

Chapter 8

Benthic Processes and the Burial of Carbon

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8.1 Introduction

A major goal of the Joint Global Ocean Flux Study (JGOFS) has been to understand the export of carbon from the surface ocean to the deep sea, a process which removes carbon from the active exchange with the atmosphere for long periods of time. Deep-sea sediments are the final sink of organic matter which is not degraded in the water column nor at the water-sediment interface. This interface is a physical boundary collecting and concentrating sinking particulate organic matter from fine debris to dead whales and consequently supports a fairly active benthic community. The level of biotic activity, the rates of remineralization, and last, but not least, the amount of material buried and preserved in the sediment, all depend on the mass flux and the composition of the material reaching the sea floor. As will be shown in this chapter, the connection between the surface ocean and the seafloor is not a simple one. However, the integration of signals at the sea floor allows conclusions to be drawn about upper ocean processes which go beyond the period of direct observation.

The remnants of surface water productivity deposited at the sea floor are not only the drivers of benthic biological activity and biogeochemical processes, but they also carry signals of productivity which are eventually buried in the sediments and retain the information of past ocean productivity. These signals undergo major changes not only in the water column but also at the water-sediment interface. Thus, this biologically active interface acts as a final filter which determines in which chemical form and quantity the settling material is preserved in the deeper layers of the sediment. Although much of the original material is lost in these degradation processes, empirical relationships between the signals stored in the sediments and various aspects of ocean productivity have been detected and used to assess levels of productivity in the past. One uncertainty of this approach is the alteration of the material by biological and chemical processes at the sea floor prior to burial. Hence, there is a common interest of biogeochemists, biologists and paleoceanographers to understand the link between productivity, benthic processes and preservation of signals in deep-sea sediments.

Paleoproductivity studies have made large efforts to reconstruct past changes in environmental and climatic conditions by following variations in signals of ocean biology, in particular of the 'biological pump', that are preserved in the sediments. The knowledge of changes in paleoproductivity is a key to understanding how external factors affect biogeochemical cycles and why the ocean is today as it is. Unfortunately, the intuitively-obvious approach to reconstruct past changes in ocean productivity from the profiles of organic carbon in the sediments is not valid. There is no simple, direct relationship between the burial rate of organic carbon and the biological productivity of the overlying waters. Preservation of organic matter is low and very variable. Furthermore, while there is strong evidence that preservation efficiency depends on bottom water oxygen content, sediment exposure time and mass sedimentation rates there is as yet no valid algorithm for assessing preservation efficiency. A further complication involves the supply of refractory 'old' organic matter originating from reworked ancient sediments and redeposited on top of new material, particularly at sites near ocean margins. Due to these and further problems paleoceanographers have turned to 'proxies' to determine past changes in ocean productivity. Proxies are indirect indicators of past processes which are, ideally, better preserved in marine sediments than bulk organic matter. Studies in the modern ocean by JGOFS and other projects have helped to establish a linkage between the proxy and either export flux, concentration of nutrients in the surface water or nutrient utilization efficiency. With this set of tools, which still presents us with many questions and unresolved problems, changes of paleoproductivity can be elucidated and related to environmental change.

This chapter deals with two aspects of deep-ocean fluxes: firstly, the removal of carbon from the surface waters by export to the deep ocean, deposition and burial in the deep-sea sediments as far as we understand it today; secondly, the use of proxies preserved in the deep-sea sediments as indicators of past ocean productivity. The study of benthic processes and burial of carbon in the sediments has not been pursued by all national JGOFS programmes, hence this information is compiled from a number of different studies.

8.2 Processes of Transport and Turnover of Material in the Deep Ocean

8.2.1 Transfer of Organic Material from the Surface to the Deep Ocean

The export of biogenic particles from the productive upper layer of the ocean removes a small and variable fraction of algal biomass from the euphotic zone transferring biologically bound carbon and associated elements into the deeper water layers. Mass occurrences of phytoplankton often lead to agglomeration of individual algal cells forming relatively large and rapidly sinking aggregates, which also scavenge other particles from the water column (Alldredge and Silver 1988). Oceanic regions characterized by seasonal phytoplankton blooms are known for high and episodic sedimentation while oligotrophic oceanic gyres are characterized by low and more constant particle fluxes (Antia et al. 2001). During settling in the water column a large part of labile organic matter is lost from the particles due to zooplankton grazing, microbial degradation and leaching. These losses are most pronounced in the zone between the upper mixed layer and about 1500 m water depth (e.g., Berger et al. 1987; Martin et al. 1987; Louanchi and Najjar 2000). Hence, what reaches the sea floor is the net result of production in the surface ocean and subsequent alteration in the deeper water column. This statement is true for the organic material, which feeds the deep-sea organisms, as well as for the proxies which are used to reconstruct past productivity levels from the sediment record.

Sinking particles can be collected by moored sediment traps deployed in different depths in the water column. Such particle interceptor traps collect and preserve the sinking material for later analysis of its constituents. This method has provided valuable long term measurements of the vertical flux of matter in selected regions of the ocean (e.g., Haake et al. 1993; Deuser 1996; Honjo et al. 2000). It has demonstrated the temporal and spatial variability of both, the flux rates and the composition of the sedimenting material. Furthermore, trap material provides information about the major groups of phytoplankton contributing to the export from the upper ocean, and particularly those with siliceous or calcareous shells can be well identified. A major problem associated with traps is the uncertainty of the efficiency by which they collect sinking particles. Sediment traps moored in shallow water depth are subjected to stronger currents and turbulence and are, therefore, prone to major errors (Buesseler 1991; Buesseler et al. 2000; Gust et al. 1994; Yu et al. 2001a). Shallow traps also frequently capture live zooplankton when they search for food, called 'swimmers', which can be separated from the sinking dead debris only with difficulty. A further complication involves release of dissolved organic mat-

ter from particles which can amount to a large fraction of the vertical organic carbon flux in shallow traps and which is usually not accounted for in flux measurements (Kähler and Bauerfeind 2001). In contrast, flux measurements from deep moored traps agree reasonably well with data from other methods (Bacon et al. 1985; Emerson et al. 1987; Buesseler 1991; Yu et al. 2001a; Scholten et al. 2001). The uncertainty in the vertical flux at shallow depth severely limits attempts to estimate the total export from the upper ocean to the deep sea.

The organic carbon flux recorded using sediment traps generally resembles primary productivity patterns in time and space. Hence, sediment trap data were used to develop algorithms which link the primary production to the flux of particulate organic carbon (POC) and water depth (e.g., Suess 1980; Betzer et al. 1984; Martin et al. 1987; Pace et al. 1987; Berger et al. 1987). Such algorithms are frequently applied to estimate the fraction of primary production that is exported out of the upper productive layer and reaches the deep ocean. This approach is tempting and convenient, since basin-wide or global export can be estimated from surface water primary productivity derived from satellite images (e.g., Antoine et al. 1996; Behrenfeld and Falkowski 1997), but it is also subject to a number of uncertainties. Many intermediate steps are required to infer export production from satellite chlorophyll data and the various algorithms describing the vertical flux differ considerably. Trap data indicate that between 10% and 40% of the primary production as derived from satellite data is being exported out of the upper mixed layer at 125 m water depth (Antia et al. 2001) and between 0.4% and 3% at 1000 m (Fischer et al. 2000) with highest export fractions generally associated with high primary production and lowest ones in oligotrophic regions. Particularly high and highly variable percentages of primary production are exported at 100 m water depth in polar regions and in the Arabian Sea at certain periods of the monsoon cycle, while export in subtropical and equatorial regions is lower and less variable (Buesseler 1998). Furthermore, the seasonality of production seems to influence export. Regions with highly variable export production tend to export more organic carbon to the deep ocean than more stable ones (Lampitt and Antia 1997; Antia et al. 2001). Algorithms with an exponential relationship between primary production and export flux seem to describe this relationship best (e.g., Betzer et al. 1984; Antia et al. 2001).

The speed of sinking of particles is an important factor determining the export flux. A range of different types of particles with different sedimentation rates ranging from 1 m to ca. 300 m d⁻¹ (Alldredge and Silver 1988) are produced in the euphotic zone and fast-sinking particles are the first ones to reach the deep waters preceding the bulk of slower particles. Among fast sinking particles are diatom aggregates and large fecal pel-

lets such as those of salps, pteropods or krill which may sediment with a speed of several hundred up to thousand meters per day (e.g., Madin 1982; Pfannkuche and Lochte 1993; Noji et al. 1997). These particles arrive in deep waters only a few days after their production in the upper water column and are important vehicles for transfer of organic matter into the deep ocean. For instance, shallow (500 m) and deep (3 200 m) moored traps at the long-time series station near Bermuda recorded the seasonal peaks of sedimentation almost without a significant time lag indicating that below the upper mixed water layer fast transfer may prevail (Conte et al. 2001), which may be caused by repackaged particles produced by zooplankton grazing in mid-water. The importance of fast sinking diatoms, or rather aggregates of diatoms, for export fluxes has been emphasized in a modeling study by Boyd and Newton (1999) highlighting diatom blooms as the plankton community with the highest export potential. Biogenic minerals, such as calcite, aragonite and opal, increase the ballast of settling particles and, hence, their sinking speed (Armstrong et al. 2002). Additional ballast from lithogenic particles introduced to the surface waters by dust, river plumes or melting of 'dirty' ice and scavenged from the water by the organic particles also increases the sinking speed (Ittekkot 1993). Large food falls to the deep-sea floor, as for instance observed from a mass mortality of swimming crabs (Christiansen and Boetius 2000), may also introduce a sizeable amount of fresh organic matter to the sea floor. Such stochastic fluxes may be large in certain regions, but cannot be assessed by conventional means and remain generally unaccounted for.

Another factor determining the flux of organic matter is the degree to which it is mineralized in the water column. Most of the organic material is lost in water depths between 500 m to 1 500 m while at greater depths only small losses occur (e.g., Berger et al. 1987; Martin et al. 1987; Louanchi and Najjar 2000). In regions with strong seasonal phytoplankton 'blooms' forming fast sinking aggregates higher losses in the water column were found, while in systems with less pulsed export (e.g., subtropical and tropical regions) less material is degraded below the upper mixed layer on the way to the deep ocean (Antia et al. 2001). This difference in loss of organic material may be caused by the types of particles being exported. Particles sedimenting after phytoplankton blooms are composed of relatively fresh organic matter from senescent algal cells and are remineralised rapidly within days (Turley and Lochte 1990). In contrast, physically more stable systems seem to recycle most material in the upper water column and loss in deeper waters is small. Exceptionally high exports and little degradation were associated with melting ice probably due to very fast sinking aggregates (Peinert et al. 2001). In contrast to shallow traps recording local differences in productivity, deep moored traps in around

3 000 m water depth show less regional variability (Antia et al. 2001). This implies that there is an effective biological filter removing organic material in mid water. These degradation processes in the mesopelagic zone beneath the upper mixed water layer are still poorly known and represent a major uncertainty in our understanding of carbon transport processes in the ocean. In particular, the influence of different types of zooplankton and their different feeding strategies on particle dynamics in the deeper water column is still an open question.

8.2.2 Benthic Carbon Turnover Processes

The sedimenting material accumulates at the sea floor and at times of high sedimentation, e.g., after the phytoplankton spring bloom, it can form a fluffy layer of organic-rich particles on the sediment surface altering the chemical and biological conditions in this layer (Billett et al. 1983; Rice et al. 1986; Thiel et al. 1989). Although in the deep water column below 1 500 m the organic material seems largely unaffected by biotic consumption, there is a substantial remineralization of this material once it settles on the sea floor (Lochte and Turley 1988; review by Turley et al. 1995). Generally >90% of the organic carbon reaching the sea floor is remineralized and only a small residual fraction is permanently buried in the sediments (Bender and Heggie 1984; Emerson et al. 1985). The community inhabiting the deep-sea floor seems well adapted to low food supply of poor quality and possesses specific capabilities to deal with this material (e.g., Lochte and Turley 1988; Boetius and Lochte 1996). As a result of high biological activity and changing physico-chemical conditions in the water-sediment interface, both sedimenting organic material and proxies experience major modifications.

The water-sediment interface comprises the lower few meters of water above the sediment with increased concentrations of resuspended sediment particles and elevated bacterial activity (called 'the benthic boundary layer', Ritzrau 1996), and the upper few centimeters of the sediment with high biological activity (Ritzrau et al. 2001a). In deep-sea sediments, highest biological activity is found in the upper two centimeters declining down to 5 or 10 cm, below which activity is very low (e.g., Boetius et al. 2000a). However, active bacteria and archaea are still present in great sediment depths, but except for specific geological settings their impact on cycling of material in sediments is assumed to be small (Parkes et al. 2000).

Gradients of oxygen in pore water indicate the rate of mineralization of organic matter in the sediment and allow one to model the degradation rates of this partly recalcitrant material. Various organic fractions with different degradation rates can be identified (Soetaert et al. 1996; Hedges et al. 1999) ranging from mean life times

of a few months in regions with high vertical flux (e.g., Smith et al. 1997; Luff et al. 2000) up to 0.7 to 3.5 years (Sayles et al. 1994) or 1.7 to 33 years (e.g., Smith et al. 1997; Sauter et al. 2001). Life times ranging from 0.3 to 80 years have been reported for Southern Ocean sediments (Sayles et al. 2001). The considerable differences in the degradation rates of organic material depend on its chemical composition and shortest degradation rates are observed in relatively 'fresh' organic matter which has settled quickly to the sea floor. If material is turned over slowly, benthic remineralization does not follow directly the temporal pulses of sedimentation, but the signal is spread out in time. According to diagenetic models, the amplitude in seasonal variations in benthic remineralization depends critically on the reactivity of the deposited material and can only show a direct response to a seasonal pulse of sedimentation when mean lifetimes of less than 0.25 years prevail (Martin and Bender 1988; Sayles et al. 2001). Therefore, seasonal changes in vertical flux as recorded by sediment traps are not always reflected by similar seasonal changes in sediment oxygen consumption. Absence of seasonal shifts in oxygen consumption in response to sedimentation events has been observed by direct measurements of benthic respiration in some investigations (e.g., Sayles et al. 1994), while other studies indicate seasonal fluctuations in respiration linked to sedimentation events (Fig. 8.1) (e.g., Pfannkuche 1993; Drazen et al. 1998). Thus, the benthic response depends on the deposition of relatively 'fresh' organic matter which has the strongest impact on benthic metabolic rates.

In particular the small sized organisms, such as bacteria, foraminifera, nematodes and other meiofauna, react to sedimentation of particulate organic matter (reviews by Gooday and Turley 1990; Lochte and Pfannkuche 2002; see also Pfannkuche et al. 1999). On a long-term station in the North Atlantic, the sediments showed a seasonal increase of concentrations of algal pigments, adenylates as indicator of biomass of small organisms, bacterial biomass and respiration (Fig. 8.1) indicating that there is seasonal growth of small sized organisms triggered by the sedimentation of the phytoplankton spring bloom. Increased metabolism, rising enzyme activity, increasing growth rates or migration towards the source of food were observed in different groups of these small organisms (Gooday and Turley 1990; Lochte 1992; Pfannkuche 1993). Owing to the poor nutritional quality of the organic material, it seems that bacteria and archaea are best adapted to degrade this material as they possess the greatest diversity of hydrolytic enzymes (e.g., Boetius and Lochte 1996). The largest share of organic carbon in deep-sea sediments is primarily utilized by microorganisms, but larger organisms feeding on the organic particles and the attached microbes also benefit from the sedimenting material (Rice et al. 1986; Gooday and Turley 1990; Heip et al. 2001).

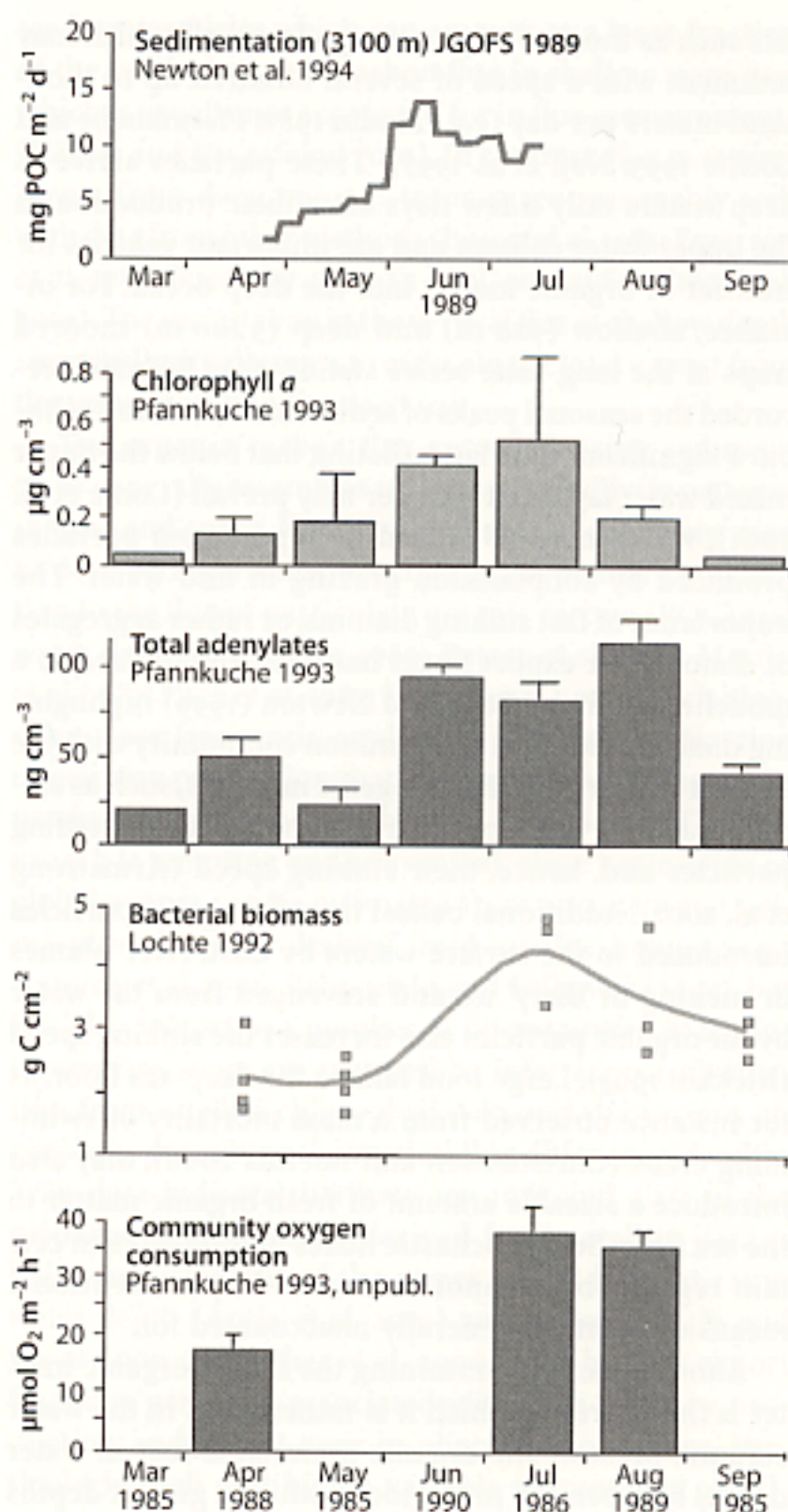


Fig. 8.1. Seasonal pattern of sedimentation of particulate organic carbon (POC) in the Northeast Atlantic in 1989, and seasonal fluctuations in the sediment at the same station of chlorophyll *a*, total adenylates, prokaryotic biomass and oxygen consumption of the sediment community. The sediment data are compiled from several years. This compilation indicates that approximately 4–6 weeks after the surface phytoplankton bloom sedimenting phytodetritus reaches the sea floor (4500 m depth) and gives rise to increased benthic microbial biomass and respiration. The sources of data are indicated with each variable (modified after Lochte et al. 1993, Lochte and Pfannkuche 2002)

From the more productive continental slopes towards the mid-oceanic regions with low sedimentation rates the proportion of large benthic organisms (macrofauna) within the total benthic community, both in respect to biomass and contribution to organic carbon degradation, decreases (Heip et al. 2001). This shift in community composition has an additional impact on the degradation process as the burrowing and pumping activity of larger organisms facilitates rapid incorporation of freshly deposited particles into the upper sediment layers.

Bioturbation and bioirrigation are positively related to the level of food input (e.g., Smith et al. 1997; Shimmield and Jahnke 1995; Pope et al. 1996), but they also depend on the type of organisms involved (Turnewitsch et al. 2000). Long-term studies in the Porcupine Abyssal Plain indicate that major shifts in the composition and abundance of benthic macrofauna may occur. For instance, increases of a species of sea cucumber (*Amperima rosea*) were observed over a period of >10 years but the reasons remain obscure (Bett et al. 2001; Billett et al. 2001). Long-term observations in the eastern North Pacific revealed a decline in sedimentation of POC to the sea floor and, hence, indicate declining food supply for the benthos (Smith and Kaufmann 1999; Smith et al. 2001). Such interannual or decadal variations are likely to have profound effects on the structure of deep-sea communities and on the turnover of material at the sea floor. Understanding the extent of these changes is critical to any interpretation of biogeochemical cycling in the deep sea. However, we are just beginning to appreciate such changes, we are not aware to which extent they are happening at present and in the past, and we are uncertain about their consequences.

Since most deep-sea sediments are well oxygenated, the organic compounds are primarily remineralized via oxygen (Emerson et al. 1985). In areas with high deposition of organic matter the increased respiration in the sediments can not be balanced by diffusion of oxygen from the overlying bottom water. In these sediments oxygen becomes depleted and the pathways of microbial degradation processes change. Such conditions are found in the deep-sea sediments adjacent to intense upwelling regions and at continental margins. For instance, the upwelling regions off Namibia, Peru and Chile are characterized by extensive anoxic zones in the sediments occasionally even extending into the water column. Anoxic conditions are also observed in upper sediment layers of the Arabian Sea where the oxygen minimum zone of the water column impinges on the continental margins and in regions where high sedimentation from monsoonal upwelling occurs. In these regions, sulfate reduction is found in the upper sediment layers, a rare occurrence in deep-sea sediments (Ferdelman et al. 1999; Boetius et al. 2000a). Furthermore, anoxic layers may also develop when turbidites cover the sea floor and prevent oxygen exchange with the overlying water. Under these conditions higher proportions of organic carbon are buried, since oxygen exposure time has been identified as the key factor influencing organic carbon preservation in sediments (Hartnett et al. 1998; review by Canfield 1994). Also the preservation of proxies may change under low oxygen or anoxic conditions (see below).

Productive continental margins also contain large amounts of methane in form of methane hydrates which represents a very large store of organically bound carbon. This ice-like material is kept stable under low tem-

perature and high pressure, but it disintegrates when temperature rises or pressure is reduced (Zatsepina and Buffett 1998). Methane hydrate deposits close to their stability limits can be released in large amounts under changing environmental conditions allowing methane to escape to the atmosphere. Such events may be initiated by switches in thermohaline circulation and evidence of massive methane release from the sea floor is found in geological records (Kennett et al. 2000). Under present day conditions, however, a very effective benthic filter consisting of methane oxidizing bacteria normally consumes this climatically active gas within the sediment when it is released gradually (Hinrichs et al. 1999; Boetius et al. 2000b) and prevents an efflux to the atmosphere. These sedimentary sources of methane also sustain very active benthic communities which are not directly dependent on the organic matter supply from the upper ocean (Sibuet and Olu 1998). The quantitative role of this additional energy source for organic matter cycling in the deep sea is probably limited to local effects only.

8.3 Quantitative Estimates of Carbon Deposition and Carbon Turnover

8.3.1 Strategies for Quantification of Benthic Fluxes

The total flux of organic matter to the sea floor can be estimated as the sum of the burial rate and remineralization rate at any specific location with the remineralization rate estimate dominating the calculation (Jahnke 1996). Deep-moored sediment trap results have indicated that particle fluxes in the water column generally decrease with depth by only a factor of 2–3 between 1 km and 4 km water depth. Thus, quantifying deposition fluxes to the sea floor also provides an important constraint on the magnitude and distribution of the water column fluxes below the main thermocline. As mentioned above, the processes within the sediments that control solute fluxes, remineralization and burial tend to dampen the effects of short-term variability of the particle input fluxes and facilitate estimation of mean fluxes. The reduced temporal variability also facilitates the combining of individual results into basin-wide compilations of flux distributions.

Two basic strategies have been employed to quantify recent fluxes to the deep-sea floor. Reaction/transport models of organic carbon distributions within the sediment column have been developed to estimate remineralization and burial (e.g., Rabouille and Gaillard 1991; Soetaert et al. 1996; Boudreau 1997). Since sediment cores can be routinely recovered from the sea floor and analyzed, there is a large data set from which to work. It is of disadvantage, however, that since the majority of the deposited organic matter has already been reminer-

alized, this method attempts to predict the total initial flux from a small residual. Inaccuracies in the model could lead to large inaccuracies in the estimated flux. Furthermore, the upper few centimeters of the sediments in the deep sea are generally comprised of materials deposited over the preceding few to tens of thousands of years. Recent variations in the particle flux would, therefore, not be reflected in sediment characteristics. Thus, while fluxes derived from sediment studies alone may reflect the average deposition occurring over the last few thousands of years, there is considerable uncertainty when extending these estimates to the present.

The other principal strategy for estimating sea-floor fluxes is to compute the benthic solute flux of metabolic oxidants (mainly oxygen and nitrate) or carbon through pore water or benthic flux chamber studies (e.g., Glud et al. 1994; Jahnke et al. 1990). In principle, solute fluxes only provide an estimate of remineralization, and burial must be estimated independently. However, only a few percent of the deposited organic carbon survive remineralization in deep-sea sediments and a rough estimate of burial is sufficient to account for this term. Limitations are that accurate flux estimations require (a) high resolution measurements of mm scale near the sediment surface, (b) in situ measurement to avoid pressure and temperature related sampling artifacts and (c) molecular diffusive transport to dominate solute exchange processes (Glud et al. 1994).

In the last decade, methods for determining benthic solute fluxes (mainly used for oxygen fluxes) have become more sophisticated due to the development of free falling lander systems (Tengberg et al. 1995). They are equipped either with benthic chambers in which the rate of loss of oxygen in the water above the sediment can be measured or with oxygen microsensors which record oxygen profiles in the sediment. These in situ measurements have added new data to the traditional shipboard measurements of oxygen consumption and have improved our understanding of the biological degradation of organic matter at the deep-sea floor. In situ benthic flux chamber measurements are generally thought to be the most accurate technique for evaluating benthic fluxes in deep-sea sediments, but are limited in that they require sophisticated instruments and are time consuming, restricting the number of measurements that can be obtained. In some cases such in situ benthic chamber measurements indicate higher sediment carbon turnover than the vertical organic carbon flux measured by sediment traps (e.g., Smith 1987; Smith and Kaufmann 1999; Witte and Pfannkuche 2000; Ritzrau et al. 2001b). This discrepancy can not yet be fully resolved. Possible explanations are lateral input of organic matter from higher productive regions not captured by sediment traps, which is particularly obvious near continental margins (see below), or systematic underestimation of total vertical flux by sediment traps. Good agreement

between carbon regeneration estimated from benthic studies and vertical organic carbon fluxes measured by sediment traps in certain mid-oceanic environments (e.g., equatorial Pacific Ocean: Berelson et al. 1997; Southern Ocean: Sayles et al. 2001) supports the view that discrepancies are greatest in ocean-margin environments.

8.3.2 Regional Assessments of Deep-Ocean Fluxes

A correlation between benthic fluxes and surface water productivity, estimated from satellite images, has been found in several well-studied regions. For instance, in the Arabian Sea biogeochemical processes in the benthos match the pattern of monsoon-driven primary productivity (Pfannkuche and Lochte 2000). In the northern North Atlantic, a consistent relationship between primary production, water depth and benthic oxygen fluxes was found (Schlüter and Sauter 2000). The global assessment of Jahnke (1996) shows a general agreement between benthic oxygen fluxes and export measured by sediment traps as well as primary productivity patterns estimated from satellite images, but in some regions deviations are observed.

Notable exceptions to this general pattern are found at stations close to continental margins. Their benthic fluxes exceed by far the rates measured by sediment traps or estimated from surface water productivity. This was observed, for example, at stations in the western Arabian Sea (Witte and Pfannkuche 2000), in the Argentine Basin (Hensen et al. 2000) or on the Iceland Plateau (Schlüter et al. 2001; Ritzrau et al. 2001b). Based on a nutrient and carbon budget Chen and Wang (1999) estimated for the East China Sea an export of organic matter from the shelf via downslope transport of POC of 0.7×10^{12} mol C yr⁻¹. This has to be compared to a total primary production of ca. 12×10^{12} mol C yr⁻¹ indicating that most of the primary produced material is recycled on the shelf and that <6% is exported to the adjacent deep sea. During the SEEP study at the northeastern American Atlantic Margin and the Mid-Atlantic bight, <5% of primary production was estimated to be exported from the shelf (Anderson et al. 1994) and studies at the European continental margin (OMEX) indicate an export of ca. 10% (McCave et al. 2001; Wollast and Chou 2001). Such estimations are hampered by many poorly constrained factors, but they are an example of the magnitudes of downslope export to be expected. Although this is only a small fraction of total production on the shelves, it represents a large influx to the sediments of the continental margins. It has to be noted that under different hydrographic and topographic conditions the export from a specific shelf system may be very different. Most of the transport from the shelf occurs in the bottom turbidity layer, which occupies a few tens of meters above the sediment. This

process is difficult to observe and has been largely neglected in the past. Major conduits for export are canyons of the shelf slope (Biscaye and Anderson 1994) through which most of the export is funnelled. Upwelling and frontal systems at the shelf edge give rise to high productivity and exceptionally high sedimentation contributing additional material to the flux at continental margins. Although there is an increasing recognition that export of organic matter from the productive shelf areas is a quantitatively important flux to the deep ocean, this export is still very difficult to quantify (see also Chen et al., this volume).

Another region of possible discrepancies is the Southern Ocean. Relatively high benthic fluxes of oxygen and nitrate, an indicator of benthic remineralization, are found in the upwelling regions off Namibia and Chile and in the Atlantic part of the Antarctic Circumpolar Current zone (Hensen et al. 2000; Grandel 2000) which are not matched by estimates of primary production from satellite images. The relatively high benthic mineralisation rates in parts of the Southern Ocean may be attributed to fast sinking large diatom aggregates and krill fecal pellets. These observations are supported by recent analyses from the ANTARES and AESOPS (Southern Ocean – JGOFS) programmes which showed that the fraction of exported production in some regions of the Southern Ocean is higher than in lower latitudes (Pondaven et al. 2000; Honjo et al. 2000; Nelson et al. 2002). Organic carbon fluxes recorded in sediment traps at 1 000 m depth in the Polar Frontal Zone and in the Antarctic Zone were about twice as high as the global average (Honjo et al. 2000). This is in contrast to other sediment trap studies which indicate that fluxes in the north and south polar regions were similar to the global average and that around 1.2% of primary production reaches the sea floor (Schlüter et al. 2001). These different observations indicate that we do not yet understand sufficiently production and export processes in the Southern Ocean and that we may underestimate the vertical flux in this region. Another important aspect is extensive sediment focusing in some regions of the Southern Ocean (Francois et al. 1993; Kumar 1994; Frank et al. 1999; Dezileau et al. 2000; Sayles et al. 2001) which produces local rates of sediment deposition far in excess (by as much as a factor of 20) of regionally-averaged particle rain rates. Sediment focusing creates high benthic fluxes in regions of modest productivity, thereby accounting for some of the discrepancies noted above.

8.3.3 Global Estimates of Deep Ocean Carbon Deposition and Remineralization

The major obstacle in obtaining large scale estimates of sea-floor fluxes is the paucity of data. There are some well studied regions, some examples are given above,

but for wide areas of the deep sea no measurements exist. The best strategy for assessing the distribution of sea floor fluxes at the basin scale is to combine benthic flux and sediment modeling strategies (see above). Point measurements of benthic fluxes provide the most accurate data and constrain the overall magnitude of the fluxes. Sediment models provide the greatest spatial coverage and could be used to interpolate between and extrapolate from point flux measurements to basin scale estimates. This, of course, implies that there is a reasonable relationship between burial rates of organic carbon, which span a long period of time, and benthic fluxes, which record the instantaneous rate of organic matter turnover. A compilation of benthic remineralization rates (from in situ benthic flux chamber deployments or in situ microelectrode oxygen profile measurements) and burial rates (from organic carbon contents of the sediments and sediment mass accumulation rates estimated primarily through ^{14}C chronology) shows a significant linear correlation (Jahnke 1996). Thus, despite the time scale difference between sediment accumulation and benthic flux response to varying inputs, there is an overall correlation between sediment burial and benthic fluxes. Burial efficiencies ($100 \times$ burial rate / deposition rate) in the deep ocean gyre regions average about 1%, in higher flux areas of open ocean and coastal upwelling regions they range from a few percent to 10%, and on the upper continental slope very high efficiencies $>10\%$ are estimated. Thus, although burial efficiencies are not constant, a regular progression from low to high deposition locations is observed.

Utilizing these techniques, global estimates of the distributions of organic carbon fluxes to the deep-sea floor and global benthic oxygen fluxes have been estimated between 60°S and 60°N (Jahnke 1996) (Fig. 8.2). Overall, the distribution of the sea floor fluxes displays the same general features as previously published distributions of primary and new production (e.g., Berger

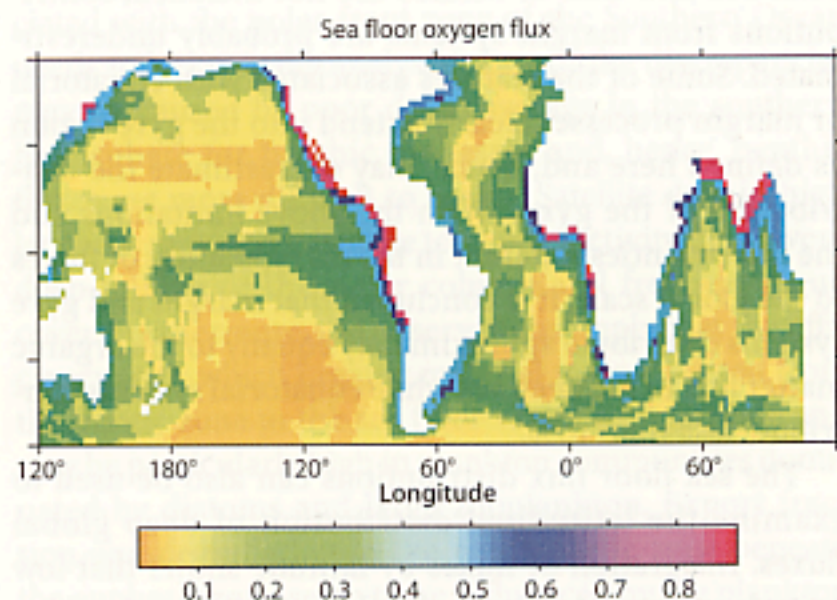


Fig. 8.2. Global distribution of sea floor oxygen flux ($\text{mol m}^{-2}\text{yr}^{-1}$) estimated from benthic flux estimates. Values are extrapolated to basin scales using empirical correlations between benthic oxygen flux and organic carbon burial rates (redrawn from Jahnke 1996)

et al. 1987; Antoine et al. 1996). On average, low fluxes are estimated for the deep, central gyre regions and high fluxes are calculated for continental boundary regions, especially those areas adjacent to coastal upwelling regions such as the Pacific margins of the Americas, the Atlantic African margin, and the monsoonally influenced regions of the Arabian Sea. Elevated fluxes are also estimated for the equatorial Pacific region and the polar-front region of the southern Atlantic and Indian Oceans.

The sea-floor fluxes imply a global organic carbon deposition rate to the deep-sea floor of 33×10^{12} mol C yr⁻¹, excluding areas shallower than 1 000 m (Jahnke 1996). Of this flux approximately 3% are permanently buried. The resulting total remineralization rate in the sediments accounts for 45% of the total oxygen utilization of the deep ocean estimated from Apparent Oxygen Utilisation-¹⁴C relationships. This estimate of global organic carbon flux agrees well with estimates from deep moored sediment traps, which indicate a flux at 2 000 m of 0.34 Gt C yr⁻¹ (28×10^{12} mol C yr⁻¹). Thus, the magnitude of the deep fluxes estimated from the sediment studies is consistent with other measures of deep-ocean metabolism.

Based on Jahnke's (1996) results from benthic oxygen fluxes, the relative importance of continental margin, equatorial and gyre regions in POC transport to the deep ocean can be assessed. For this purpose, the margin regions are defined as any location within 6° of latitude or longitude of the continental shelf, the equatorial region is defined as those areas between 5° N and 5° S and the gyre region is all of the sea floor area remaining. Respectively, these areas represent 24.5%, 7.3% and 68.2% of the total deep-sea floor area. In general, despite comprising the majority of ocean area, the gyre region contributes only approximately 50% of the estimated total deep flux. Margin areas contribute 40% or more and equatorial areas contribute less than 10%. Since some marginal seas and basins such as the Caribbean Sea and Gulf of Mexico are not included, contributions from margin systems are probably underestimated. Some of the features associated with equatorial or margin processes clearly extend into the gyre region as defined here and, hence, may overestimate the contribution of the gyres. With the above limitations and the uncertainties inherent in the extrapolation of fluxes to the global scale, it is concluded that margin and gyre systems contribute approximately equally to the organic matter flux to the deep sea while equatorial systems contribute less than 10%.

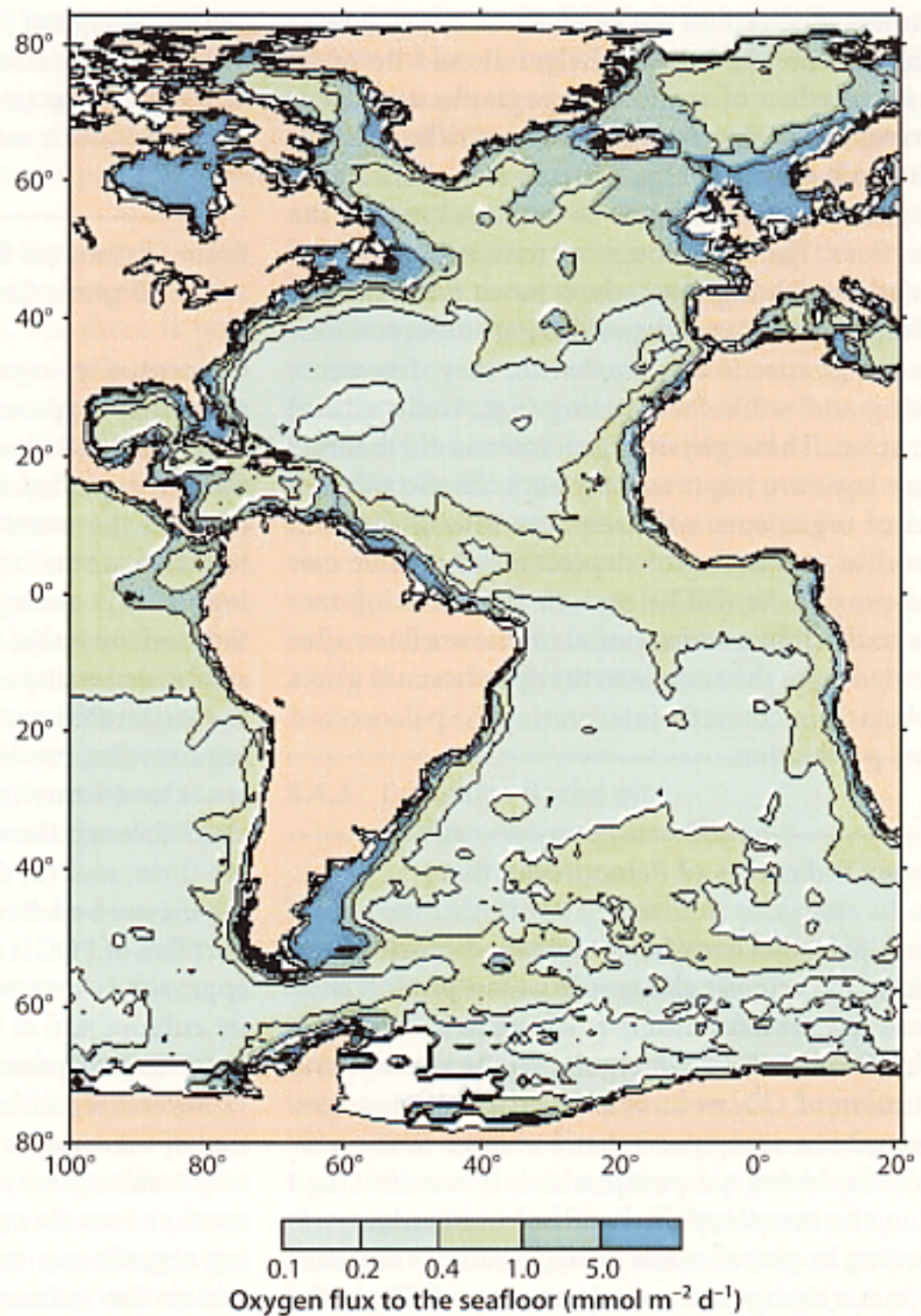
The sea floor flux distributions can also be used to examine the latitudinal distribution of deep global fluxes. Integration of fluxes by latitude shows that low latitude regions dominate the flux of POC to the deep ocean and suggests that 2/3 of the total POC flux to the sea floor occurs within 30° of the equator. This low latitude dominance follows very closely the latitudinal dis-

tribution of deep-ocean surface area as approximately 60% of the total ocean area lies within 30° of the equator (Menard and Smith 1966). Given this distribution, high latitude regions could contribute equally to the deep POC flux only if deep POC fluxes there were at least a factor of 5 larger than low-latitude fluxes. Such high deep POC fluxes are not indicated by sediment trap data (Fischer et al. 2000; Antia et al. 2001; Schlüter et al. 2001), even if the recently reported higher fluxes in the Southern Ocean are considered (see above).

The above described benthic oxygen flux distribution based on sea-floor results can also be compared to a distribution estimated from surface water productivities based on CZCS satellite data and direct productivity measurements, vertical transfer relationships and water depth (Romankevich et al. 1999; Tseitlin 1993; Vinogradov et al. 1996) (Fig. 8.3). Overall, there is a good agreement in the estimated total carbon and oxygen fluxes to the deep-sea floor (sea floor greater than 1 000 m water depth) between the two approaches. A value of 53×10^{12} mol O₂ yr⁻¹ ($= 32 \times 10^{12}$ mol C yr⁻¹) is estimated from the surface productivity and vertical carbon flux relationship for the global deep-ocean floor. A value of 33×10^{12} mol C yr⁻¹ resulted from benthic measurements (see above, Jahnke 1996). Approximately 72% of the total sea floor flux derived from the primary production-depth relationship occurs within 30° of the equator. Considering that these results are obtained from completely different approaches and data sets, such agreement may be to some extent fortuitous since regional differences are apparent between both approaches.

A totally different approach to deep-ocean fluxes is made by inverse models. The large data base of deep ocean dissolved nutrients, oxygen and hydrographic data is used to fit a coupled circulation-biogeochemistry global ocean model until the observed properties are realistically reproduced (Schlitzer 2002). This inverse model yields total integrated export fluxes which are necessary for a realistic reproduction of nutrient and oxygen data in the deep water column. This model indicates that the tropical and subtropical areas between 30° N and 30° S contribute the largest export flux of organic carbon (ca. 53% of global export flux). This is a consequence of the very large area covered by this zonal belt. The second largest contribution comes from the Southern Ocean south of 30° S (ca. 33%) while the export of the oceans north of 30° N is smaller (ca. 14%). Most of the Southern Ocean export is found in a zonal belt along the Antarctic Circumpolar Current, associated with the high productivity at the Polar Front, and in the coastal upwelling regions off Chile and Namibia. While in most areas of the ocean the model estimates of export flux are in agreement with estimates based on satellite images, they are higher by factors of two to five in the Southern Ocean. These model results of high export relative to satellite estimates support the observa-

Fig. 8.3. Distribution of sea floor oxygen flux ($\text{mmol m}^{-2} \text{d}^{-1}$) in the Atlantic Ocean based on estimates of surface primary production rates, vertical transfer relationships and water depth (Romankevich et al. 1999)



tions of high benthic fluxes in parts of the Southern Ocean (Grandel 2000), AESOPS sediment trap studies (Honjo et al. 2000) and analyses of nutrient budgets at ANTARES (Pondaven et al. 2000) as well as throughout the Southern Ocean (Louanchi and Najjar 2000). All these studies also indicate that the organic carbon fluxes are accompanied by exceptionally high silicate fluxes in the Southern Ocean stressing the importance of diatoms for efficient export fluxes (see also Tréguer, this volume). Since the ratio of silicate to organic carbon varies strongly in settling material (e.g., Honjo et al. 2000; Pondaven et al. 2000), care has to be taken when using sedimentary opal accumulation rates as indicators of paleoproductivity.

When the sea floor fluxes are compared to distributions of primary productivity reported by Behrenfeld and Falkowski (1997) differences are obvious in the high latitudes. Unlike benthic assessments that were dominated by low latitude regions (within 30° of the equator), 55% of the reported primary productivity occurs at latitudes greater than 30° . While the estimates of the global deep-ocean carbon fluxes converge to values

around $0.3\text{--}0.4 \text{ Gt C yr}^{-1}$ ($25\text{--}30 \times 10^{12} \text{ mol C yr}^{-1}$), the discrepancies between regional estimates offer a chance to refine our perception of the export processes. It seems that in particular the productivity and the export associated with the polar front zone of the Southern Ocean needs to be critically analysed. Part of the discrepancies may be caused by poor data coverage in the southern hemisphere for benthic processes and, hence, benthic fluxes are more difficult to assess. Satellite data in high latitudes may also misjudge total productivity due to very deep mixing of the water column and frequent cloud cover. Furthermore, the observations imply that the efficiency with which organic material is transported from the photic zone to the sea floor varies with latitude and may be particularly high in plankton communities dominated by diatoms and large zooplankton. Export fraction and degradation in the mesopelagic zone beneath the euphotic zone seem to be influenced by the plankton community, but as yet there are few hard facts which allow estimates of the regionally variable transfer efficiencies from the upper to the deep ocean to be made.

A process which could not be analysed adequately in this context, but which nevertheless should be mentioned, is the effect of sea-floor topography and deep-sea currents on the deposition of organic-rich particles. Extensive mid-oceanic ridge systems as well as ridges and canyons at ocean margins cover large areas of the deep-sea floor. The deep-ocean currents, which can intermittently reach high speeds, remove fine material from elevated parts and deposit them in depressions where current speeds are low, hence, they determine winnowing and sediment focusing (e.g., Hollister and McCave 1984). These physical processes in the benthic boundary layer are important for both the distribution patterns of organisms and their activities (e.g., Flach et al. 2001) as well as for the deposition of organic carbon and proxies. As will be seen in the following section, the redistribution of material on the sea floor after it has settled from the surface to the deep ocean is also a major obstacle in correctly interpreting the paleorecord of export production.

8.4 Proxy Indicators of Paleoproductivity

Two principal objectives have motivated much of the recent research on past changes in ocean productivity. First, investigators have sought evidence in marine sediments for the ocean's role in regulating the atmospheric concentration of CO₂ as an important greenhouse gas. It has long been recognized that a change in the efficiency of the biological pump, which is manifest as a change in the inventory of dissolved inorganic nutrients residing in global-ocean surface waters, translates directly into a change in the concentration of CO₂ in the atmosphere (e.g., Broecker 1982; Sarmiento and Toggweiler 1984). Various factors, ranging from changes in wind-driven upwelling (Pedersen and Bertrand 2000), ocean nutrient inventory (Falkowski 1997; Ganeshram et al. 2000) and to fertilization by iron (Martin 1990) have been hypothesized to induce climate-related changes in ocean productivity. Much of the recent paleoproductivity research has been designed to test these hypotheses. The second, and no less important, objective motivating paleoproductivity research has been the desire to understand the response of ocean ecosystems to changing environmental boundary conditions associated with climate change. A sound understanding of the sensitivity of ocean ecology to perturbation by climate change in the past will help guide efforts to predict the response of ocean ecosystems to anticipated global warming. A number of methods have been developed to reconstruct past changes in ocean productivity. Careful calibration of such methods is essential in order to test the assumptions and resolve the limitations inherent in these methods. Progress has been made in calibrating productivity proxies through the comprehensive biogeochemical

process studies of JGOFS. However, because this research was not always afforded high priority during the design of JGOFS programmes, progress occurred at a limited pace, and much more remains to be done.

8.4.1 Estimates Based on Organic Carbon Burial Rates

Conceptually, organic carbon burial rates provide the most direct approach for reconstructing export production of POC. Although organic matter leaving the productive upper layer is largely oxidized during its transit through the water column and at the water-sediment interface, a small fraction is eventually buried. Assuming there is a simple relationship between the export flux and the burial rate of carbon, then it should be possible to estimate past changes in export production from the accumulation rate of organic carbon. This approach requires that two key parameters do not vary greatly in space and time: (1) the remineralization of POC as it sinks through the water column and as it settles on the sea floor; and (2) the preservation of POC after reaching the sea bed. Because only a small fraction of the export flux of POC is eventually preserved and buried, this approach is very sensitive to variable losses in the water column and at the water-sediment interface as well as to variable preservation during sediment diagenesis.

Several algorithms for POC regeneration as a function of water depth have been developed using sediment trap results, however, they differ substantially from one another (see above). Furthermore, 'ballasting' of sinking organic material by denser inorganic particles increases the sedimentation speed and, hence, the depth of remineralization (Ittekkot 1993; Armstrong et al. 2002). An algorithm relating carbon preservation to sediment accumulation rate has been derived empirically at continental margin sites (Mueller and Suess 1979). Subsequently, it has been learned that much of the POC of continental margin sediments originates from lateral transport down the continental slope. Much of this POC is old (¹⁴C age of several hundred years, Anderson et al. 1994) and refractory, thereby creating artificially high apparent POC preservation efficiencies in continental margin sediments (e.g., Jahnke 1990; Anderson et al. 1994). For this reason, the preservation algorithm overestimates the sensitivity to sediment accumulation rate, and should not be used in paleoproductivity reconstructions.

As the supply of POC by lateral transport is often large at ocean margins, sometimes exceeding the vertical rain from surface waters (Anderson et al. 1994, see above), the burial rate of POC is largely decoupled from the export flux sinking from overlying waters. In some cases, POC of terrestrial origin dominates the organic matter preserved and buried in ocean-margin sediments

(e.g., Lyle et al. 1992; Villaneuva et al. 1997), even in regions far removed from the mouths of major rivers. Where terrestrial POC constitutes a significant portion of buried organic matter, the carbon accumulation rate obviously cannot be used to reconstruct past changes in ocean productivity.

The sensitivity of sedimentary POC preservation to bottom water oxygen concentration has long been debated (see review by Canfield 1994), but there is now increasing evidence that POC preservation is sensitive to multiple factors, including bottom water oxygen concentration (Keil et al. 1999), oxygen exposure time (Hartnett et al. 1998), abundance of bacterial grazers (Lee 1992), bioturbation rate (Kristensen et al. 1992; Andersen and Kristensen 1992), and protection by sorption to minerals (Mayer 1994; Keil et al. 1994). This introduces substantial uncertainty into paleoproductivity reconstructions based on the accumulation rate of organic carbon. For this reason, together with the other sources of uncertainty identified above, paleoceanographers have sought independent methods free of these problems to estimate past levels of ocean productivity.

8.4.2 Estimates Based on Biomarker Accumulation Rates

Specific organic biomarker compounds, known to be produced by marine phytoplankton, are used as proxies alternative to organic carbon burial rates for paleoproductivity studies. Biomarkers may be specific to selected groups of phytoplankton (e.g., alkenones from coccolithophorids, dinosterol from dinoflagellates, brassicasterol from diatoms), or they may include the full suite of the pigment transformation products of chlorophyll, known as chlorins. Use of these biomarkers eliminates the error associated with input of terrestrial POC, and also supplies information about the dominant groups of phytoplankton preserved in the sediments (e.g., Schubert et al. 1998).

Like any method that relies on the absolute accumulation rate to reconstruct changes in export production, the use of biomarkers is sensitive to errors introduced by sediment focusing; i.e., the redistribution of particles by deep-sea currents, and by variable rates of preservation of the biomarkers. While sediment focusing is well known in environments influenced by bottom currents (e.g., the Southern Ocean, see above), recent evidence suggests that sediment focusing is also prevalent in other regions, such as the central equatorial Pacific Ocean, where its effects were previously not recognized (Marcantonio et al. 1996, 2001). Fortunately, it is possible to correct for sediment focusing by normalizing concentrations of biomarkers to ^{230}Th , a radiogenic product of ^{234}U dissolved in seawater, which is highly particle reactive and whose flux to the sediments in most

oceanic regions nearly equals its known rate of production in the overlying water column (Suman and Bacon 1989; Francois et al. 1990). Analysis of sediment trap samples collected world-wide is contributing to the further calibration of ^{230}Th as a constant flux proxy by evaluating the degree to which its flux deviates from its known production rate and defining the conditions under which these deviations occur (Yu et al. 2001a; Scholten et al. 2001). This approach only provides estimates of 'preserved rain rates', i.e., rain rate minus dissolution or remineralization before burial. Variable losses of biomarkers due to biological action or changes in redox conditions are still a major problem. As yet, no method has been proposed to correct for such variation in the preservation of biomarkers, although research conducted during JGOFS process studies may help to improve the understanding of the factors regulating biomarker preservation.

8.4.3 Estimates Based on Barium Accumulation Rates

High concentrations of barium, in excess of average concentrations in aluminosilicate minerals, have long been known to occur in marine sediments underlying regions of high productivity. This has led to the suggestion that accumulation rates of excess barium can be used to estimate export production. Support for this view came from sediment trap data which showed a tight, but non-linear, relationship between the flux of organic carbon and that of Ba (Dymond et al. 1992; Francois et al. 1995) and from empirical correlations between barite accumulation rate and primary productivity (Paytan et al. 1996). These relationships provide a means of quantifying the export flux of carbon from the accumulation rate of excess Ba in sediments, if the preservation of excess Ba can be constrained. The main advantage of Ba is that it is much better preserved in sediments than is organic carbon. An empirical algorithm for excess Ba preservation as a function of sediment accumulation rate has been developed (Dymond et al. 1992). It has also been suggested that barite, the common carrier of excess Ba, would only derive from biogenic material freshly produced in the overlying water, so that the Ba record would not be affected by lateral transport of more refractory POC from shelves and continents (Francois et al. 1995). Because of these advantages, the use of excess Ba for paleoproductivity reconstructions has become extremely popular.

While initial results suggested that Ba offers many advantages as a paleoproductivity proxy, more recent research has discovered that it also suffers from some serious limitations. Calibration studies using sediment trap samples have shown that the Ba/POC rain ratio in sinking particles varies substantially from one location

to another, even among sites where lateral supply of reworked POC is expected to be negligible (Dymond and Collier 1996; Dehairs et al. 2000). Preservation of barite in sediments is poor where pore water sulfate concentrations are lowered by sulfate reduction (e.g., Brumsack 1986; von Breyman et al. 1992). It was discovered more recently that preservation of excess Ba plummets even under modestly reducing (sometimes referred to as suboxic) conditions (Kumar et al. 1996; McManus et al. 1998), such as occur commonly at ocean margins and in other regions of high export production. Furthermore, barite is subject to extensive reworking and export from continental shelves (Fagel et al. 1999), similar to organic carbon. An example from the JGOFS Equatorial Pacific Study shows the absolute accumulation rates of barite in sediment cores derived from ^{18}O -based stratigraphy and in comparison to the accumulation rate corrected for sediment focusing by normalisation to ^{230}Th (Fig. 8.4). These two traces indicate very different pictures of the sensitivity of export production to climate change over the last 200 kyr in the equatorial Pacific Ocean. The absolute accumulation rate (^{18}O) implies much greater export during glacial climate intervals, whereas the accumulation rate corrected for sediment focusing (^{230}Th) indicates very little climate sensitivity. Supply of excess barite from sediment focusing obviously increased the barite accumulation rate during glacials (Marcantonio et al. 2001). Therefore, this temporal variability may be interpreted as changes in climate-related deep-sea currents responsible for sediment focusing rather than changes in export production. Another example from the Atlantic sector of the Southern Ocean shows ^{230}Th normalized accumulation rates of

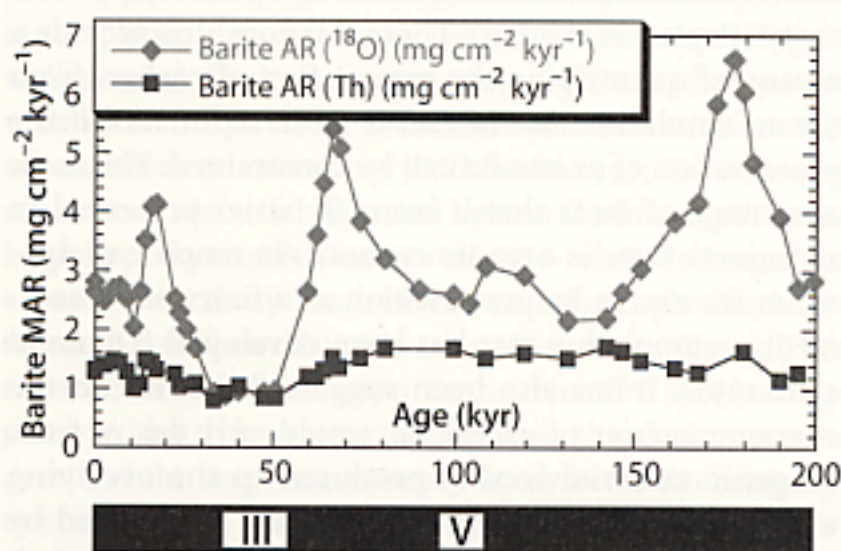


Fig. 8.4. Absolute accumulation rate of barite derived from ^{18}O -based stratigraphy (diamonds) and accumulation rate normalised to ^{230}Th to correct for sediment focusing (squares). The absolute accumulation rate implies much greater export production during glacial climate intervals, whereas normalization to ^{230}Th indicates very little climate sensitivity. The difference is caused by supply of excess barite due to sediment focusing. Scale bar shows marine isotope stages. Roman numerals III and V represent interglacial periods; filled intervals represent glacial periods (data from US JGOFS Equatorial Pacific study at 0°N and 140°W ; barite data from Paytan (1995); this figure has been redrafted from results presented by Marcantonio et al. 2001)

organic carbon (C_{org}) and excess Ba in two sediment cores (Fig. 8.5). Through the time interval from the last glacial maximum (ca. 20 kyr) to the present, the carbon accumulation rates have decreased more than 5-fold, yet there has been no significant change in the accumulation rate of Ba. This exemplifies that one obtains entirely different views of the climate sensitivity of export production depending on which tracer is used. Either the initial Ba/ C_{org} ratio has changed through time or the relative preservation of C_{org} or excess Ba is the factor that has changed. These two examples illustrate that one must be cautious in using Ba as a productivity proxy in regions where supply of barite is decoupled from export production by winnowing from shelves, or where preservation of Ba is low and variable in suboxic sediments. Suboxic sediments exist not only in many productive regions (e.g., Kumar et al. 1995), but also in areas where sediment focusing is pronounced (e.g., Francois et al. 1993), precluding the use of Ba accumulation in these regions as well.

In pelagic regions, where sediments remain well oxygenated to great depth, it was believed until recently that the principal interference influencing the accumulation rate of excess Ba is sediment focusing, which can be corrected for by normalizing to ^{230}Th . However, first-order budgets for Ba in the central equatorial Pacific Ocean, constructed using benthic incubation chambers, sediment trap samples and cores collected during the US JGOFS EqPac programme, show that the present rates of Ba rain and benthic remobilization are nearly in balance, indicating that the net rate of Ba accumulation is negligible (McManus et al. 1999). Thus, there seems to be a minimum threshold in carbon flux that needs to be reached to leave a biogenic Ba signal in the sediment. The usefulness of Ba-based paleoproductivity algorithms may thus be limited to a relatively narrow window of productivity, whose exact limits still need to be established.

8.4.4 Estimates Based on Radionuclide Ratios

Radionuclide ratios as productivity proxies exploit the systematic relationship between mass particle flux and the adsorption of certain radionuclides to sinking particles. Here, the fact that ^{230}Th is sufficiently particle-reactive that it is removed from the ocean at a rate equivalent to its known rate of production (see above) is exploited. Thus, this proxy indicates changes in the rate of mass particle flux and indirectly past changes in productivity. In contrast to this ultra-reactive behavior of Th, less-reactive tracers are scavenged from the ocean on time scales comparable to, or greater than, the mixing time of an ocean basin, and their flux from the water column increases with increasing particle flux. Tracers that fall into this category include ^{231}Pa and ^{10}Be . ^{231}Pa , like ^{230}Th , is produced uniformly throughout the

Fig. 8.5. Accumulation rates of (left) organic carbon and (right) excess Ba in two cores from the Atlantic sector of the Southern Ocean from a sampling site between the present positions of the Antarctic Polar Front and the Subantarctic Front. The accumulation rates have been normalized to ^{230}Th to account for sediment focusing. The last glacial and interglacial periods as recorded in the sediments are indicated. Note the major changes of export production indicated by C_{org} accumulation rate between interglacial and glacial, but not by excess Ba (R. Anderson, unpubl.)

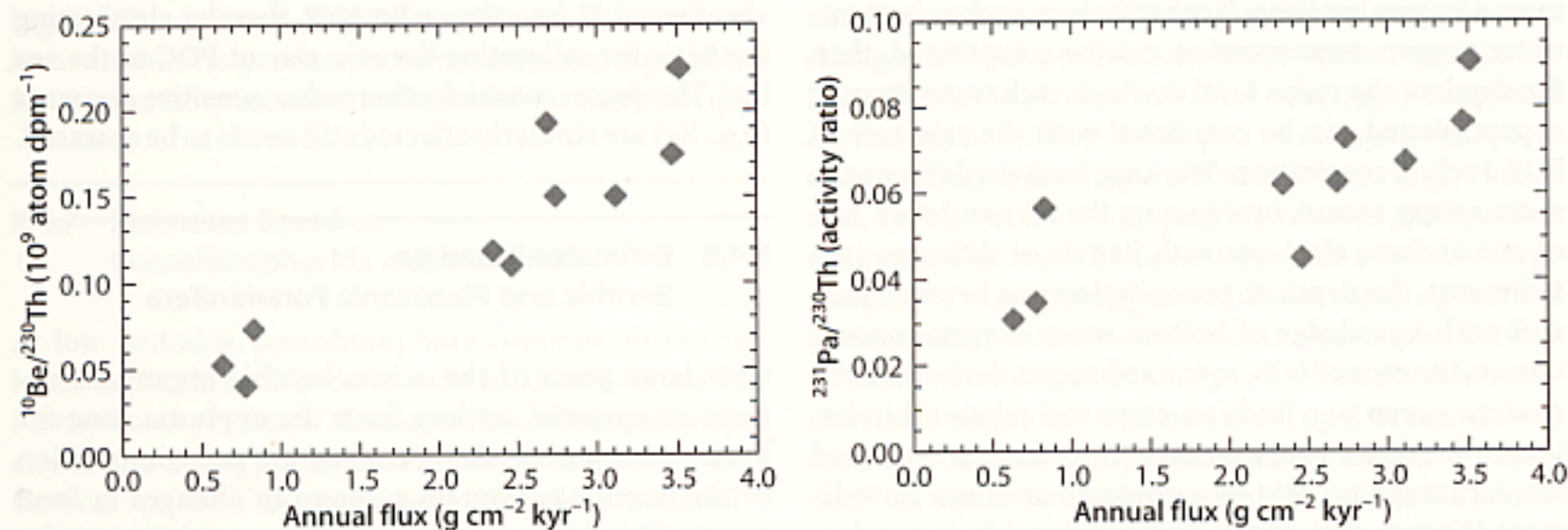
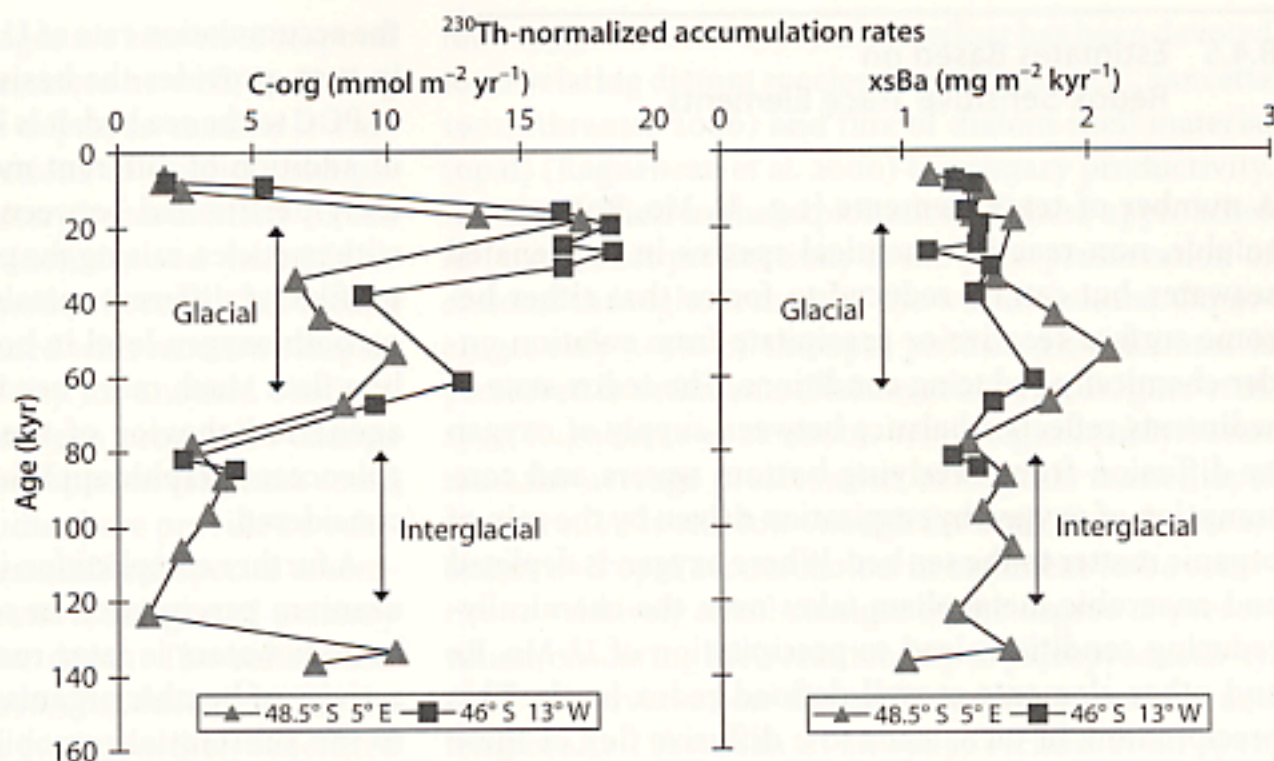


Fig. 8.6. Flux-weighted mean radionuclide ratios are plotted against annual average mass flux for sediment trap samples recovered during the US JGOFS study along a transect normal to the equator at 140°W from 9°N to 12°S . Radionuclide ratios correlate with mass flux, supporting their use as proxies for vertical flux. Sediment traps used in this calibration were deployed at depths greater than 2000 m (R. Anderson, unpubl.)

ocean by U decay (^{235}U in this case), while ^{10}Be is produced in the atmosphere and supplied to the ocean primarily in precipitation. The tendency for $^{231}\text{Pa}/^{230}\text{Th}$ and $^{10}\text{Be}/^{230}\text{Th}$ ratios to increase with increasing sediment accumulation rate was proposed as a paleoproductivity proxy (Kumar et al. 1995; Anderson et al. 1998). A recent calibration of these proxies using JGOFS sediment trap samples from the equatorial Pacific Ocean shows good correlations between $^{231}\text{Pa}/^{230}\text{Th}$ and $^{10}\text{Be}/^{230}\text{Th}$ ratios and the mean annual flux of particles, supporting the original contention that these radionuclide ratios can be used as proxies of particle flux (Fig. 8.6) (see also Marcantonio et al. 2001; Yu et al. 2001b).

There are some shortcomings with this approach, however. To the extent that these nuclide ratios reflect particle flux, rather than export production per se, they may be influenced by changes in the flux of detrital particles eroded from continents, e.g., riverine inputs or aeolian dust input, over the considered time scales. In addition, scavenged fluxes of these tracers at any one site

in the ocean also depend on the intensity of scavenging in surrounding regions, which determines whether the surrounding regions serve primarily as a source (i.e., surrounding regions have lower particle fluxes and scavenging intensity) or a sink (higher particle fluxes) for the laterally-transported tracers (^{231}Pa and ^{10}Be) relative to the site being studied. Furthermore, scavenged elemental ratios are controlled not only by particle flux, but also by the chemical composition of particles (e.g., Walter et al. 1997; Yu et al. 2001b; Chase 2001). Finally, deep water thermohaline circulation also affects radionuclide ratios independently of particle flux (Yu et al. 1996; Marchal et al. 2000; Yu et al. 2001b; Chase 2001). In order to exploit these tracers reliably, it will be necessary to fully characterize the effects of particle composition-dependent elemental fractionation, and to take into account possible change in deep water circulation. The greatest potential for these ratios is in providing synoptic maps reflecting the combined effects of deep water circulation and relative particle fluxes between oceanic regions.

8.4.5 Estimates Based on Redox-Sensitive Trace Elements

A number of trace elements (e.g., U, Mo, Re) exist as soluble, non-reactive chemical species in oxygenated seawater, but can be reduced to forms that either become surface reactive or precipitate from solution under chemically-reducing conditions. The redox state of sediments reflects a balance between supply of oxygen by diffusion from overlying bottom waters and consumption of oxygen by respiration driven by the rain of organic matter to the sea bed. Where oxygen is depleted and anaerobic metabolism takes over, the chemically-reducing conditions lead to precipitation of U, Mo, Re and other elements at well-defined redox levels. This precipitation, in turn, leads to a diffusive flux of these elements into the sediments to replace the atoms removed by precipitation. If other factors, such as bottom-water oxygen concentration, can be constrained, then the depth of the redox level at which each trace element is precipitated can be correlated with the rain rate of POC fueling respiration. Working backwards from the sedimentary record, by equating the accumulation rate of one of these elements with its rate of diffusion into sediments, the depth of precipitation can be calculated and, with knowledge of bottom water oxygen concentration, the rain of POC to the sediments derived. In the modern ocean one finds an empirical relationship between the flux of organic carbon to the sea floor and the accumulation rate of authigenic uranium in sediment (Kumar et al. 1995). This relationship is non-linear, and involves a threshold carbon flux below which no uranium is buried. If other parameters can be constrained, then the change in accumulation rate of authigenic uranium, or other redox-sensitive elements, could be used to reconstruct past changes in export production.

Several problems limit the use of this proxy. First, the redox conditions of sediments depend on bottom-water oxygen concentration as well as on POC supply. If changes in bottom-water oxygen concentration cannot be excluded, or quantified, then it is not possible to derive a carbon flux uniquely from the accumulation rate of uranium and other redox-sensitive metals. Also, the interpretation of authigenic metal accumulation delineated above relies on the principle that metal accumulation is primarily due to diffusive fluxes from bottom waters into the sediment. It was recently discovered, however, that particulate authigenic U formed in surface waters, although very labile, can contribute a substantial fraction of authigenic U buried in sediments under suboxic or anoxic conditions (Zheng et al. 2002a). If particulate authigenic U formed in surface waters is preserved and buried, then this flux partially decouples

the accumulation rate of U from its diffusive flux which, in turn, provides the basis for estimating the rain rate of POC to the sea bed. It is likely, however, that the mode of addition of different metals into sediment is differently partitioned between diffusive flux and addition with particles, raising the possibility that combining the profiles of different metals could provide information on both oxygen level in bottom water and organic carbon flux. Much more needs to be known about the diagenetic behavior of these metals, however, before paleoceanographic applications of this approach can be considered.

A further complication is that much of the authigenic uranium precipitated in sediments under oxygenated bottom waters is later remobilized by the burrowing activity of benthic organisms (Zheng et al. 2002b). Due to the substantial remobilization of authigenic U, its accumulation rate is again decoupled from the diffusive flux of U into the sediments, thereby eliminating the basis for estimating the rain rate of POC to the sea bed. The degree to which other redox-sensitive elements (e.g., Re) are similarly affected still needs to be assessed.

8.4.6 Estimates Based on Benthic and Planktonic Foraminifera

Over large parts of the ocean, benthic organisms depend on material settling from the euphotic zone for food. Consequently, the size, structure and composition of the benthic ecosystem respond to changes in food supply. This basic principle has been exploited to derive empirical relationships between carbon flux and the abundance, accumulation rate, and species composition of benthic foraminifera (e.g., Herguera and Berger 1991, 1994; McCorkle et al. 1994; Thomas et al. 1995). These relationships, in turn, applied to down core records have been used to reconstruct past changes in surface productivity. While a response to food supply is easily understood, one would also expect the composition of the benthic community to respond to other environmental factors, such as food quality, seasonality of food supply, and bottom water oxygen concentration. Recent expansion of calibration studies is beginning to address these multiple factors, and offers hope of extracting information concerning carbon flux as well as its seasonality (Loubere and Fariduddin 1999). The carbon isotopic composition of benthic foraminiferan CaCO_3 shells also contains information about the environment in which they grew (Woodruff and Savin 1985; Zahn et al. 1986; McCorkle et al. 1990).

Species assemblage of planktonic foraminifera deposited in sediments are also used to estimate surface water productivity and statistical transfer functions have been derived (e.g., Mix 1989a,b). However, planktonic

foraminifera species assemblages are known to respond to other environmental parameters as well, including temperature and mixed layer depth, so caution is warranted in using transfer functions to predict multiple properties from the sedimentary record. Many of the properties (for example, productivity and mixed layer depth) are correlated in the modern ocean. This means that transfer functions calibrated with modern samples may confuse one ocean property for another. Furthermore, if the relationships between properties change through time, then the transfer function estimates could be in error. JGOFS process studies have provided a valuable opportunity to relate foraminiferal species assemblages to sea surface temperature, integrated primary productivity, and mixed layer depth. The calibration study by Watkins and Mix (1998), conducted during the US JGOFS Equatorial Pacific study, further benefitted from the opportunity to collect samples under contrasting El Niño and non-El Niño conditions. Further studies are needed to produce more robust global algorithms for productivity reconstruction based on this principle.

8.4.7 Estimates Based on Coccolithophorids and Diatoms

At low latitudes, coccolithophore communities of the lower euphotic zone (~60 to ~180 m) are dominated by *Florisphaera profunda*. Most other coccolithophore species live in the upper euphotic zone (0 to ~60 m). This vertical zonation has been used for paleoproductivity studies (Molfinio and McIntyre 1990; McIntyre and Molfinio 1996) where the abundance of *F. profunda* in fossil assemblages was used to monitor the depth of the nutricline. The relative abundance of *F. profunda* increases when the upper euphotic zone is impoverished in nutrients and the nutricline is deep. Conversely, the relative abundance of *F. profunda* decreases when wind stress induces a rise of the nutricline and an increase in productivity of the upper euphotic zone. Beaufort et al. (1997) correlated the relative abundance of *F. profunda* in surface sediments from the Indian Ocean with primary productivity estimated from satellite information. They further used principal component analysis to correlate species assemblages of planktonic foraminifera in Indian Ocean core top samples to primary productivity estimated from satellite information. Primary productivity estimates derived from foraminifera were similar to those derived from the abundance of *F. profunda*, and both proxies showed similar patterns of variability in a 270-kyr record from a site near the Maldives Islands.

Because diatoms form a major component of phytoplankton in upwelling regions of high productivity, and because diatoms contribute a substantial portion of the export flux even in less productive regions (Gold-

man 1993; Buesseler 1998), much effort has been devoted to correlating diatom species assemblages (e.g., Sancetta 1992; Abrantes 2000) and flux of diatom shell material (opal) (Ragueneau et al. 2000) to primary productivity. A complication in the exploitation of these approaches to reconstruct productivity is the poor preservation of diatoms throughout most of the world's oceans. On average, only 3–5% of the opal produced by diatoms is preserved in sediments (Nelson et al. 1995; Tréguer et al. 1995; Ragueneau et al. 2000). While significantly better than the average preservation of organic matter, opal preservation is still low enough for both diatom assemblages and opal accumulation in sediment to be sensitive to relatively small changes of the degree of preservation, obscuring their relationship to paleoproductivity. Opal preservation on the seafloor varies spatially and temporally (Shemesh et al. 1989; Pichon et al. 1992; Abrantes 2000; Pondaven et al. 2000; Sayles et al. 2001) and must be accurately constrained to estimate past changes in opal productivity from opal accumulation (e.g., Charles et al. 1991; Mortlock et al. 1991). Empirical algorithms have been developed to estimate opal preservation from diatom species assemblages (e.g., Pichon et al. 1992), but they only provide relative preservation estimates and are still associated with relatively large margins of error. While refinement of these algorithms is warranted, we also need to better understand the factors that control opal dissolution both in the water column and sediments. Furthermore, opal accumulation rates can be profoundly influenced by sediment focusing. This was shown to be particularly true in the Southern Ocean where focusing factors in excess of ten are not uncommon (e.g., Kumar 1994; Francois et al. 1993; Frank et al. 1999; Dezileau et al. 2000). In order to utilize opal accumulation rates to reconstruct productivity, better preservation algorithms will need to be developed (Sayles et al. 2001), and it will be necessary to correct for sediment focusing using ^{230}Th , or an alternative proxy of known flux. Recent work has also emphasized that the relationships between fluxes of organic carbon and opal vary strongly geographically depending on the plankton community (e.g., Honjo et al. 2000; Pondaven et al. 2000; Schlitzer 2002; see above). Biogeochemical process studies, such as those conducted during the international JGOFS programmes, have provided opportunities to start evaluating those factors. Much more remains to be done, however, particularly in terms of alteration of the species assemblage preserved in the sediments.

8.4.8 Proxies of Surface Nutrient Concentration

The export production is equal to the new production relying on the supply of nutrients by upwelling and mix-

ing. If this supply can be assumed constant, or constrained by independent methods, then a change in surface nutrient concentration can be interpreted in terms of a change in export flux. Consequently, substantial effort has been devoted to developing proxies of surface nutrient concentration. The two proxies used most commonly, the carbon isotopic composition and the Cadmium/Calcium (Cd/Ca) ratio of planktonic foraminifera, both rely on the modern empirical relationship between nutrient (e.g., PO_4) concentration and the relevant parameter recorded in foraminifera shells (i.e., the carbon isotopic composition of dissolved inorganic carbon, or the Cd concentration of seawater).

Carbon isotopic composition of planktonic foraminifera have been used widely to estimate past changes in surface nutrient concentration (e.g., Labeyrie and Duplessy 1985; Charles and Fairbanks 1990; Ninnemann and Charles 1997). Extending this approach, the difference between the carbon isotopic composition of planktonic foraminifera and that of benthic foraminifera has been used to infer past changes in the overall strength of the biological pump (e.g., Curry and Crowley 1987). Recent studies have shown, however, that the carbon isotopic composition of foraminifera is offset from that of dissolved inorganic carbon due to the influence of other environmental parameters. For example, the carbon isotopic composition of planktonic foraminifera varies systematically with the carbonate ion concentration in seawater (Spero et al. 1997) and depends, as well, on the carbon isotopic composition of ingested prey and on temperature (Kohfeld et al. 2000). Isotopic fractionation during air-sea exchange of CO_2 also affects the $\delta^{13}\text{C}$ of surface water DIC, independently of nutrient concentration (Charles et al. 1993). In addition, planktonic foraminifera species grow over a range of water depths that include not only surface but also pycnocline waters (Fairbanks et al. 1980). When all present uncertainties are taken into account, the propagated error in the final estimate of past nutrient concentration can exceed the largest climate related changes recorded in the sediments, at least over the interval from the Last Glacial Maximum (LGM) to the present (Kohfeld et al. 2000). It is thus essential that these uncertainties be reduced before reliably interpreting the $\delta^{13}\text{C}$ of planktonic foraminifera.

Cadmium/calcium ratios of planktonic foraminifera have not been widely exploited to reconstruct surface nutrient concentrations because the low concentrations of Cd in low-latitude surface waters leave little Cd to be acquired by foraminifera. Foraminiferal Cd/Ca ratios hold potential for reconstructing nutrient concentrations in high-latitude waters, however, where elevated nutrient concentrations persist throughout the year, provided that other factors affecting the Cd/Ca ratio can be constrained (Elderfield and Rickaby 2000). Early work in the Southern Ocean found no change in nutrient concentration from the LGM to the present (Keigwin and

Boyle 1989). More recently, Rosenthal et al. (1997) interpreted planktonic foraminiferal Cd/Ca ratios from the Subantarctic Indian Ocean to indicate that surface nutrient concentrations had been lower, and productivity higher, than today during the LGM. This interpretation has been challenged, recently, following the calibration of the temperature dependence of the partition coefficient for uptake of Cd by planktonic foraminifera (Rickaby and Elderfield 1999). When this temperature dependence is taken into account, for example by using the Mg/Ca ratio or the oxygen isotopic composition of the foraminifera shells, Rickaby and Elderfield find little change since the LGM in the surface nutrient concentration of Subantarctic waters. Further tests are needed to assess the general applicability of the temperature dependence of metal uptake by foraminiferal carbonate shells, as well as to constrain the preferential loss of trace metals during partial dissolution of foraminifera shells (McCorkle et al. 1995).

8.4.9 Proxies of Surface Nutrient Utilization Efficiency

The efficiency of the biological pump, expressed as the fraction of new nutrient added to the euphotic zone which is utilized by phytoplankton, can be evaluated from N isotopes for nitrogen and, possibly, Si isotopes for silicate. The isotope systematics of both elements follow the same principle, in that the light isotope is taken up preferentially and, as a result, the residual nutrient and planktonic material produced from it become increasingly heavy with nutrient depletion. While the study of Si isotopes is just beginning (De la Rocha et al. 1998), the possibilities afforded by N isotopes have been investigated for several years (Calvert et al. 1992; Francois and Altabet 1992; Altabet and Francois 1994; Francois et al. 1997). These studies have shown that the $^{15}\text{N}/^{14}\text{N}$ ratio of particulate organic matter in the water column and surface sediments reflects the fraction of surface nitrate utilized by phytoplankton, with heavier isotope ratios found in areas of greater nitrate depletion. The isotopic composition of organic nitrogen preserved in sediments has been used as a means of assessing changes in this important variable through time, although its interpretation is complicated by a diagenetic increase in the $^{15}\text{N}/^{14}\text{N}$ ratio at the water-sediment interface. Recent findings indicate, however, that this latter problem could be resolved by analyzing organic nitrogen associated with the protein template locked within diatom frustules (Sigman et al. 1999). This pool of sedimentary nitrogen appears to be unaffected by diagenesis, while recording the primary signal produced in surface waters.

Calibration work conducted during JGOFS process studies, and elsewhere, has found remarkable spatial uniformity in the fractionation factor associated with

the uptake of nitrate by phytoplankton (Altabet and Francois 2001), although unique species assemblages (e.g., blooms of *Phaeocystis antarctica* common in the Southern Ocean) and phytoplankton growing in certain unique habitats (e.g., sea ice algae) remain to be tested. Thus, the original isotopic composition of nitrate taken up by phytoplankton determines their N isotope signal. For instance, nitrogen fixation reduces ^{15}N in the nitrate pool and, hence, causes light N isotopic composition in phytoplankton. Major changes in the level of nitrogen fixation will, therefore, also affect the $^{15}\text{N}/^{14}\text{N}$ signal in the sediments. Denitrification, on the other hand, enriches the ^{15}N isotope in nitrate, hence, nutrient sources affected by denitrification will lead to a heavy isotopic composition in phytoplankton. If the supply of nitrate to the surface waters from different source water masses with distinct $^{15}\text{N}/^{14}\text{N}$ characteristics changes, this will affect the isotopic composition of phytoplankton and finally of the sediment record. Therefore, the interpretation of the N isotope signals in the sediments will require a sound understanding of the sources of nitrate being utilized by phytoplankton. This introduces a complicating factor into the interpretation of the paleo-record, since it cannot be assumed that the ^{15}N isotope signal in surface water nitrate has remained constant.

8.5 Conclusions

Sea floor studies provide a powerful strategy for estimating the magnitude and the global distribution of organic matter fluxes in the oceans. The general coherence between primary productivity estimates from satellites and benthic fluxes is, in fact, quite astounding considering the many intermediate steps required to link both processes, all of which are subject to errors. Although regional deviations are observed, general correlations are found when considering longer periods of time. This strengthens the view that there is a systematic link between upper and deep ocean processes. This systematic link is also the ultimate justification for using proxies from deep-sea sediments to reconstruct paleoproductivity. The reason for this correlation has to be sought in a fairly consistent relationship between nutrient supply and phytoplankton export production, in the relatively uniform chemical composition of sedimenting material, and in only small deviations from average settling speeds of the majority of sinking particles. On shorter time scales, like seasonal cycles, the coherence between primary production and benthic fluxes is relaxed due to the different speeds on which both systems function.

Patterns of fluxes at the deep-sea floor do not always follow the distributions of surface water primary production as derived from satellites. In particular, discrepancies are observed along continental margins and in

some areas of the Southern Ocean. Additional supply of organic material enters the deep ocean from productive shelf areas and it is important to better quantify this flux. In highly productive regions, such as in upwelling regions and in the polar front zone of the Southern Ocean, the transfer efficiency of organic material to the deep ocean may be greater than elsewhere. Hence, the role of plankton communities in regulating the transfer efficiency in differently productive regions of the ocean needs to be elucidated. This also concerns the removal and modification of organic particles in the mesopelagic zone of the ocean beneath the productive upper layers which probably has a noticeable influence on the amount and composition of particles reaching the deep-sea floor.

The biological processes that modulate vertical flux and modify material at the sea floor also create substantial uncertainties when using proxies for paleoproductivity studies. The inherent uncertainties are partly due to the fact that each productivity proxy is affected by different secondary processes which can act independently of productivity. These uncertainties also stem in part from our lack of understanding of the processes affecting the links between productivity and proxy. To remedy the first problem we need a to use a multiproxy approach. Biases induced by secondary processes are more likely to be identified in such an approach, and consistency between proxies may also provide important information on some of these secondary processes. In particular, a direct comparison of geochemical proxies with ecological proxies has yet to be undertaken. Addressing the second issue requires comprehensive biogeochemical process studies, in which expression of the proxy signal can be related directly to the biogeochemical parameter of interest, and in which the preservation of the proxy during sediment diagenesis can be evaluated. Future biogeochemical process studies, along the lines of those conducted by JGOFS, provide ideal opportunities for proxy calibration, and should include a proxy calibration component. In return, improved understanding of the carbon cycle under forcing conditions (radiations, sea level, circulation etc.) very different from those prevailing today will highlight important aspects of the fundamental processes at play that may have been missed by studying the modern ocean alone. The synergy between paleoceanographic and modern process studies is evident and should mold future comprehensive research programmes on the carbon cycle.

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