CHAPTER FOURTEEN

Elemental Proxies for Palaeoclimatic and Palaeoceanographic Variability in Marine Sediments: Interpretation and Application

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Contents

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1. Introduction

The elemental composition of sediments and sedimentary rocks provides a wide range of information on sediment sources, the mode and direction of sediment transport, past climates, ocean circulation, organic production, sea-floor and sedimentary oxygenation and post-depositional changes in sediment sequences. The content of a given element in a sediment sample depends on the relative proportions of its constituent phases, which are ultimately derived from the continents, the sea floor and the water column. Physical and biological processes during deposition coupled with post-depositional chemical reactions yield a complex component mixture that can provide significant palaeoceanographic and palaeoclimatic information to complement and strengthen interpretations derived from the study of microfossils and the isotopic compositions of sedimentary components.

Early work on the construction of climate records from marine sediments focused primarily on stratigraphic studies of microfossil distributions and changes in assemblages over time (Schott, 1935; Cushman & Henbest, 1940; Phleger, Parker, & Peirson, 1953; Parker, 1962). But it was also realized that the lithology and mineralogy of deep-sea sediments could also identify the sequence of glacial–interglacial deposits on the sea floor (Bramlette & Bradley, 1940). Elemental data assembled in the reports of some of the classic deep-sea expeditions (Murray & Renard, 1891; Correns, 1937; Bramlette & Bradley, 1940; Arrhenius, 1952) amplified this information, and laid the groundwork for much of our current understanding of the geochemistry of deep-sea deposits and how geochemical data can be used to study the ocean system. One or two decades later information on elemental variability was developed to study marine geochemical cycles (Goldberg, 1954; Goldberg & Arrhenius, 1958; Wedepohl, 1960; Degens, 1965; Berner, 1971), and this greatly advanced understanding of ways in which the distributions, enrichments and depletions of elements can be used to interpret the sedimentary record.

In this chapter, we review the application of sedimentary geochemistry to the reconstruction of climatic and oceanographic changes over the Cenozoic, with emphasis on the Late Pleistocene. Records from both pelagic regimes and ocean margin provinces will be used to show how information on both ocean conditions and terrestrial climates can be assembled from the major, minor and trace element composition of sea-floor deposits. Processes governing the distribution and accumulation of organic carbon and nitrogen in marine sediments will not be specifically discussed in this chapter because they have been extensively reviewed in a number of publications (see for example, Emerson & Hedges, 1988; Pedersen & Calvert, 1990; Stein, 1991; Rullkötter, 2000). Carbon and nitrogen cycling in the ocean are fully discussed in Volume 2. Likewise, the application of rare earth element geochemistry to palaeoceanographic and palaeoclimatic problems is not treated here; the interested reader can refer to recent reviews by McLennan (1989), McLennan, Hemming, McDaniel, and Hanson (1993) and Holser (1997).

The next two sections present background sedimentary information and describe some common data manipulation techniques that are used to construct and study palaeoclimatic and palaeoceanographic records in marine sediments.

2. Sedimentary Components of Marine Sediments

Marine sediments and sedimentary rocks are mixtures of a number of components that are derived from different parts of the Geosphere (Goldberg, 1963). They comprise *lithogenous* components, crystalline and non-crystalline phases derived from continental surfaces, (soils and all rock types) and the crustal rocks of the sea floor, *biogenous* components, skeletal materials and the degraded tissues of marine and terrestrial organisms, *hydrogenous* components, inorganic phases that precipitate from seawater, *cosmogenous* components, meteoritic material from space, and *diagenetic* phases and constituents that form, or are precipitated, within accumulating sediments. The elemental composition of sediments reflects this admixture of components since virtually all sediments have contributions from more than one of these sediment sources. In the case where an element resides in only one of the components, its total content will be variably diluted by all other components. However, where an element is present in more than one component its concentration is determined by its amount in each separate component and the proportion of each component in the mixture. Considerable effort has been devoted to unraveling complex component mixtures in order to gain insight into the geochemistry of sedimentary deposits.

3. Normalization of Elemental Data

The lithogenous fraction of sediments carries information on the variable composition of Earth's crust, which can be modified by chemical erosion and sorting of materials on the land surface and on the sea floor, as well as transportation processes that abrade particles and sort them according to size. The concentration of aluminium is often used to estimate the total lithogenous content of a sediment because its concentration is very similar in acidic to basic extrusive and intrusive and most metamorphic rocks. This is in turn quite similar to its concentration in bulk upper crust and shales, the most common sedimentary rock (Turekian & Wedepohl, 1961; Wedepohl, Correns, Shaw, Turekian, & Zemann, 1969–1978; Wedepohl, 1971; Taylor & McLennan, 1985).

The conservative behaviour of Al is well known in weathering profiles and soil formation due to the *in situ* formation of clay minerals and the retention of hydroxides (Loughnan, 1969; Hem, 1969–1978; Bohn, O'Connor, & McNeal, 1979). This has led to its use in sediment studies as a normalizing parameter for the assessment of the relative degrees of enrichment or depletion of specific elements in a given sample, or to estimate the "background" contribution of an element derived from crustal sources. Data compilations of the World Shale Average (Wedepohl, 1971), the Post-Archaean Average Shale (Taylor & McLennan, 1985) and the North American Shale Composite (Gromet, Dymek, Haskin, & Korotev, 1984) have been used for this purpose. Van der Weijden (2002) recently reviewed the use of the element/Al ratio in sedimentary geochemistry and cautioned against its use for element correlations while confirming that it can provide useful qualitative information on element enrichments/depletions and in correcting for dilution.

An alternative method for normalizing elemental data utilizes the bulk Ti content of marine sediments. The Al/Ti ratio in carbonate-rich equatorial sediments of the central Pacific appears to be substantially higher than the crustal ratio, possibly due to adsorption of dissolved Al onto particle surfaces and its transport to the sea floor (Murray & Leinen, 1993; Murray, Leinen, & Isern, 1993). If correct, this discovery would obviate the use of Al as a conservative lithogenous proxy, but, on the other hand, would provide a useful tracer of variable particle accumulation on the sea floor, linked to biogenous fluxes in the dominantly carbonate-bearing sediments of remote pelagic regions of the sea (Section 6.3). For this reason, Murray and Leinen (1993) elected to use the bulk Ti content of their equatorial sediments as a general lithogenous proxy. This practice has been followed subsequently (Zabel, Bickert, Dittert, & Haese, 1999; Yarincik, Murray, & Peterson, 2000; Zabel et al., 2001; Mora & Martinez, 2005) in situations where the total biogenous fraction of the deposits is small and virtually all Al is contained in lithogenous aluminosilicate lattices.

The use of Ti as a lithogenous proxy is problematic because, although the inorganic fraction of North Pacific clays was found to have a remarkably uniform titanium concentration (Revelle, 1944) and the bulk Ti content of equatorial Pacific sediments has been used as a constant flux index (Arrhenius, Kjellberg, & Libby, 1951; Arrhenius, 1952), its content varies to a greater extent in different rock types compared with Al. Thus, Ti contents can range over a factor of five or more in silicic to mafic igneous rocks compared with a range of only *ca*. 10% for Al (Wedepohl et al., 1969–1978). As discussed in Section 4.1, Ti is hosted principally in discrete Ti-bearing heavy minerals in sediments and sedimentary rocks (Spears & Kanaris-Sotiriou, 1976). These are transported with the silt and fine sand fractions of marine sediments. Ti/Al ratios have consequently been used as a grain-size proxy (Boyle, 1983), suggesting that the assumption underlying the use of Ti as a general lithogenous index, namely its more or less uniform content in a wide range of crustal reservoirs, is more complicated than that of Al.

Discrete rutile and anatase crystals (TiO_2) were identified in Pacific pelagic sediments by Goldberg & Arrhenius (1958), who considered at least the anatase to be formed authigenically on the sea floor. This phase also forms authigenically in deeply weathered soils from dissolved Ti released from residual aluminosilicates (Walker, Sherman, & Katsura, 1969; Bain, 1976). Closer to volcanic islands and seamount chains in the North Pacific, Ti contents of the bulk sediments increase due to the derivation of augite, a well-known host for Ti, from basaltic rocks. Trace quantities of ilmenite ($FeTiO_3$) would also be expected from this source; and since Ti is hosted in biotite, amphiboles, pyroxenes and some clay minerals (Correns, 1969–1978) it is clear that Ti has multiple sources and hosts in marine sediments.

For these reasons, Al will be used as the lithogenous reference element in this chapter where data normalization is used to describe elemental variability.

4. Palaeoclimatic Records from the Sea Floor

Information on past climate changes has often been difficult to obtain from continental records because of the poor preservation of proxies on land, which are subjected to severe alteration by chemical and physical weathering and erosion. Although sedimentary sequences on the sea floor can be affected by erosion and redeposition, the deep-sea repository is generally more complete, and judicious selection of core sites can produce high quality, high-resolution records of climatic variations. Elemental data have been used to glean information on changing terrestrial climates, for example whether the source regions were relatively arid, humid or ice covered, by identifying specific sedimentary components that have been transported to ocean core sites via the atmosphere, by river runoff and by ice transport, respectively. This type of information on provenance comes predominantly from the lithogenous fraction of marine sediments. Provenance studies using mainly mineralogical data have a long history (Pettijohn, 1957; Milner, 1962a, 1962b), but considerable progress has been made more recently using elemental data from sedimentary rock sequences to acquire information on likely sources of components (Nesbitt & Young, 1982; Argast & Donnelly, 1987; McCann, 1991; McLennan et al., 1993; Nesbitt & Young, 1996; Nesbitt, Young, McLennan, & Keays, 1996; Hurowitz & McLennan, 2005).

The identification of the primary source or sources — igneous, metamorphic or sedimentary rocks — using elemental data is made difficult by changes introduced by chemical weathering coupled with the sorting of granular sediment masses during physical erosion and transportation. Unless source material has been subjected only to mechanical disaggregation (Nesbitt & Young, 1996), the eroded material carried to the oceans, by whatever transport mode, reflects the composition of the weathered mantle of the land surface, not the unaltered primary rocks (Kronberg, Nesbitt, & Lam, 1986; Nesbitt et al., 1996; Nesbitt & Young, 1997). However, chemical weathering — its intensity and compositional trends — depends on terrestrial climate, and it is that fact that allows elemental compositions of marine sediments to be used as recorders of climatic changes over geological time (Stewart, 1990; Visser & Young, 1990).

4.1. Aeolian Sediment Inputs

The realization that records of aeolian sedimentation can be obtained from marine sediments began with the work of Radczewski (1939), following earlier reports of wind-blown dust at great distances from coastlines (Darwin, 1846). Early work on the distribution of quartz (Rex & Goldberg, 1958) revealed distinct distributional patterns of abundance that could be related to modern wind directions, and that study ushered in a large number of investigations of the abundance of aeolian materials in pelagic sediments. In addition to mineralogical data, the grain-size distribution of the lithogenous fraction of marine sediments can be used to derive relative wind strengths (Parkin & Shackleton, 1973) on the assumption that more vigorous atmospheric circulation will transport larger particles (mineral and rock grains) to a given site of deposition. Thus, both mineralogical and textural approaches yield information on changes in arid land areas and on the relative aridity in sediment source regions.

Aeolian inputs to marine sediments can be tracked using geochemical proxies for sediment grain-size. Among such proxies, Si/Al, Ti/Al and Zr/Al ratios have been successfully used. Silicon occurs both as the basic building block of all aluminosilicates and separately as quartz (SiO_2). Quartz most commonly occurs in the silt and sand fractions of soils and sediments and sedimentary rocks, reflecting the average sizes of quartz grains in source rocks (Feniak, 1944). Quartz is highly resistant to chemical leaching, which, together with its hardness (7 on the Mohs scale) and lack of cleavage, causes the mineral to survive multiple cycles of erosion and deposition (Rankama & Sahama, 1950). Its abundance in sediments is roughly the same as its abundance in common igneous and metamorphic rocks (Blatt, Middleton, & Murray, 1980), attesting to its longevity (Rex & Goldberg, 1958).

Normalization of bulk Si contents to Al (see above) in lithogenous materials yields values that vary widely depending on the ratio of quartz to aluminosilicate phases in the sediments, and since quartz is on average always coarser than the clay minerals in sediment, the Si/Al ratio identifies coarser and finer-grained sections of ocean cores. Silicon also occurs, of course, in the opaline skeletons of diatoms, silicoflagellates and radiolarians; thus, corrections must be made in samples containing appreciable biogenous Si, using direct measures of opal or assuming an average lithogenous Si/Al ratio, if the bulk sediment Si/Al ratio is used as a grain-size proxy.

As previously discussed, Ti resides in both aluminosilicates as a substituent for some of the major elements and as discrete Ti oxide and silicate mineral phases. It is enriched in soils, especially laterites and bauxites, due to the formation of Ti oxides during weathering (Raman & Jackson, 1965; Dolcaster, Syers, & Jackson, 1970; Milne & Fitzpatrick, 1977). In the form of rutile (TiO_2), sphene ($CaTiSiO_5$) and ilmenite ($FeTiO_3$), Ti is carried in the silt and fine-sand fractions during particle transportation, accompanying slightly coarser quartz grains. Correns (1954), for example, found that Ti was enriched in the coarser fractions of pelagic North Atlantic sediments. Spears and Kanaris-Sotiriou (1976) showed that the Ti/Al ratio correlates closely with the total quartz content of a series of Carboniferous sedimentary rocks, and that only a small amount of Ti resides in the clay fraction where it substitutes for Al, Fe, Mn and perhaps Si in the lattices of a wide range of aluminosilicates (Correns, 1969–1978), especially biotite, but also amphiboles, pyroxenes and some clay minerals. In general, but not invariably, therefore, the Ti/Al ratio can be used as a grain-size proxy because the heavy minerals are the main Ti carrier in many sediments.

Zirconium occurs in sediments almost exclusively as the mineral zircon ($ZrSiO_4$), which has a hardness close to that of quartz, has no cleavage and is chemically resistant in the weathering profile (Sudom & St. Arnaud, 1971; Milne & Fitzpatrick, 1977). In primary source rocks it occurs in the very fine sand and silt fractions (Feniak, 1944), and, due to its higher specific gravity than quartz, it is transported with the fine and medium sand quartz grains. Like quartz, therefore, it survives recycling and accumulates in soils (Mason & Jacobs, 1998) and sediments (Dypvik & Harris, 2001). The geochemical behaviour of Zr therefore suggests that the Zr/Al ratio can be used as a grain-size proxy, and it has been applied in this way in a number of studies (e.g. Pedersen et al., 1992; Ganeshram, Calvert, Pedersen, & Cowie, 1999).

An increase in aeolian flux to a site in the eastern equatorial Pacific during Marine Isotope Stage (MIS) 2–4 relative to MIS 1 and the MIS 5 interstadials was detected using changes in the Ti/Al ratio (Boyle, 1983). This is consistent with a source of dust from the arid areas of northern South America lying west of the Andes (Prospero & Bonatti, 1969). Likewise, Shimmield and Mowbray (1991) used variations in Ti/Al (and Zr/Al, Cr/Al) in ODP cores in the northwestern Arabian Sea to track changes in monsoonal wind strength during the Late Pleistocene.

Modern Saharan aerosols, which are currently derived from the extensive dry lake beds in northern Africa (Stuut et al., 2005), can be transported across the North Atlantic as far as the Caribbean and Bermuda (Delany et al., 1967; Prospero & Bonatti, 1969; Glaccum & Prospero, 1980; Denison, Koepnick, Burke, Hetherington, & Fletcher, 1994). Immediately downwind of the Sahara, such material is coarser grained than the enclosing clay-rich sediment (Parkin & Shackleton, 1973; Parkin, 1974; Parkin & Padgham, 1975; Sarnthein, 1978; Sarnthein, Tetzlaff, Koopmann, Wolter, & Pflaumann, 1981; Sarnthein et al., 1982; Grousset et al., 1989), and this can be observed by downcore changes in Si/Al, Ti/Al and Zr/Al (Grousset et al., 1989) (Figure 1). The supply of wind-blown dust appears to have increased under glacial conditions when the areal extent and the aridity of the Sahara increased significantly (Chylek, Lesins, & Lohmann, 2001).

Changes in aeolian fluxes to the Mediterranean Sea on glacial–interglacial timescales can be tracked by Si/Al and Zr/Al ratios (Figure 2), which peak in the marls that were deposited between the sapropel events (Calvert & Fontugne, 2001). This reflects the establishment of more arid conditions in the Mediterranean borderlands that alternated with more humid conditions that led to the formation of the sapropels on a precessional timescale. As in the case illustrated in Figure 1, Ti/Al does not follow the increases in quartz (monitored using Si/Al, as biogenous silica is virtually absent at this site) and zircon (Zr/Al) in the marls, suggesting that it is only partly a grain-size proxy in this basin.

The clay mineralogy of atmospheric dust varies latitudinally, a reflection of the climatic control of clay mineral formation. Thus, kaolinite is the dominant clay mineral in dusts collected from low latitudes in the Atlantic Ocean, whereas illite is the most abundant clay species at higher latitudes (Chester, Elderfield, Griffin, Johnson, & Padgham, 1972). Thus, the clay mineralogy of atmospheric dust carries information on terrestrial climates, which is preserved in ocean archives.

4.2. Terrestrial Runoff and Precipitation Records

Elemental indices of grain-size changes have also been used to infer changes in terrestrial runoff and weathering regimes. Schmitz (1987b), for example, interpreted the increase in Ti content of Bengal Fan sediments through the Cenozoic as reflecting an increase in the supply of coarse-grained material from the

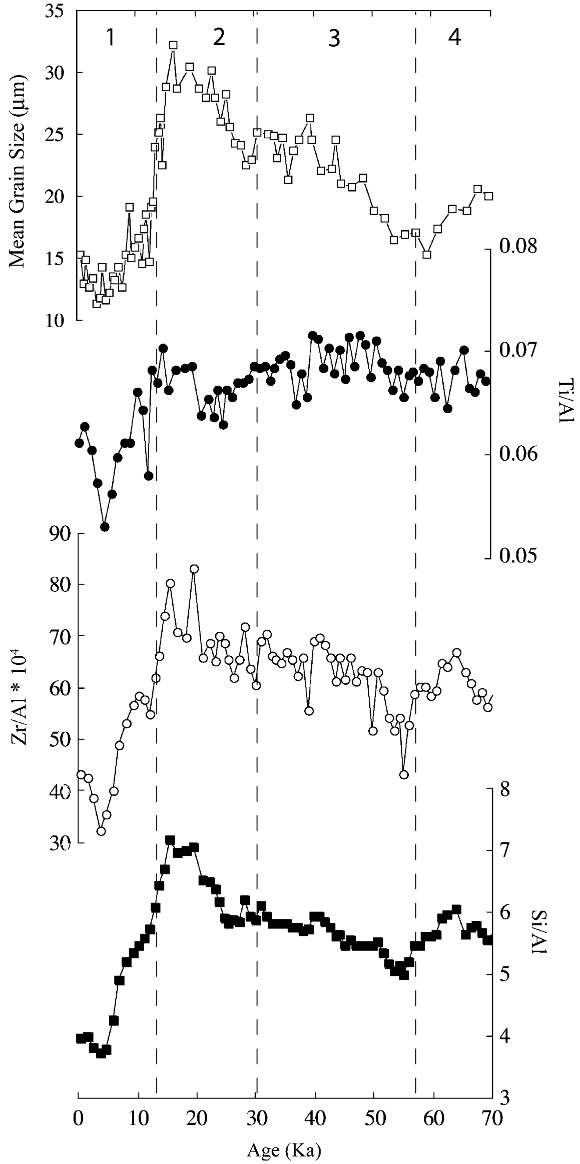


Figure 1 Temporal record of mean grain size (non-carbonate fraction), Ti/Al, Zr/Al & Si/Al changes over the last 70 kyr in core SEDORQUA 11 K (21.48°N, 17.95°W, 1,200 m depth) on the continental slope off Mauritania. Marine Isotope Stages (MIS) are indicated at the top of the upper panel. Data from Martinez et al. (1996). The larger mean grain-size in MIS 2 and the upper part of MIS 3 is closely mirrored by higher Zr/Al and Si/Al, reflecting higher contents of zircon and quartz, respectively, relative to aluminosilicate phases. Note that Ti/Al does not follow the grain-size trends as clearly, due to the location of Ti in aluminosilicates as well as in discrete titaniferous minerals.

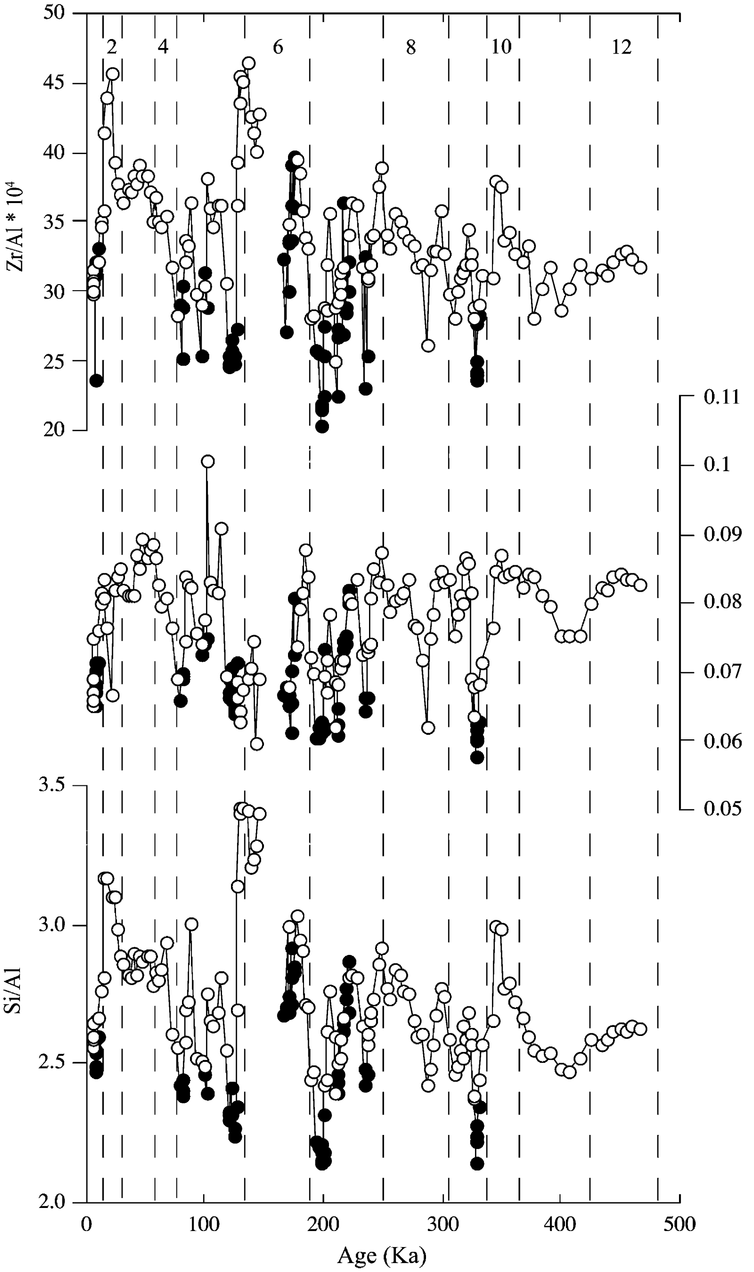


Figure 2 Temporal record of Zr/Al, Ti/Al and Si/Al over the last 480 kyr in core MD84641 (33.03°N, 32.63°E, 1,375 m depth) from the eastern Mediterranean. Data from Calvert and Fontugne (2001). Closed symbols are sapropel intervals, open symbols are marls. Zr/Al and Si/Al have similar downcore variations, reflecting the presence of coarser grained material in the marls and finer-grained sediment in the sapropels. Ti/Al is broadly similar, but there are significant deviations in MIS 2 and late Stage 6.

Ganges-Brahmaputra River system to the Bay of Bengal. This was supported by a strong curvilinear relationship between Ti content and grain size (settling velocity) in a size-fractionated Holocene varved clay. Thus, Schmitz used the Ti/Al ratio as a "palaeosteam indicator", interpreting the downcore changes in the ratio as recording the tectonic uplift of the Himalaya since the Late Miocene. The development of such a high mountain source region caused intensified monsoonal precipitation, led to the rejuvenation of river systems and intensified terrestrial denudation rates. Millennial-scale increases in Ti/Al and coherent increases in grain-size have also been identified in high-resolution cores from the NW European continental margin, reflecting in this case not tectonic effects but rather changing bottom water transport paths and/or winnowing (Kroon, Shimmield, & Shimmield, 2000).

Rubidium does not form discrete Rb mineral phases, but it substitutes readily for K in aluminosilicate minerals. The enrichment of Rb relative to K is greater in micas, especially biotite, compared with co-existing feldspars (Heier & Adams, 1963; Lange, Reynolds, & Lyons, 1966). In the absence of Al data, the K/Rb ratio has been used as a grain-size proxy in sedimentary rocks (Dypvik & Harris, 2001), Chinese loess sequences (Liu, Chen, Ji, & Chen, 2004) and in cores off north-west Africa (Matthewson, Shimmield, Kroon, & Fallick, 1995). Zr/Rb has likewise been used to track changes in sediment grain-sizes (Schneider, Price, Müller, Kroon, & Alexander, 1997), since on average Zr resides in coarser particles than does Rb.

Clay minerals are mainly formed by the hydrolytic decomposition of primary aluminosilicates during terrestrial weathering, which is principally controlled by the flow rate of water through the soil profile (Singer, 1979/80). This results in alteration of the primary minerals and the neoformation of new aluminosilicate frameworks. Different clay mineral species are therefore formed under different leaching regimes as governed by the prevailing precipitation. It follows that information on clay mineral assemblages could be used to reconstruct changes in terrestrial climate. Since clay mineral species have different elemental compositions, mineralogical changes will be reflected in the bulk lithogenous geochemistry of a given sediment.

The general sequence of clay mineral formation and stability has been summarized by Singer (1979/80), based on extensive earlier work. Given the same rock type, montmorillonite will form at the lowest precipitation rates, illite and vermiculite at intermediate rates and kaolinite/halloysite at the highest leaching intensities. This sequence reflects the extent of major cation (Mg, Fe, K, Na, etc.) retention (montmorillonite) or loss (kaolinite) from the weathering zone. The distribution of clay minerals in the Holocene sediments of the world ocean accords with latitudinal gradients in the intensity of land–surface weathering. Thus, kaolinite is the most abundant clay mineral in Holocene sediments of the eastern equatorial Atlantic (Griffin, Windom, & Goldberg, 1968) due to its derivation via river runoff from the deeply-weathered soils of the Niger and Zaire river basins. High kaolinite contents in Holocene sediments of the eastern Indian Ocean derive from the deflation of post-Miocene lateritic soils exposed in the interior of Australia. These "dead laterites" (Campbell, 1917) were formed under more humid conditions than those now prevailing. Illite is the most abundant clay mineral in the mid-latitudes of the Pacific and Atlantic Oceans, reflecting its derivation from the continents via rivers and the wind, where it forms both in soils and via long-term burial diagenesis in sedimentary sequences (Meunier & Velde, 2004). This material has K-Ar ages of hundreds of millions of years (Hurley, Heezen, Pinson, & Fairbairn, 1963), attesting to its strictly detrital nature. It is the dominant clay mineral in aerosols collected in the North Pacific (Arnold, Merrill, Leinen, & King, 1998). Montmorillonite is derived from lowland parts of river basins where leaching within the soil is minimal; its formation on the sea floor by the alteration of basaltic debris is inferred from its distribution and mineral associations in modern sediments (Griffin et al., 1968; Heath, 1969), but this has not been conclusively demonstrated. Iron-rich varieties of montmorillonite — nontronites — are probably formed on the sea floor from the reaction of dissolving biogenous silica and hydrothermal Fe oxyhydroxides (Hein, Yeh, & Alexander, 1979; Cole & Shaw, 1983; Cole, 1985). This is further discussed in Section 5.2.

Coherent downcore variations in Ti/Al, K/Al, Zr/Al and Rb/Al have been observed in cores located off large tropical drainage basins, where aeolian dust supply is minor. In cores off the Zaire River, for example (Schneider et al., 1997), changes in the relative abundances of kaolinite (with a high Al content) and feldspar (with a lower Al content) are thought to cause large variations in total Al contents, which drive the changes in the elemental ratios (Figure 3).

The mineralogical variations probably reflect past climatic changes in equatorial Africa, with kaolinite forming in soils during warm and humid periods when feldspar would also be less stable, and more feldspar surviving soil-forming processes during drier periods when kaolinite production decreased. The chemical and mineralogical data collectively suggest that African climate was warmer and more humid during the Holocene and MIS 5.1, 5.3, 5.5, 6.3 and 6.5. The Zr/Rb ratio in the same cores is highest when the other elemental ratios are lowest (thus, more Al-rich kaolinite) reflecting the enrichment of zircon relative to feldspar in deeply weathered soils. This climatic interpretation is supported by variations in clay mineral abundances off the Niger River (Pastouret, Chamley, Delibrias, Duplessy, & Thiede, 1978). Here, kaolinite is derived from well-drained lateritic soils in the humid equatorial climatic belt of Africa, whereas illite and smectite come from poorly-drained soils of the lower parts of the equatorial and tropical rivers; the relative abundance of these species in sediments off the Niger Delta records changes in the rainfall in this part of Africa over the last glacial–interglacial cycle. During MIS 2 and 3, the flow of the Niger River decreased and was able to deliver only illite- and smectite-rich material from its lower reaches to the offshore area, whereas during the Holocene increased precipitation augmented the supply of kaolinite from interior parts of the Niger drainage basin.

Climatically driven variations in river runoff from northern South America have been reconstructed from downcore changes in inferred major element contents of cores from the Cariaco Trench in the Caribbean. At ODP Site 1002 (Peterson, Haug, Hughen, & Rohl, 2000), downcore oscillations in the relative abundances of Ti and Fe, determined as count rates by a profiling X-ray fluorescence scanner (Jansen, Gaast, Koster, & Vaars, 1998), are considered to reflect changing input of fine-grained terrigenous siliciclastic sediment from the adjacent continental margin

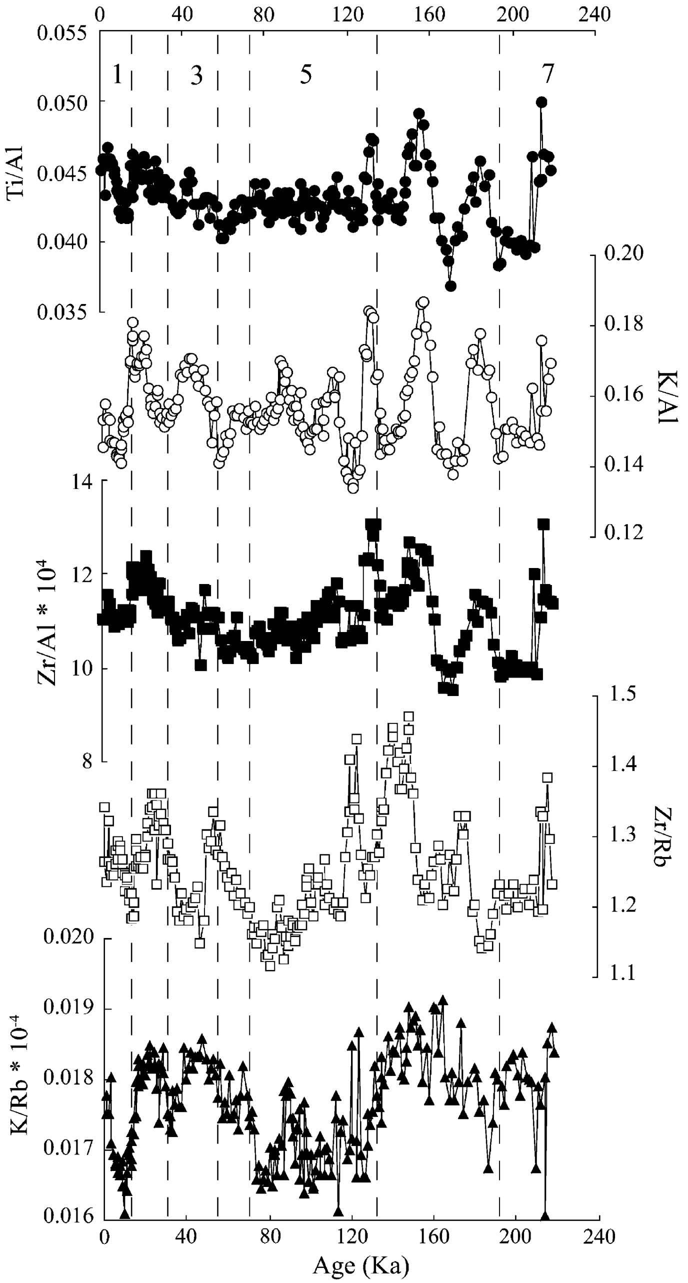


Figure 3 Temporal record of Ti/Al, K/Al, Zr/Al, Zr/Rb and K/Rb over the last 220 kyr in core GeoB 1083 in the eastern tropical Atlantic (6.58°S 10.32°E, 3,124 m water depth). Data from Schneider et al. (1997). Relative changes in Al, K and Rb at this site reflect the preferential enrichment of kaolinite (low K, high Al) in warm/humid intervals and the better survival of feldspar (high K/Al) during drier periods. Changes in Zr/Rb reflect the enrichment of zircon relative to feldspar in deeply weathered soils.

of Venezuela. Such oscillations are in turn likely to be driven by changes in rainfall and runoff from the watersheds of the local rivers, and are especially marked during MIS 3, when lower sea level and isolation of the Cariaco Basin from the Caribbean proper increased the importance of local sediment supply. Higher accumulation rates of the terrigenous indices (Ti and Fe) at Site 1002 coeval with the warm interstadial events in Greenland point to higher precipitation in northern South America at the same time.

A somewhat more complicated picture of sediment sources, and hence climatic changes, emerges from a more extensive set of quantitative elemental data from the same ODP site (Yarincik et al., 2000). Changes in K/Al and Ti/Al (used here rather than Al/Ti as in the original publication) are interpreted to reflect an increase in the relative proportions of kaolinite relative to illite (lower K/Al) during glacials, when local rivers supplied more kaolinite to a semi-isolated basin during lowered sea levels (Figure 4). At the same time, increased aeolian supply of Ti-rich dust from North Africa led to increases in Ti/Al. On the basis of this approach, the major element composition of the deposits has recorded changes in both riverine and

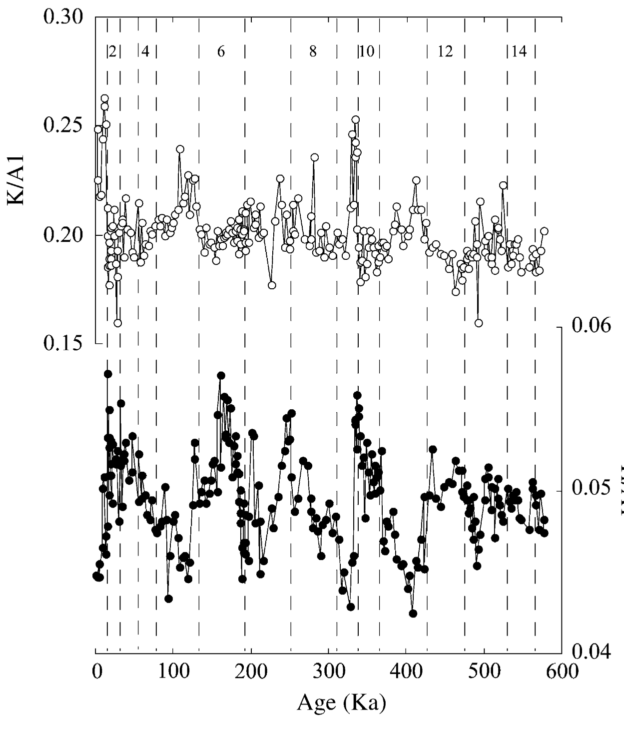


Figure 4 Temporal record of K/Al and Ti/Al over the last 590 kyr at ODP Site 1002, Cariaco Basin. Marine Isotope Stages are indicated at the top of the upper panel. Data from Yarincik et al. (2000). Changes in K/Al reflect an increase in the relative proportions of kaolinite relative to illite (lower K/Al) during glacials, when local rivers supplied more kaolinite to a semi-isolated basin during lowered sea-levels. Increases in Ti/Al point to increased aeolian supply of Ti-rich dust from North Africa led to increases in Ti/Al. These two proxies are anti-phased at this site.

aeolian sediment supply. The link to palaeoclimate is via increase in river flow and by implication increased rainfall, bringing more lithogenous detritus to the Cariaco Basin. In parallel, the enhanced atmospheric transport of dust implies greater aridity and/or increased wind speeds in the desert latitudes.

Similar changes in the proportions of lithogenous and biogenous components over the last 85 ka, possibly linked to changes in terrestrial climate, have been reported in cores recovered off central Brazil (Arz, Pätzold, & Wefer, 1998). As in the Cariaco Basin (Peterson et al., 2000), Ca abundances in the cores vary inversely with Fe and Ti abundances (as recorded by the XRF scanner technique), with higher lithogenous indices correlating with interstadial events in Greenland. The enrichments in lithogenous elements were interpreted as recording increased supplies of terrestrial detritus to the Brazilian margin during warmer periods due to an increase in precipitation in the Brazilian lowlands. However, ^{230}Th-normalized carbonate accumulation rates (François, Bacon, & Suman, 1990) in this part of the eastern Atlantic (Ruhlemann et al., 1996) varied by a factor of three over the last 180 kyr coherently with % $CaCO_3$, which is higher in MIS 1, 3, 5.1, 5.3, 5.5 and 6.5. Thus, variations in Fe and Ti are likely to reflect biogenous dilution and it will be necessary to obtain ^{230}Th-normalized lithogenous accumulation rates before it can be definitively concluded that detrital sediment supply from the adjacent land changed over this time period.

Higher resolution records of Fe and Ti abundances from the Cariaco Basin over the last 14 kyr (Haug, Hughen, Sigman, Peterson, & Rohl, 2001) show a marked decrease in inferred precipitation associated with the Younger Dryas (11.5 to 12.6 ka), smaller decreases during the Medieval Warm Period (0.7 to 1.05 ka), a large decrease during the "Little Ice Age" (0.55 to 0.2 ka), and a broad increase during the Holocene "thermal maximum" (5.4 to 10.5 ka). Such variability in the hydrological balance over northern South America, based on inferred runoff, is broadly coherent with similar variations throughout the tropical Atlantic (Hastenrath, 1985; Hodell et al., 1991; Hastenrath & Greishar, 1993; van der Hammen & Hoogheimstra, 1995; deMenocal, Ortiz, Guilderson, & Sarnthein, 2000). Latitudinal migration of the Intertropical Convergence Zone (ITCZ) appears to be the cause; this responds to seasonality of insolation at the precessional (21 kyr) periodicity (Haug et al., 2001).

4.3. Changes in Lithogenous Fluxes to the North Pacific during the Cenozoic

The history of lithogenous sediment supply to the North Pacific over the last 70 million years has been reconstructed from mineralogical and geochemical data obtained from a site (LL44-GPC) currently located in the pelagic clay province north of Hawaii (Leinen & Heath, 1981; Leinen, 1987, 1989; Kyte, Leinen, Heath, & Zhou, 1993). Two aeolian components have been identified on the basis of the mineralogy of this core, one originating from an easterly source by trade winds during the Palaeogene — possibly from North Africa — and the other originating from Asia via the westerlies during the Neogene. The change in composition reflects the progressive movement of the core site from low latitudes close to the East Pacific Rise to the central North Pacific Basin due to sea-floor spreading.

Further insights into the nature and sources of lithogenous supply to this site have been obtained from elemental data (Kyte et al., 1993). The low-latitude aeolian material was modeled as having an andesitic composition, whereas the more recent aeolian material is identical to quartz- and illite-rich wind-blown dust, and compositionally similar to average shale (Wedepohl, 1971). Figure 5 shows that Si/Al ratios are approximately constant over the last 30 Myr, whereas maxima in the ratio occur in the Late Cretaceous-Early Palaeocene and Eocene due to biogenic silica diagenesis (there are only rare radiolaria observed). Si/Al ratios in the post-Miocene deposits are lower than in Chinese loess (Taylor, McLennan, & McCulloch, 1983) because of loss of larger quartz grains during atmospheric transport from the source region(s); the ratio (mean $= 2.86 \pm 0.012$) reflects the admixture of clay minerals and quartz (Rahn, 1976). The Ti/Al ratio has a broad peak in the Oligo-Miocene when the site was closest to Hawaii during its movement north and westwards by sea-floor spreading. Ti concentrations in Hawaiian basalts can reach 12% by weight, and weathering of such rocks can account for the high ratio of Ti/Al in the mid-Tertiary deposits (Walker et al., 1969). K/Al and Rb/Al ratios show relatively high K and low Rb contents in the Cretaceous-Palaeocene, Early Eocene and Late Eocene-Early Oligocene sections of the core, implying silicic volcanism (Peterson & Goldberg, 1962). In the Miocene-Pliocene, Rb is enriched and K is depleted, possibly depicting a switch to higher illite contents (higher Rb, lower K) in Asian dust.

5. Metalliferous Sedimentation in the Ocean

Iron- and manganese-rich deposits accumulate on the sea floor by two processes. The first is the slow precipitation of poorly crystalline and amorphous oxyhydroxides from normal seawater, which yields *hydrogenous* deposits. These coat detrital and biogenous particles and are thoroughly dispersed within the bottom sediments, or they form discrete ferromanganese nodules and crusts on the sea floor that constitute large potential ore deposits. *Hydrothermal* processes comprise the second mechanism, and include the rapid deposition of sulphides, oxyhydroxides and the crystallization of authigenic clay minerals at mid-ocean ridge crests from hot, acidic waters that flow into bottom waters from hydrothermal vents (Boström & Peterson, 1966; Haymon & Kastner, 1981).

5.1. Hydrogenous Deposits

Hydrogenous ferromanganese oxyhydroxides occur as spheroidal and discoidal concretions that cover extensive areas of the ocean floor in all water depths, especially in areas of slow sedimentation, and as crusts and coatings on rock and mineral surfaces, especially on seamounts and similar topographic elevations throughout the ocean basins (Cronan, 1976). Both types of deposits are formed at

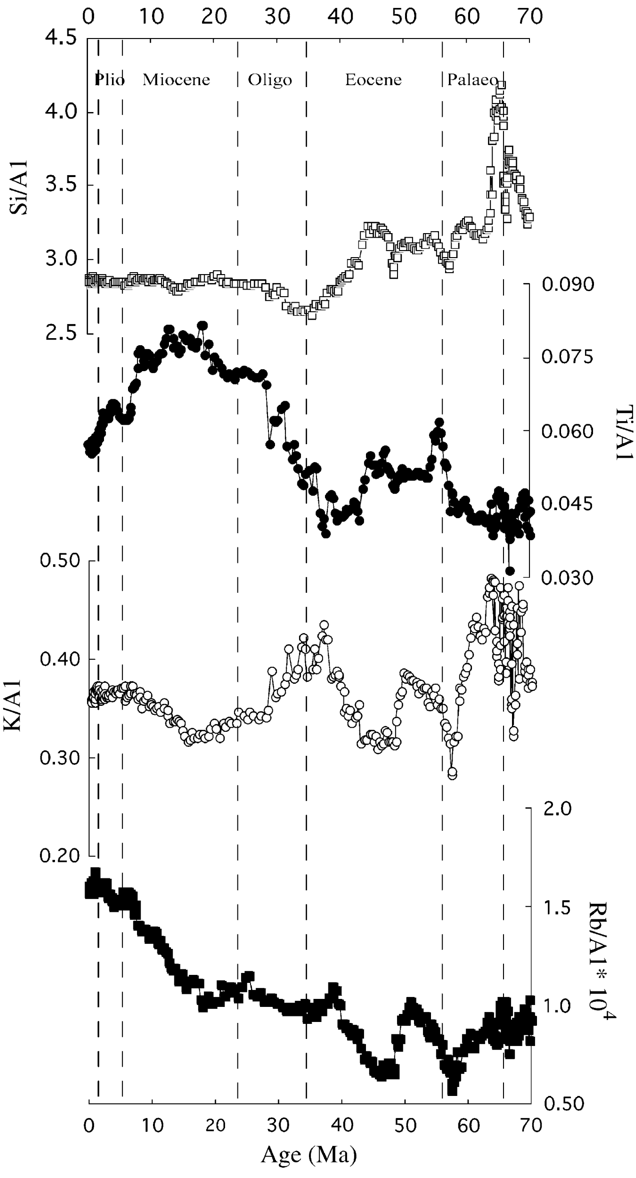


Figure 5 Temporal record of lithogenous proxies over the last 70 Myr in core LL44-GPC3, North Pacific. Data from Kyte et al. (1993). The roughly constant Si/Al ratios over the last 30 Myr record the supply of aeolian dust from the deserts of inland China, whereas maxima in the ratio in the Late Cretaceous-Early Palaeocene and Eocene probably reflect biogenic Si enrichment. Ti enrichment in the Oligo-Miocene has tracked the movement of the core site close to Hawaii during its movement north and westwards by sea-floor spreading. High K/Al and Rb/Al ratios in the Cretaceous-Palaeocene, Early Eocene and Late Eocene-Early Oligocene record silicic volcanism. In the Miocene-Pliocene, Rb enrichment and K depletion records a switch to higher illite contents in Asian dust.

rates ranging from <1 to >50 mm/Ma, significantly slower than the accumulation rate of the associated sediments (Ku, 1976). The nodules are therefore maintained at the sediment surface, probably by the activities of benthic organisms (Piper & Fowler, 1980), but they are sporadically found buried in the sedimentary section (Cronan & Tooms, 1967). Finely dispersed Fe and Mn oxyhydroxides are ubiquitous components of oxidized pelagic clays (Krishnaswami, 1976). Such phases are unstable under the reducing conditions normally encountered at depth in marginal and some deep-sea environments, so that they are only found in the sea-floor record in slowly accumulating deposits that have remained oxygenated since the deposits formed.

The abundance of ferromanganese nodules in the surface 2.5 m of the sediment column in gravity and piston cores from the central Pacific is roughly the same as the surface concentration (Cronan & Tooms, 1967). Deep-sea drilling has revealed that ferromanganese nodules, micro-nodules and crusts are common constituents of all slowly-accumulating pelagic sediments since the Late Cretaceous (Glasby, 1978, 1988), occurring preferentially on or close to hiatuses (Usui & Ito, 1994). They are mineralogical and chemically similar to modern nodules and crusts, and there is little evidence of post-depositional alteration of their compositions. This is in contrast to some nodules preserved in the geological record on land, where evidence of chemical and mineralogical alteration is found (Jenkyns, 1977; Margolis, Ku, Glasby, Fein, & Audley-Charles, 1978). The isotopic composition of Sr in the buried deep-sea deposits is closely similar to coeval seawater (Ito, Usui, Kajiwara, & Nakano, 1998), confirming the fossil nature of the nodules and that they are not slumped deposits from surface sediment horizons. In view of the fact that a decrease of dissolved oxygen content by 50–70% would have caused dissolution of the Mn phase of such deposits, the combined evidence suggests that the environmental conditions in most regions of the pelagic ocean, and in particular the oxygen content of bottom waters, have remained more or less constant for the last *ca.* 60 million years.

5.2. Records of Sea Floor Hydrothermal Inputs to the Ocean

Hydrothermal metalliferous sediments accumulate at mid-ocean spreading centres. The metals are derived from sub-sea floor rocks that are chemically altered by reaction with circulating seawater and are precipitated when hot solutions mix with cold, ambient seawater above the sea floor (Edmond et al., 1979a, 1979b). Sulphide chimneys and mounds form from sulphide- and metal-laden high-temperature hydrothermal waters close to vents (Bonatti, 1975; Haymon & Kastner, 1981). Fine-grained sulphide-rich particulates are deposited at greater distances from the ridge crests, and this material is subsequently oxidized when in contact with normal bottom waters (German et al., 1993). More widely dispersed poorly crystalline and amorphous Fe and Mn oxyhydroxides form when hydrothermal waters are cooled by rapid mixing with ambient oxygenated seawater (Boström & Peterson, 1966; Piper, 1973; Edmond et al., 1979a; Dymond, 1981). A wide range of metals and metalloids are coprecipitated or scavenged by the oxyhydroxides. In addition, poorly crystalline clay minerals form authigenically within the hydrothermal deposits (Dymond et al., 1973; McMurtry & Yeh, 1981; Haymon & Kastner, 1986). The degree of major element enrichment in ridge crest sediments can be seen in the exceptionally high Fe/Al, Mn/Al and Si/Al ratios in a transect across the East Pacific Rise (Figure 6). Similar relative enrichments of other metals and metalloids, including As, B, Cd, Cu, Ni, Pb, Tl and Zn, are found on other EPR transects (Piper, 1973). The enriched metals accumulate at significantly higher rates compared with hydrogenous sedimentation in the central ocean basins (Bender et al., 1971; Dymond & Veeh, 1975).

The hydrothermal sediments are buried beneath normal pelagic sediment when sea-floor spreading transports the newly-formed sea floor away from the ridge

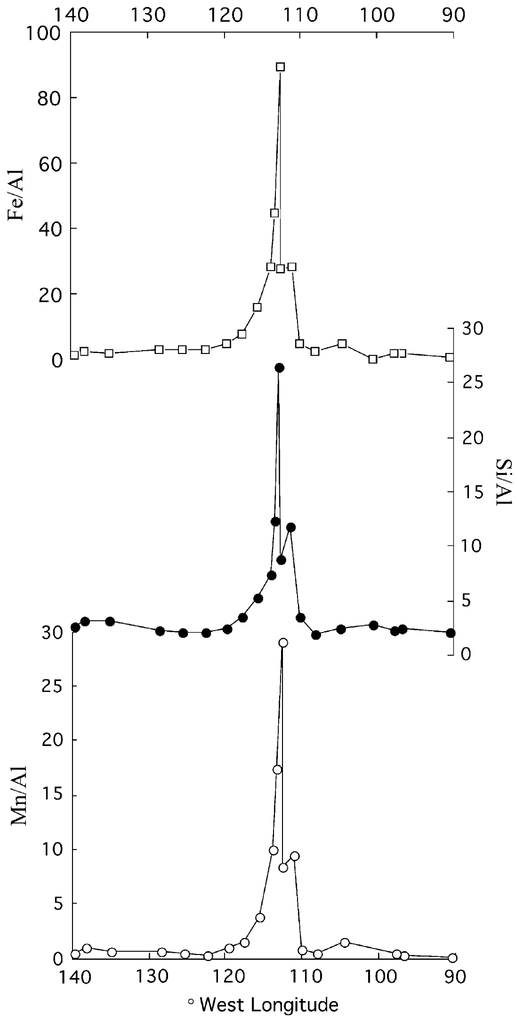


Figure 6 Longitudinal transect of metal enrichments in surface sediments across the East Pacific Rise. Data from Boström and Peterson (1969).

crests, so that all sedimentary sections in the ocean basins are floored by unique basal Fe- and Mn-rich deposits (Boström, Joensuu, Valdes, & Riera, 1972; Cronan et al., 1972; Dymond et al., 1973; Dymond & Corliss, 1977).

The history of metalliferous sedimentation in the North Pacific since the Late Cretaceous is shown by the record from core LL44-GPC discussed previously (Kyte et al., 1993). Fe/Al and Mn/Al maxima in the Cretaceous/Palaeocene and Eocene sections of the core reflect the accumulation of oxyhydroxides and Fe-rich smectite, as also recorded by maxima in Si/Al, formed when the site lay close to the East Pacific Rise (Figure 7). The smectites contain large amounts of Fe in octahedral positions, accounting for the low Al contents of the bulk sediments (Corliss, Lyle, & Dymond, 1978). Phosphorus maxima probably reflect adsorbed phosphate on volcanogenic Fe oxyhydroxides (Berner, 1973) as well as small amounts of insoluble fish debris (Doyle & Riedel, 1979). Maxima in As, Sb and V (not shown) coincide closely with the principal Fe/Al peaks, probably reflecting adsorption of the metal oxyanions on freshly precipitated Fe oxyhydroxides. The minor Mn maximum in the Oligocene section of the core records hydrogenous accumulation of oxyhydroxides, and is accompanied by high abundances of Co and Ni (not shown), two metals that are characteristically enriched in hydrogenous deposits throughout the Pacific.

6. Elemental Proxies for Palaeoproductivity

A variety of sedimentary proxies for estimating marine palaeoproductivity have been developed in an effort to assess, through time, the contribution of export production in the sea to the global carbon cycle, as well as the factors that promote the preservation of organic matter in marine deposits. The methods utilize microfossil assemblages, stable isotope ratios, biomarker distributions, the concentrations and/or burial fluxes of organic carbon and biogenous silica (opal), as well as several major and minor elements. All of these approaches when used in concert can provide critical insights into the production and preservation of biogenous materials in marine sediments that can then be related to other information on climate states, ocean circulation and environmental conditions at the sea floor.

6.1. Barium

Pelagic sediments of the equatorial Pacific are enriched in barium relative to crustal abundances (Revelle, 1944), the additional Ba occurring as barite ($BaSO_4$) (Goldberg & Arrhenius, 1958). Although these authors were not able to identify an organism responsible for secreting the barite, they nevertheless concluded that the euhedral barite crystals, such as those illustrated by Arrhenius (1963), formed authigenically in the sediment following the release of Ba from benthonic faecal pellets. They further concluded that such Ba enrichment reflects the higher productivity characteristic of the equatorial Pacific (Graham, 1941; Barber et al., 1996). Goldberg and Arrhenius (1958) also showed that the Ba/Ti ratio increased

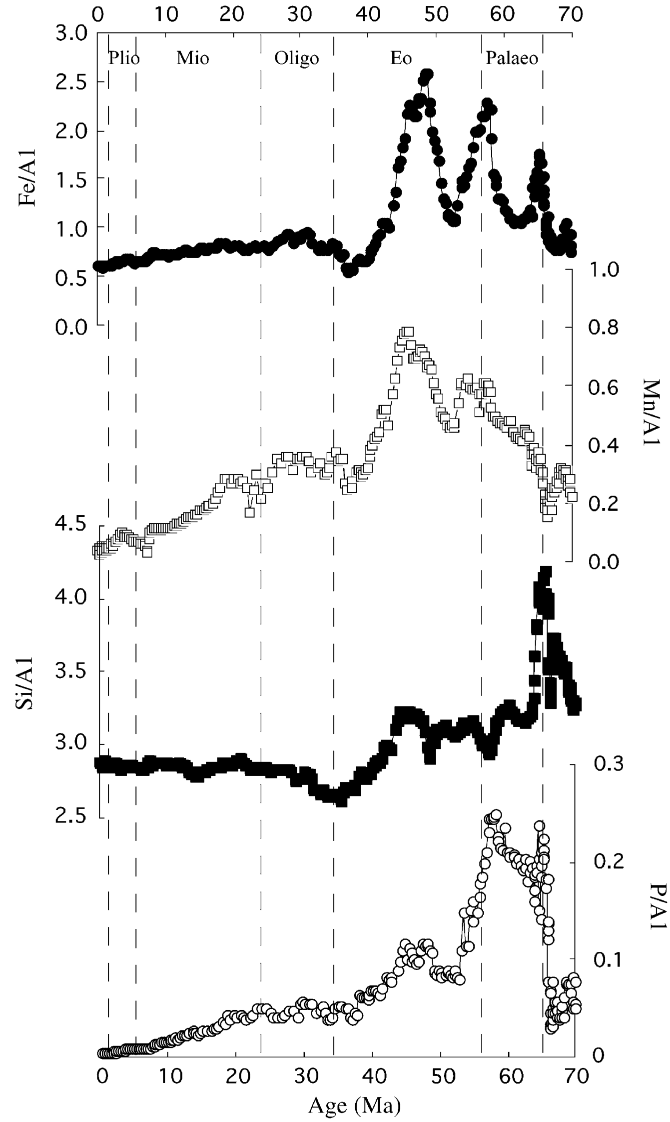


Figure 7 The Cenozoic history of metalliferous sedimentation in the North Pacific since the Late Cretaceous as recorded by the distribution of Fe/Al, Mn/Al, Si/Al and P/Al in core LL44-GPC from the North Pacific (30.32°N, 157.83°W, 5,705 m water depth). Data from Kyte et al. (1993). Hydrothermal inputs were high during the Cretaceous/Palaeocene and Eocene when there are Fe/Al, Mn/Al and Si/Al maxima. Phosphorus is enriched due to adsorption on volcanogenic Fe oxyhydroxides. The minor Mn maximum in the Oligocene section of the core records hydrogenous accumulation of oxyhydroxides.

during the last glacial in a Pacific core at 5°N, supporting the inferred glacial productivity increase (Arrhenius, 1952). Since these early discoveries, the variability of sedimentary Ba has become one of the most widely used proxies for palaeoproductivity.

Relatively high concentrations of discrete barite particles, on average 1 μm in diameter, occur in near-surface waters of the oceans (Dehairs, Chesselet, & Jedwab, 1980; Dehairs, Lambert, Chesselet, & Risler, 1987; Bishop, 1988; Dehairs et al., 1990; Dehairs, Stoobants, & Goeyens, 1991), and especially in areas of high new production (Dehairs, Baeyens, & Goeyens, 1992; Cardinal et al., 2005). The barite is mainly associated with biogenous aggregates in surface and near-surface waters, especially siliceous debris (Bishop, 1988), but occurs as free particles in deeper waters (Dehairs et al., 1990; Bertram & Cowen, 1997). Such barite particles constitute most of the suspended barite in the water column, although in some regions up to 50% of the standing stock of particulate Ba may be present in skeletal and organic debris. Since near-surface seawater is undersaturated with respect to barite (Monnin, Jeandel, Cattaldo, & Dehairs, 1999), precipitation of this phase requires the existence of microenvironments where concentrations of either dissolved Ba or sulphate are elevated, possibly in decaying organic matter (Chow & Goldberg, 1960). The possible direct biogenic formation of barite in the oceanic water column has prompted a search for the identity of Ba-secreting organisms. While some planktonic marine organisms do form barite intracellularly (Gayral & Fresnel, 1979; Rieder, Ott, Pfundstein, & Schoch, 1982), and xenophyophoria, giant benthic protozoa, also produce euhedral barite crystals within the protoplasm (Tendal, 1972; Gooday & Nott, 1982), no associations between barite and organisms has been described in plankton samples, and no excessive Ba enrichment has been found in modern plankton samples (Martin & Knauer, 1973). Laboratory culture experiments have shown that Ba can be removed from the solution during growth of a wide range of phytoplankton (Riley & Roth, 1971; Fisher, Guillard, & Bankston, 1991; Ganeshram, François, Commeau, & Brown-Leger, 2003) and a heterotrophic soil bacterium (Gonzales-Munoz et al., 2003) in proportion to the Ba concentration in the growth medium, but Ba is not incorporated in living cells (Sternberg, Tang, Ho, Jeandel, & Morel, 2005). Barite microcrystals are only formed during the decay of phytoplankton cultures in the dark (Ganeshram, Pedersen, & Murray, 1992), consistent with their formation in microenvironments within decaying masses of organic matter suspended in near-surface waters (Chow & Goldberg, 1960; Bishop, 1988). However, the culture conditions frequently employed in such experiments evidently cause Ba to be removed by Fe hydroxide scavenging on (organic) particle surfaces, rendering the interpretation of many laboratory results equivocal (Sternberg et al., 2005).

Barium is also incorporated into other biogenous phases in ocean waters, notably acantharian celestite ($BaSO_4$ is isostructural with $SrSO_4$) (Bernstein, Byrne, Betzer, & Greco, 1992) where it can constitute up to 0.5% by weight (Arrhenius, 1963). Acantharian tests are completely solubilized in the upper water column, however, rendering this vector an insignificant source of biogenic Ba in marine sediments.

The settling flux of Ba through the oceanic water column, as measured by moored sediment traps, is tightly correlated with organic carbon flux out of surface waters, changing seasonally with total primary production (Dymond, 1985; François, Honjo, Manganini, & Ravizza, 1995; Jeandel, Tachikawa, & Dehairs, 2000; Balakrishnan Nair, Ittekkot, Shankar, & Guptha, 2005). Below *ca.* 1,500 m water depth, the settling flux of Ba increases while that of organic carbon decreases due to the microbial degradation of organic matter and the additional formation of barite in settling particles. Away from regions of significant terrestrial organic matter supply, $C_{organic}/Ba$ ratios decrease in a predictable manner in all ocean basins, providing a basis for using Ba fluxes for palaeoceanographic reconstructions of past productivity variations (Dymond, 1985; François et al., 1995; Fagel, Dehairs, Peinert, Andre, & Antia, 2004).

As well as barite microcrystals, Ba in marine sediments is hosted in several other phases, notably lithogenous material derived from crustal rocks, and biogenous debris, both skeletal material and degraded soft tissue produced in the ocean. The insoluble nature of barite leads to its high degree of preservation in slowly-accumulating sediments — constituting a "dissolution residue" (Dymond, 1981) — which have not been subjected to reducing conditions (see below). In aluminosilicates, Ba mainly occurs in K-feldspars and micas, where it substitutes isomorphically for K (Puchelt, 1969–1978). Various attempts have been made to correct total Ba contents of sediments for the contribution from such lithogenous sources in order to arrive at estimates of the abundance of biogenous Ba. Normalization to Al (Section 3) is a common method, combined with estimates of the Ba/Al ratio of average crustal rocks or of the aluminosilicate debris in a specific sediment sample. Alternatively, a correction for aluminosilicate contributions has been made by reference to the total K content (Schneider et al., 1997). A secure knowledge of the Ba content of associated mineral phases or the bulk lithogenous material is required in order to derive measures of excess or biogenous Ba (Reitz, Pfeifer, de Lange, & Klump, 2004). Direct determination of the barite content of sediments, either by means of chemical extraction (Paytan, Kastner, & Chavez, 1996) or by direct enumeration using electron microscopy/X-ray spectrometry (Robin et al., 2003), circumvents some of the problems inherent in correction procedures when the Ba content of the other carrier phases is poorly constrained.

Barium is enriched in Plio-Pleistocene sediments beneath the equatorial upwelling zone of the Indian Ocean, but Palaeocene-Eocene sections of deep sea drilling project (DSDP) cores lying north of this productive zone at present are similarly enriched, suggesting that the accumulation of excess or biogenous Ba has tracked the northward movement of the Indian Plate beneath the equatorial region during the Neogene (Schmitz, 1987a). Sedimentary opal concentrations are also significantly higher in the Ba-enriched sections of the cores, supporting the inference that Ba accumulates together with skeletal planktonic material in marine sediments. Similar Ba enrichments in higher-resolution sections from the Atlantic, Pacific and Southern Oceans that are also variably enriched in opal and organic carbon have also been identified, and used to study changes in ocean production on glacial–interglacial timescales. Thus, using the Ba proxy, productivity appears to have been higher during glacial (Matthewson et al., 1995; Gingele, Zabel, Kasten, Bonn, & Nurnberg, 1999), interglacial (Shimmield, 1992; Shimmield, Derrick, Mackensen, Grobe, & Pudsey, 1994; Bonn, Gingele, Grobe, Mackensen, & Fütterer, 1998) or both glacial and interglacial intervals (Rutsch et al., 1995; Schneider et al., 1997; Thomson et al., 2000) of deep ocean cores, pointing to the modulation of ocean productivity by glacial–interglacial climate changes. In the Antarctic region, higher productivity is found during relatively ice-free interglacial stages, whereas in the central Arabian Sea, interglacial maxima in production record increased nutrient supplies via upwelling of more vigorously circulating intermediate and Antarctic Bottom Waters. These changes occur on the eccentricity and obliquity (ice-volume) frequencies rather than the precessional frequency that would be expected based on the low-latitude insolation forcing of coastal upwelling in the coastal Arabian Sea. In contrast, biogenous Ba enrichments coherent with organic carbon maxima are observed at approximately 21 kyr intervals on the Zaire Fan in the eastern equatorial Atlantic (Rutsch et al., 1995; Schneider et al., 1997), showing that productivity variations occur at the precessional frequency at this low-latitude site (Figure 8). This pattern is not replicated by the variations in opal content in the same core, suggesting that siliceous plankton is not the main carrier of the barite in this region.

Palaeoproductivity estimates for the equatorial Pacific using the Ba and other inorganic geochemical proxies (see Sections 6.2 and 6.3) have been controversial. The well-expressed cycles of $CaCO_3$ content in the Swedish Deep-Sea Expedition cores were initially taken to reflect changing glacial–interglacial productivity, with a superimposed effect of carbonate dissolution (Arrhenius, 1952, 1959). Although carbonate dissolution was thought to have increased during glacial stages due to enhanced flow of Antarctic Bottom Water, greatly increased production levels were invoked to explain the carbonate-rich glacial horizons in the equatorial cores. Subsequent studies (Berger, 1973) have emphasized variations in sea-floor preservation as controlling the carbonate cycles, and indeed it is now known that the depth of the lysocline has fluctuated markedly on glacial–interglacial timescales (Farrell & Prell, 1989). However, the change in carbonate saturation required to produce the observed carbonate cycles is quite large, and variable carbonate supply (production) appears to be a better explanation (Archer, 1991). In addition, invariant foraminiferal preservation indices in cores collected above the lysocline which also show marked carbonate cycles also argue for variations in production (Adelseck & Anderson, 1978). Similar sets of issues (production vs. preservation) have been encountered with the use of organic carbon (Emerson & Hedges, 1988) and biogenous opal (Archer, Lyle, Rodgers, & Froelich, 1993) for palaeoproductivity reconstructions, so that application of another palaeoproductivity proxy to this problem may provide independent evidence for changes in glacial–interglacial production in the oceans.

The settling flux of Ba intercepted by moored sediment traps is highest on average within five degrees of the equator at 140°W (Dymond & Collier, 1996), coincident with the highest primary production rates (Barber et al., 1996) and water column organic matter fluxes (Honjo, Dymond, Collier, & Manganini, 1995). Likewise, Ba is enriched in the surface sediment at the equator, although the peak in Ba content is much more narrowly centred on the equator compared with

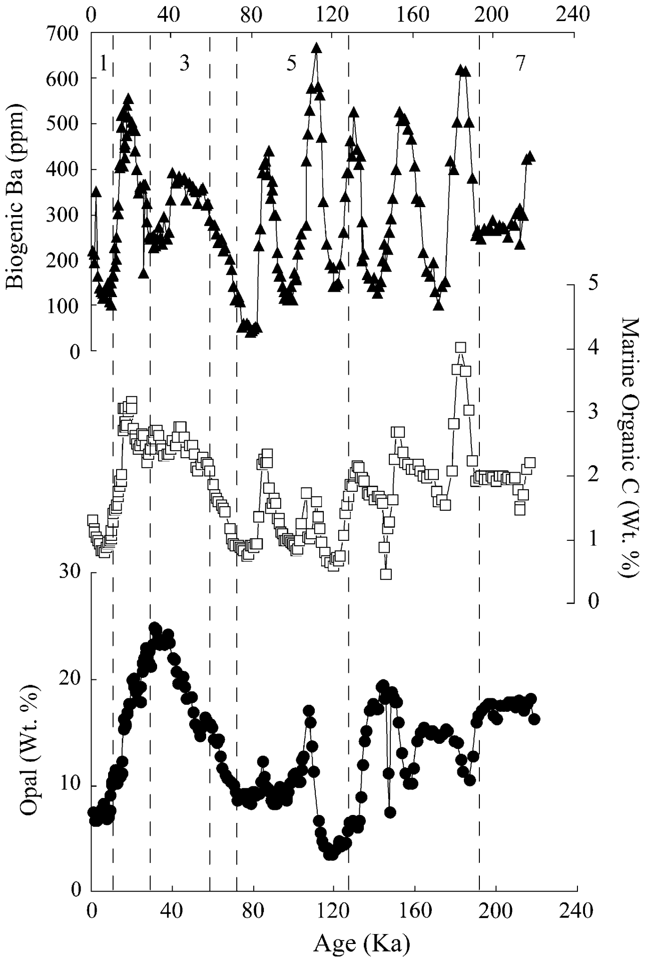


Figure 8 Temporal record of biogenous Ba, marine organic carbon (MOC) and opal over the last 230 kyr in core GeoB 1083 from the Zaire Fan, eastern tropical Atlantic. Data from Schneider et al. (1997). MOC was derived from total organic carbon values using the C isotopic composition of the bulk sediment and a mixing equation. Biogenous Ba, derived by subtracting aluminosilicate Ba from total Ba using the Ba/K ratio in crustal rocks, fluctuates coherently with MOC, with higher values in MIS 2, 3, 5 and 6. Opal values show increases in MIS 2, 3, 5 and 6, but they are not coherent with Ba or MOC.

the water column settling fluxes. The accumulation rate of barite in the surface sediment also peaks at the equator (Paytan et al., 1996) as does the bulk sediment Ba/Ti and Ba/Al ratio (Murray & Leinen, 1993; Murray, Knowlton, Leinen, Mix, & Polsky, 2000) (Figure 9). Thus, biogenic barium is enriched in Holocene equatorial sediments.

Estimates of the accumulation rate of Ba in surface sediments have been combined with sea surface primary production determinations to construct productivity algorithms for estimating palaeoproductivity (Dymond, Suess, & Lyle, 1992;

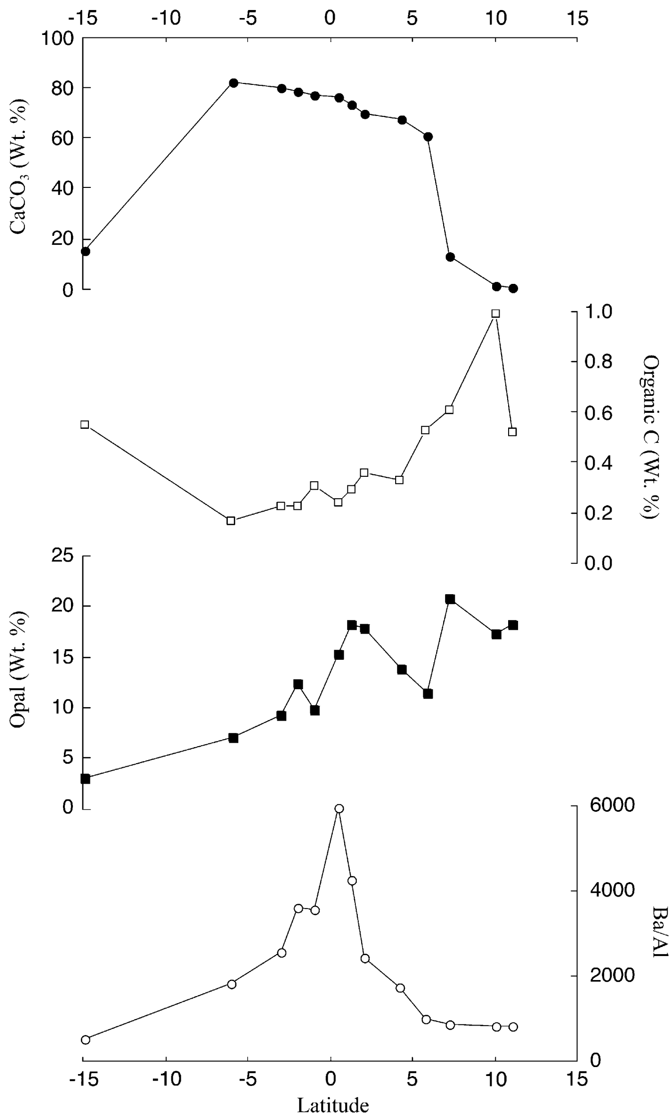


Figure 9 Distribution of $CaCO_3$, opal, Organic C and Ba/Al in surface sediments across a north-south transect in the central equatorial Pacific (data from Murray and Leinen, 1993).

François et al., 1995; Paytan et al., 1996), and these have been widely applied to long core sections recovered throughout the oceans (Gingele & Dahmke, 1994; Bonn et al., 1998; Gingele et al., 1999; Klump, Hebbeln, & Wefer, 2001). The widespread evidence for syndepositional focusing in deep-sea sediments (Marcantonio et al., 2001), including the Holocene sections of many equatorial Pacific cores (François, Frank, Rutgers van der Loeff, & Bacon, 2004; Loubere, Mekik, François, & Pichat, 2004; Kienast, Kienast, François, Mix, & Calvert, 2007, in press), renders such algorithms unreliable because the sediment-derived Ba accumulation rates (both barite and excess Ba) of many of the cores used for this estimate are too high by unknown factors.

This problem can be appreciated by examining the glacial–interglacial records of barite and bulk sediment barium enrichment and accumulation in piston cores from the central equatorial Pacific (Paytan et al., 1996; Murray et al., 2000). Barite concentrations are highest in both glacial and interglacial stages when $CaCO_3$ contents are lowest, reflecting variable carbonate dilution of insoluble barite (Figure 10). Conversion of these data to accumulation rates, using the stratigraphically derived linear sedimentation rates, reveals clear maxima in glacial stages MIS 2–8, and also in MIS 11, coherent with the barite content. The use of sediment accumulation rates derived in this way is likely to exaggerate these glacial increases in the accumulation rates if significant sediment focusing during the glacials has occurred (Frank et al., 1995; Frank, Gersonde, Rutgers van der Loeff, Kuhn, & Mangini, 1996; Marcantonio et al., 2001; François et al., 2004; Anderson & Winckler, 2005; Winckler, Anderson, & Schlosser, 2005). The barite maxima in low carbonate intervals (MIS 6, 8 and 10) due to lowered dilution by this major phase together with the inflated sedimentation rates caused by focusing in the glacial intervals produces sharp barite accumulation rate maxima that are more likely artifacts. Correction for focusing using $^{230}Th_{excess}$ shows that there has been no significant increase in glacial productivity in the equatorial Pacific west of the Panama Basin using the abundance of barite as a palaeoproductivity proxy (Marcantonio et al., 2001), consistent with observations using $^{231}Pa/^{230}Th$ (Pichat et al., 2004), benthic foraminiferal transfer functions (Loubere, 1999, 2000) and ^{230}Th-normalized sediment fluxes (Loubere et al., 2004).

Similar changes in glacial and interglacial palaeoproductivity in the Atlantic sector of the Southern Ocean south of the polar front but higher glacial Ba accumulation north of the polar front are also revealed by applying radionuclide constant flux tracers to derive true vertical fluxes of Ba (Nürnberg, Bohrmann, Schlüter, & Frank, 1997; Frank et al., 2000). In view of these considerations, the relative Ba enrichment in bulk sediments in the equatorial Pacific core appears to be a better proxy for changes in palaeoproductivity because both Ba and Al are diluted to the same extent when carbonate content changes. Broad maxima in Ba/Al ratios occur in MIS 2–3, 6, 7, 8, 9/10 and 11/12, which are not coherent with the sharp maxima in the barite accumulation rate, themselves artificially elevated by carbonate dissolution and sediment focusing.

Downcore Ba records can be compromised by the post-depositional loss of accumulated barite in suboxic sediments (McManus et al., 1998; McManus, Berelson, Hammond, & Klinkhammer, 1999) and especially in anoxic sediments in which either minimal (van Os, Middelburg, & de Lange, 1991; Schenau, Prins, deLange, & Monnin, 2001) or significant sulphate depletion (Brumsack & Gieskes, 1983; Brumsack, 1989; van Os et al., 1991; Von Breymann, Emeis, & Suess, 1992) has occurred. For this reason, barium records in many continental margin settings — where relatively high organic matter accumulation leads to lower redox potentials at shallow depth — do not record palaeoproductivity changes (Shimmield et al., 1994; Ganeshram et al., 1999). Direct measurements of Ba efflux from and

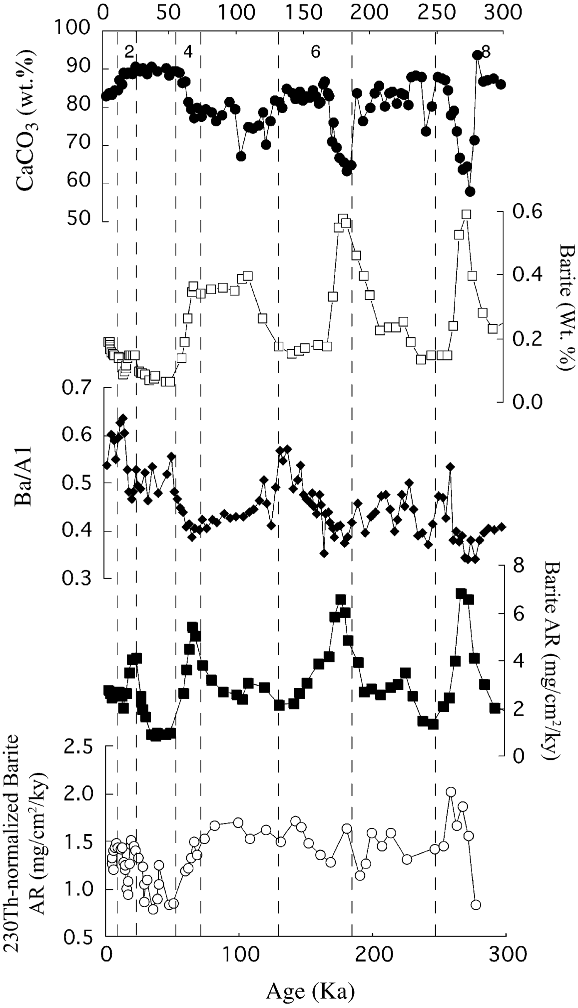


Figure 10 Temporal record over the last 280 kyr of % CaCO3, % barite, Ba/Al, and the barite accumulation rate, estimated using the stratigraphically derived mass accumulation rate (Paytan, 1995) and the ^{230}Th-normalized mass accumulation rate to correct for winnowing/focusing (François et al., 2004) in core TT013-PC72 from the central equatorial Pacific (0.11°N, 139.40°W, 4,298 m depth). Carbonate, Ba, and Al data from Murray et al. (2000), and barite data from Paytan (1995).

dissolved pore water Ba enrichment in sediments underlying the California Current (McManus, Berelson, Klinkhammer, Kilgore, & Hammond, 1994), the Arabian Sea and the equatorial Pacific (Paytan & Kastner, 1996; McManus et al., 1998) show that Ba is remobilized within suboxic sediments, as well as anoxic sediments, even though pore-water sulphate depletion is not detected. Evidently, sulphate reduction occurs in microenvironments in many oxic and suboxic settings (Berelson et al., 1996), and this leads to dissolution of some of the deposited barite. The concurrent determination of solid-phase U and Ba contents of a sediment core can be used to screen out those sites that have had significant post-depositional Ba remobilization (McManus et al., 1998) because U is known to become enriched in sediments under suboxic conditions (Anderson, 1982; Klinkhammer & Palmer, 1991). Uranium concentrations can therefore be used as a proxy for high rates of diagenetic organic matter oxidation and hence vertical organic flux to the sea floor (Kumar et al., 1995; Anderson et al., 1998). This aspect of U geochemistry is discussed in Section 7.2.1.

6.2. Phosphorus

Phosphorus is a limiting macro-nutrient for algal growth, along with fixed nitrogen, in many parts of the modern ocean, and its accumulation in marine sediments has been used as a palaeoproductivity proxy. Organically bound and skeletal P is exported from the surface ocean in biogenous particles and aggregates and is diagenetically recycled within accumulating sediments and, together with a relatively small amount of organic P, may become fixed in an inorganic phosphate mineral phase and adsorbed by Fe oxyhydroxides.

The relative abundance of different forms of sedimentary P has been estimated by selective chemical extractions (Ruttenberg & Berner, 1992). These show that in most deep-sea sediments the major phosphorus-bearing component is francolite (or carbonate fluor-apatite: $(Ca, Mg, Na)_5(PO_4, CO_3)_3(F, OH)$). This phase also accumulates within modern nearshore and continental shelf settings (Ruttenberg & Berner, 1993), and occasionally forms enriched deposits in highly productive regions (Burnett, 1977; Price & Calvert, 1978; Baturin & Bezrukov, 1979; Schuffert, Kastner, & Jahnke, 1998; Schenau, Slomp, & DeLange, 2000). Subsequent winnowing of the deposits on some shelves concentrates the phosphatic materials into concentrated phosphorite beds (Baturin, 1971), which resemble some of the giant phosphorite ores in the geological record. A minor amount of P in unconsolidated marine sediments is retained in refractory organic matter, fish debris (Suess, 1981) or is adsorbed by authigenic Fe oxyhydroxides (Froelich, 1988). The latter phase is reductively dissolved during burial under suboxic and anoxic conditions (see Section 7), the released P potentially precipitating as francolite.

The phosphorus originally delivered to sediments is evidently preserved — even though the organic material which it partly constitutes is largely degraded diagenetically — by "sink switching" (Ruttenberg & Berner, 1993), namely the loss of P from organic association and the subsequent precipitation of francolite. This phase, together with fish debris (biogenous P), is included in an operationally defined authigenic/biogenous fraction soluble in dilute acetic acid (pH 4). The accumulation of organic P can therefore be tracked by the distribution over time of organic and authigenic/biogenous P (Filippelli & Delaney, 1995) or total P (Murray et al., 2000), since these components together generally constitute $>70\%$ of total P.

A record of palaeoproductivity from the burial of P from the highly productive continental slope off northwestern Mexico (Figure 11) shows that phosphogenesis, and hence productivity, was higher in interglacial stages compared with the glacials over the last 130 kyr (Ganeshram, Pedersen, Calvert, & François, 2002).

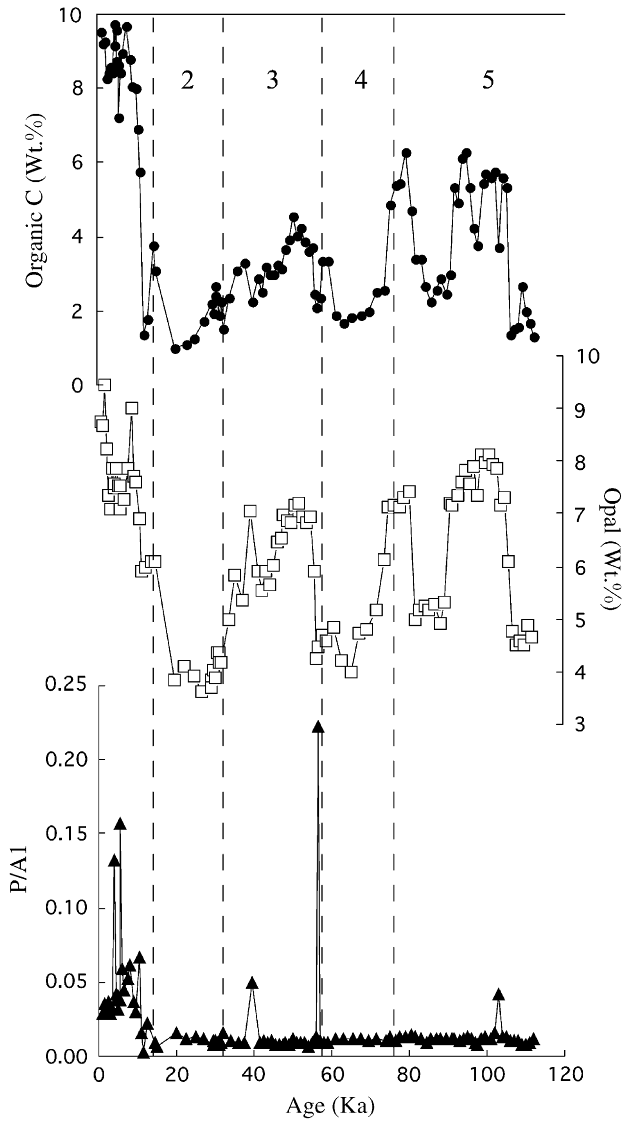


Figure 11 Temporal record of organic C, opal and P/Al over the last 114 kyr in core NH15P (22.68°N 106.48°W, 425 m water depth) from the northwestern Mexican slope (Ganeshram et al., 2002) show that phosphogenesis, and hence productivity, was higher in interglacial stages compared with the glacials over the last 130 kyr, as also recorded by organic C and biogenous silica contents.

Phosphorus enrichments at this site are coherent with other palaeoproductivity proxies, namely organic C and biogenous silica contents, and with the N isotopic proxy for higher water column denitrification. The accumulation of biogenous P is also higher during interglacials off the Peru margin (Burnett, 1980; Garrison &

Kastner, 1990) and in the Arabian Sea (Schenau et al., 2000) where the relationship with carbon burial and $\delta^{15}N$ is also similar, suggesting that the oceanic cycles of N and P are closely coupled on glacial–interglacial timescales (Ganeshram et al., 2002).

In contrast to the sedimentary records from productive continental margins, the record of P burial in the central equatorial Pacific appears to show increases in glacial stages compared to interglacial stages (Figure 12). The correspondence between the P/Al and Ba/Al ratios is strong and coherent with the $CaCO_3$ record, lending support to the suggestion that the fluctuations in $CaCO_3$ content at least partly reflect productivity variations.

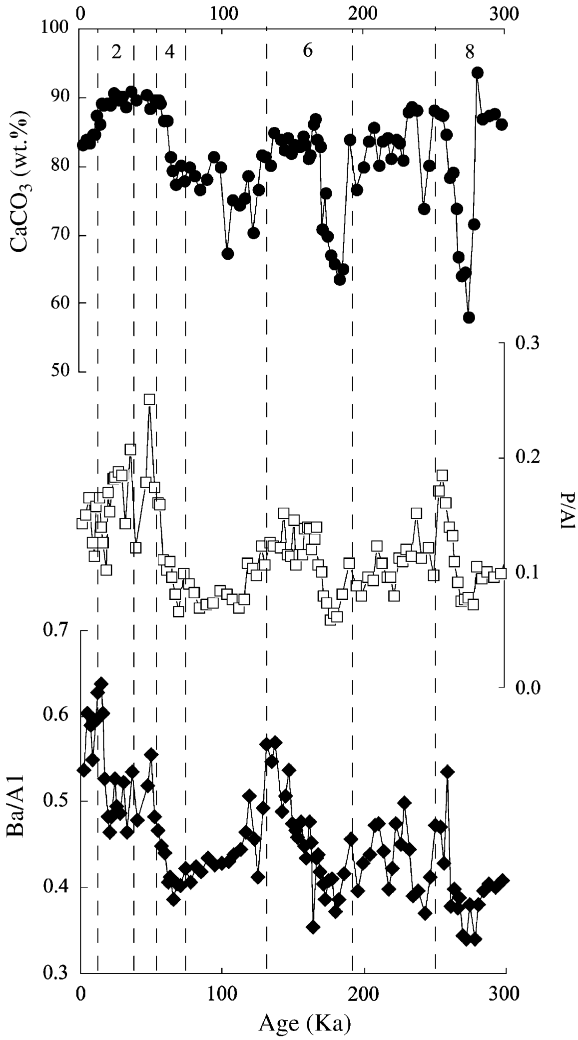


Figure 12 Temporal record of $CaCO_3$, P/Al and Ba/Al over the last 300 kyr in core TT013-72PC PC72 from the central equatorial Pacific (0.11°N, 139.40°W, 4,298 m water depth) showing P and Ba increases in glacial stages compared with interglacials. Data from Murray et al. (2000).

6.3. Aluminium

Surface sediments in the central equatorial Pacific are enriched in Al relative to Ti, Al/Ti ratios being significantly higher than whole crust (~16) or upper crustal values (~27) (Murray et al., 1993; Murray & Leinen, 1996). This enrichment parallels the markedly higher settling fluxes of biogenous debris on transects across the equator (Figure 13), and has been ascribed to preferential adsorption (scavenging) of Al relative to Ti by settling particles (Orians & Bruland, 1986), overwhelmingly comprising organic matter, $CaCO_3$ and opal in the equatorial Pacific (Honjo et al., 1995). Since the flux of particles is greatest close to the equatorial divergence due to the higher productivity (Chavez & Barber, 1987), the Al enrichment is directly related to organic particle flux, and has therefore been used as a proxy for productivity (Murray et al., 1993; Murray & Leinen, 1996).

Multivariate statistical analysis of the composition of the settling material on the 140°W transect suggests that the excess Al is largely associated with opal and that this component carries most of the Al to the sea floor (Dymond et al., 1997). This is consistent with reports of the biological removal of dissolved Al from seawater (Moran & Moore, 1988) and the presence of significant amounts of Al in diatom frustules in some bottom sediments (Van Bennekom, Jansen, Van der Gaast, van Iperen, & Pieters, 1989). Sedimentary Al/Ti ratios could therefore be used to track the accumulation of opal in the ocean, making this parameter a specific proxy for siliceous productivity.

Further investigation of the relationship between Al and Ti contents of the trapped particles yields a highly variable picture (Dymond et al., 1997). Although Al/Ti ratios are higher than upper crustal values close to the equator, the ratios fall below this value to the north and south (Figure 14). Moreover, significant non-zero intercepts on the Al axis in regressions of Al on Ti are only found at 5°N and 5°S; at the other stations on this transect, including moorings at the equator and 2°N and

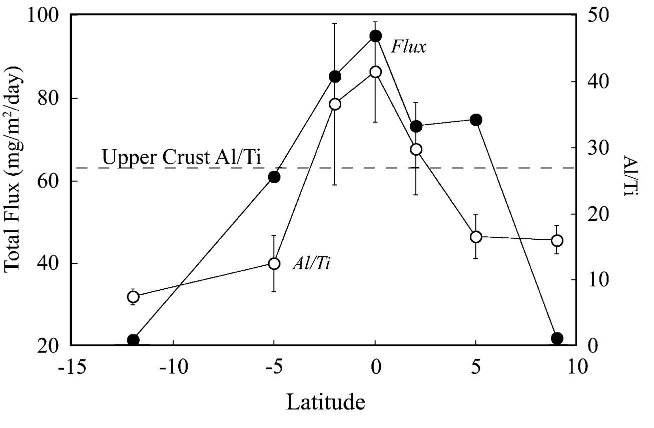


Figure 13 Total settling flux of particulate material (Honjo et al., 1995) and the Al/Ti ratio of bulk sediment trap material (Dymond, Collier, McManus, Honjo, & Manganini, 1997) at US JGOFS moorings across the equator at 140°W. Locations and depths of the traps are given in Table 1.

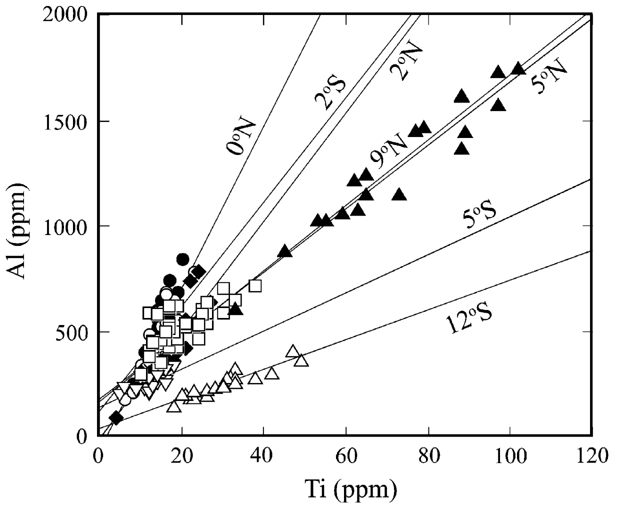


Figure 14 Regressions of Al on Ti for sediment trap samples from a trans-equatorial Pacific mooring transect at 140°W (Dymond et al., 1997). Model II regressions (Ricker, 1984). Intercepts are different from zero only for the moorings at 5°N and 5°S. Slopes of the regressions (Table 1) give the Al/Ti ratios of the settling material (aluminosilicate plus opal) that is added to the "excess" amounts of Al at these sites.

Table 1 Regressions Coefficients for Al and Ti Contents of Sediment Trap Samples from the US JGOFS Trans-Equatorial Mooring Transect at 140°W.

Latitude	Trap depth (m)	Slope	Intercept	r^2
9°N	2,250	16.03±2.1	126.28±156.0	0.93
5°N	2,100	16.63±3.3	143.17±79.6	0.81
2°N	2,200	29.84±7.0	−74.77±124.6	0.74
0°N	2,284	41.50±7.6	−100.55±106.7	0.85
0°N	3,650	45.56±12.1	−134.32±190.0	0.66
2°S	3,593	36.57±12.2	−53.78±182.8	0.46
5°S	2,316	12.55±4.2	94.64±54.3	0.52
12°S	1,292	7.50±1.2	26.83±38.2	0.87

Source: Dymond et al. (1997).

2°S, there is no significant amount of excess Al in the particles, but the slopes of the regressions are variable (Table 1). The nature of the regressions (a non-zero intercept at some stations and variable slopes) imply that there are at least two particle fractions in addition to any excess scavenged Al in the settling material (Timothy & Calvert, 1998), possibly aeolian dust (Murray et al., 1993) and opal (Dymond et al., 1997), and that the proportions of this additional material are site specific. This may be related to the position of the ITCZ at 4°N and the equatorial divergence where the highest production is observed.

Systematic downcore variations in Al/Ti close to the equator ranging from upper crustal values to values similar to the surface sediment values suggest that the Al enrichment carried by particles is preserved in the bottom sediment, even though some of the biogenous phases dissolve or are recycled (Murray et al., 1993). In the unique situation where the sediment is composed overwhelmingly (>99%) of biogenous phases, as in this particular case, Al is a poor proxy for aluminosilicate debris, and is the reason for the selection of Ti as a proxy for terrigenous aluminosilicate debris in this region.

As in the case of settling particulate material (Figure 14), downcore variations in Al and Ti contents are also strongly linearly correlated, with a variable non-zero intercept that represents the excess Al content (Timothy & Calvert, 1998). This relationship is best interpreted as the addition of aluminosilicate material with a more or less constant Al/Ti ratio to an aluminous sediment component that is devoid of Ti. This additional component could be scavenged Al, as originally hypothesized (Murray et al., 1993), Al originally incorporated in opaline shells (Van Bennekom et al., 1989; Dymond et al., 1997) or an aluminous phase that forms diagenetically in the sediment (Mackin & Aller, 1984). It is not possible to choose between these possibilities with our current understanding of Al geochemistry of biogenous sediments.

The downcore distribution of Al/Ti in the central equatorial Pacific over the last 300 kyr (Figure 15) shows that the ratios are generally higher where the $CaCO_3$ content is high (MIS 3–4, 6, 7), although the correlation is not strong. Such a postulated relationship suggests an increasing importance of excess Al in lithogenous-poor samples. However, regression analysis of the Ti and Al values shows that excess (or "scavenged") Al (Murray & Leinen, 1996) contributes 177 ± 58 ppm Al to the sediments at this site, a minor component at most core depths. The Al enrichments in the carbonate-rich sections of this core have been interpreted as support for the carbonate variations being due primarily to productivity fluctuations (Murray et al., 1993). However, the changes in Al/Ti correlate poorly with either the Ba/Al ratio or the ^{230}Th-normalized barite accumulation rate in the same core (Figure 15). Thus, the higher excess Al contents at this site do not correlate with other palaeoproductivity proxies.

7. Proxies for Redox Conditions at the Sea Floor and in Bottom Sediments

Many trace and minor elements accumulate in the solid phase of marine sediments as a result of post-depositional precipitation or adsorption from the bottom waters or from pore waters. These processes are primarily controlled, in turn, by redox reactions in response to the oxidative decomposition of deposited organic matter (Froelich et al., 1979). The reactions proceed in a well-defined sequence (Figure 16) during which oxidants are consumed and reduced species accumulate in the pore waters. Some trace metals that have multiple valency states at Earth surface conditions may be enriched as a consequence of such reactions,

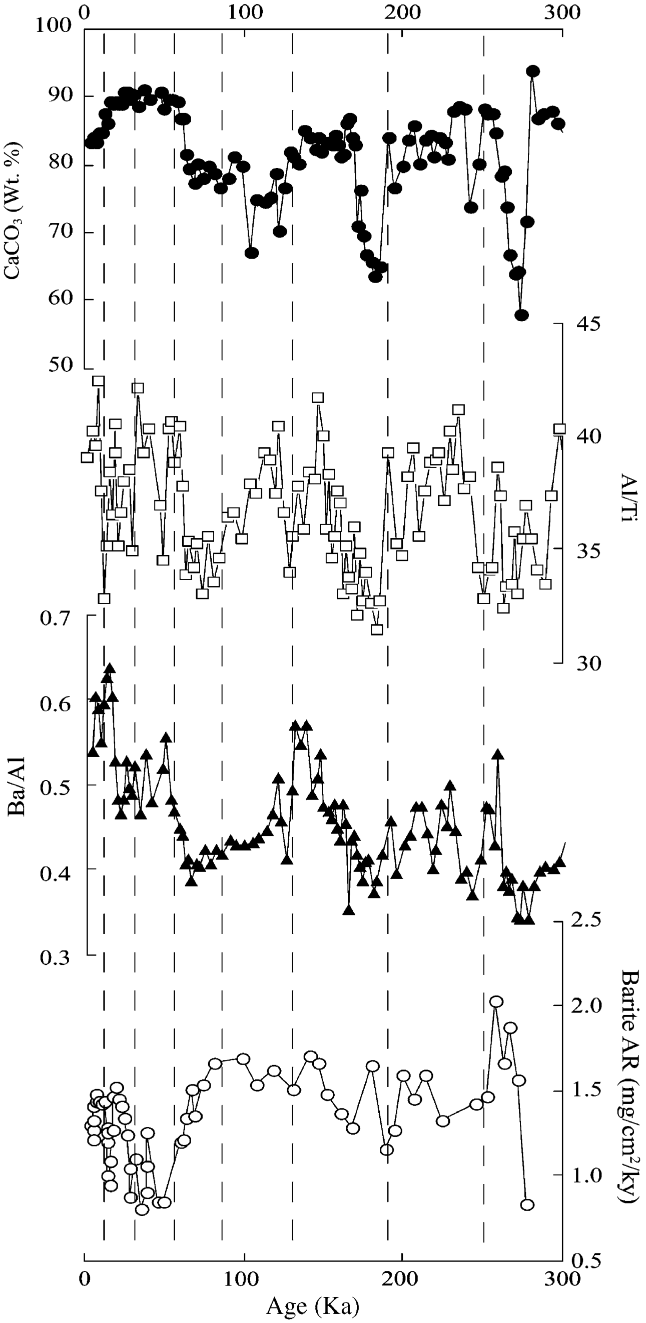
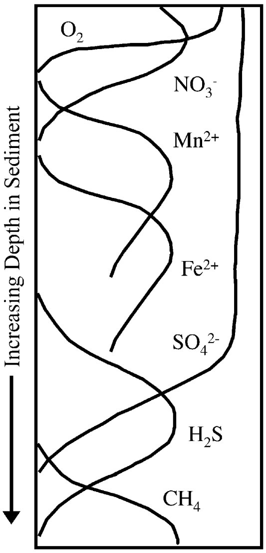


Figure 15 Temporal record of % $CaCO_3$, Al/Ti, Ba/Al (data from Murray et al., 2000) and the ^{230}Th-normalized accumulation rate of barite (Marcantonio et al., 2001) over the last 280 kyr in core TT013-PC72 (0.1°N, 139.4°W, 4,298 m water depth). Al/Ti is generally higher where the $CaCO_3$ content is high (MIS 3–4, 6, 7), but the changes in Al/Ti correlate poorly with either the Ba/Al ratio or the ^{230}Th-normalized barite accumulation rate in the same core.



1. *Aerobic Respiration*
   $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \rightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O$

2. *Nitrate Reduction*
   $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 94.4HNO_3 \rightarrow 106CO_2 + 55.2N_2 + H_3PO_4 + 177.2H_2O$

3. *Manganese Reduction*
   $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236MnO_2 + 472H^+ \rightarrow 236Mn^{2+} + 106CO_2 + 8N_2 + H_3PO_4 + 366H_2O$

4. *Iron Reduction*
   $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 424FeOOH + 848H^+ \rightarrow 424Fe^{2+} + 106CO_2 + 16NH_3 + H_3PO_4 + 742H_2O$

5. *Sulphate Reduction*
   $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} \rightarrow 106CO_2 + 16NH_3 + H_3PO_4 + 53S^{2-}$

6. *Methanogenesis*
   $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 16NH_3 + H_3PO_4 + 53CH_4$

Figure 16 Schematic portrayal of the vertical sequence of oxidation-reduction reactions in marine sediments. Microbial consortia utilize the oxidants O_2, NO_3^-, Mn(IV), Fe(III) and SO_4^{2-} to metabolize buried organic matter, as shown by the idealized reactions on the right, formulated following Richards (1965) and Hartmann, Müller, Suess, and van der Weijden (1973) which are ordered sequentially (1–6) either by the decreasing free energy yield for each mole of carbon oxidized (Froelich et al., 1979) or by the physiological requirements of the respective microbial consortia (McCarty, 1972). Downcore profiles on the left depict the concentration gradients of the pore water constituents that are monitors of these reactions. Adapted from Eganhouse and Venkatesan (1993).

contributing to the *authigenic* fraction of the sediments. Such enrichment occurs either because the elements have different solubilities in oxygenated or oxygen-deficient seawater or are partitioned between the solid and solution phases to different extents under different redox conditions. Other metals are precipitated as sulphides within sediments in the presence of dissolved H_2S species produced by reduction of seawater sulphate when it is used as an oxidant during microbial organic matter degradation. Sedimentary records of relative enrichments and depletions of such authigenic metals and metalloids have been used to study both the geochemical behaviour of the elements in the ocean as well as the chemical state of ocean waters and bottom sediments in the past. This has been made possible by the rapid advances over the last two decades in our understanding of the biogeochemistry of trace and minor elements in the ocean, as summarized by Bruland & Lohan (2003).

Elements with variable valency can be added to accumulating sediments in three ways: (i) by diffusion from bottom waters and subsequent precipitation or adsorption; (ii) by release to pore waters from degrading organic matter followed by precipitation or adsorption; and (iii) by dissolution of a solid phase and subsequent fixation within the deposits. These vectors therefore contribute a "marine fraction" of elements to sediments (Piper, 1994) or "excess" metals over and above those supplied in detrital minerals and rock fragments. The proportion of such metals in a given sediment sample can be determined by correcting the total content for the likely contribution from lithogenous sources, taking into account the chemical composition of marine planktonic organic matter (Martin & Knauer, 1973; Collier & Edmond, 1984; Brumsack, 1986). The balance between organic sources and seawater sources will, of course, vary widely depending on the flux of organic matter to the sea floor, the sedimentation rate of the deposit and the redox conditions of the bottom water and the sediment. In many situations, organic sources of authigenic trace elements are dominant for Ag and Cd, whereas seawater itself dominates as a source for Mo, Re and U; Cr, V, Ni, Cu and Zn appear to fall between these two extremes (Piper, 1994; Piper & Medrano, 1994; Piper & Isaacs, 1995).

As indicated previously, trace and minor elements whose behaviours are most likely to be different under oxic and anoxic marine conditions fall into two categories. The first includes those elements whose valency can vary as a function of the prevailing redox potential. Included in this group are: Mn, which forms a highly insoluble oxyhydroxide where oxic conditions prevail; I, which, as the iodate ion, has a strong adsorptive affinity for organic matter in the presence of oxygen; and Cr, Mo, Re, U and V, which occur as highly soluble anionic species in oxic waters but are reduced to reactive or insoluble species of lower valency under anoxic conditions. The second category includes elements whose valency does not change, such as Ag, Cd, Cu, Ni and Zn, but which form highly insoluble sulphides and are usually removed from solution in the presence of H_2S. Study of the geochemistry of these groups of metals in sedimentary rocks has a long history, and has contributed significantly to the understanding of the environment of formation of sedimentary metalliferous ores (Maynard, 1983; Coveney & Glascock, 1989; Parnell, Ye, & Chen, 1990; Jones & Manning, 1994). The relative degrees of enrichment and depletion of the trace elements in oxic, reducing and anoxic deposits to be discussed in this section are summarized in Figure 17.

Because the authigenic accumulation of many metals occurs in reducing sediments, their enrichments have been used to infer conditions, both in the water column and in bottom sediments, that were more reducing in the past. Water column anoxia, and therefore surficial sedimentary anoxia, occurs where the rates of consumption of dissolved oxygen and other oxidants exceed their rates of replenishment and the large reservoir of sulphate in seawater becomes the dominant oxidant. This may occur in coastal basins where the ventilation of deep waters is restricted by a topographic barrier, or at intermediate water depths in the open ocean when ventilation is slow and oxidant demand is high due to a high settling flux of organic matter from the sea surface. Examples of the former category include the Black Sea, the Cariaco Trench and several high-latitude fjords (Richards, 1965), whereas larger areas of intermediate depth waters in the eastern Pacific and the Arabian Sea are examples of the second category (Brandhorst, 1959; Naqvi, Noronha, & Gangadhara Reddy, 1982; Naqvi, 1987). In addition, metals may also be sequestered authigenically where the rate of accumulation and burial of particulate organic matter (a higher organic rain rate) exceeds the rate of replenishment of dissolved oxygen from bottom waters by diffusion or irrigation, even

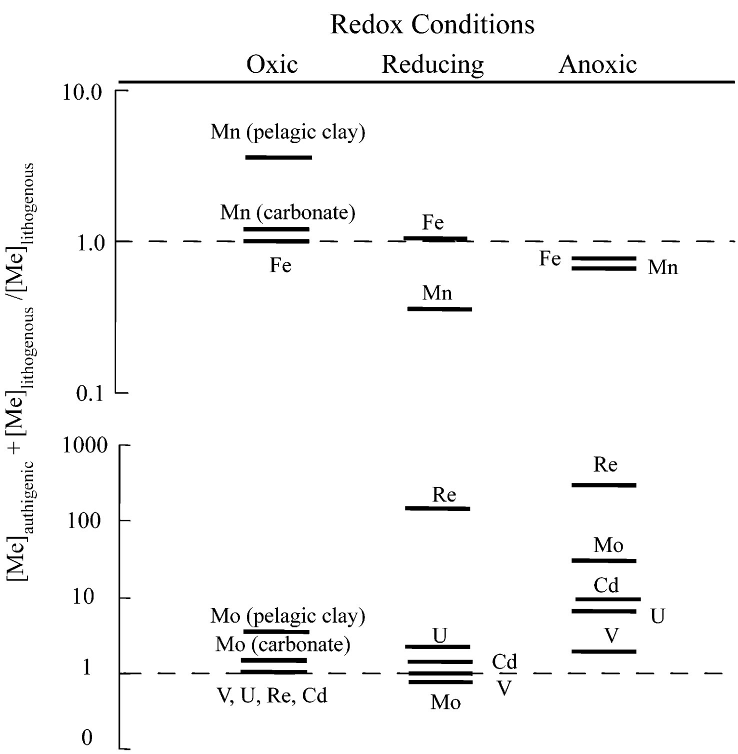


Figure 17 Enrichment and depletion factors for redox-sensitive metals in marine sediments (from Morford & Emerson, 1999). Iodine is omitted from this figure because its content in lithogenous detritus is poorly known (but probably very small).

though the bottom waters are fully oxygenated. This situation prevails in large areas along continental margins; the surficial sediments are oxic, but they become anoxic (sulphidic) at a variable depth below the sediment/water interface due to the microbial utilization of oxygen, nitrate and Fe and Mn oxyhydroxides during organic matter degradation, after which H_2S is produced as a byproduct of bacterial sulphate reduction (Figure 16).

Authigenic metal enrichments in sediments may therefore be used to infer anoxic bottom water conditions in the past, or a higher burial flux of organic matter, and hence higher productivity, in the past. In both cases, enrichments are directly due to the redox status of the depositional environment, but in the latter case the enrichments constitute an indirect proxy for productivity.

7.1. Proxies for Oxic Conditions of Sedimentation

7.1.1. Manganese

Manganese occurs as the Mn(II), Mn(III) and Mn(IV) valency states in Earth surface environments. The species Mn^{2+} and $MnCl^{+}$ are the principal soluble forms in seawater, but Mn(II) is thermodynamically unstable in the presence of oxygen and is sluggishly oxidized to insoluble Mn(III) and Mn(IV) oxides. Dissolved manganese is normally enriched in surface waters, reflecting the input of Mn as oxyhydroxide coatings on sediment particles and its partial release into solution. The element is scavenged throughout much of the oceanic water column below the mixed layer (Bender, Klinkhammer, & Spencer, 1977). An intermediate-depth Mn maximum occurs in the Oxygen Minimum Zone (OMZ) wherever oxygen concentrations fall below 100 μM probably reflecting reductive dissolution of settling particulate Mn oxyhydroxides or the lateral transport of dissolved Mn that has diffused out of anoxic shelf and slope sediments (Klinkhammer & Bender, 1980).

Dissolved Mn(II) accumulates in the deep sulphidic waters of anoxic basins due to the reduction of Mn(IV) oxides that settle into the deeper waters from oxic waters above the redox boundary (Spencer & Brewer, 1971). A particulate concentration maximum is found immediately above the boundary, and this is formed by the oxidative precipitation of upward-diffusing Mn^{2+} from the anoxic waters. Manganese is thus actively recycled between oxidized and reduced forms across a redox boundary, whether that boundary be in a water column or in sea-floor deposits.

As discussed in Section 5.1, manganese is concentrated over its crustal abundance in sediments of the deep ocean (Murray & Irvine, 1895) and in surficial sediments on many continental margins (Figure 17), where it occurs as MnO_2 and MnOOH, collectively referred to as Mn oxyhydroxides (Grill, 1982; Kalhorn & Emerson, 1984; Murray, Balistrieri, & Paul, 1984). Its enrichment in pelagic sediments (Goldberg & Arrhenius, 1958) is due to the slow accumulation rates of terrestrial and biogenic detritus relative to the precipitation of authigenic Mn under oxic conditions (Krishnaswami, 1976). Manganese is preserved in pelagic sediments due to the very low settling fluxes of organic matter (Suess, 1980). The combination of the limited flux and the typically refractory nature of organic material at abyssal depths in the ocean ensures that oxic conditions are maintained to great depth in the bottom sediments.

In continental margin environments, where accumulation rates of organic matter are much higher, oxygen is completely consumed at relatively shallow depths during aerobic oxidation of labile organic matter, and under these conditions Mn recycles between surface and subsurface horizons (Figure 18). Burial of surface oxyhydroxides transports Mn(IV) into the subsurface reducing environment where it dissolves. Manganese(II) concentrations are therefore commonly much higher in the pore waters of such sediments immediately below the oxyhydroxide horizon. Dissolved Mn diffuses downwards into the sediment and upwards into the overlying oxic horizon where it is reprecipitated. This “zone refining” of Mn (Froelich et al., 1979) leads to surficial solid-phase Mn concentrations in hemipelagic and nearshore sediments that are often much higher than they are in pelagic sediments.

In spite of the accumulation of dissolved Mn in the bottom waters of anoxic basins, the concentrations of Mn, even in the presence of relatively high alkalinity, are insufficient for the precipitation of Mn(II) solid phase (i.e. $MnCO_3$) in the water column or underlying sediments. Hence, fully anoxic deposits — i.e. those that accumulate under oxygen-free bottom waters — characteristically have solid-phase Mn concentrations that are controlled entirely by the aluminosilicate fraction

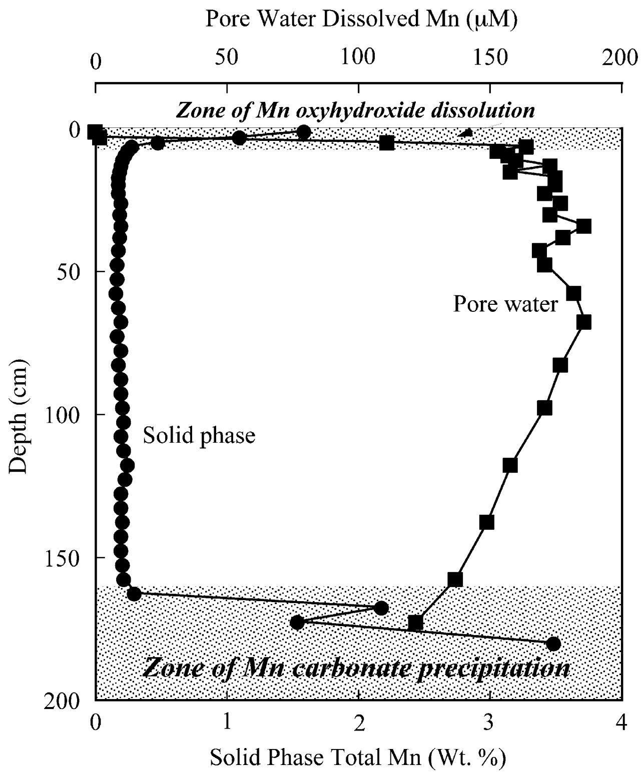


Figure 18 Downcore distribution of pore water and solid phase total Mn in core P8 from the Panama Basin (4.62°N, 82.99°W, 2,700 m water depth). Elevated solid phase Mn in the uppermost part of the core occurs as finely dispersed oxyhydroxides, which have accumulated from the oxidative precipitation of upwardly diffusing dissolved Mn, whereas the marked increase at the base of the core reflects the presence of authigenic mixed Mn carbonate ($(Mn_{48}Ca_{47}Mg_8)CO_3$). The dissolved Mn distribution reflects its production from buried surface oxyhydroxides and its downwards diffusion along the concentration gradient to the depth of Mn carbonate formation (Pedersen & Price, 1982).

(Figure 17). On the other hand, mixed Mn(II)-Ca-Mg carbonates are found in subsurface anoxic sections of marine sediments where surface horizons have high oxyhydroxide contents (Calvert & Pederson, 1996). The continual burial of surface oxyhydroxides as sedimentation proceeds increases the pore water concentration of dissolved Mn, which may reach levels where the ion activity product of Mn^{2+} and dissolved bicarbonate exceeds the solubility product of a carbonate phase (Figure 18). Even where the abundance of such authigenic carbonates is below typical analytical detection limits, pore water Mn profiles commonly show clear evidence of Mn removal within the sediments (Li, Bischoff, & Mathieu, 1969) that is almost certainly due to subsurface precipitation of a manganese carbonate phase.

The occurrence of Mn carbonate in marine sediments can be used as a proxy for original oxygenated bottom water conditions because the mechanism for increasing the concentration of dissolved Mn in sediment pore waters can only operate where the surface sediments accumulate Mn oxyhydroxides. These phases dissolve when they are buried below the oxygenated surface sediments and may saturate the interstitial waters. Such "manganese pumping" can only occur beneath oxygenated bottom waters. In contrast, the bottom sediments of anoxic basins or oxygen minima lack authigenic Mn enrichments because there is no Mn oxyhydroxide cap on the sediments, and therefore no effective mechanism for increasing Mn concentrations in the pore waters above the solubility product of a mixed carbonate. Thus, the 'manganese pump' only operates under oxic bottom waters, an observation that establishes the validity of sedimentary manganese carbonate occurrences as indicators of bottom water oxygenation history, as discussed by Calvert, Bustin, and Ingall (1996) and Calvert and Pederson (1996).

7.1.2. Iodine and bromine

The distribution and concentration of the halogens iodine and bromine in marine sediments are governed by the organic fraction of marine sediments and by diagenetic reactions involving organic matter degradation (Bojanowski & Paslawska, 1970; Price, Calvert, & Jones, 1970). Iodine occurs as I(V) in the form of the iodate (IO_3^-) ion in oxic seawater, with minor occurrences as the iodide ion (I^-) in some near-surface waters, presumably due to biochemical processes (Wong, 1980). In anoxic basins it occurs as the iodide ion (I^-) (Wong & Brewer, 1977; Emerson, Cranston, & Liss, 1979). In contrast, bromine behaves conservatively and occurs everywhere in marine waters as the bromide (Br^-) ion. The concentrations of both elements are closely related to the content of organic matter in oxic sediments, whereas under anoxic conditions iodine is depleted relative to bromine (Price et al., 1970; Price & Calvert, 1977; Shimmield & Pedersen, 1990). The enrichment of iodine in oxic sediments is due to the adsorption of the iodate ion by the high molecular weight organic fraction of the sediment, whereas iodide, the stable form in anoxic waters, is not adsorbed as effectively (François, 1987). Iodine is released from the organic matrix when surficial sediments with high adsorbed I contents are buried under anoxic conditions as a result of the reaction between dissolved pore water sulphide and sedimentary humic substances. Iodine contents therefore decrease with burial, whereas the concentration of bromine changes to a lesser degree, probably as a consequence of the degradation of the organic matrix itself (Pedersen & Price, 1980). Hence, I enrichments relative to organic carbon and Br contents in marine sediments can be used as proxies for oxygenated bottom water conditions in the past, as long as the sediments have remained oxic since deposition.

Using this approach, it was found that the organic-rich sediments deposited during the Last Glacial Maximum (LGM) in the Panama Basin have $I/C_{organic}$ ratios significantly greater than those characteristic of anoxic sediments, and, consequently, that the organic carbon maximum formed when the bottom waters of the basin were oxygenated (Pedersen, Pickering, Vogel, Southon, & Nelson, 1988). This conclusion was supported by micropalaeontological information and the behaviour of Mo, which is examined in Section 7.3.2. Similarly, I/Br ratios in a core from the central California continental slope (discussed in Section 7.7) indicate that bottom water conditions were probably oxic during stadial events and the Younger

Dryas during the last 60 kyr. This conclusion is consistent with information from trace metal proxies on the ventilation of bottom waters at this site.

7.2. Proxies for Suboxia

7.2.1. Chromium, vanadium, rhenium and uranium

These four trace elements occur in seawater in at least two oxidation states, and are probably removed to bottom sediments as the less soluble lower oxidation state. In oxic sea water, they occur predominantly as: chromate (CrO_4^{2-}) and also to a lesser extent as the cationic (III) aquahydroxy species $Cr(OH)_2$+$(H_2O)_4$ (Elderfield, 1970); vanadate (HVO_4^{2-} and $H_2VO_4^-$, which are probably hydrolyzed to $VO(OH)_3^-$ or $VO_2(OH)_3^{2-}$) (Turner et al., 1981; Sadiq, 1988; Wehrli and Stumm, 1989; Emerson and Huested, 1991); perrhenate (ReO_4^-) (Colodner, et al., 1993) and the uranyl (VI) carbonate complex ($UO_2(CO_3)_2^{2-}$) (Langmuir, 1978). The vertical distribution these metals in seawater show either very small surface depletions (Cr and V), signifying minor involvements in biogeochemical cycles (Murray et al., 1983; Collier, 1984), or are invariant (Re and U), pointing to their conservative behaviour in oxic waters (Ku et al., 1977; Anbar et al., 1992; Colodner et al., 1993).

In the eastern tropical Pacific, dissolved Cr(VI) exhibits a minimum at the depths of the OMZ (O_2 10–40 μM), while Cr(III) has a maximum concentration at the same depth, indicating the reductive transformation of Cr species (Murray et al., 1983; Rue, Smith, Cutter, & Bruland, 1997). This clearly shows that the reduction of Cr(VI) takes place under suboxic conditions as predicted thermodynamically. In anoxic basins, Cr(VI) is also removed from solution, probably by the adsorption of $Cr(OH)_2^+$ on particle surfaces (Emerson et al., 1979). Similarly, V is removed from the anoxic bottom waters of Lake Nitinat (British Columbia), the Black Sea and the Cariaco Trench, probably by surface adsorption of its reduced species VO^{2+} or $VO(OH)_3^-$ (Emerson & Huested, 1991), or by the precipitation of V_2O_3 or $V(OH)_3$. However, in Saanich Inlet (British Columbia) and Framvaren (Norway), V concentrations are higher in the anoxic water mass possibly due to the complexation of VO^{2+} by dissolved organic matter (Emerson & Huested, 1991).

Chromium, V, Re and U accumulate in marine sediments above their crustal abundances under suboxic conditions, that is in the absence of both oxygen and sulphide, as shown by their increases in concentration in pore waters at, or close to, the burial depths where Fe oxyhydroxides are also reduced. Where the identity of the predominant chemical species of the metals is known with some confidence, this behaviour is consistent with the thermodynamically predicted reactions that caused the conversion of the oxidized into the reduced forms of the metals. Where the chemical species have not been well established, the predicted reactions at suboxic redox potentials do not appear to be valid. On the basis of the observed behaviour of the metals, however, sedimentary enrichments of Cr, V, Re and U have been used as proxies for sedimentation under suboxic conditions.

In accordance with thermodynamic predictions, Cr and V are strongly removed from the pore waters of some continental margin sediments close to the depth of manganese oxide reduction, suggesting that they are diffusing into the sediments down a concentration gradient to be fixed at depth (Shaw, Gieskes, & Jahnke, 1990). The enrichment of the two metals in the solid phases of the sediments is difficult to discern in many cases due to their high background in the lithogenous fraction. Dissolved Cr and V also increase in concentration with depth in pore waters in organic-rich sediments in the poorly-ventilated Gulf of California (Brumsack & Gieskes, 1983) showing again that they are solubilized under low redox potentials. The solid phase V concentration increases with depth in these sediments, demonstrating that V is being removed from pore solutions (Brumsack, 1986).

Enrichments of Cr and V in the organic-rich Miocene Monterey Formation are much larger than those of Mo and U, suggesting that deposition of the sediments occurred under suboxic (denitrifying) conditions (Piper & Isaacs, 1995). This conclusion is in accord with the accepted palaeoenvironmental model for the formation of this deposit, which invokes deposition on an upwelling-intense continental margin (Isaacs, 2001).

Rhenium is greatly enriched in the suboxic sediments of nearshore and continental margin settings (Colodner et al., 1993; Crusius, Calvert, Pedersen, & Sage, 1996; Sundby, Martinez, & Gobeil, 2004) as well as in the sediments of anoxic basins (Koide, Hodge, Yang, Stallard, & Goldberg, 1986; Ravizza, Turekian, & Hay, 1991; Colodner, Edmond, & Boyle, 1995). In contrast, concentrations of the element in pelagic clays and ferromanganese nodules are less than or equal to crustal abundances. The degree of enrichment of Re in anoxic sediments is significantly larger (up to a factor of 300 relative to crustal abundances) than any other metal whose marine geochemistry is sufficiently well understood (Colodner et al., 1993). In these suboxic and anoxic environments, Re is delivered to the sediments via diffusion from bottom waters and is being removed from sediment pore waters by the reduction of Re(VII) to Re(IV), possibly ReO_2 or ReS.

Uranium has a constant concentration in seawater from all ocean basins (Ku et al., 1977), and is largely conservative in estuaries (Borole, Krishnaswami, & Somayajulu, 1982; Cochran, 1984). This conservative behaviour is due to the high degree of solubility of the uranyl(VI) carbonate complex ($UO_2(CO_3)_2^{2-}$) in seawater. In anoxic basins, U is removed from solution to the bottom sediments by reduction to the IV oxidation state (Anderson, 1987; Todd, Elsinger, & Moore, 1988; Anderson, Fleisher, & LeHuray, 1989a; Anderson, LeHuray, Fleisher, & Murray, 1989b; McKee & Todd, 1993). In spite of the evident removal of U in the deep water of these basins, it exists in solution in its higher oxidation state. Moreover, a little authigenic U is found in settling particulate matter collected by particle interceptor traps in Saanich Inlet (British Columbia) and the Black Sea (Anderson et al., 1989a; Anderson et al., 1989b). Its removal to the sediments must, therefore, occur by diffusion from the bottom water into the underlying deposits, and may involve the catalytic reduction of U(VI) to U(IV) on particle surfaces (Kochenov, Korolev, Dubinchuk, & Medvedev, 1977), as reflected in pore water and solid phase total U profiles in the Black Sea (Barnes & Cochran, 1991). Experimental work has also demonstrated bacterial reduction of U(VI) to U(IV) in the presence of hydrogen sulphide (Lovley, Phillips, Gorby, & Landa, 1991), a mechanism that would be favoured in sediments compared to the water column because of the higher concentrations of bacterial cells in sediments (Kriss, 1963).

Uranium also appears to be removed from bottom oxygenated waters by diffusion across the sediment/water interface into continental margin and some deep-sea sediments (Thomson, Wallace, Colley, & Toole, 1990; Klinkhammer & Palmer, 1991; Barnes & Cochran, 1993; McManus, Berelson, Klinkhammer, Hammond, & Holm, 2005). Such removal is demonstrated by the decrease with depth of dissolved pore water uranium and the concomitant increase in solid phase U in subsurface suboxic and anoxic sediments. The authigenic U at such depths has a $^{234}U/^{238}U$ ratio identical with that in normal seawater, attesting to its seawater source (Yamada & Tsunogai, 1984; Thomson et al., 1990). The sink is evidently below the depth where Mn and Fe oxyhydroxides are reduced, and probably lies at the depth where sulphate reduction begins. The largest of the global U sinks, accounting for the removal of at least 75% of the total dissolved U supplied to the ocean by rivers, evidently occurs in suboxic, continental margin sediments (Klinkhammer & Palmer, 1991).

The suboxic/anoxic sedimentary U sink is controlled by the settling flux of metabolizable organic matter to the sea floor. Under oxygenated bottom water conditions, oxygen is fully depleted in the pore waters at a sub-surface depth that depends on the organic content of the sediment, below which suboxic conditions (nitrate, Mn and Fe oxyhydroxide reduction) prevail (Figure 16). Increasing the organic flux to the sea floor — that is, increasing surface productivity — causes the oxic/suboxic boundary to shoal, steepening the concentration gradient of dissolved U from the bottom water to the boundary, thereby increasing the rate of fixation of U in the suboxic zone (Rosenthal, Lam, Boyle, & Thomson, 1995b). Changes in productivity can therefore be inferred from changes in U content of the bottom sediments, which constitutes a palaeoproductivity proxy. Uranium and several other trace metals are oxidized and re-precipitated close to the oxic/suboxic boundary in some deposits due to a decrease in bulk sedimentation rate in the Holocene compared with the LGM (Thomson et al., 1990; Thomson, Higgs, Croudace, Colley, & Hydes, 1993; Thomson, Higgs, & Colley, 1996; Mangini, Jung, & Laukenmann, 2001). This "burn-down" causes the formation of characteristic concentration peaks above and below the boundary between two sediment facies, one organic-poor and the other organic-rich. Where the Holocene sedimentation rate is <2 cm/ky, authigenic U that accumulated in sediments during the glacial period can subsequently be removed during "burn-down diagenesis" (Mangini et al., 2001), so that periods which lack U enrichments do not necessarily signify periods of low productivity.

Changes in the drawdown of atmospheric CO_2 by processes in the high latitude regions of the ocean on glacial–interglacial timescales have been of considerable interest (Knox & McElroy, 1984; Sarmiento & Toggweiler, 1984; Siegenthaler & Wenk, 1984). The Southern Ocean region in particular has been identified as one of the systems where the efficiency of the biological pump might have changed (Sigman & Boyle, 2000), leading to some of the large changes in atmospheric pCO_2 recorded in Antarctic ice cores (Jouzel et al., 1987). This has focused interest on changes in the proportion of nutrients removed from the mixed layer and the rate of export of carbon to the deep sea via settling organic particles. Proxy records of palaeoproductivity using isotopic (François, Altabet, & Burckle, 1992; Shemesh, Macko, Charles, & Rau, 1993; Mackensen, Grobe, Hubberten, & Kuhn, 1994) and elemental data (Kumar et al., 1995; Rosenthal et al., 1995b; Anderson et al., 1998) have been constructed for large regions of the Antarctic and sub-Antarctic circumpolar region to test this hypothesis.

The burial of organic carbon in Southern Ocean sediments appears to have changed drastically, but this change is areally variable. In the Subantarctic zone and in the Cape Basin of the South Atlantic, north of the Antarctic Polar Front, production appears to have been substantially higher during the LGM compared to the Holocene (Figure 19), as recorded by the U palaeoproductivity proxy (Rosenthal

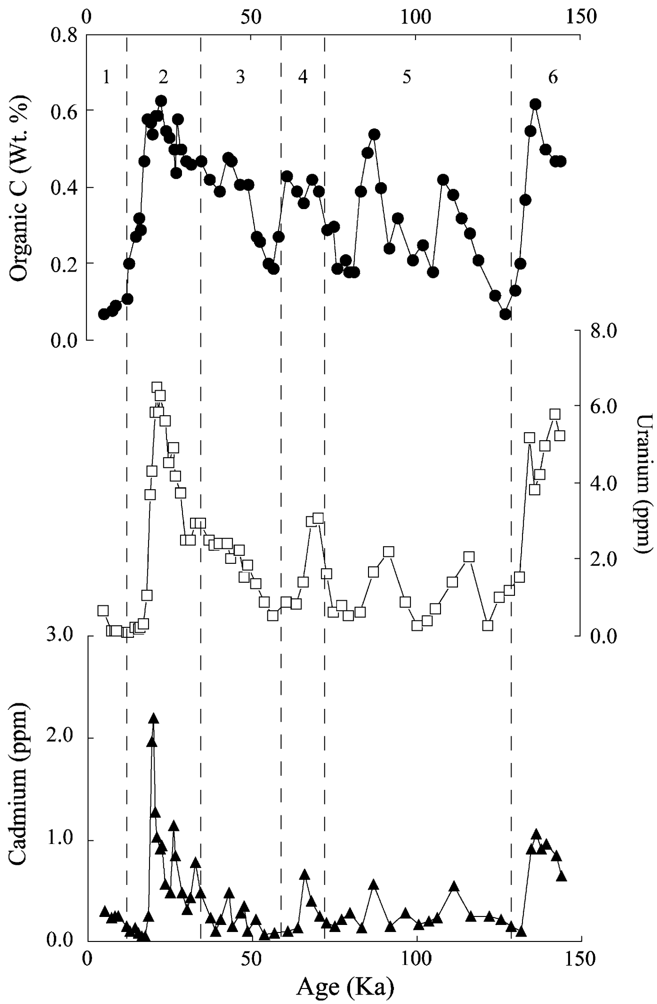


Figure 19 Downcore variations in organic C and authigenic U and Cd over the last 145 kyr in core MD88-769 in the Subantarctic Indian Ocean (46.07°S, 90.12°E, 3,420 m water depth). Data from Rosenthal, Boyle, Labeyrie, and Oppo (1995a). Organic carbon and the metal proxies point to substantially higher production during the LGM in the Subantarctic zone.

et al., 1995b). This may have been induced by a higher glacial supply of Fe by dust (Kumar et al., 1995). South of the Antarctic Polar Front, on the other hand, where sea ice was extensive during the LGM, changes in production show the inverse pattern. This has suggested that the modern belt of high productivity moved northwards during the LGM, and the degree of enrichment of U (and Cd) in glacial sediments suggests that the burial flux was higher in the Subantarctic zone possibly due to a greater partitioning of carbon into the deep sea, consistent with a more efficient biological pump. This conclusion is supported by sedimentary records of the $^{231}Pa/^{230}Th$ and $^{10}Be/^{230}Th$ particle flux proxies (Kumar et al., 1995), of opal and organic carbon burial (Charles, Froelich, Zibello, Mortlock, & Morley, 1991; Mortlock et al., 1991), of biogenous Ba enrichments (Figure 20) where U data show there has been no diagenetic loss of barite (Anderson et al., 1998; Anderson, Chase, Fleisher, & Sachs, 2002) and by diatom-bound $\delta^{15}N$ measurements (Robinson et al., 2005). Whether there was a net increase in export production and carbon burial in the glacial Southern Ocean or little change due to areal compensation of sea-surface production has not been fully resolved due to uncertainties in our understanding of Southern Ocean nutrient cycles, the phytoplankton groups responsible for production and the physical factors controlling export production during the Last Glacial (Anderson et al., 2002).

The enrichment of uranium in organic-rich sediments that accumulated during OIS 2 and 3 in the Arabian Sea has been ascribed to anoxic bottom water conditions at this time (Sarkar et al., 1993). However, the organic carbon flux appears to have been significantly higher where U is enriched, as is the case for cores in the Subantarctic region, suggesting that the oxic–anoxic boundary shoaled within the sediment, thereby increasing the authigenic fixation of U in the sediments. Although the oxygen content of the bottom waters could have decreased concomitantly because of the higher carbon flux into bottom waters, there is no requirement for the bottom waters to have been fully anoxic to explain the observed U enrichment. This conclusion is strongly supported by the areal distribution of glacial U enrichments in the Southern Ocean, and by the discovery of similar glacial enrichments in cores recovered from the depths of South Atlantic Intermediate Water, which could not have been oxygen deficient during this time period (Chase, Anderson, & Fleisher, 2001).

7.3. Proxies for Anoxic Conditions of Sedimentation

7.3.1. Silver, cadmium, copper, nickel and zinc

These five metals are chalcophile elements that, together with lead and mercury, are concentrated in sulphide deposits in the Earth's crust. They are commonly enriched in sedimentary rocks, especially black shales, where they occur mainly as disseminated sulphides. The range of metal contents in such shales is very wide, and some deposits contain ore-grade levels of some of the metals. The stable species of these metals in aqueous solution are the monovalent (Ag) and divalent forms, and their distributions in the ocean are dominated by biochemical reactions. Silver, Cd, Ni and Zn behave as micronutrients, being removed quantitatively in surface waters by plankton growth and liberated from settling organic debris in the upper part of the

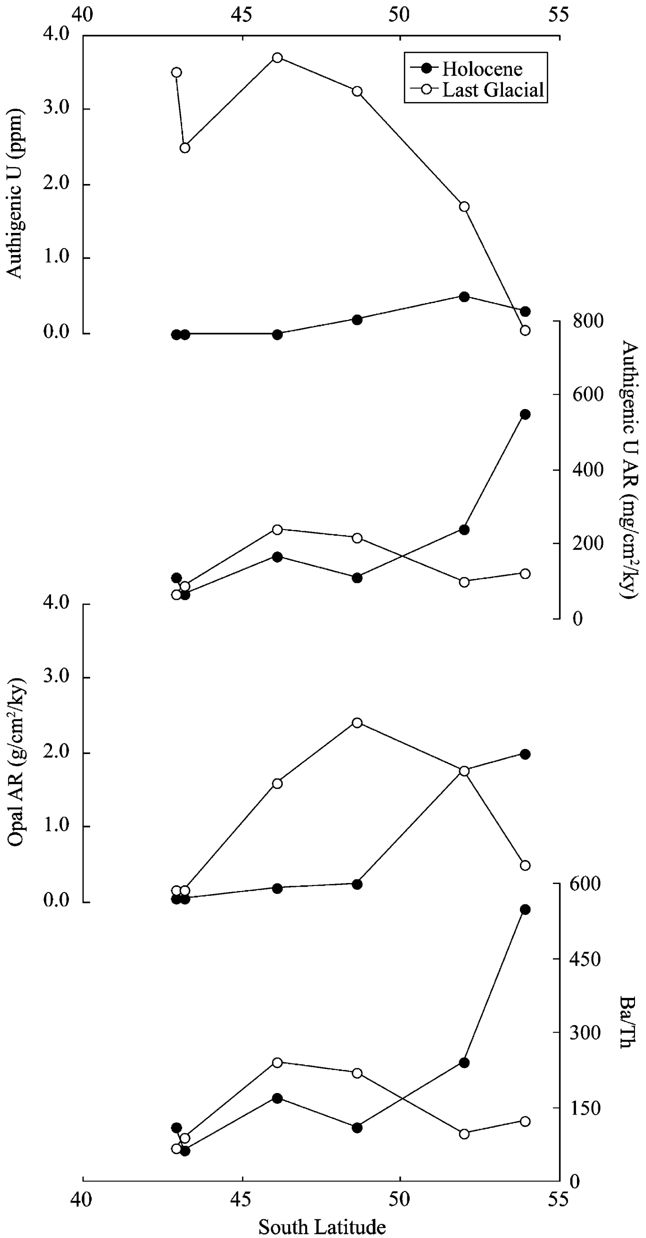


Figure 20 North-south transect of surface sediment authigenic U, authigenic U accumulation rate, opal accumulation rate and the Ba/Th ratio in the Atlantic sector of the Southern Ocean. Data from (Kumar, 1994). Accumulation rates are Th-normalized component accumulation rates.

oceanic water column. Concentration-depth profiles of Cd are very similar to those of phosphate, whereas distributions of Ag, Ni and Zn are closest to those of silicic acid, with surface minima, increasing concentrations with depth and substantial ocean–ocean fractionation (Bruland, 1983; Flegal, Sanudo-Wilhelmy, & Sceflo, 1995; Nozaki, 1997; Bruland & Lohan, 2003). Copper is somewhat unique among the trace metals in seawater in that it behaves partly like a micronutrient but is also scavenged from solution onto particle surfaces in deep water. Its depth distribution therefore shows surface depletions, more or less linear increases with depth in deep water and high concentrations in bottom waters, implying a sediment source (Boyle, Sclater, & Edmond, 1977). Cadmium can be used as a robust upwelling proxy because its concentration in surface waters responds in the same fashion as the macro-nutrients, especially phosphate, to upwelling events (van Geen & Husby, 1996). Assimilation of this upwelled Cd by phytoplankton that respond to the increased supply of nutrients is then transmitted to the sediment in the biogenous debris that settles into deeper waters.

In anoxic basins, such as the Cariaco Trench, Framvaren Fjord, Saanich Inlet and the Black Sea, the dissolved concentrations of Cd, Cu and Zn decrease by factors ranging from 2 to 10 from the upper oxic water mass into the underlying anoxic waters (Jacobs & Emerson, 1982; Jacobs, Emerson, & Skei, 1985; Jacobs, Emerson, & Huested, 1987; Haraldsson & Westerlund, 1988, 1991; Landing & Lewis, 1991). Equilibrium speciation calculations show that such decreases reflect the precipitation of the respective solid sulphides in the presence of dissolved sulphide in the anoxic waters. Silver is similarly stripped from solution in the anoxic waters of Saanich Inlet, with concentrations year-round being <0.5 pM in waters below the oxygen-zero boundary (Kramer, 2006). In contrast to the systematic behaviours of Ag, Cd, Cu and Zn, Ni does not show any decrease in concentration in anoxic waters even though a number of insoluble sulphides have the potential to limit its concentration in the presence of dissolved sulphide. Hence, we should expect that the bottom sediments of such basins would display enrichments in the concentrations of at least Ag, Cd, Cu and Zn above those characteristic of the detrital sediment input.

Cadmium, Cu, Ni and Zn are enriched in the bottom sediments of some modern anoxic basins, but these enrichments are highly variable (Jacobs et al., 1987). This is due to the relatively large contribution of the metals to the sediments in lithogenous phases, which dilute the authigenic fraction to different extents depending on their accumulation rates, Thus, Framvaren sediments are highly enriched in Cd, Cu, Ni and Zn because it is a sediment-starved basin that receives very little detrital supply. On the other hand, the fluxes of most of the metals in the Cariaco Trench are dominated by detrital input so that only in the case of Cd and Zn are significant enrichments found, and in Saanich Inlet, Cu is enriched whereas the Zn can be accounted for entirely by the supply of the metal from settling particulate organic matter (François, 1988). Paradoxically, Ni is significantly enriched in the bottom sediments of the Black Sea and Framvaren in spite of an evident lack of removal of the metal in the deep anoxic waters of the basin.

Authigenic Ag, Cd, Cu, Ni and Zn appear to be added to the solid fraction of many nearshore sediments by the diffusion of the dissolved metals from the overlying oxygenated waters or the pore waters into the subsurface anoxic horizons. Theoretical studies of the sedimentary removal of Cd and Cu show that the respective sulphide phases should control the concentration of both metals in the pore waters of estuarine sediments containing moderate concentrations of dissolved sulphide (Davies-Colley, Nelson, & Williamson, 1984, 1985). Where sulphide concentrations are higher (~1 mM), polysulphide formation may cause the metals to stabilize in solution. Gobeil, Silverberg, Sundby, and Cossa (1987) showed that authigenic Cd is added to the sediments of the Laurentian Trough by downward diffusion from a dissolved Cd maximum in the upper part of the sediment column. Likewise, Pedersen, Waters, and Macdonald (1989) suggested that Cd is markedly enriched in the organic-rich sediments of a small sediment-starved coastal embayment by the diffusion of dissolved Cd from the overlying waters and fixation as the sulphide within the sediments. In each of these cases, the sediments are accumulating under oxygenated bottom waters, but the metals are being precipitated as the sulphides under anoxic conditions at shallow depth in the sediment. The affinity of Cd for adsorption by organic matter is rather low (Guy & Chakrabarti, 1976) so that a high degree of correlation between the concentrations of Cd and organic carbon (Pedersen et al., 1989) reflect an indirect control of the production of dissolved sulphide by sulphate reduction that is fueled by the burial of large quantities of marine organic matter in this coastal setting. Evidently, wherever there is sufficient organic matter delivered to sediments and the redox boundary occurs at relatively shallow depth (itself due to the high settling flux of carbon), then Cd, Cu, Ni and Zn (and probably Ag) can be potentially sequestered by the sediments as the respective sulphides.

7.3.2. Molybdenum

The concentration of dissolved Mo is similar in the Atlantic and Pacific oceans (Sugawara, Okabe, & Tanaka, 1961; Morris, 1975; Collier, 1985), and it is slightly depleted in surface waters, reflecting a minor involvement in biogeochemical cycles. Molybdenum is removed from solution in anoxic basins (Berrang & Grill, 1974; Emerson & Huested, 1991), where concentrations observed vary widely, there being no relationship between the dissolved metal concentrations and the dissolved sulphide levels, which range over two orders of magnitude. This has suggested that there are no solubility equilibria involving Mo and that the metal is removed from the anoxic waters within the bottom sediments.

Molybdenum is enriched in both oxic and anoxic sediments. Thus, in spite of its occurrence as the stable soluble molybdate ion in oxygenated seawater (Turner, Whitfield, & Dickson, 1981), Mo is significantly enriched in ferromanganese nodules (Calvert & Price, 1977) and in surficial Mn oxyhydroxides in continental margin and nearshore sediments (Shimmield & Price, 1986). In the latter situation, Mo is released from the solid phases of surface sediments when the oxyhydroxides of Mn are reductively dissolved during burial into more reducing subsurface sediments (Figure 18). Where dissolved sulphide occurs in such sub-surface sediments, Mo may be removed from the pore waters to be immobilized in the solid phases.

Experimental and observational studies have revealed that a key step in Mo removal from seawater and pore waters is the conversion of inert MoO_4^{2-} to particle-reactive thiomolybdates ($MoO_xS_{4-x}^{2-}$), which may then be scavenged from solution by Fe sulphide phases and humic substances (Helz et al., 1996). Protonated mineral surfaces promote the interconversion of thiomolybdate species, which could lead to a higher rate of immobilization of Mo in sediments compared with overlying waters (Vorlicek & Helz, 2002). The relationship between Mo removal and aqueous sulphide concentration suggests that thiomolybdate formation increases markedly at an H_2S concentration of 11 μM at 25°C, an effective "switch point" (Helz et al., 1996), which enhances Mo immobilization on solid phases. Because of the kinetics of molybdate–thiomolybdate interconversion, a secondary control is the time of exposure of MoO_4^{2-} to sulphide (Erickson & Helz, 2000). Thus, Mo enrichment in marine sediments proceeds in the presence of sulphide, which can increase in concentration to relatively high levels in subsurface continental margin sediments as well as anoxic basins due to diagenetic sulphate reduction.

In Saanich Inlet and the Black Sea, Mo occurs at concentrations below the detection limit (1–2 ppm) in settling particulate matter in the deep anoxic waters (François, 1988; Crusius et al., 1996), whereas it is greatly enriched in the bottom anoxic sediments of both basins (90–100 ppm). This lends strong support to the mechanism of Mo enrichment under sulphidic conditions by the immobilization within the sediments, the decrease in concentration in the anoxic bottom waters being due to the diffusion of the dissolved metal into the sediment along a concentration gradient.

The largest sedimentary Mo enrichments are found in permanently anoxic basins, such as Framvaren (Piper, 1971), the Black Sea (Calvert, 1990), Saanich Inlet (François, 1988) and the Cariaco Basin (Piper & Dean, 2002). In continental margin sediments, on the other hand, where surface sediments are oxic, Mo concentrations are significantly lower (Pedersen, 1985; Shimmield & Price, 1986; Crusius et al., 1996; Zheng, Anderson, van Geen, & Kuwabara, 2000; Chaillou, Anschutz, Lavaux, Schafer, & Blanc, 2002; Sundby et al., 2004). This contrast may be produced by the ambient concentrations of dissolved sulphide in anoxic basins, the residence time of deep basin waters, as well as the kinetics of Mo species transformations. Thus, dissolved Mo depletion in the anoxic Black Sea waters, where H_2S concentration is *ca.* 400 μM and the deep water residence time is long, is $>90\%$ (relative to the overlying oxic waters), whereas it is only *ca.* 10% in Saanich Inlet where H_2S is *ca.* 10 μM and ventilation takes place on a quasi-annual time scale, with Lake Nitinat and the Cariaco Basin having intermediate values (Piper & Isaacs, 1996; Algeo & Lyons, 2006).

In spite of the lower degree of Mo enrichment in continental margin deposits, subsurface enrichments above crustal abundances are readily detected and have been used to hindcast past anoxic deep-water conditions and carbon fluxes to the sea floor. In such environments, pore water Mo is depleted and solid phase Mo concentrations increase below the zone of Mn oxyhydroxide recycling (Malcolm, 1985; Shaw et al., 1990; Zheng et al., 2000; Chaillou et al., 2002; Sundby et al., 2004). Because Mo is enriched in surficial horizons where Mn oxyhydroxides exist under surficial oxic conditions (Shimmield & Price, 1986), the metal is effectively pumped into the underlying anoxic zone by burial where it is released to solution. Molybdenum is also most likely fixed as Fe-Mo-S clusters, probably in solid solution in FeS phases (Helz, Vorlicek, & Kahn, 2004). The increasing concentration of solid phase Mo with depth in many situations suggests that the kinetics of Mo removal are sluggish (Sundby et al., 2004), and that the modest enrichment in continental margin settings is restricted by this kinetic hindrance, which lengthens the path over which dissolved Mo must diffuse before it is fixed. The metal begins to be removed from the Santa Barbara Basin sediment at dissolved sulphide levels of ~0.1 μM, as shown by the decrease in dissolved Mo and the increase in solid phase concentrations, which reach 7 ppm (Zheng et al., 2000). This removal may involve scavenging by humic substances to form organic thiomolybdates (Adelson, Helz, & Miller, 2001). A second critical concentration of ~100 μM total sulphide marks the further depletion of pore water Mo and the concomitant enrichment in solid phase Mo in this basin. It is here that the association with Fe sulphide phases is probably involved (Helz et al., 2004) rather than precipitation as a Mo sulphide. Pyrite (FeS_2), which forms from FeS during diagenetic sulphide reactions, is the host of significant Mo contents in anoxic sediments (Huerta-Diaz & Morse, 1992). These observations support the experimentally determined sulphide "switch point", which enhances the conversion rate of molybdate to thiomolybdate species in solution (Helz et al., 1996). In order to sustain H_2S concentrations above the switch point in near-surface sediment pore waters so that significant Mo fixation can occur, it has been argued that dissolved sulphide must be present in the bottom waters of a basin. Sulphide would otherwise be lost by reaction with O_2 diffusing downwards from ventilated bottom waters (Adelson et al., 2001). Data from the California margin discussed in Section 7.7 challenge this conclusion because Mo is enriched in sediments that have accumulated under oxic bottom water conditions (Hendy & Pedersen, 2005).

7.4. Post-Depositional Migration or Loss of Authigenic Metals

Several authigenic trace metals can be remobilized and relocated in buried sediments if they become exposed to oxygen after initial accumulation. This process has been reported in sediment sections of the Atlantic where a diminution in the Holocene sedimentation rate has allowed the diffusion of dissolved oxygen into deeper anoxic Late Glacial sediments that had built up relatively high concentrations of the metals due to a higher burial flux of organic matter at that time (Thomson, Higgs, Croudace et al., 1993; Thomson, Higgs, & Colley, 1996). The effect is to produce a redistribution of elements in a specific redox-controlled order above and below the boundary between an upper oxic section, which has not been altered, and an underlying section, which has been secondarily oxidized by O_2 diffusing downwards from oxygenated sediment. This so-called "burn-down" process causes the formation of sharp concentration peaks of, for example, Ag, Cd, Cu, V, Zn, V, I and U. Rhenium is also mobilized in the oxidized section and re-immobilized below the oxidation front, but its distribution extends over a broader depth range, and this distribution remains over at least 3.4 Ma (Crusius & Thomson, 2000). On the other hand, U forms sharp concentration peaks roughly 500 cm broad in the upper part of the glacial reducing sediments. Bioturbation can also lead to loss of U from sediments due to the post-depositional transport of reducing sediment into the near-surface, more oxidizing environment (Zheng, Anderson, van Geen, & Fleisher, 2002). Molybdenum can be lost from an anoxic sediment that has been subsequently exposed to O_2 unless it is associated with authigenic pyrite formation (Crusius & Thomson, 2000). Thus, Mo enrichments may be preserved in re-oxidized deposits if they were originally sufficiently anoxic for pyrite to have formed. Similar patterns of element remobilization and re-immobilization have been discovered around the sapropel horizons in the Mediterranean following re-ventilation of the basin after periods of increased production and bottom water anoxia (Pruysers, De Lange, Middelburg, & Hydes, 1993; Thomson et al., 1995; Crusius & Thomson, 2000).

These artifacts must be carefully evaluated when making palaeoceanographic deductions from authigenic metal distributions in sediment sections that have suffered post-depositional burn-down events. Authigenic metal records are well preserved in sediments that have high sedimentation rates and where the metal enrichments are permanently buried under suboxic or anoxic conditions.

7.5. Distinguishing between Suboxic and Anoxic Environments of Sedimentation

It is well established that Ag, Cd, Cr, Cu, Mo, Ni, Re, U, V and Zn are all removed from seawater under suboxic and/or anoxic bottom water conditions. Those metals that are readily fixed in solid phases under suboxic conditions (Cr, Re, U and V) without the requirement for the presence of dissolved sulphide will also be removed under anoxic conditions because the change in oxidation state will be promoted at lower redox potentials. A less than ideal method for distinguishing between suboxic and anoxic sedimentary environments could therefore involve the enrichment of Cr, Re, U or V accompanied by the absence of significant enrichments of Ag, Cd, Cu, Mo, Ni or Zn.

The contrasting geochemical behaviours of Re and Mo can provide a simple way to make this distinction (Crusius et al., 1996). As shown previously, these two metals show the largest degrees of enrichment above crustal abundances among the metals considered here. Rhenium is not associated with authigenic oxide phases, but is strongly removed to suboxic sediments. Molybdenum is adsorbed on Mn oxyhydroxides and is also removed to anoxic sediments at high dissolved sulphide levels, which are maintained in the surficial sediment by anoxic bottom waters. A ratio of total Re/Mo greater than that of seawater (0.4 mmol/mol) in a given deposit will be diagnostic of suboxic conditions, whereas a ratio close to that of seawater is expected under anoxic conditions. Under oxic conditions in the bottom water and the sediments, the ratio could be less than that in seawater due to the fixation of Mo on oxyhydroxides and the lack of uptake of Re on such phases.

7.6. History of Anoxia in the Cariaco Basin

The Cariaco Basin, lying on the Venezuelan continental shelf, is a 1,400 m deep permanently anoxic basin that is isolated from the Caribbean Sea by a sill with a maximum depth of 146 m. Sulphate reducing conditions prevail below 250 m depth, where dissolved sulphide concentrations are 40–70 μM (Richards & Vaccaro, 1956; Richards, 1975; Scranton, Astor, Bohrer, Ho, & Muller_karger, 2001), and the deep water residence time is approximately 100 years (Deuser, 1973). The bottom sediments of the basin are siliceous-calcareous organic-rich silty clays that are finely laminated, light-coloured diatom/silicoflagellate-rich laminae alternating with darker, clay-rich laminae (Hughen, Overpeck, Peterson, & Anderson, 1996). During the last glacial, the basin was further isolated from the Caribbean due to sea level lowering, when fully oxygenated conditions in the deep water prevailed. The sediments deposited during this period are moderately organic rich and weakly bioturbated (Peterson, Overpeck, Kipp, & Imbrie, 1991).

The history of environmental change in the Cariaco Basin has been reconstructed using a combination of foraminiferal census and isotopic data (Peterson et al., 1991; Lin, Peterson, Overpeck, Trumbore, & Murray, 1997) and a range of major and trace element proxies for sedimentation under oxic, suboxic and anoxic conditions (Dean, Piper, & Peterson, 1999; Piper & Dean, 2002). Production and sediment supply in the Cariaco Basin vary seasonally in response to changes in the position of the ITCZ in the tropical Atlantic. Between January and March, the ITCZ lies south of the equator, and strong trade winds blowing along the coast of Venezuela produce strong upwelling. Production in the Cariaco Basin is up to 20 times greater than in the open Caribbean to the north. This is also the dry season in the region, due to the location of the ITCZ far to the south. Beginning in June–July, the ITCZ moves northwards and lies near the Venezuelan coast; winds diminish, upwelling weakens and the high rainfall results in increased river discharge.

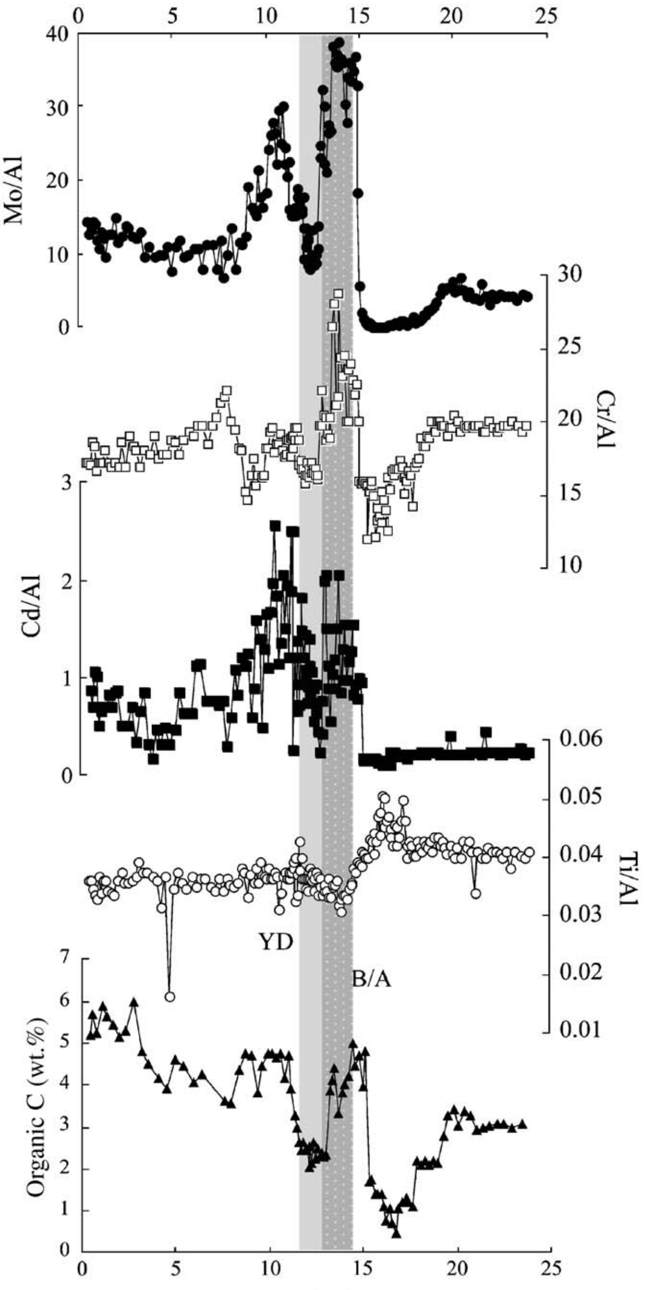
Prior to 12.6 kyr ago, the foraminiferal faunas were dominated by species characteristic of the modern non-upwelling season, suggesting low productivity at this time. At 12.6 ka, a sharp increase in the abundance of species characteristic of upwelling regimes and high plankton productivity is found to be coincident with the first major rise in sea-level that accompanied the melt water pulse (1A) from the Laurentide ice sheet. Production is interpreted to have increased in response to an increase in water exchange between the basin and the Caribbean, and anoxia in deep waters was quickly established in response to the higher organic matter fluxes below sill depth. These changes in hydrography and production are coincident with the observed changes in the sedimentary record, from oxic, bioturbated clays to anoxic, micro-laminated clays.

Between 18 and 15 ka, when the basin was maximally isolated, and the most organic-lean sediment accumulated, the trace element proxies show, as expected from the bioturbated sediment structure, that the deep water basin waters were oxic; there are no enrichments of Cd, Cr or Mo (Figure 21), or of Cu, Ni, V and Zn (not shown) relative to average shale. Between 18 and 23 ka, however, when the organic C content of the sediment is higher, small enrichments of Cr and Mo (and Cu, Ni, V and Zn) may indicate modest uptake of the metals from bottom waters and from deposited organic materials by subsurface suboxic and anoxic sediment even though the surface sediments were oxic and bioturbated, in the same way that many continental margin sediments have small metal enrichments. Also note that the Ti/Al ratio is highest when the trace metals are lowest, possibly recording the delivery of coarser-grained material from local, exposed parts of the shelf and islands surrounding the basin.

The abrupt increase in organic C at 15 ka is followed shortly thereafter by very large enrichments in Cd, Cr, Mo (Figure 21) and Cu, Ni, V and Zn (not shown). Over a period of roughly 1.8 kyr, concentrations are maximal for the entire core. This interval, lasting from 14.6 to 12.8 ka, is coeval with the Bølling-Allerød interstadial event in the North Atlantic, which followed Heinrich Event 1 and marked the end of the last glacial period (Alley & Clark, 1999). Melt water pulse 1A (Fairbanks, 1989), triggered by abrupt melting of Antarctic ice (Weaver, Saenko, Clark, & Mitrovica, 2003), begins at 14.6 ka during which sea level rose by ~20 m in less than 500 years. The response to this dramatic event was clearly the rapid onset of anoxic bottom water conditions in the Cariaco Basin, due to the large increase in export production and the increase in water column stability induced by lower sea surface salinity. This set of conditions caused the largest Mo enrichments for the entire core. The state of the basin changed drastically once again at the beginning of the Younger Dryas event at 12.8 ka, when surface water temperatures decreased by 3–4°C (Lea, Pak, Peterson, & Hughen, 2003), and Mo and Cr contents decreased drastically; Cd, after an initial decrease, increased to levels observed during the B/A. Organic C contents also decreased, but biogenous carbonate and opal increased and diatom and zooplankton biomarkers reached a maxima for the last 12 ka (Werne, Hollander, Lyons, & Peterson, 2000), indicating an interval of increased productivity. Thus, Cd enrichments tracked the increase in export production, while the anoxia proxies suggest that deep water conditions were not as reducing as during the B/A. Following the end of the Younger Dryas, Mo and Cd increased markedly and Cr increased modestly, suggesting productivity continued to rise and intense anoxia returned to the deep waters. Conditions were wettest and river flow was highest in the Cariaco Basin borderlands between approximately 10.5 and 5.4 ka, the time interval of the Holocene "thermal maximum", as deduced from the record of Fe and Ti abundances. At ODP Site 1002 within the Basin, these track variations in lithogenous sediment supply (Haug et al., 2001). This is the same time interval of higher Cd, Cr and Mo enrichments in core 39PC (Figure 21) when the deep basin waters must have been more intensely anoxic probably due to increased water column stability induced by the higher freshwater flux into the basin. The time interval with the largest Mo enrichments (~15–10 ka) is also the period of accumulation of distinct laminations, whereas the laminations are weakly developed or less distinct after 10 ka (Peterson et al., 1991; Lin et al., 1997), when the sulphide level in deep waters decreased. Anoxic conditions persisted through to the Late Holocene, however.

7.7. Sedimentary Records of Changes in Ventilation and Organic Flux

As explained previously, the burial flux of metals sequestered in sediments under suboxic and anoxic conditions can be affected or controlled by the oxygen content


Mo/Al
Cr/Al
Cd/Al
Ti/Al
YD
B/A
Organic C (wt.%)
Age (Ka)

of bottom waters in contact with the sediments and by the accumulation rate of organic matter that is metabolized within the deposits, thereby changing the sedimentary redox conditions. Methods for unravelling these two controls are required in order to understand past changes in water column ventilation and productivity.

High-resolution sedimentary records of high-frequency palaeoclimatic and palaeoceanographic variability that address this problem have been obtained from the central California margin, where changes in bottom water oxygenation appear to be highly coherent with the Dansgaard-Oeschger climate oscillations in Greenland (Behl & Kennett, 1996; Cannariato & Kennett, 1999; Hendy & Kennett, 2000; Hendy, Kennett, Roark, & Ingram, 2002). Multi-element data have been used to discriminate between bottom water ventilation and organic flux variations as the main drivers of the oxygenation of the sea floor over the last 60 kyr (Ivanochko & Pedersen, 2004; Hendy & Pedersen, 2005). On the upper slope to the northwest of the Santa Barbara Basin, a core site located at the base of the OMZ shows enrichments of minor and trace element during Late Quaternary interstadials and the Holocene, consistent with reduced intermediate water ventilation (Figure 22). Marked enrichments in Ag, Cd and Mo indicate sulphate-reducing conditions in the pore waters during some of the major interstadials that are also coherent with proxies for productivity (organic C and $CaCO_3$ content, biogenic silica and planktonic foraminiferal assemblages) and nutrient content of source waters ($\delta^{15}N$), showing that the export flux of biogenous detritus as well as intermediate water ventilation played a role in modulating the intensity of the OMZ over the last 60 kyr. Such changes have been found in other parts of the central California margin from downcore records of Mo (Dean, Gardner, & Piper, 1997), and the benthic foraminiferal Cd/Ca palaeonutrient proxy (van Geen, Frairbanks, Dartnell, McGann, & Gardner, 1996). In the Santa Barbara Basin, on the other hand, which has very low dissolved oxygen contents (currently $<2\,\mu M$), a similar approach found that oxygenation changes were mainly controlled by basin ventilation, with a minor role for productivity variations over the last 50 kyr (Ivanochko & Pedersen, 2004).

8. Future Developments

In this chapter, we have shown how elemental abundance data have been applied to a variety of problems in palaeoclimatology and palaeoceanography. Continuing research will lead to the refinement of many of the proxies discussed, and

Figure 21 Temporal indices of changing bottom water oxygenation, sediment supply and productivity from core PL07-39PC (10.67°N, 64.94°W, 790 m water depth) in the Cariaco Basin. Data from Piper and Dean (2002). YD = Younger Dryas, B/A = Bølling-Allerød. Prior to the B/A, deep basin waters were oxic. Between 18 and 23 ka, minor Cr and Mo enrichments indicate modest uptake of the metals from bottom waters and from deposited organic materials by subsurface suboxic and anoxic sediment even though the surface sediments were oxic and bioturbated. Higher Ti/Al at this time records the delivery of coarser-grained material to the basin. Maximal enrichments in Cr and Mo and a peak in Cd are found in the B/A. All three metals are greatly depleted in the YD, and then increased after 11 ka.

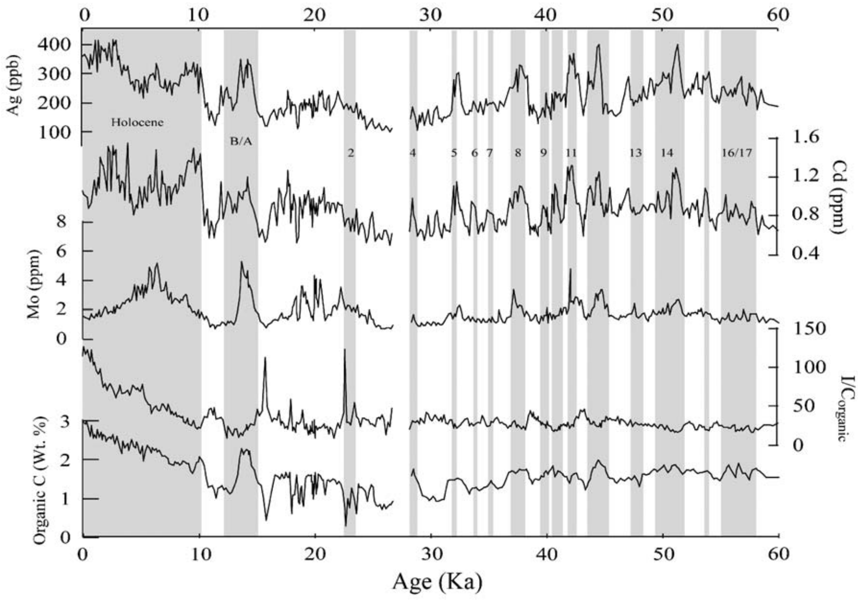


Figure 22 Comparison of temporal records of Ag, Cd, Mo, $I/C_{organic}$ and organic C at ODP Site 1017E on the central California continental slope (34.53°N, 121.1°W, 955 m water depth). Shading represents warm intervals as deduced from the ratio of dextral to sinistral *Neogloboquadrina pachyderma* (Hendy, Pedersen, Kennett, & Tada, 2004). Interstadial events are numbered beneath the Ag profile. YD = Younger Dryas, B/A = Bølling-Allerød. Ag, Cd and Mo enrichments show that many of the interstadials experienced sulphate-reducing conditions in the pore waters, suggesting that the export flux of biogenous detritus as well as intermediate water ventilation played a role in modulating the intensity of the OMZ over the last 60 kyr.

to the introduction of new proxies for tracking climatic and oceanographic variability in the past as more information on the geochemistry of marine sediments accumulates and as new requirements for insight into environmental changes are realized.

Further application of palaeoclimate proxies using major and minor element contents of lithogenous components, and cross validation of interpretations against other palaeoclimatic indices, e.g. terrestrial biomarkers (e.g. Zhao, Eglinton, & Zhang, 2000; Pancost & Boot, 2004), will increase our understanding of past variations in terrestrial climates and land–ocean interactions. The recent development of automated continuous scanning X-ray fluorescence determination of selected major element abundances (Jansen et al., 1998) promises to provide much-needed high-resolution sedimentary records, which could be used for these purposes. Calibration of the XRF response so that more quantitative information can be acquired, and extension of the method to include the determination of Al concentration, in addition to Fe, Ti and Ca reported so far, would mark a significant advance in the technique. In this way, true variability of the composition of the lithogenous component of sediments could be assessed via Al-normalization (Section 3), thereby avoiding the ambiguity of results currently available in the form of raw count rates.

Further work on the validation of palaeoproductivity proxies is urgently required. For the Ba proxy, experimental approaches using phytoplankton cultures need to be extended in view of the probability that the culture conditions themselves have compromised some earlier results, and that the precipitation of Fe hydroxide on particle surfaces leads to the removal of Ba from solution (Sternberg et al., 2005). The formation of hydroxide coatings on all particle surfaces could account for the presence of barite within masses of sinking planktonic debris (Dehairs et al., 1987), the association of barite with suspended diatom frustules (Bishop, 1988) and the precipitation of barite in cultures of both diatoms and coccolithophorids (Ganeshram et al., 2003), implying that barite may constitute an index of particle flux through the water column rather than productivity *per se*. The Ba or barite proxy also needs to be cross-checked against other palaeoproductivity proxies, e.g. phytoplankton group biomarkers (alkenones for coccoliths, sterols for diatoms (e.g. Engel & Macko, 1993).

Establishment of the degree of preservation of barite in bottom sediments is also an urgent requirement in view of conflicting results from oxic, suboxic and anoxic settings. This is especially puzzling in view of the fact that all deep ocean bottom waters are saturated with respect to barite (Monnin et al., 1999), and the observation that Ba is being diagenetically mobilized from fully oxic pelagic sediments that lack subsurface suboxia or anoxia (Paytan & Kastner, 1996; McManus et al., 1998). Assessment of the recommendation for the use of authigenic U enrichment in sub-surface sediments as an index of probable barite remobilization (McManus et al., 1998) should be carried out in parallel with this work.

Algorithms for palaeoproductivity using barite or excess Ba (Dymond et al., 1992; François et al., 1995) require re-evaluation in view of the evidence for significant focusing of Holocene sediment sections, as discussed later. This effect will have inflated some, if not many, of the Ba or barite accumulation rates estimated from conventional mass accumulation rates, which are required for the regressions of modern Ba accumulation rates on estimates of primary production at individual core sites.

Evidence for a large range of Al/Ti ratios and the highly variable amount of excess Al relative to Ti in settling particular material in the central equatorial Pacific (Dymond et al., 1997) suggests that the apparent excess Al in bottom sediments of this region is not related in a simple way to the particle flux to the sea floor. This will potentially compromise the use of excess Al as a particle flux, or palaeoproductivity, proxy as originally conceived (Murray et al., 1993; Murray & Leinen, 1996). More work on the geochemistry of the preponderantly biogenous sediments in this region is required in order to provide a means for distinguishing between adsorbed or scavenged Al and Al added to the sediment by authigenic formation of aluminosilicate phases or phases (Timothy & Calvert, 1998). Knowledge of the precise composition of these phases will then provide a means for distinguishing between authigenic and detrital (lithogenous) Al, which in turn will improve our ability to characterize the aluminosilicate contribution to sediments, for example in the form of aeolian dust (Anderson, Fleisher, & Lao, 2006), and the reliability of Al-normalization for assessing element enrichments and depletions over time.

Variations in the sedimentary concentrations of chalcophile elements that have a significant authigenic component can be valuable as indicators of bottom-water or upper-pore-water oxygenation. But there is a constraint on such inferences, in that the rate of sub-bottom precipitation as a metal sulphide, for example, is largely a function of the concentration gradient, $\partial C/\partial z$, which provides the primary control on the rate of molecular diffusion. A subtle change in precipitation depth of say, 1 to 2 mm, could halve the rate of precipitation of the authigenic fraction of a metal, without necessarily being directly related to the oxygen content at the sediment water interface. A short-term decline in sedimentation rate could yield such a change. Thus, there is considerable scope for high-spatial-resolution study of the distributions of dissolved chalcophile metals as a function of shallow sub-bottom depth in sedimentary pore waters, ideally as time-series measurements over the course of several seasons on selected continental margins. Such work would be expensive, technically challenging and time-consuming, but would provide data of considerable value in the calibration of trace-metal proxies.

Since the bulk composition of sediments and sedimentary rocks is determined by the accumulation rates of the individual components of the deposit, a better way to evaluate variations in the supply rates of proxies to the sea floor is to recast compositional information into component accumulation rates (Koczy, 1951). This approach avoids the constant sum problem when data are expressed as closed arrays (Rollinson, 1993). We have eschewed this approach here because reliable data on the vertical flux of materials, that is sediment flux to the sea floor through the seawater interface or from the sea surface, are scarce. The calculation of component accumulation rates — which relies on estimates of linear sedimentation rates determined as the sediment thickness deposited per unit time between two horizons or depths of known age — is unreliable because sediment winnowing and lateral transport, or focusing, on the sea floor appears to be pervasive (François et al., 2004). Thus, the thickness of a sediment section is not a reliable estimate of the mass of sediment supplied to the sea floor from the overlying water column, a requirement for assessing, for example, palaeoproductivity or aeolian dust fluxes. This is a controversial issue at the time of writing (Lyle et al., 2005), but if these effects are confirmed by on-going work, a great deal of effort will be required to re-evaluate the true vertical flux of materials to the sea floor by using a constant flux tracer. Two possibilities have been proposed, ^{230}Th (Bacon, 1984; François et al., 1990) and ^{3}He (Marcantonio, Anderson, & Mix, 1996), both of which have more or less constant fluxes to the sea floor due to their source functions — U decay in the first case and extra-terrestrial dust flux in the second. These tracers have the added advantage that they can provide normalized accumulation rates at high resolution, that is at each sampling point in a core profile (François et al., 2004), whereas conventional sedimentation rates can only yield average mass accumulation rates between more widely spaced sample depths, normally at much coarser resolution than the available compositional information. Modern mass spectrometric techniques are fully capable of generating the high-resolution data sets that will be required to generate reliable records of component accumulation rates throughout the ocean. The major limitation of the ^{230}Th normalization method is the relatively short half-life of the isotope (75.7 kyr), which restricts its application to the last

200–300 kyr. No such limitation exists for ^{3}He normalization, and we expect to see its wide application for this purpose in older sediment sections.

9. Afterword

Nearly 150 years ago, natural philosophers began applying techniques of elemental analysis of sediments and sedimentary rocks in an effort to understand geological processes and to apply such knowledge to unravelling Earth history. The laborious techniques and crude detection limits of the past have been supplanted in the modern era by sophisticated, automated methods that generate large volumes of multi-element information. Although this wealth of data has provided an interpretative boon for modern sedimentary geochemists, challenges remain, none more compelling than developing a stronger understanding of climate history, particularly during the Quaternary Era.

This chapter has reviewed current approaches to palaeoclimate interpretation that are based on a wide range of analyses of marine sediments. Although single element distributions can serve as proxies for certain processes, such an approach is often insufficient to yield confident palaeoclimatic interpretations. A multiproxy approach — the collective interpretation of the typical multi-element assemblages that today can be gleaned from the analysis of sediment cores – presents a better option, as implied by the examples discussed in the preceding pages. We recommend that such an approach be applied wherever possible to circumvent some of the current proxy noise, for the additional investment in analytical effort pays disproportionately higher dividends in insight gained.

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