CHAPTER 4

DEEP-SEA SEDIMENTS AND PALAEOCEANOGRAPHY

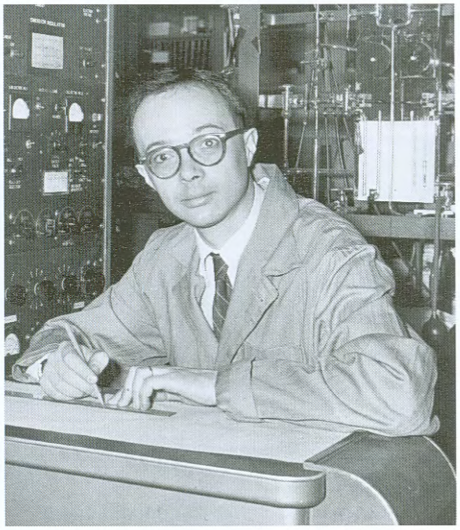

Figure 4.1 Cesare Emiliani (1922–1995). Emiliani was born in Italy; this photograph was taken in the early 1950s when he was working at the University of Chicago. (*Photo: Robert Ginsburg.*)

As recently as the late 1960s, the deep sea was regarded by some as an unchanging primordial environment and the most constant feature on the surface of the Earth throughout most of geological time. While the HMS *Challenger* expedition (Section 1.1) provided information about the present-day distribution of deep-sea sediments, an historical perspective was added only in the mid-1940s following the invention of the **piston core**. This was first deployed on the Swedish Deep-Sea Expedition (1947–1948), and analysis of the recovered sediment cores revealed that over time there had been significant variations in the accumulation of carbonate material, which could be correlated with glacial and interglacial conditions. Although sedimentary studies such as this were important in demonstrating that the oceanic environment had in fact changed with time, the science of **palaeoceanography** (the study of ancient oceans) was really founded in the 1950s, when Cesare Emiliani (Figure 4.1) published a series of three classic papers that outlined past variations in sea-surface temperature as derived from the analysis of oxygen isotopes in the $CaCO_3$ shells of foraminiferans (see Section 4.3.1). These papers demolished the notion that the marine environment is constant over periods of thousands of years (Figure 4.2).

Piston cores can recover material up to a few hundred thousand years in age. Much longer cores could be recovered only after the start of the Deep Sea Drilling Project (DSDP) in 1968. DSDP ended in 1983, and continued as a multinational effort with the Ocean Drilling Program (ODP, 1985–2003), which has now been superseded by the Integrated Ocean Drilling Program (IODP, 2003–). IODP utilizes two drillships, along with additional drilling platforms as required

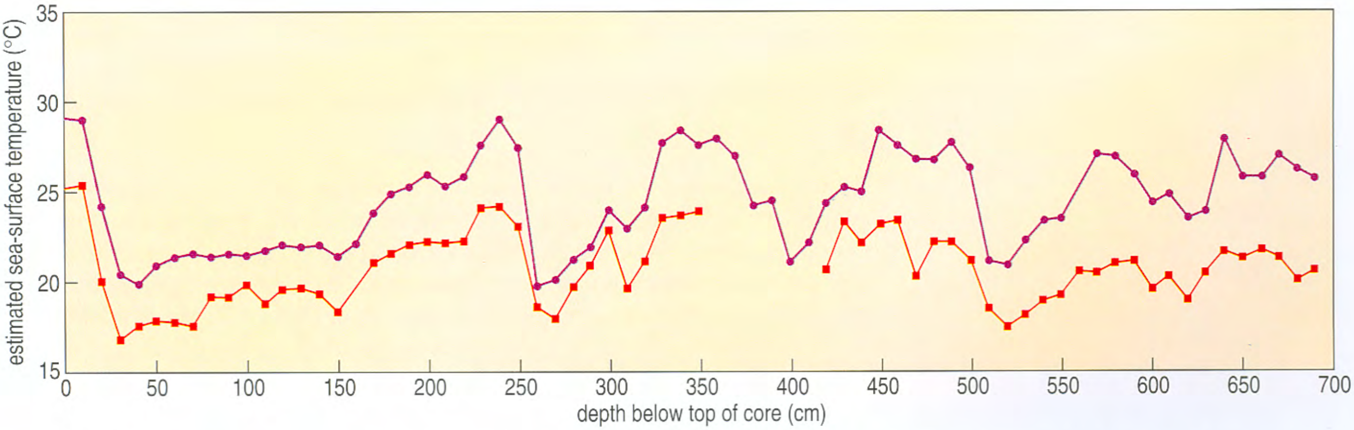

Figure 4.2 Emiliani's first measurements of the variation in sea-surface temperature with core depth, as determined from oxygen-isotope analysis of planktonic foraminiferans, for a core obtained from the Caribbean. (i) *Globerigerinoides sacculifera* (purple circles); (ii) *Globigerina dubia* (red squares). Note that the value determined for sea-surface temperature varies with species. Radiocarbon dating of this core gave an age of 27 600 ± 1000 years for sediment at a depth of 73.5 cm below the top of the core.

(Figure 4.3). Core material recovered by DSDP, ODP and IODP has confirmed that there have been changes in sea-surface temperature in the past, and it has shown that sediments accumulating on the sea-floor in fact record a plethora of other conditions (and events) in the overlying waters, such as biological productivity and patterns of ocean circulation. This is explored in the following Sections: first though, we will investigate how the sediment record has helped to unravel the history of the evolution of the ocean basins.

Figure 4.3 The IODP drillship *Chikyu*, launched by the Japanese in 2004. '*Chikyu*' is Japanese for 'Earth'.

4.1 EVOLUTION OF THE OCEAN BASINS

The sea-floor sediment record extends back to ~180 million years ago at the most.

Why is that, when the oldest rocks on Earth are around 3850 million years old?

The reason is that the ocean basins are relatively short-lived features of this planet. An individual basin grows from an initial rift, reaches a maximum size, then develops subduction zones around the margins, begins shrinking and ultimately closes completely. This cycle takes, on average, about 200 million years (Ma): no oceanic crust older than about 180 Ma is known from the present oceans. As sediments accumulate on top of oceanic crust, they too can be no older than about 180 Ma.

The thickness of sediments increases with distance from spreading axes, and with increasing depth either side of an axis.

What is the reason for this?

The further crust is from the ridge, the older it is and the more time has elapsed for sediments to accumulate; furthermore, depth increases with age according to the **age–depth relationship** (Figure 4.4). Near spreading axes, sediments are no more than a metre or two thick, even in depressions in the rugged topography, except where an axis lies close to land (e.g., in the Gulf of California). By contrast, in abyssal plain areas, sediment thicknesses of a kilometre or so are commonplace. The continental shelf–slope–rise region may be blanketed by more than 10 km of sediment.

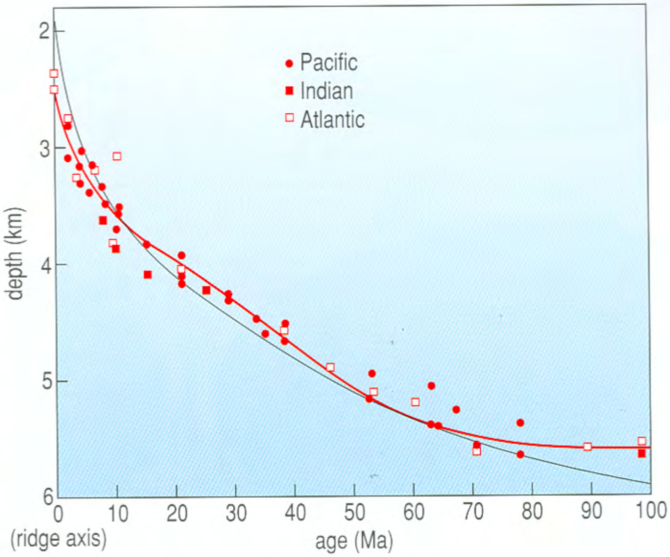

Figure 4.4 Observed and theoretical relationship between the depth to the top of the oceanic crust and its age. The red line is a best-fit curve through observed points. The fine black line is a theoretical elevation curve, calculated on the assumption that the increase of depth with age is due to thermal contraction of the lithosphere as the plate cools on moving away from the ridge axis.

Distance from a spreading ridge may also affect the *type* of sediment accumulating.

QUESTION 4.1 Examine Figure 4.5 and, recalling what you read in Chapter 3, explain why: (a) the main sedimentary component at the sea-floor at locality 1 is calcium carbonate; (b) the carbonate ooze at locality 2 is overlain by pelagic clay; (c) the main sedimentary component *at the sea-floor* at locality 3 is siliceous ooze.

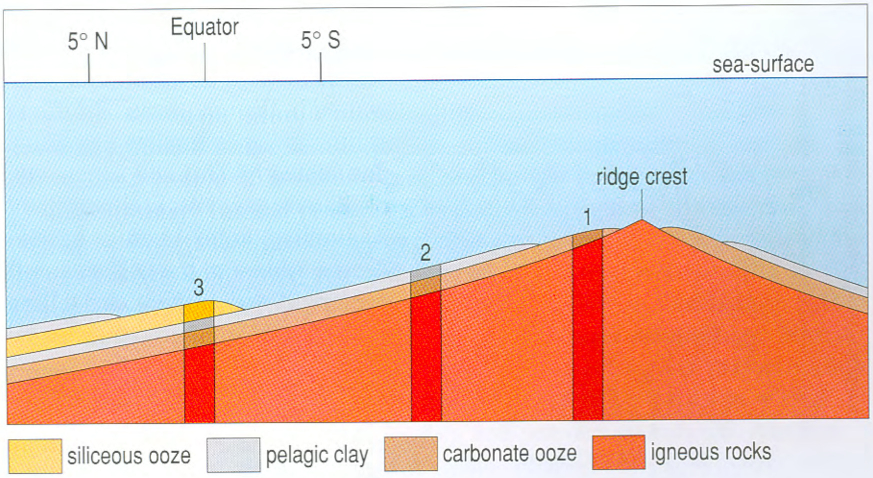

Figure 4.5 A simplified cross-section (perpendicular to the ridge crest) of the sediments in part of the Pacific Ocean. The main components of the sediment types are given in the key. (For use with Question 4.1.)

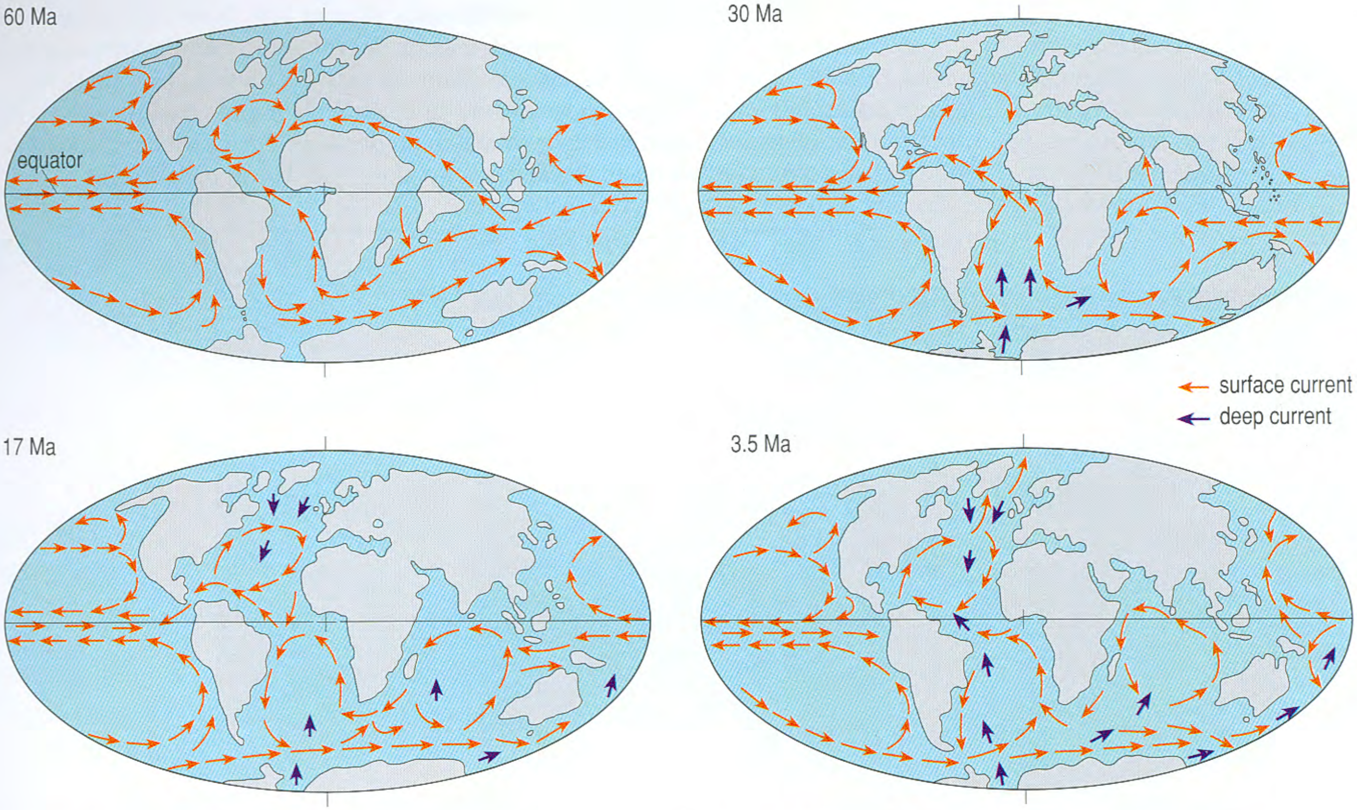

Figure 4.6 Changing continental configurations since 60 Ma, and postulated ocean currents (surface: thin orange arrows; deep: thick blue arrows). The maps show two key events: (i) the opening of an oceanic gateway between South America and Antarctica 25 to 30 Ma ago, allowing the Antarctic Circumpolar Current to develop; and (ii) the closing of the gateway between Central and South America at around 3.5 Ma, isolating the Atlantic and shutting down equatorial circulation between it and the Pacific.

The sediment record can additionally provide information as to the changing configuration of the continents, which in turn affects wind and current patterns (Figure 4.6). By way of example, we will examine the effects of the closure of the gateway between Central and South America at around 3.5 Ma ago. The closure severed communication between the equatorial Pacific and the Atlantic Ocean and Caribbean Sea, and may have played a role in the initiation of the **glaciation** of the Northern Hemisphere.

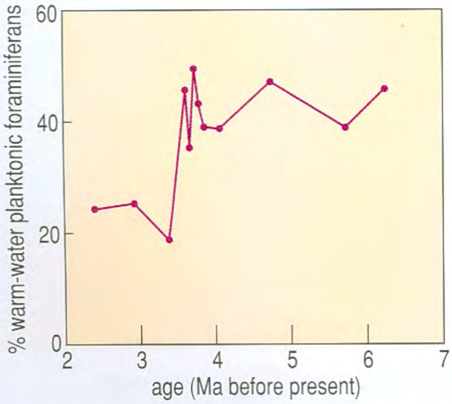

Figure 4.7 Changes in the percentage of warm-water planktonic foraminiferans (relative to total foraminiferal assemblage) over the past ~7 Ma, in sediments recovered from off the coast of NW Ecuador in the Pacific Ocean.

Figure 4.7 shows that off Ecuador the relative amount of planktonic foraminiferans that prefer to live in warm water decreased sharply in sediments laid down around 3.95 to 3.35 Ma ago, indicating that surface waters in the equatorial Pacific cooled after the closure of the gateway. The nature of the sediments has also changed. Before ~3.5 Ma, they were dominated by silts and sands, but since 3.5 Ma the sediments consist mainly of diatom ooze. As you read in Chapter 1, diatom oozes generally accumulate today in areas of coastal upwelling; upwelling brings cooler, deeper waters to the surface, so the sediments, and the foraminiferan tests preserved within them, are telling us that closure of the gateway between Central and Southern America initiated upwelling off the coast of Ecuador.

Deducing the evolution of the ocean basins is just one aspect of palaeoceanography. The study of palaeoceanography has expanded rapidly in recent years; the main reason for this is that it has become clear that changes in characteristics of the ocean (such as temperature distribution, circulation and productivity) are linked to changes in global climate. A good example of this is shown in Figure 4.8: the variation in the oxygen-isotope composition of surface seawater over the past 400 000 years tracks the variation in atmospheric carbon dioxide and temperature recorded by

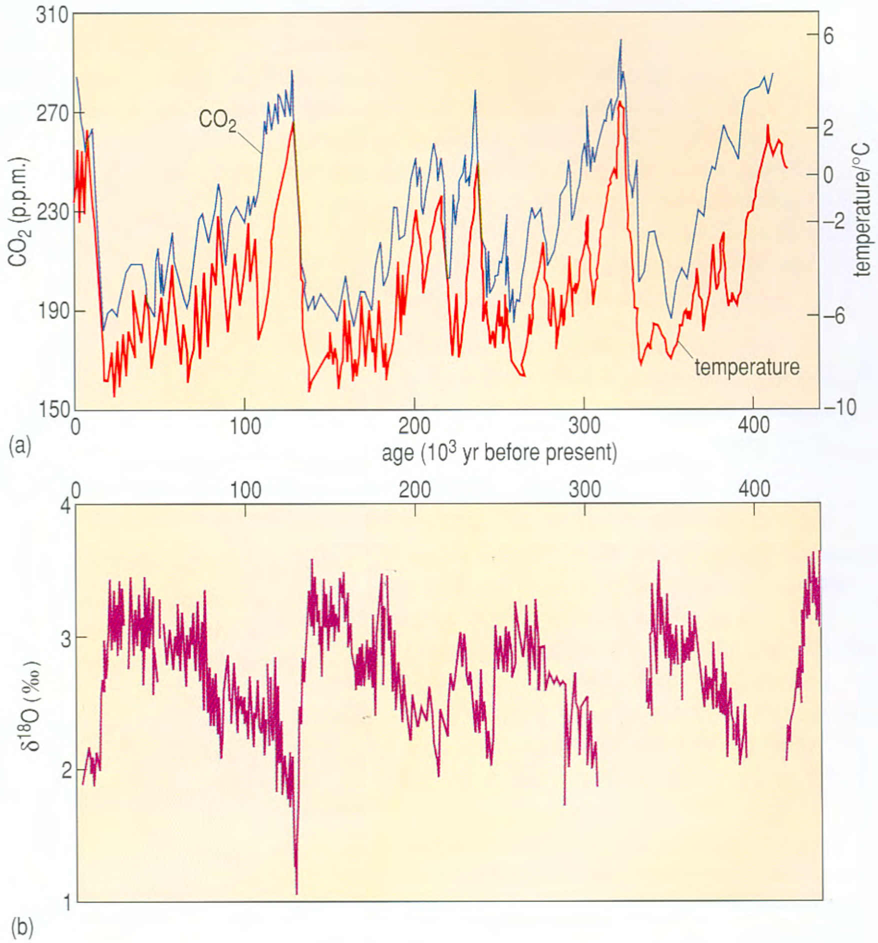

Figure 4.8 (a) Record of the last 400 000 years of atmospheric CO_2 and temperature variation from the Vostok ice core, Antarctica. Also shown is (b), the corresponding record of planktonic foraminiferal $\delta^{18}O$ (see Section 4.3.1) from sediments recovered from the South Atlantic (40° 56′ S, 9° 54′ E). Note the close correlation between these records; this tells us that there is some kind of link between atmospheric CO_2, temperature and surface seawater $\delta^{18}O$. The exact nature of this relationship is the subject of ongoing scientific debate.

ice cores from the Antarctic. If we can understand these links between ocean and climate, then we will be better able to predict the effects of human activity on future climate.

4.2 USE OF PROXIES IN PALAEOCEANOGRAPHY

How can we obtain information about the ancient oceans when, for example, scientific observations of sea-surface temperature go back no more than a couple of hundred years, and no laboratory holds samples of glacial seawater? Instead of direct measurements, palaeoceanographers must rely on *proxies* (substitutes) — things that can be measured in sediments (or ice) laid down in the past, and which have responded systematically to changes in important (but now unmeasurable) variables, like salinity. One of the most useful sediment proxies is the **microfossil assemblage**: marine organisms, plant and animal, have their particular ecological preferences, which are related to the environmental conditions in the water in which they lived, such as temperature, salinity and nutrient abundance. Another useful proxy is the composition of microfossil shells, organic matter and other sediment components, in terms of the chemical elements and the relative proportions of the different isotopes of those elements.

The ideal sediment proxy should correlate with a single variable, and this correlation should be preserved in perpetuity in the sedimentary record.

Generally, this isn't the case; the correlation is often imperfect and several more or less independent variables will determine the behaviour of the proxy, while chemical changes within the sediment can overprint the primary correlation between the variable and the proxy. The best way to overcome these problems is to estimate a variable using more than one proxy: the 'multiproxy approach'.

The relationship between a proxy and a variable is calibrated by comparing proxy data for surface (modern-day) sediments with corresponding data collected in the overlying water column.

What critical assumption would you be making here?

You would be assuming that the calibration would also have applied in the past; in, say, glacial times, for example.

QUESTION 4.2 Explain how (a) emplacement of a turbidite, and (b) a low sedimentation rate, can affect the quality of a palaeoceanographic record.

In the following Section, you will learn about some proxies, and what they can tell us about past oceanic conditions and long-term climate change. It will become clear that palaeoceanography is an emerging science, and that much more research is needed into the development and calibration of proxies.

4.3 RECONSTRUCTING PAST OCEANS: INSIGHTS AS TO THE CAUSES OF CLIMATE CHANGE

Figure 4.9 represents a qualitative estimate of the changing mean global temperature for the past ~200 Ma (the maximum age of deep-sea sediments), in relation to that of the present day (marked by a dashed line), which is about 15 °C. Throughout most of this time, mean global temperature has been consistently higher than that of today, and the Earth is informally referred to as having been in a 'greenhouse' condition.

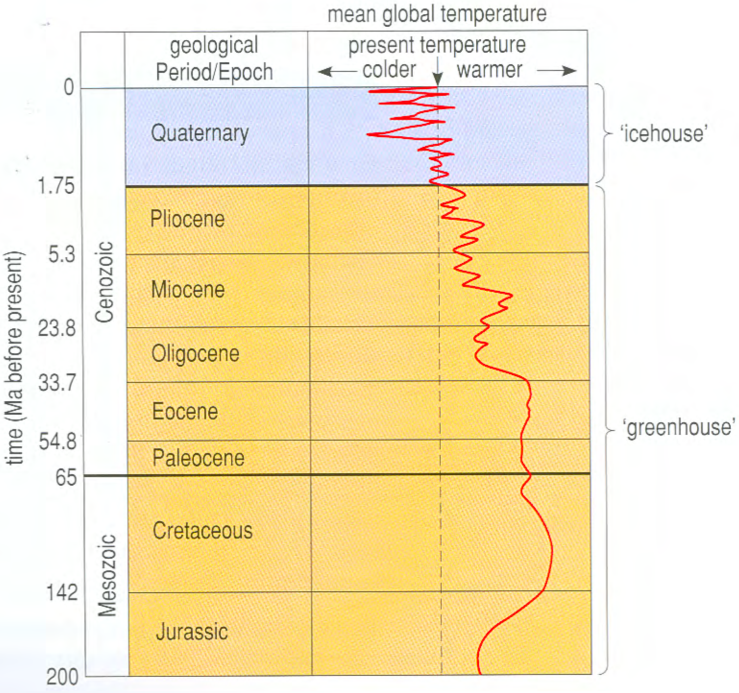

Figure 4.9 Schematic representation of changes in mean global temperature relative to that of the present day (about 15 °C), for the past 200 Ma, based on an array of geological evidence. Note that the time axis is *not* linear, but has been adjusted to show more detail for recent geological periods.

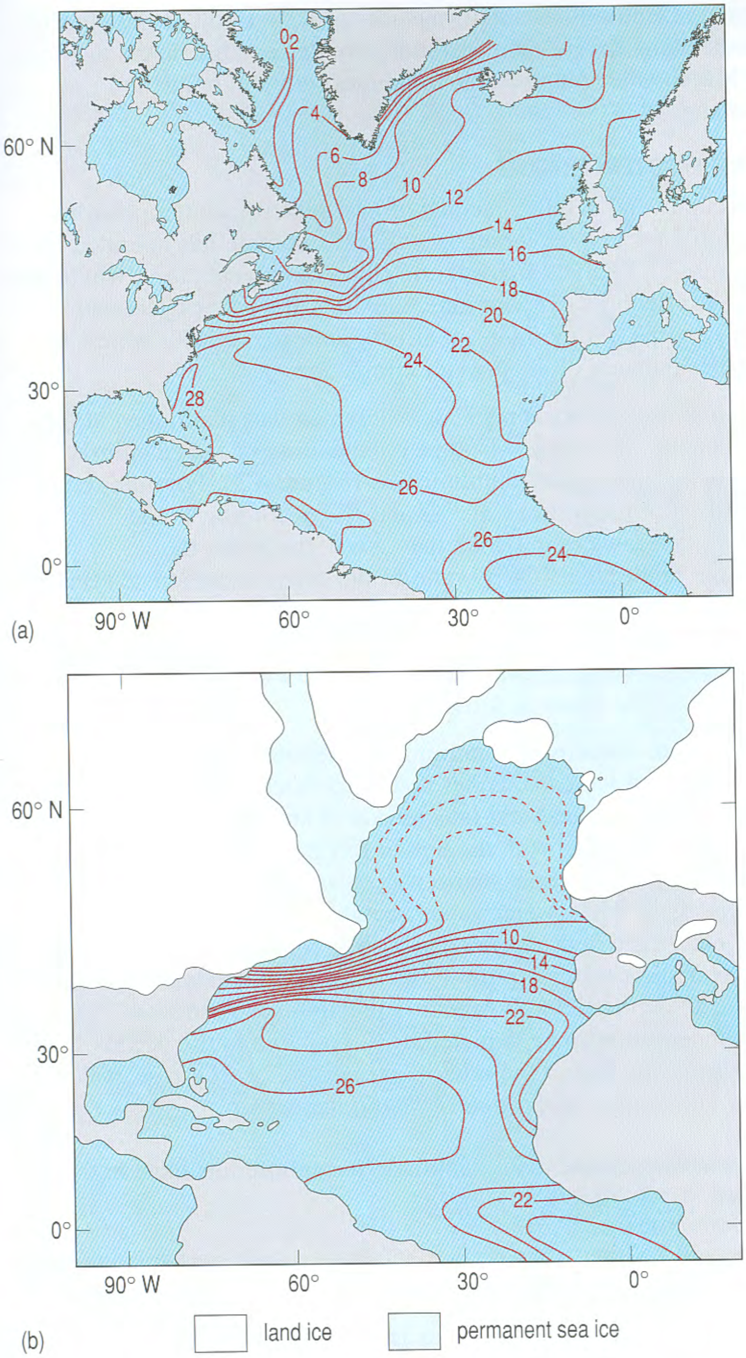

Figure 4.10 Maps comparing the distribution of ice and sea-surface temperatures in the northern Atlantic summer (a) at the present time, and (b) 18 000 years ago. Isotherms are in °C.

The Quaternary, the present geological era, is however characterized by 'icehouse' conditions, with huge permanent ice-sheets present over Antarctica and Greenland. Another feature of the Quaternary is the dramatic and apparently cyclic changes in the Earth's climatic regime. These cycles involve the growth and retreat of yet further large ice-sheets over much of North America and northern Eurasia (including the British Isles) and elsewhere, and they are referred to as **glacial/interglacial cycles**.

Today, the Earth is in an interglacial period. If we travelled back in time 18 000 years, to the height of the last glacial period, we would hardly recognize our planet; environmental conditions were very different (Figure 4.10).

Many parts of the Northern Hemisphere that are densely populated today were frozen wastes: glaciers reached the sites of New York and Berlin, and the ground where London and Paris would become established was permanently frozen. Ice sheets over 3 km thick covered much of North America and Scandinavia. Winds blowing down from the ice sheets reached speeds of over 100 km per hour. Much of western Europe was largely treeless with a tundra-like landscape, and much of the northern part of the North Atlantic Ocean was frozen, although the Norwegian Sea remained seasonally ice free. Sea ice extended down to the latitude of the British Isles, and even during the summer months, floating ice and large icebergs would have been common between Ireland and Newfoundland.

The isotherms (lines of equal temperature) in Figure 4.10 show that the distribution of sea-surface temperature in the northern Atlantic 18 000 years ago was markedly different from what it is today. At around 40° N, the isotherms were much more crowded together during glacial times as a result of the southward expansion of the high-latitude cold belt. Note, however, that the zone of warm water in equatorial and tropical latitudes (up to about 30° N) was apparently not much narrower at the height of the glaciation than it is now. Off north-west Africa, the relatively low temperatures were even more marked 18 000 years ago than they are today, suggesting that upwelling there was even more powerful in glacial times than at present.

QUESTION 4.3 What do the isotherms in Figure 4.10 suggest about the flow of the Gulf Stream 18 000 years ago?

We now move on to look into how maps of past oceanic conditions, such as that shown in Figure 4.10(b), are determined. For the most part, we will use examples from the past ~2 Ma, because the climatic, environmental and ecological processes that have operated during this time, though subject to rapid change, are similar, but not always identical, to those of the present. If we can understand the mechanisms that have driven climate change over the past ~2 Ma, then we may be able to predict future climatic and ecological changes.

4.3.1 SEA-SURFACE TEMPERATURE

Obtaining accurate and detailed records of past sea-surface temperature (SST) is essential for understanding how Earth's climate has operated in the past, because SST drives atmospheric circulation, generating winds and weather, and it influences evaporation, regulating the water cycle and precipitation patterns. Furthermore, it affects seawater density which, in turn, determines patterns of deep-water circulation.

The most widely used proxy for SST is that which was mentioned at the start of this Chapter: the oxygen-isotope composition of the calcium carbonate tests of planktonic foraminiferans (Figure 4.2). Foraminiferans incorporate different proportions of ^{16}O and ^{18}O according to the temperature of the seawater in which they grow: the lower the temperature, the higher the $^{18}O/^{16}O$ ratio in the calcium carbonate secreted. Although all organisms secreting calcium carbonate produce $CaCO_3$ with higher $^{18}O/^{16}O$ in cold than warm water, the actual ratio for a particular temperature depends on the species concerned (see Figure 4.2) (and also on the $^{18}O/^{16}O$ ratio of the water it is living in).

The $^{18}O/^{16}O$ ratio of remains of foraminiferans is also affected by the waxing and waning of ice-caps. Water that evaporates from the ocean eventually condenses as cloud and falls as rain or snow. When seawater evaporates, water molecules with the lighter oxygen isotope ($H_2{}^{16}O$) evaporate more readily, so atmospheric water vapour is relatively enriched in the lighter isotope. When water vapour condenses and is precipitated back into the ocean, the heavier isotope ($H_2{}^{18}O$) condenses preferentially. Both processes deplete water vapour in the atmosphere in $H_2{}^{18}O$ relative to $H_2{}^{16}O$. When ^{18}O-depleted water vapour is precipitated as snow at high latitudes, the snow will also be depleted in ^{18}O relative to the oceans. The larger the ice-caps, the higher the relative proportion of ^{18}O in seawater and the lower the relative proportion of ^{18}O in ice-caps.

Under what conditions, then, will planktonic foraminiferans have high $^{18}O/^{16}O$ ratios?

$^{18}O/^{16}O$ ratios will be high if the surface seawater is cold, and the amount of water held in ice-caps is large.

The amount of ^{18}O in foraminiferan tests is very small, but it can be measured accurately by mass spectrometry. The result is usually reported not as a simple ratio, but as a delta (δ) value, which is determined by comparison of the sample with a standard, and results in a value expressed in parts per thousand (‰ or 'per mil'):

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{standard}}}{(^{18}O/^{16}O)_{\text{standard}}} \times 1000 \qquad (4.1)$$

Generally, the standard used nowadays is seawater; Standard Mean Ocean Water (SMOW), or Vienna Standard Mean Ocean Water (VSMOW), which superseded SMOW in 1995.

QUESTION 4.4 (a) A foraminiferan test has a δ^{18}O value of $-1‰$ relative to VSMOW. By reference to Equation 4.1, explain whether it contains more or less ^{16}O than the VSMOW standard. (b) What is the meaning of a δ^{18}O value of $0‰$?

To reconstruct past variations in sea-surface temperature, the 'ice volume' signal must be separated from the temperature signal. One way to do this is to make oxygen-isotope measurements for tests of benthic foraminiferans, since waters near the ocean floor generally remain relatively unaffected by global changes in surface temperature, but are always affected by ice volume changes. By subtracting the δ^{18}O value for a benthic foraminiferan from the δ^{18}O value of a contemporaneous planktonic foraminiferan, an estimate of SST at the time in question can be obtained (Figure 4.11).

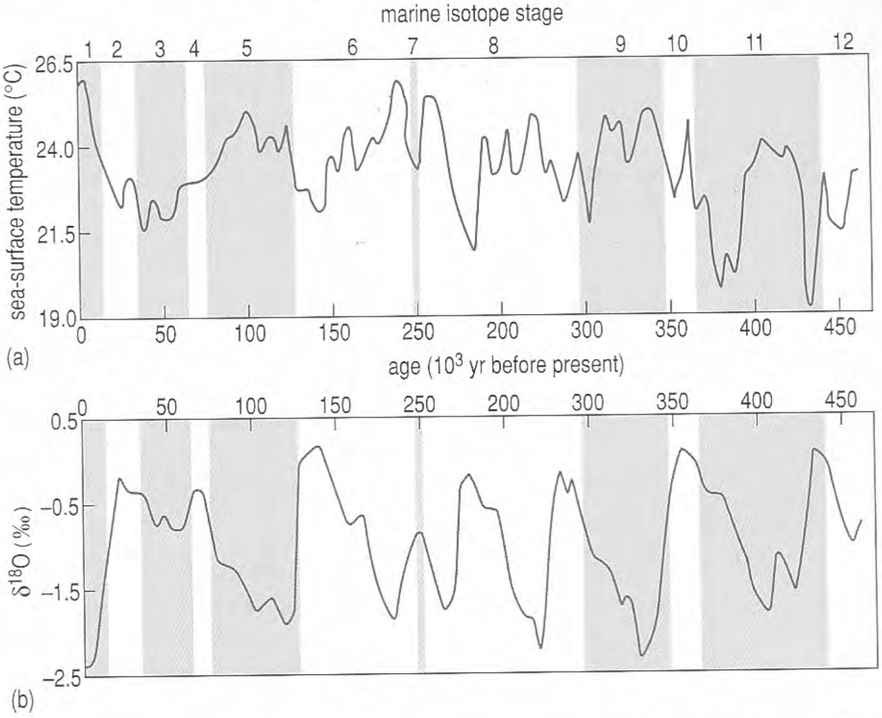

Figure 4.11 (a) Variations in sea-surface temperature in the Caribbean inferred from oxygen-isotope ratios measured for the tests of planktonic and benthic foraminiferans. The oxygen-isotope record for planktonic foraminiferans (b) is also shown. Interglacial (blue) and glacial (white) periods are identified by odd- and even-numbered Marine Isotope Stages, respectively. (See text for details.)

The last glacial period can be seen recorded in Figure 4.11 as higher δ^{18}O values and lower sea-surface temperatures from ~30 000 to ~12 000 years ago. The isotope record in fact reveals a number of glacial and interglacial periods; these are known as **Marine Isotope Stages** (MIS), and by convention, odd-numbered stages represent interglacials and even numbers glacials. Glacial stages tend to be longer than interglacials, and their termination is rapid (on a geological timescale). Furthermore, the record shows small perturbations in the average climate during both glacials and interglacials (these perturbations are called *stadials* and *interstadials*, respectively).

Figure 4.11 shows that there have been six major glacial/interglacial cycles during approximately the past 0.5 Ma. Since 0.71 Ma ago, there have been eight such cycles.

What is the approximate time period for these climate cycles?

It is close to 100 000 years. This 100 000-year periodicity is less obvious in records of earlier climatic fluctuations preserved in sediments, which, back to about 2.6 Ma ago, are dominated by cycles lasting *c.* 40 000 years.

What processes are seen as controlling the periodicity of these climatic cycles?

They are the cyclical changes in the configuration of the Earth in its orbit, which result in periodic changes in the amount of solar radiation reaching the Northern Hemisphere. These cyclical changes are known as **Milankovitch cycles**; there are three different cycles, superimposed on one another, having periods of about 22 000 years, 40 000 years and 110 000 years.

These orbital variations *alone*, however, cannot explain the causes of glacial periods. One reason is that the pattern of Milankovitch orbital variations, as recognized in oceanic oxygen-isotope records from the Quaternary, must have operated throughout most, if not all, of the Earth's geological history. For much of that time, there is no evidence of any significant glaciation. Another reason is that Milankovitch theory relates the pattern of glacial and interglacial stages to changes in the amount of solar radiation reaching the Northern Hemisphere, but analysis of sediment cores from sites throughout the world ocean reveals that this pattern is in fact global. The mechanism most likely to 'mix and merge' climatic signals in both hemispheres is the pattern of deep ocean circulation and the global thermohaline conveyor.

Other tools used to assess past SST include statistical analysis of the microfossil assemblage (different species tolerate different ranges of water temperature), and measurement of Mg/Ca ratios in shells of well-preserved planktonic foraminiferans (like $\delta^{18}O$, Mg/Ca of a shell varies with temperature, although it does *not* vary with ice volume).

What are the drawbacks of using foraminiferans as palaeoclimate proxies?

Recall that roughly 80% of the ocean floor lies below the CCD. Foraminiferan tests are composed of calcium carbonate and are likely to dissolve below the CCD. This means that records of environmental change based on foraminiferans are often incomplete. An alternative method for obtaining past sea-surface temperatures, this time from *organic* remains of coccolithophores, is described in Box 4.1.

4.3.2 OCEAN CIRCULATION

Along with surface currents, the pattern of thermohaline circulation is an important factor in Earth's climate because its overall effect is to transport vast quantities of heat poleward into high latitudes. The thermohaline circulation involves the formation of North Atlantic Deep Water in the Greenland (and Labrador) Seas, its flow southward in the western Atlantic, round southern Africa (where it is joined by Antarctic Bottom Water) and then into the Indian and Pacific Oceans, and its subsequent return to the surface through upwelling (Figure 2.23). As you read in Chapter 2, this pattern is reflected in the concentration of nutrient elements in bottom seawater: concentrations are highest in the oldest waters in the deep northern Pacific, and lowest in newly formed deep water in the northern Atlantic (Figure 2.22). If deep-water circulation was different in the past, we might expect to see a different distribution of the nutrient elements.

BOX 4.1 MOLECULAR INDICATORS OF ENVIRONMENTAL CHANGE

Alkenones (a type of ketone) are a class of organic molecules found in almost all marine sediments from the present day back to at least 140 Ma ago. They are important constituents of the membranes of coccolithophores, such as *Emiliania huxleyi* (Figure 1.5). It turns out that coccolithophores alter the number of double bonds in their alkenone constituents, depending on the temperature of the water that they are growing in. Careful laboratory experiments show that the relative abundance of alkenones with 37 carbon atoms and two carbon–carbon double bonds increases at higher temperatures, while the relative abundance of alkenones with 37 carbon atoms and three carbon–carbon double bonds increases at lower temperatures. Expressed in simple terms: more double bonds means cooler waters. The so-called **alkenone unsaturation index**, U^{K}_{37} (where U is for unsaturation, i.e. the presence of double bonds; the superscript K is for ketone; and the subscript 37 is for the number of carbon atoms), is given by:

$$U^{K}_{37} = \frac{[C_{37:2}]}{[C_{37:2}]+[C_{37:3}]} \tag{4.2}$$

where $[C_{37:2}]$ and $[C_{37:3}]$ refer to the concentration of alkenones with two and three double bonds, respectively. The relationship between U^{K}_{37} and temperature (T, °C) is as follows:

$$U^{K}_{37} = 0.034T + 0.039 \tag{4.3}$$

QUESTION 4.5 At what time of year would you expect coccolithophore productivity to be highest at temperate latitudes, and what are the implications for measurement of sea-surface temperature using the alkenone unsaturation index?

Figure 4.12 compares records of SST derived from the U^{K}_{37} index and on the basis of the distribution and relative abundance of different species of planktonic foraminiferans for a core recovered from the eastern North Atlantic. Records derived from the U^{K}_{37} index are generally in good agreement with those derived from warm (August) foraminiferal assemblages between 28 000 and 8000 years ago, which suggests that maximum coccolithophore production occurred in the summer months in the glacial ocean. The relationship between these two proxies breaks down for sediments deposited during the last 8000 years. This may be linked to a switch in the seasonal timing of maximum coccolithophore productivity from mid-summer in the glacial ocean to late spring—early summer in the modern ocean.

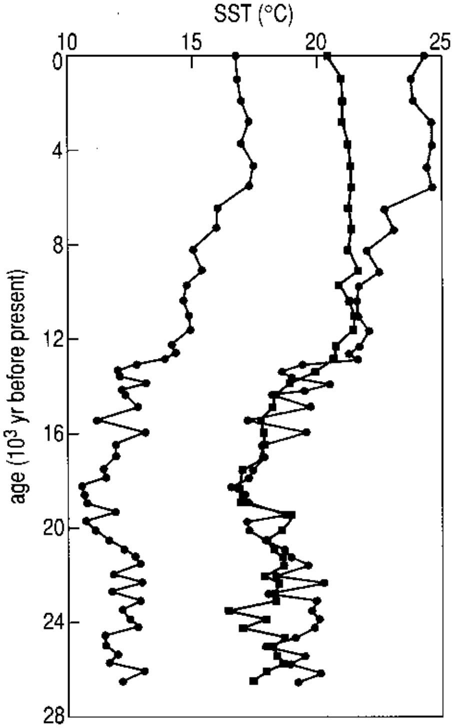

Figure 4.12 A comparison of planktonic foraminiferal SST estimates for August (orange circles, right) and February (blue circles, left), with the U^{K}_{37} (black squares) palaeotemperature index.

The nutrient elements (principally nitrogen and phosphorus, in the form of nitrate and phosphate) are incorporated into the soft tissues of biogenic material and are therefore not well preserved in sediments. For this reason, we need to find a nutrient proxy; that is, something that mimics the behaviour of the nutrients, and is preserved in the sedimentary record. Cadmium is one such proxy. As with nitrate and phosphate, surface waters have the lowest concentration of dissolved cadmium, and deep waters in the northern Pacific the highest, while the concentration in deep Atlantic waters falls midway between these extremes (Figure 4.13). It turns out that cadmium and calcium are sufficiently similar chemically for cadmium to substitute for calcium in the calcite secreted by foraminiferans. Because of this, the cadmium : calcium ratio in foraminiferan shells should be proportional to the cadmium : calcium ratio in the seawater in which the shell formed. Since the concentration of Ca hardly varies in seawater, and Ca has a residence time in excess of a million years, then any change in the Cd/Ca ratio in seawater over the past 10^6 years or so is likely to result from the redistribution of Cd within the ocean.

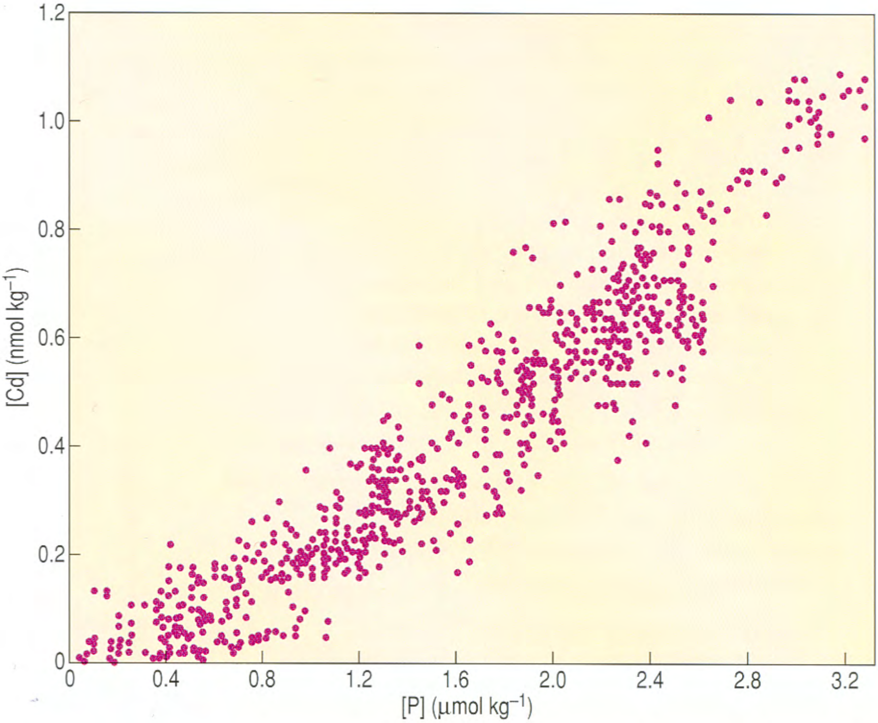

Figure 4.13 Dissolved cadmium versus phosphorus concentration for samples of seawater collected from sites throughout the oceans.

QUESTION 4.6 Explain which end of the line defined by the data points in Figure 4.13 corresponds to surface seawater, and which to deep northern Pacific water.

A number of studies have investigated changes in benthic foraminiferal Cd/Ca over the past 400 000 years. These show that Cd/Ca in benthic foraminiferans from sediments deposited in the North Atlantic during glacials is some 22% higher, indicating that deep water in the North Atlantic must have had higher concentrations of the nutrient elements in glacial times relative to today. One explanation for these higher nutrient levels is that the flux of nutrient-poor NADW was reduced (Section 2.4), allowing nutrient-rich waters from the south (including AABW) to penetrate further north. Measurements of carbon isotopes in benthic foraminiferan shells (see Box 4.2) support this idea.

BOX 4.2 CARBON ISOTOPES AND THE SEDIMENTARY RECORD

Carbon occurs in nature as a mixture of two stable isotopes, carbon-12 (^{12}C) and the much rarer carbon-13 (^{13}C). All the common photosynthetic pathways discriminate against ^{13}C in favour of ^{12}C, so organic matter produced by photosynthesis is enriched in ^{12}C and depleted in ^{13}C relative to the inorganic carbon in the atmosphere and hydrosphere (CO_2 gas, plus hydrogen carbonate and carbonate ions in solution). A typical profile of the ratio of ^{13}C to ^{12}C (expressed as $\delta^{13}C$) of dissolved inorganic carbon in the ocean is shown in Figure 4.14.

How does the shape of the curve relate to the shape of a typical curve for phosphate (Figure 2.10)?

The curve for $\delta^{13}C$ is very similar to that for phosphate. This is because photosynthesis leads to depletion of ^{12}C (and phosphate), and therefore relative enrichment of ^{13}C, in surface waters, and respiration returns ^{12}C (and phosphate) to seawater at depth, so deep waters contain relatively less ^{13}C.

Similarly, today's pattern of deep-water circulation means that deep waters in the North Atlantic have relatively high $^{13}C/^{12}C$ (and low levels of phosphate), while deep northern Pacific waters have relatively low $^{13}C/^{12}C$ (and high levels of phosphate).

The record of the $\delta^{13}C$ value of deep ocean water can be obtained from analysis of the $^{13}C/^{12}C$ ratio of the shells of benthic foraminiferans. The most reliable records seem to come from species that live *on* the sea-floor (epifaunal species) rather than those that live within the sediments (infaunal species); the $\delta^{13}C$ value of infaunal species tends to be affected by the amount of organic carbon reaching the sea-floor.

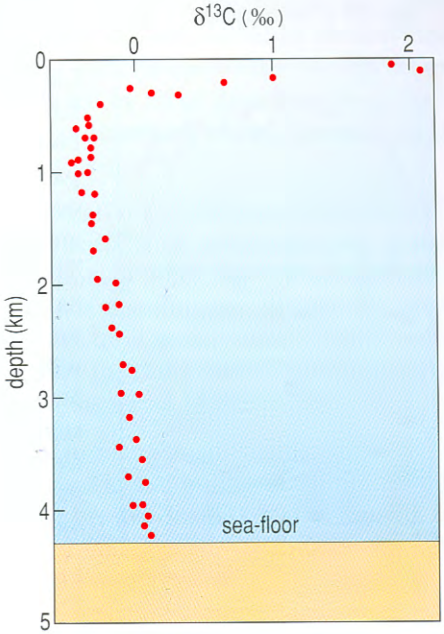

Figure 4.14 Profile of $\delta^{13}C$ of dissolved inorganic carbon in the north-western Pacific Ocean. $\delta^{13}C$ is calculated from measured carbon-isotope ratios in an analogous way to $\delta^{18}O$:

$$\delta^{13}C = \frac{(^{13}C/^{12}C)_{\text{sample}} - (^{13}C/^{12}C)_{\text{standard}}}{(^{13}C/^{12}C)_{\text{standard}}} \times 1000$$

Having read Box 4.2, would you expect $\delta^{13}C$ in benthic foraminiferans to be relatively high or low if they lived in waters that were relatively nutrient-rich?

We would expect the foraminiferans to have relatively low $\delta^{13}C$. Indeed, in glacial times, the $\delta^{13}C$ value of benthic foraminiferan shells accumulating on the North Atlantic sea-floor was ~0.4‰ lower than the value for today.

Glacial–interglacial changes in deep-water circulation in the South Atlantic are less clear-cut. Benthic foraminiferal shells recovered from the Southern Ocean show that those deposited at the height of the last glaciation have lower $\delta^{13}C$ than those being deposited today. As for the studies in the North Atlantic, this suggests that fluxes of NADW were lower during glacial periods. However, measurements of Cd/Ca in benthic foraminiferans from the Southern Ocean indicate that there was little change in the nutrient concentration of deep water between the height of the last glaciation and today (Figure 4.15), which suggests that the flow of North Atlantic Deep Water into the South Atlantic has *not* changed. Why there is this discrepancy between the results from Cd/Ca and $\delta^{13}C$ is not clear. One possible reason is changes in the amount of organic carbon exported from surface waters to the deep sea (which may affect $\delta^{13}C$ in the shells of benthic animals); and another is that the chemical composition of the foraminiferan shells may have changed due to partial dissolution after burial.

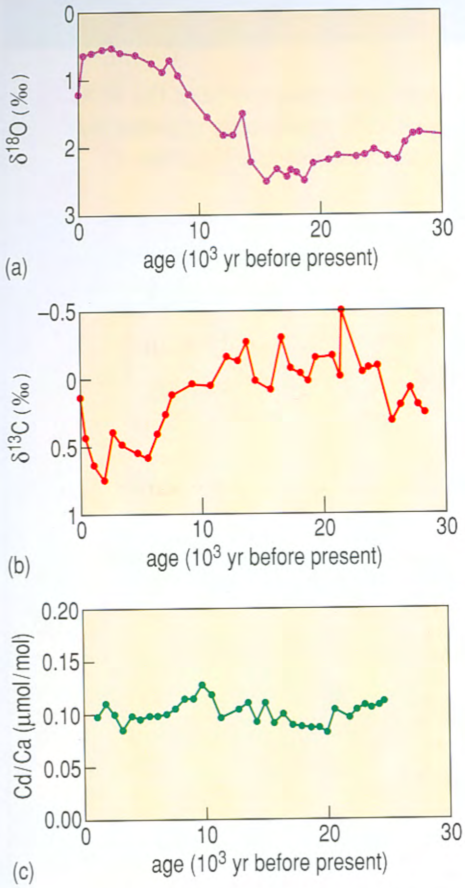

Figure 4.15 Palaeoceanographic records from the Southern Ocean over the past 30 000 years: (a) planktonic foraminiferal $\delta^{18}O$, (b) benthic foraminiferal $\delta^{13}C$ and (c) benthic foraminiferal Cd/Ca. The last glacial period is identified by high $\delta^{18}O$ values and low $\delta^{13}C$ values up to about 15 000 years ago. Meanwhile, Cd/Ca shows little variation.

The sedimentary carbon-isotope record and gas hydrates

Large shifts (~ −3‰) in the $\delta^{13}C$ value of biogenic carbonates have been recorded in ~55 Ma-old sediments (near the Palaeocene/Eocene boundary), at widely separated locations (Figure 4.16). Other palaeoceanographic studies have shown that around the same time, deep-ocean and high-latitude surface temperatures soared by at least 5–7 °C, and around 35–50% of species of benthic foraminiferans became extinct. The size and the global nature of this $\delta^{13}C$ 'excursion' means that it cannot be attributed to a change in ocean circulation. What, then, was the cause? The consensus view is that the $\delta^{13}C$ excursion was associated with a sudden and massive injection of ^{12}C-rich carbon to the atmosphere or ocean due to decomposition of **gas hydrate** reservoirs in sediments of continental margins; methane from gas hydrates has an average $\delta^{13}C$ value of −60‰. Methane, and the CO_2 released by its oxidation, are both greenhouse gases, so this could have led to sudden warming of the planet.

Proxy studies of periods with high atmospheric CO_2 (such as those in Figure 4.16) are particularly important because on no occasion in the Quaternary have atmospheric CO_2 levels been as high as the present day (370 p.p.m.). If we want to predict climates of the future, with atmospheric CO_2 potentially reaching 2000 p.p.m. when all of the world's coal supplies have been used up, we need to evaluate how the climate system responds to high CO_2 concentrations in the atmosphere and oceans. Palaeoceanographic studies of ancient sediments are the best way of doing this.

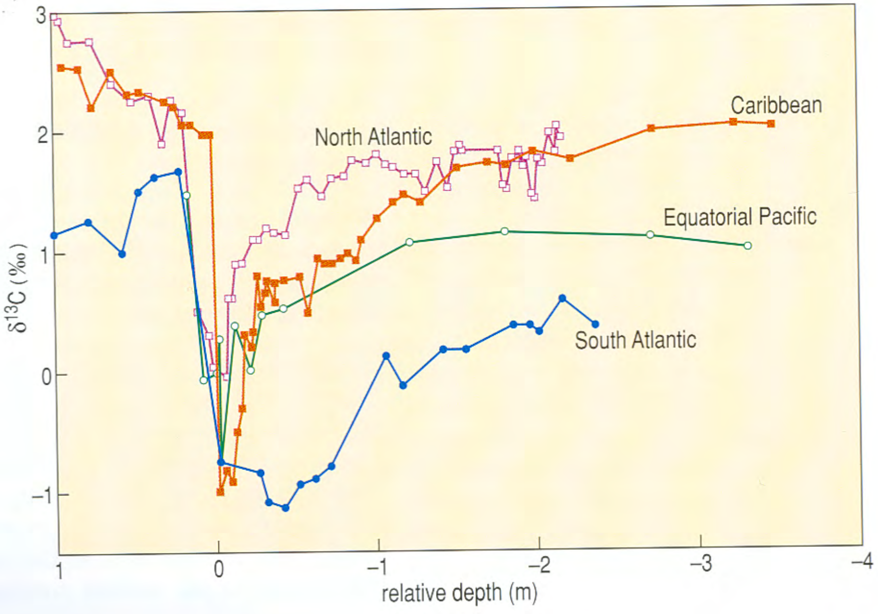

Figure 4.16 Records of the variation of $\delta^{13}C$ of biogenic carbonates from various sites around the globe: ODP Site 690 (South Atlantic), Site 865 (Equatorial Pacific), Site 1001 (Caribbean) and Site 1051 (North Atlantic). The data have been placed on a common depth scale. The abrupt drop in $\delta^{13}C$ close to 0 m is common to all sites. Chronological studies at Site 1051 suggest that this carbon-isotope excursion began between 54.93 and 54.98 Ma ago and lasted ~150 000 years.

4.3.3 THE CARBONATE SYSTEM

The oceans contain by far the largest reservoir of carbon that can be transferred to and from the atmosphere as CO_2, so any change in the way the marine carbonate system operates has the potential to trigger a change in Earth's climate. As you have already seen, CO_2 does not simply dissolve in seawater but reacts with it to form dissolved CO_2, hydrogen carbonate and carbonate ions (Figure 3.3). The relative proportion of each of these varies with the pH of seawater (Figure 3.4). Meanwhile, the carbonate system is perturbed by biological processes, including photosynthesis and respiration, and the formation of skeletal carbonate. The operation of the carbon cycle in seawater is affected by all of these variables; finding suitable proxies for them in the sedimentary record, however, is not an easy task.

One way to track changes in the carbonate ion concentration of deep water is to reconstruct past depths of the CCD by determining the variation in the calcium carbonate content of sediment cores. As you saw in Section 3.2.1, the tendency for calcium carbonate dissolution is dictated by deep water $[CO_3^{2-}]$; $CaCO_3$ dissolves if seawater is undersaturated with respect to CO_3^{2-}. If the carbonate content of the sediments is 20% or less, then the overlying waters must be below the depth of the CCD.

Firm evidence exists for glacial to interglacial changes in the depth of the CCD. Cores from the tropical Pacific and Indian Ocean reveal that during glacial times the CCD shifted to greater depth. For the Atlantic, the change was in the opposite direction, and dissolution was more intense during glacial times. As the Pacific and Indian Oceans together cover a much larger area than the Atlantic, on a global scale the average CO_3^{2-} concentration of deep water generally appears to have been somewhat higher during glacial times.

What does this mean for levels of dissolved, and therefore atmospheric, CO_2?

Higher $[CO_3^{2-}]$ means lower dissolved $[CO_2]$ and, in turn, lower atmospheric concentrations of CO_2. Ice core data show that levels of atmospheric CO_2 were indeed lower during glacial times, by some 90 p.p.m. (Figure 4.8). So the global average of the change in the depth of the CCD is in the right direction, but it turns out that it can only account for ~20% of the measured change in the concentration of atmospheric CO_2.

The depth of the CCD may, however, be a misleading index of deep ocean $[CO_3^{2-}]$. Release of CO_2 by bacterial respiration of organic carbon in sediments may react with $CaCO_3$ in shells to produce hydrogen carbonate ions:

$$H_2O + CO_2(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq)$$

The result is that sea-floor dissolution of calcite is to some extent driven by the amount of CO_2 released by respiration into sediment pore waters, as well as by bottom water $[CO_3^{2-}]$. Proxies that are thought to be sensitive to bottom water $[CO_3^{2-}]$ alone have more recently been developed, such as the amount of foraminiferal fragmentation (see Question 4.7), and variations in the weight of foraminiferal tests of specified species and dimensions. These techniques are still being researched but, so far, the perfect proxy for deep water $[CO_3^{2-}]$ remains elusive.

QUESTION 4.7 Figure 4.17 shows palaeoceanographic records for Marine Isotope Stages 12 and 11 for a core from the South Pacific.
(a) First, without looking at Figure 4.17, can you say which MIS (i.e. 11 or 12) corresponds to a glacial period, and which to an interglacial?
(b) Which part of the benthic $\delta^{18}O$ record (i.e. the left-hand or right-hand side) corresponds to MIS 11, and which to MIS 12, and how can you tell?
(c) Use Figure 4.17 to help you decide whether foraminiferans are better preserved during glacials or interglacials. Does your answer agree with the results of the CCD study in the tropical Pacific described above?

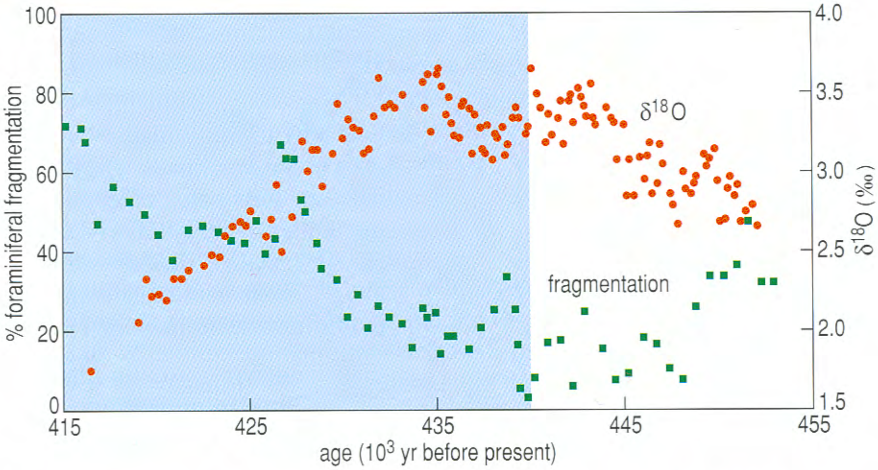

Figure 4.17 Records of benthic foraminiferal $\delta^{18}O$ and % foraminiferal fragmentation from a core in the South Pacific. The percentage of foraminiferal fragmentation is a guide to foraminiferal preservation: a high percentage of fragments (i.e. few whole tests) is indicative of poor preservation (more dissolution), and *vice versa*. Different backgrounds correspond to different marine-isotope stages.

So, if the deeper CCD accounts for ~20% of the reduction in atmospheric concentrations of CO_2 in glacial times, what accounts for the remaining ~80%? Photosynthesis 'consumes' CO_2, so an increase in global biological productivity could also lower atmospheric CO_2, as long as the percentage of organic matter that is preserved on the sea-floor remains the same, or even increases. Therefore, if primary productivity increased in glacial times, there would be increased drawdown of atmospheric CO_2. One way to determine past levels of primary production is to evaluate past levels of nutrient utilization in surface waters.

As we have seen already, the Cd/Ca ratio of benthic foraminiferans can be used as a proxy for deep-water phosphate concentrations. In the same way, Cd in the shells of planktonic foraminiferans can be used as a proxy for phosphate in surface seawater; relatively low levels of Cd (phosphate) mean relatively high nutrient utilization, and therefore high rates of biological production. There are complications with the application of this technique, however. First, in the modern ocean, the ratio Cd/P in surface waters increases from low to high latitudes, and we do not know if it always did. Secondly, uptake of Cd into foraminiferal tests varies with sea-surface temperature, so records of variability in SST are required for accurate interpretation of foraminiferal Cd/Ca. Nevertheless, careful reconstructions of surface water phosphate from planktonic foraminiferal Cd/Ca in sediments from the sea-bed of the Southern Ocean suggest that north of the modern-day Antarctic Front (which is located at ~50° S) there was a similar nutrient utilization during glacial times relative to today (Figure 4.18), which is consistent with what we see for other nutrient tracers (such as the nitrogen-isotope ratio of organic matter: see Question 4.8). South of the Antarctic Front, planktonic foraminiferal Cd/Ca indicates that nutrient utilization was actually lower than today during

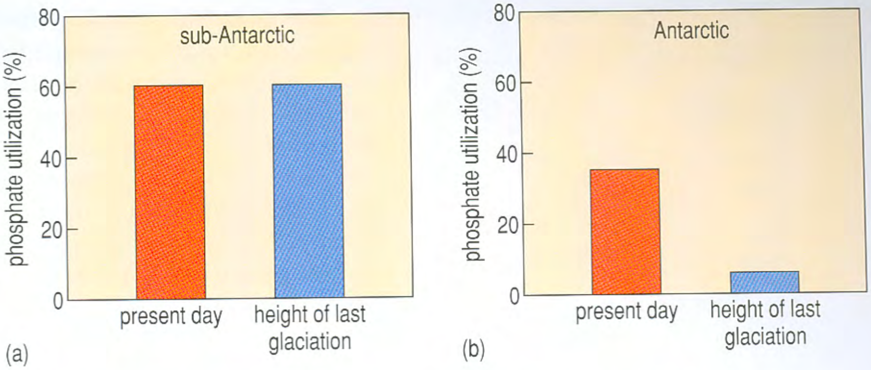

Figure 4.18 Contrasted utilization of phosphate in surface waters at the height of the last glaciation and the present day in the Southern Ocean, based on planktonic foraminiferal Cd/Ca ratios. (a) Sub-Antarctic waters (north of ~50° S); (b) Antarctic waters (south of ~50° S).

glacial times (Figure 4.18). This is consistent with some other nutrient proxies (including the rate of accumulation of biogenic silica on the sea-floor), but is at odds with results of analyses of nitrogen-isotope ratios of organic matter, which suggest that nutrient utilization was greater in glacial times. The reason for the discrepancy isn't clear at present, but it may be related (in a complicated way which we won't go into here!) to the expansion in sea-ice cover, which, in glacial times, may have been as much as double the surface area of winter ice today, in the region to the south of the modern Antarctic Front.

QUESTION 4.8 Nitrogen isotopes offer an insight into the utilization of nitrate in primary production. The dominant isotope is ^{14}N, and this lighter isotope is preferentially taken up ('fixed') by photosynthesizing organisms, leaving behind the much less abundant heavier isotope, ^{15}N. When nitrate is plentiful, therefore, the δ^{15}N value (analogous to δ^{13}C and δ^{18}O) of sea-floor sediments is low, because the primary producers have selected chiefly the lighter ^{14}N isotope. Where nitrate is in short supply, however, proportionally much more of it gets used, including the component with the heavier ^{15}N isotope. So the δ^{15}N value increases.

(a) The dots in Figure 4.19(a) are δ^{15}N values in sediments from the sub-Arctic Pacific (close to 50° N, 167° W). Explain how these nitrogen-isotope data are consistent with an abrupt reduction in nutrient upwelling in the northern Pacific gyres 2.73 Ma ago.

(b) Is the planktonic foraminiferal Cd/Ca record shown in Figure 4.19(b) consistent with your answer to part (a)?

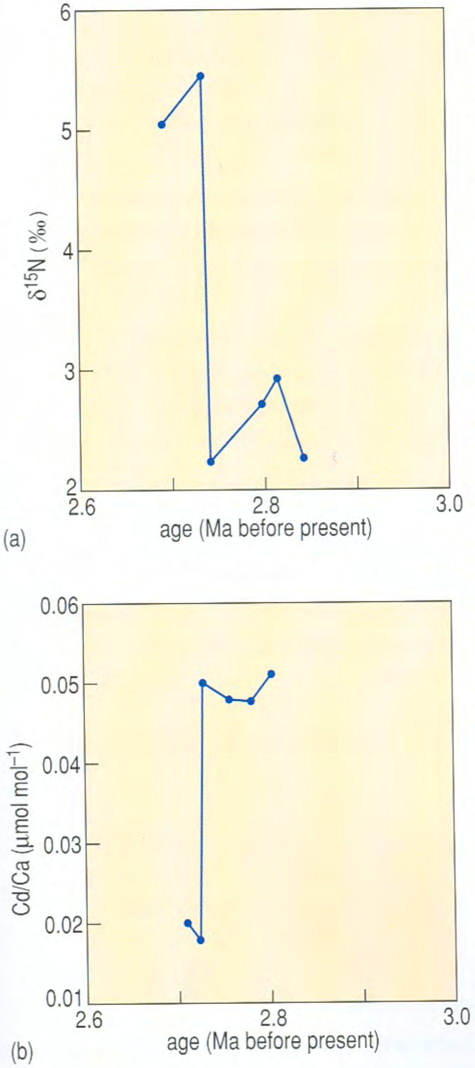

Figure 4.19 (a) Nitrogen-isotope and (b) planktonic foraminiferal Cd/Ca data for sediments recovered from a station in the sub-Arctic Pacific, for use with Question 4.8. Note that in (a) $\delta^{15}\mathrm{N}\ (‰) = ((^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{sample}} / (^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{standard}}) - 1) \times 1000$, where atmospheric nitrogen is the standard.

4.4 SUMMARY OF CHAPTER 4

1 The sea-floor sediment record extends back to ~200 Ma ago. Sediments are thinnest closest to spreading axes, where the ocean crust is young, and increase in thickness with distance (and depth) from the axis as the crust ages and more time has elapsed for sediments to accumulate.

2 Sediments recovered in deep-sea drill cores contain a wealth of information about past ocean environments. This is obtained from the nature of the sediments themselves, and from measurements of sediment properties (such as the isotopic composition of microfossil shells) which respond systematically to important environmental variables, such as past sea-surface temperature, which cannot be directly measured. Such sediment properties are known as 'proxies'.

3 The most widely used proxy for sea-surface temperature is the oxygen-isotope ratio (usually expressed as $\delta^{18}O$) of planktonic foraminiferans. Foraminiferans incorporate proportionally more ^{18}O into their calcium carbonate shells at low temperatures, and more ^{16}O at high temperatures. Planktonic foraminiferal $\delta^{18}O$ is not the perfect proxy, however. Oxygen-isotope ratios are also affected by the $^{18}O/^{16}O$ ratio of the water in which the foraminiferans lived; this varies with ice volume, and hence sea-level. Other proxies that are useful for determining past sea-surface temperatures include planktonic foraminiferal Mg/Ca, and the alkenone unsaturation index ($U^{K}{}_{37}$).

4 Proxies for the concentrations of the nutrient elements in the deep sea can be used to trace changes in the rate of formation of deep water, and the pattern of thermohaline circulation. One such proxy is the Cd concentration in shells of benthic foraminiferans: Cd mimics phosphate in the deep ocean. Another proxy is the carbon-isotope ratio of shells of benthic foraminiferans. Photosynthesizing organisms take up ^{12}C in preference to ^{13}C, so surface waters are relatively depleted in ^{12}C. This ^{12}C is returned to seawater by respiration at depth. Therefore the older the water mass, the more ^{12}C it contains, and the lower its $\delta^{13}C$ value.

5 Reconstructing past changes in the marine carbonate system is central to understanding the causes of climate change. Deep-water carbonate ion concentration can be estimated from past levels of the CCD, and by analysis of microfossil fragmentation.

6 Changes in biological production can be reconstructed from analyses of Cd in the shells of planktonic foraminiferans: concentrations of Cd (phosphate) in surface waters are low if photosynthetic activity is high, so the proportion of Cd incorporated into the shell decreases.

7 While sediment proxies have provided an abundance of information for reconstructing past climate, they may yield conflicting information. There are a number of reasons for this: our understanding of the parameters that control proxy relationships is incomplete; the chemical signature of microfossils may be altered upon burial; and some proxies require better calibration. Palaeoceanographers are working hard to resolve these conflicts, and to develop new proxies.

Now try the following questions to consolidate your understanding of this Chapter.

QUESTION 4.9 Planktonic foraminiferans preserved in sediments aged ~220 000 years have a $\delta^{18}O$ value of $-0.6‰$. Explain whether sea-surface temperatures were higher or lower at that time than they are today.

QUESTION 4.10 Results of the analysis of alkenones from within sediments from the Mediterranean are presented in Table 4.1.

(a) Use Equations 4.2 and 4.3 to complete the Table. The temperature of the topmost four samples has been calculated for you; begin by checking that you get the same answers as ours.

(b) Plot the sea-surface temperature record on Figure 4.20. Is your record consistent with the planktonic foraminiferal oxygen-isotope record shown in Figure 4.15(a)?

Table 4.1 Alkenone data from a Mediterranean sediment core, for use with Question 4.10.

Age (years before present)	$[C_{37:2}]$	$[C_{37:3}]$	U^{K}_{37}	Temperature (°C)
1000	22	10.1	0.68	18.8
3220	20	10.5	0.66	18.3
4860	25	13.1	0.66	18.3
7130	18.3	9.6	0.66	18.3
9450	21	8		
11 100	18	11.2		
13 200	25	24		
14 900	13	16		
17 200	19	23.5		
19 000	16	19.7		

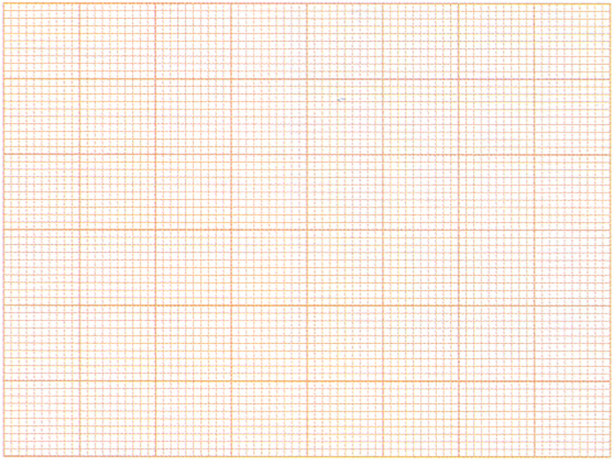

Figure 4.20 Graph paper for answer to Question 4.10(b).