CHAPTER 3 THE ACCUMULATION OF PELAGIC BIOGENIC SEDIMENTS

Deep-sea sediments of biological origin occur in quite well-defined areas (Figure 1.4). The main factors controlling this distribution include the productivity of surface waters, the water depth, and the supply of terrigenous sediment, large volumes of which would dilute the biogenic components. The geographical separation of calcareous and siliceous sediments is related more to the different solubilities of calcium carbonate and silica and the chemistry of the water column than to the distribution of organisms at the surface.

Pelagic biogenic sediments consist mainly of the skeletal remains of very small pelagic organisms, some only a few μm in size (Section 1.1.1). Stokes' law calculations suggest that these remains would take decades or even centuries to sink to the deep sea-floor. Such calculations assume that the particles have spherical shapes without protrusions, and that there is no turbulence in the water column, neither of which applies in the oceans; so, the time taken for such material to reach the sea-bed in the deep oceans would be even longer.

So, how is it that sediments formed of this skeletal debris mainly occur directly below areas of high productivity in surface waters? Why are they not spread all over the sea-bed by ocean currents?

As you read in Chapter 2, the short answer is biopackaging, either in the form of marine snow or faecal pellets—it has been estimated that a single faecal pellet can contain as many as 10^5 coccoliths, so biological aggregation is obviously an important way of speedily transferring planktonic debris (along with pelagic clays of mainly aeolian origin) to the sea-bed.

3.1 THE PRESERVATION OF PELAGIC CARBONATES

Rapid descent through the water column is only the first step towards the conversion of calcareous skeletal material into carbonate sediment at the sea-bed. The chemistry of deep ocean waters determines whether or not this conversion occurs.

In general, productivity exerts a greater influence on the actual composition of pelagic carbonates than does depth, because Foraminifera increase faster than coccolithophores in the photic zone as overall productivity rises. As a result, calcareous nanofossil oozes tend to predominate in areas of low productivity, while foraminiferal oozes are found mainly where productivity is high.

3.1.1 CARBONATE SATURATION IN SEAWATER

Carbon dioxide gas is more soluble in cold water than in hot water, and its solubility increases with pressure. This property is well known to those manufacturers and consumers of bottled and canned drinks which froth or fizz when opened. The CO_2 combines with water molecules to produce a

weak acid (carbonic acid) which then dissociates to produce hydrogen and bicarbonate ions:

$$CO_2 \text{ gas} + H_2O = H_2CO_3 = H^+ + HCO_3^- \quad (3.1)$$

As noted in Section 2.5.1, the concentration of carbon dioxide as *gas* in seawater is very small. In surface waters, only about 1 atom of carbon in 200 is in the form of dissolved CO_2 molecules, and even in the deep ocean the figure rises only to about 3 atoms in 200.

There is a further component of reaction 3.1:

$$HCO_3^- = H^+ + CO_3^{2-} \quad (3.2)$$

Carbon thus occurs as several species in solution: CO_2 gas, H_2CO_3, HCO_3^-, and CO_3^{2-}, as well as carbon combined in organic molecules (which rarely amounts to more than about 1 p.p.m., Section 2.2.1). HCO_3^- and CO_3^{2-} are quantitatively by far the most important of these. Reaction 3.2 is rapid, and seawater can be assumed to contain an equilibrium mixture of the three ions.

A large proportion of the bicarbonate and carbonate ions in seawater comes not from direct solution of atmospheric carbon dioxide, however, but from rivers flowing into the sea: the weathering of rocks by carbonic acid in rainwater releases cations (e.g. Ca^{2+}, Na^+, K^+) and bicarbonate and carbonate ions (along with other constituents, of course) into solution in river water. The average concentration of bicarbonate plus carbonate ions in river water is around $60 mg l^{-1}$, which is equivalent to about $12 mg l^{-1}$ (12 p.p.m.) of carbon, nearly half the figure for the average concentration of carbon in seawater (Table 2.1).

Figure 3.1 shows typical profiles for total dissolved inorganic carbon in seawater, expressed as ΣCO_2 (where Σ is capital sigma, and denotes 'sum of'). The profiles illustrate how carbon in its various forms is the least conservative of the major dissolved constituents, with obvious bio-intermediate character (*cf.* Figure 2.13). Concentrations are higher in the Pacific than in the Atlantic, which is consistent with the pattern described for recycled coustituents in Section 2.4.

Profiles of total dissolved inorganic carbon (ΣCO_2) in seawater take the form shown in Figure 3.1 chiefly because carbon dioxide is removed from solution in surface waters by photosynthesis (reaction 2.3 goes to the right) and returned to solution in deep water, as organic matter is decomposed (reaction 2.3 goes to the left). Another contribution to the increase of ΣCO_2 with depth comes from the dissolution of atmospheric carbon dioxide at high latitudes in cold surface waters, which sink to the deep sea-floor on account of their low temperature and increased density.

In what follows, it is essential to bear in mind the point made in Section 2.5.1 and above, that nearly all carbon dioxide in seawater is in the form of bicarbonate and carbonate ions, because of reactions 3.1 and 3.2.

For our purposes, it is sufficient to state that the equilibrium relationships in reactions 3.1 and 3.2 are such that, as ΣCO_2 increases, so does the ratio of bicarbonate to carbonate ions in the expression:

$$[H^+] = K \frac{[HCO_3^-]}{[CO_3^{2-}]} \quad (3.3)$$

where the terms in square brackets are molar concentrations and K is the equilibrium constant for reaction 3.2.

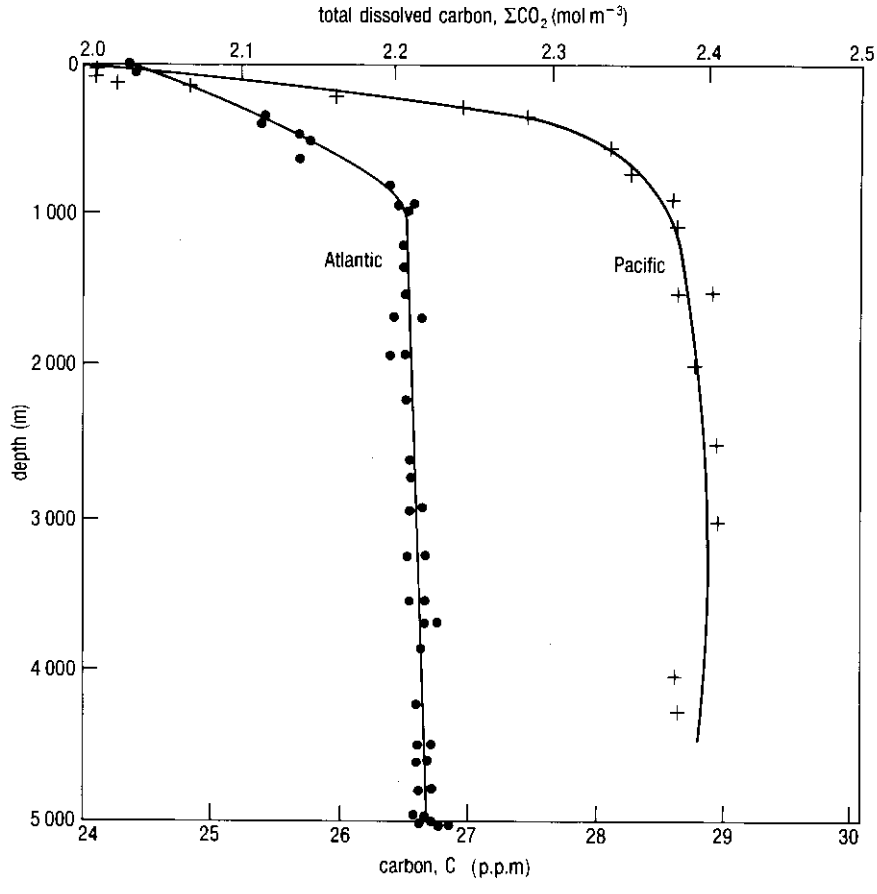

Figure 3.1 Variation with depth of total dissolved carbon (ΣCO_2), in the Atlantic (36°N, 68°W) and in the Pacific (28°N, 122°W). Note that Σ (sigma) denotes 'sum of'.

If ΣCO_2 increases, will the water become more or less acid according to equation 3.3?

As ΣCO_2 increases, the ratio of bicarbonate to carbonate ions increases and so does $[H^+]$; i.e. there are more hydrogen ions, and the water becomes more acid (pH decreases). The converse will be true where ΣCO_2 decreases. Thus, variations in ΣCO_2 significantly affect the balance between bicarbonate and carbonate ions.

However, because of the rapidity of reaction 3.2, this component of the carbonate system provides a chemical buffer for pH in the oceans. Considerable changes of $[\Sigma CO_2]$ or of the $[HCO_3^-]$:$[CO_3^{2-}]$ ratio (or even of $[H^+]$) are required before the pH is significantly changed.

Dissolution of calcium carbonate skeletons ($CaCO_3$) occurs where increased acidity of the water results from the release of hydrogen ions:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (3.4)$$

Therefore, is $CaCO_3$ more likely to dissolve where ΣCO_2 concentrations are high than where they are low?

It must follow from what you have read that where ΣCO_2 concentrations are high, then so is $[H^+]$, the water is more acid, so $CaCO_3$ is more likely to dissolve.

Accordingly, would you expect $CaCO_3$ to dissolve more readily in Atlantic than in Pacific waters, judging from Figure 3.1?

ΣCO_2 is higher in the Pacific than in the Atlantic, so $CaCO_3$ should dissolve more readily in Pacific waters.

However, Figure 1.4 indicates also that the solubility of calcium carbonate in the oceans is depth-dependent: carbonate sediments are abundant on shallower parts of the ocean floor, notably the mid-ocean ridges, but absent from the deeper abyssal plains. Calcium carbonate is more soluble in cold than in warm water and it is also more soluble at high pressure than at low pressure (dissolved calcium and carbonate ions occupy less volume than when combined in solid form).

QUESTION 3.1 Does that help you to explain part of the answer to Question 1.1, namely: why do calcareous biogenic sediments predominate along the ocean ridges?

But that is not the whole story: another expression for the dissolution of calcium carbonate is:

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{3.5}$$

In the oceans, the concentration of Ca^{2+} in solution is virtually constant. As you read in Section 2.1, calcium in seawater departs only very slightly from conservative behaviour. The concentration of carbonate ions, i.e. $[CO_3^{2-}]$, is much more variable.

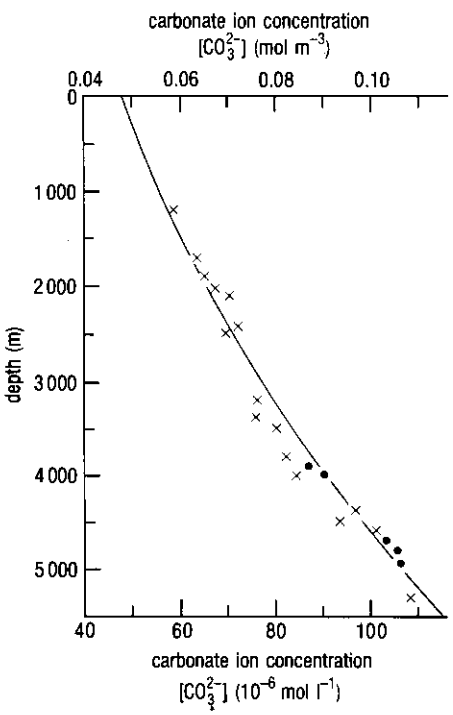

Figure 3.2 The saturation curve of CO_3^{2-} concentration versus depth for calcite, $CaCO_3$. The theoretical relationship is given by the solid line; crosses are experimentally determined points; dots represent actual observations of calcite dissolution in the oceans.

Figure 3.2 shows how the concentration of CO_3^{2-} ions in seawater determines whether the calcite variety of calcium carbonate (Section 1.1.1) will be dissolved or not. If the concentration of CO_3^{2-} ions in the seawater lies to the right of the line, calcite will not dissolve. If $[CO_3^{2-}]$ lies to the left of the line, calcite will dissolve.

In order to predict the depth at which calcite skeletal material will begin to dissolve in the water column, therefore, all we need to do is to determine $[CO_3^{2-}]$ in the water, and plot the value in Figure 3.2.

Unfortunately, $[CO_3^{2-}]$ cannot be directly measured. It has to be determined by indirect means. The concentration of ΣCO_2 in a seawater sample can be found easily by direct analysis. The sample can also be titrated with acid, to convert bicarbonate and carbonate to CO_2:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \tag{3.6}$$

$$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O \tag{3.7}$$

The result of this titration gives a value for the **alkalinity** of the sample, which for our purposes can be defined as the combined concentrations of bicarbonate and carbonate ions, expressed in 'charge-equivalent' terms. If we express concentrations in molar terms, then we can write:

$$[\Sigma CO_2] = [HCO_3^-] + [CO_3^{2-}] \tag{3.8}$$

$$\text{Alkalinity, } A = [HCO_3^-] + 2[CO_3^{2-}] \tag{3.9}$$

By re-arranging these two equations:

$$A - [\Sigma CO_2] = [CO_3^{2-}] \tag{3.10}$$

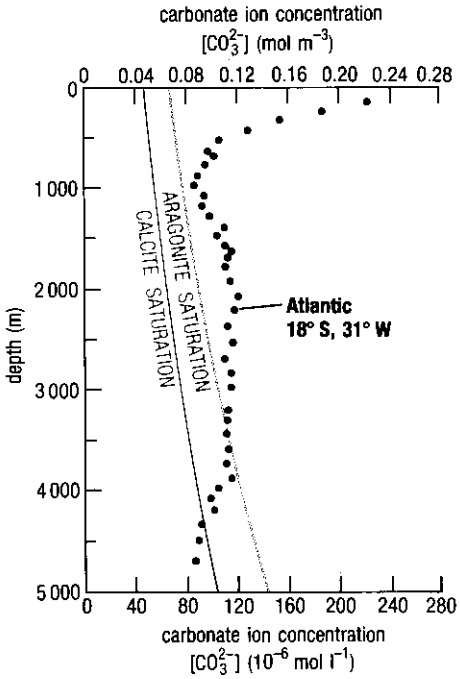

Figure 3.3 Saturation curves of CO_3^{2-} concentration versus depth for calcite and aragonite (both $CaCO_3$). The curve for calcite is from Figure 3.2. Dots represent a profile of calculated values of $[CO_3^{2-}]$ for a station in the Atlantic.

Thus, by direct measurement of ΣCO_2 and A, the value of $[CO_3^{2-}]$ can be calculated. In practice, for accurate results it is a little more complicated than this simple outline suggests, because as we have seen, bicarbonate and carbonate are not the only contributors to total dissolved inorganic carbon (ΣCO_2) in seawater; and other dissolved species contribute to alkalinity. But our approach violates no basic principles and gives adequate approximations of the real situation.

QUESTION 3.2 The alkalinity of a sample of surface water is 2.35 mol m^{-3} and its $[\Sigma CO_3]$ is 2.15 mol m^{-3}. The same quantities for a sample of water from 4 km depth at the same location are 2.45 mol m^{-3} and 2.40 mol m^{-3} respectively. Work out the $[CO_3^{2-}]$ for each sample, using equation 3.10. Where would these samples plot in relation to the line in Figure 3.2, and what does that tell you about the degree of saturation of the water samples with respect to calcite?

Some calcium carbonate skeletal material is formed of aragonite rather than calcite, and aragonite is less stable than calcite and dissolves more readily (Section 1.1.1). Figure 3.3 shows the same curve for calcite as in Figure 3.2, along with the analogous curve for aragonite, and an actual profile for $[CO_3^{2-}]$ from an Atlantic station.

At what depth(s) would you expect calcite and aragonite skeletal material to begin dissolving at this station?

Figure 3.3 suggests that aragonite should begin to dissolve at a little over 3 km depth, whereas calcite should not start dissolving till nearly 4.5 km depth.

An important general point is also illustrated in Figure 3.3: down to a few km depth, seawater is supersaturated with respect to calcium carbonate (*cf.* Question 3.2). The degree of supersaturation is greater for calcite than for aragonite (the saturation curve for aragonite lies to the right of that for calcite). The reason why $CaCO_3$ does not precipitate spontaneously from seawater is that most of the CO_3^{2-} ions in the solution are 'combined' with Mg^{2+} ions in what are known as *ion pairs*, which must be extensively broken up for $CaCO_3$ to precipitate spontaneously.

3.1.2 THE LYSOCLINE AND THE CARBONATE COMPENSATION DEPTH

The rate of descent of rapidly sinking particles generally takes most of the skeletal material through the undersaturated lower parts of the water column in too short a time for significant dissolution to occur. *Dissolution of calcareous material takes place mostly at the sea-bed.*

The depth at which the dissolution of carbonate skeletal material is observed to begin, from observation and analysis of sediment samples from the ocean floor, is called the **lysocline**. Below the lysocline, dissolution occurs at increasing rates, so that there is a progressive decrease in the proportion of carbonate skeletal material preserved in the sediments. The depth at which this proportion falls below 20% of the total sediment is called the **carbonate compensation depth, CCD.**

In theory, the depth of the lysocline, based on visual inspection of carbonate debris in sediments collected at different depths, should coincide with the depth predicted from intersections of $[CO_3^{2-}]$-depth

profiles with the saturation curves, as in the example given in Figure 3.3. In practice, the (observed) lysocline may coincide with the predicted depth, but can be as much as a few hundred metres below it.

Figures 3.2 and 3.3 show that seawater becomes progressively more undersaturated with respect to calcium carbonate (whether calcite or aragonite) as depth increases. In consequence, the rate of dissolution of carbonate increases with depth below the lysocline.

The depth of the CCD is controlled in part by how undersaturated the water is, but also by the flux of calcareous debris to the sediments. The greater this is, the greater the likelihood of carbonate material being buried before it dissolves. Figure 3.4 shows the depth of the CCD for calcite, as determined from deep-sea sediment samples. The CCD is depressed beneath the Equator on account of the high productivity resulting from equatorial upwelling, and the increased flux of calcareous remains to the sea-bed.

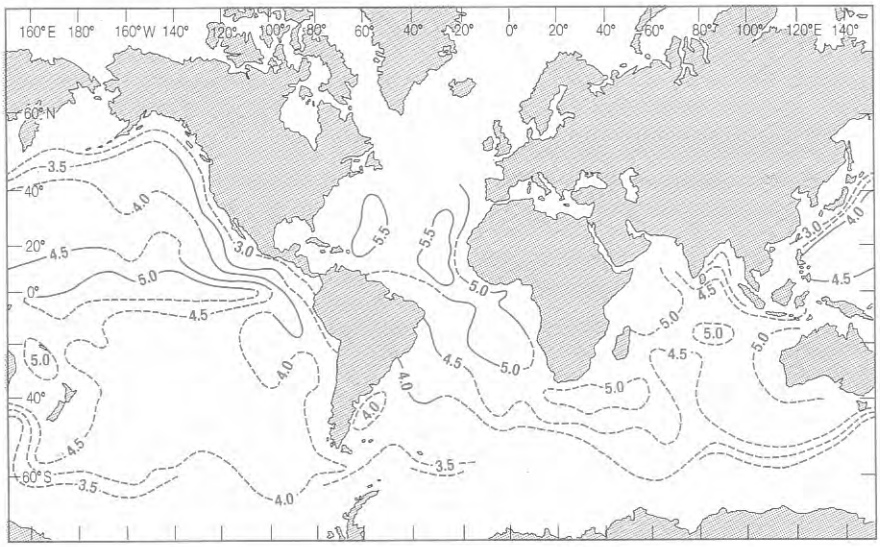

Figure 3.4 Contours (in km) for the calcium carbonate compensation depth (CCD), defined by interpolating boundaries between calcareous sediments and sediments with little or no calcium carbonate. Solid blue contours represent more than 20 control samples per 10° square; broken blue contours represent fewer than 20 control samples. Note that this map is for the more common calcium carbonate mineral, *calcite*; the compensation depth for the other variety, *aragonite*, is very different, as discussed in the text.

At this point, it is necessary to emphasize two things:

1 The lysocline is a 'surface' that can be 'mapped' within the oceans by reference to the chemistry of the water column (Figures 3.2 and 3.3). That level can be *checked* by inspection of calcareous sediments accumulating on the sea-bed at appropriate depths: if no dissolution is observed, then the sediments are above the lysocline; if dissolution has begun, the sediments are below the lysocline.

2 The CCD is also 'a surface', but it can be 'mapped' *only* by inspection and analysis of calcareous sediment samples from the sea-bed. If originally calcareous sediments contain more than 20% $CaCO_3$, they are above the CCD; if they contain less, they are below it. On maps of the CCD such as Figure 3.4, the contour lines are *interpolations* between sea-bed locations where the CCD has been determined from inspection of the sediments.

Figure 3.4 shows that the level of the CCD typically rises towards the continental margins, where biological productivity is in general greater

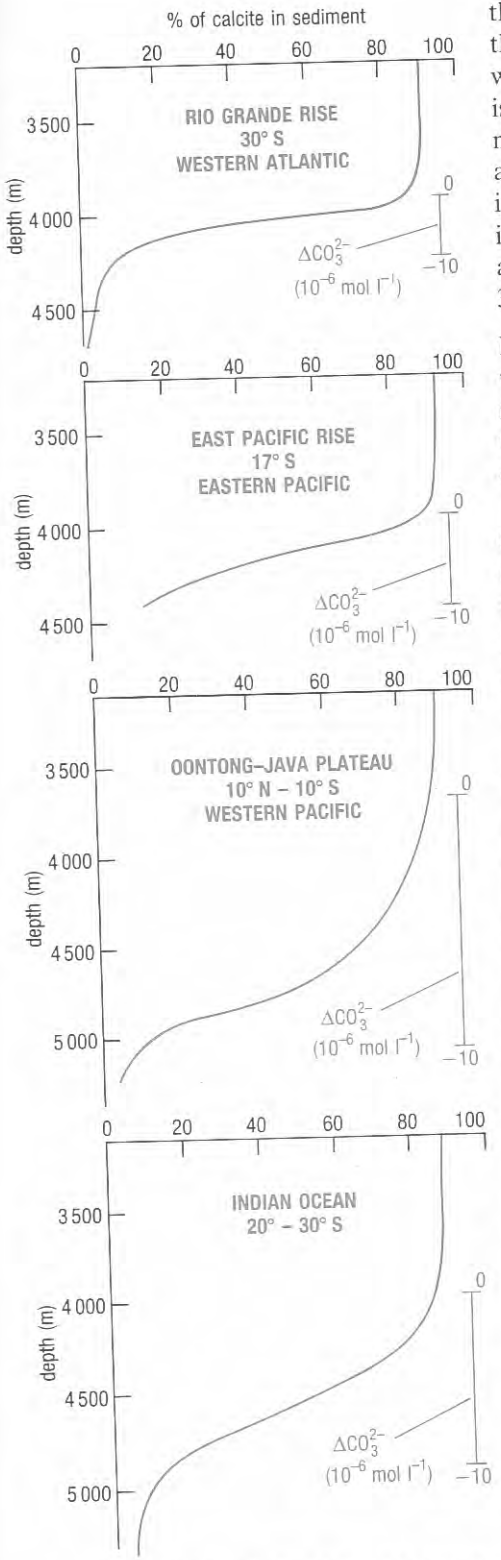

Figure 3.5 Generalized profiles of the calcite content of surface sediments versus water depth on the flanks of ocean ridges and plateaus in different parts of the ocean. For explanation of ΔCO_3^{2-}, see the text. For use also with Question 3.3. Note that 10×10^{-6}moll$^{-1} = 0.01$molm^{-3}.

than throughout most of the open oceans. This would seem to contradict the correlation between high productivity and depression of the CCD which we have just established. The reason for the apparent contradiction is that dissolution of calcareous debris is aided by a rich supply of organic matter which is available for consumption by benthic animals and bacteria at the sea-floor, releasing CO_2 into solution at the sediment–water interface. The CO_2 instantly combines with the water, as in reaction 3.1, increasing the ΣCO_2 of the bottom water, which thus becomes more acid and more undersaturated in CO_3^{2-} with respect to calcite (*cf.* equation 3.3).

In these situations, the CCD virtually coincides with the lysocline, whereas in deeper water there is a depth interval of several hundred metres between them. This is summarized in Figure 3.5, which shows how the amount of calcite in sediments decreases with depth in different parts of the oceans.

QUESTION 3.3 You know that the lysocline is the depth at which dissolution commences (i.e. where the percentage of $CaCO_3$ in the sediments begins to decrease); and that the CCD is the depth at which the proportion of $CaCO_3$ in the sediments falls to less than 20%. Hence, identify the lysocline and the CCD on the profiles on Figure 3.5. Which of the two levels shows the greater variation in depth?

Also shown in Figure 3.5 is the depth interval over which the *difference* between the saturation concentration of CO_3^{2-} for calcite and the actual concentration of CO_3^{2-} in the water rises from 0 to 10 (in 10^{-6}moll^{-1}). This difference is expressed as ΔCO_3^{2-} and on Figure 3.5 it is shown to range from 0 to −10. The rate of dissolution of calcite increases below the lysocline, as the value of $-\Delta CO_3^{2-}$ increases, i.e. as the water becomes more and more undersaturated with respect to calcite. You can see from Figure 3.5 that undersaturation of CO_3^{2-} of only 10×10^{-6}moll^{-1} is enough to dissolve virtually all the calcite in the sediments.

The reason for the transition zone between the lysocline and the CCD (the sloping part of each profile in Figure 3.5) is that the pore waters in the uppermost few millimetres of the sediment become saturated with respect to calcite. Dissolution can only continue when they become undersaturated again, through exchange with bottom waters (by diffusion and/or advection). The greater the value of $-\Delta CO_3^{2-}$, the longer it takes for saturation to occur and the easier it is for exchange with bottom waters to restore the undersaturation.

In general, the greater the flux or 'rain rate' of calcium carbonate debris, the greater the thickness of this transition zone: the time taken to restore undersaturation in the pore waters is increased where the supply of calcite debris is greater. So, the CCD is depressed beneath areas of high productivity, as we have seen.

You might well be tempted to ask at this point why the term 'lysocline' is not applied to the sloping part of profiles such as those in Figure 3.5, by analogy with the terms 'thermocline' and 'halocline'. This is a good question. It is likely that in the original definition, the lysocline *was* the depth interval over which dissolution of calcium carbonate occurred. Nowadays, however, the definition is generally confined to the depth at which dissolution *commences*.

The carbonate system in the oceans is one of considerable complexity, and we have been able to consider only some aspects. The basic relationships are really quite simple however:

1 The solubility of calcium carbonate in seawater increases with depth (e.g. Figure 3.2)

2 In general, the concentration of ΣCO_2 increases with depth (e.g. Figure 3.1), so that at some depth the seawater becomes sufficiently acidic and undersaturated with respect to calcium carbonate for it to begin to dissolve (e.g. Figure 3.3). This is the lysocline.

3 At some greater depth, nearly all the calcium carbonate has dissolved. This is the carbonate compensation depth, the CCD (e.g. Figure 3.5).

4 Calcite is more stable than aragonite, so the lysocline and CCD are both shallower for aragonite than for calcite (e.g. Figure 3.3).

Some of the complexities in the system arise from the inherent variability of the contributions to total dissolved inorganic carbon (ΣCO_2). At the start of Section 3.1.1, you read that some of the ΣCO_2 comes from the atmosphere: CO_2 gas goes into solution and combines with water (reactions 3.1 and 3.2). Gases dissolve more readily in cold than in warm water, so the deep water masses sinking in polar latitudes carry dissolved CO_2 to the ocean depths.

We have seen that as water masses 'age' on moving away from the surface source regions, their initial complement of oxygen is depleted by respiration and bacterial decomposition. The oxygen is used to form CO_2, which increases the concentration of ΣCO_2. There are thus considerable lateral and vertical variations of ΣCO_2. As exemplified in Figure 3.1, older Pacific (and Indian) Ocean waters carry more ΣCO_2 than younger Atlantic waters. Nor is the rate of decrease of $[CO_3^{2-}]$ regular with depth. In Figure 3.3 for example, there is a distinct minimum in the $[CO_3^{2-}]$ profile at about 1km depth, superimposed on the overall downward decrease.

QUESTION 3.4 Can you offer an explanation for this minimum, at about 1km depth?

The average level of the CCD is an indicator of the rate of removal of atmospheric CO_2 to the deep sea, both in organic tissue, and in carbonate skeletal material. As we noted earlier, there are two principal ways in which the CO_2 gets into the ocean in the first place. One is direct, through solution of CO_2 from the atmosphere. The other is indirect, through weathering of rocks on land (by carbonic acid in rainwater); this supplies bicarbonate and carbonate ions in river water and thence to seawater. These two routes for the entry of carbon into the oceans have different effects on the carbonate system there.

Reactions 3.1 and 3.2 show that direction solution of atmospheric CO_2 produces hydrogen ions to balance the negative charges on the bicarbonate and carbonate ions. In contrast, the bicarbonate and carbonate ions in solution in river water are balanced chiefly by cations such as Ca^{2+}, Na^+, K^+ and so on, rather than by H^+.

If the rate of supply of CO_2 to the oceans were to increase by either of these routes, which would be more likely to make seawater more acid?

Direct solution of CO_2 is accompanied by the formation of hydrogen ions in seawater, which would make the seawater more acid. The more CO_2 entering the oceans by this route, the greater the value of $[H^+]$, and the higher the ratio of bicarbonate to carbonate ions (equation 3.3). On the other hand, the bicarbonate and carbonate ions entering the oceans from rivers are mostly accompanied by cations other than H^+, so seawater does not get more acid (there are exceptions, of course, because some river waters are relatively acid, but the generalization is valid enough for our purposes). The concentration of hydrogen ions $[H^+]$ in seawater is not increased and the ratio of bicarbonate to carbonate ions is not affected. Indeed, $[H^+]$ might even fall, in which case the bicarbonate:carbonate ratio would also fall. Because of this, marine chemists sometimes speak of weathering (of rocks on land) as supplying alkalinity to the oceans—from equation 3.10, if $[CO_3^{2-}]$ is high, then A must also be high.

Do not worry if you have not been able to follow all the details of these arguments; it is more important to grasp the overall implications which are:

1 If ΣCO_2 in seawater is increased by direct solution of CO_2 from the atmosphere, the oceans will become more acid, $[CO_3^{2-}]$ in deep water will decrease, and the levels of the lysocline and the CCD will rise.

2 If ΣCO_2 in seawater is increased by the addition of bicarbonate and carbonate ions from rivers, the oceans will probably not become more acid (and might even become less so). $[CO_3^{2-}]$ in deep water will not change significantly (it might even increase), and the levels of the lysocline and CCD will not change (they might even fall).

Both of the scenarios summarized in 1 and 2 above are sensitive to changes in climate and biological activity, which are themselves linked to some extent and which have changed through geological time, with marked effects on the level of the CCD, as we shall see in the next Section.

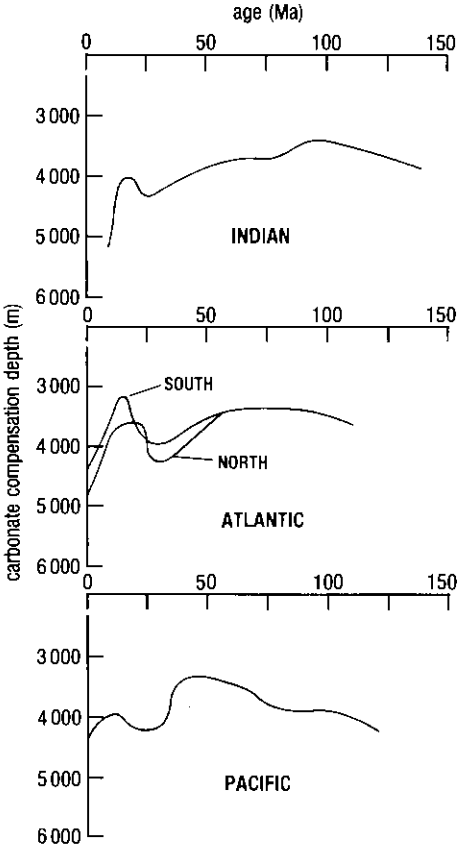

Figure 3.6 Changes in the level of the CCD with time for the major oceans, determined from sediment sequences recovered in deep-sea drill cores.

3.1.3 VARIATIONS OF THE CCD WITH TIME

The global average CCD appears to be deeper now than at any time in the past 150Ma (Figure 3.6). The CCD seems to have deepened progressively, if somewhat erratically, to its present level, over the past 100Ma.

Past levels of the CCD are worked out using information from deep-sea sediment cores and from the basic **age–depth relationship** of oceanic crust. The depth to the top of the igneous oceanic crust (below the sediments) increases with time, though at an exponentially decreasing rate (Figure 3.7), because of cooling, contraction and subsidence of oceanic lithosphere as it moves away from the ridge crest at which it formed. The 'ideal' or theoretical age–depth curve (the dashed line in Figure 3.7) is used to work out past levels of the CCD using information obtained from deep-sea sediment cores. The procedure is very simple in principle.

In any deep-sea sediment core taken from a site that formerly underlay a region where biogenic sediments were not 'swamped' by terrigenous inputs, there will be an upward transition from carbonate-rich sediments (below) to carbonate-poor or carbonate-free sediments (above). The age of the transition can be found easily from the fossil remains in the sediments. If this transition occurred, say, 40Ma ago, then according to

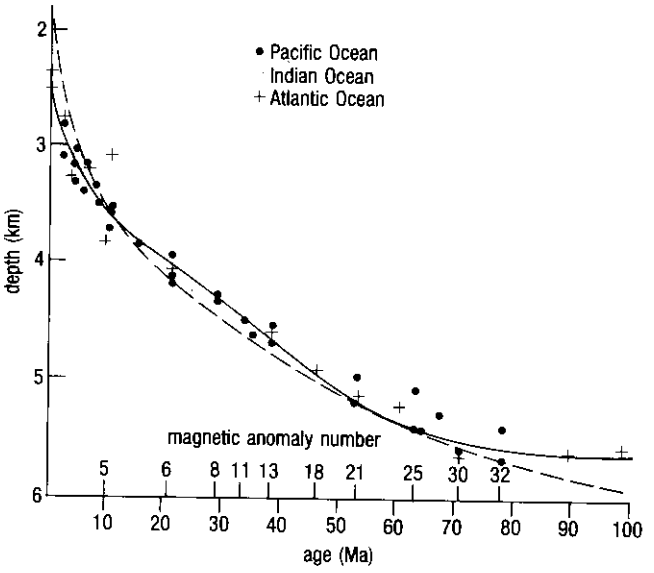

Figure 3.7 Observed and theoretical relationship between the depth to the top of the igneous oceanic crust and its age. The solid line is a best-fit curve through observed points. The dashed line is a theoretical elevation curve, calculated on the assumption that the increase of depth with age is due to thermal contraction of the lithosphere as the plate cools on moving away from the ridge axis. Magnetic anomaly numbers refer to the linear magnetic stripes on the ocean floor, which are arranged symmetrically about ridge axes.

the age–depth relationship (Figure 3.7), the top of the underlying igneous crust lay at a depth of about 4800m. Knowing the thickness of sediment below the transition, and making corrections for sediment compaction and isostatic depression due to sediment loading, the level of the CCD 40Ma ago can be determined, sometimes to within a couple of hundred metres.

It is one thing to establish a pattern, another to explain it. It would seem that in the Cretaceous the oceans were relatively more acid than at present, for the CCD to have been so much shallower (Figure 3.6). The Earth as a whole was warmer then, with ice-free poles. About 100Ma ago, as the continents dispersed and the ocean basins developed their present configurations, the world saw one of the greatest marine **transgressions** in its history, a vast inundation of low-lying land areas, the result of a global sea-level rise of some 300–400m. The planktonic organisms that secrete calcareous tests (coccolithophores and Foraminifera) did not begin to become widespread until about 100Ma ago. Before that time, carbonate sedimentation was mainly confined to the shallow waters of continental shelf regions; and so relatively less calcium was precipitated from open ocean waters than is the case now.

A relative scarcity of pelagic carbonates might have been a contributory factor in maintaining a shallow CCD, but it cannot have been the only one. Cretaceous sediment sequences containing dark, clay-rich layers with between 1% and 30% of organic carbon, offer another explanation. The oceans must have been poorly oxygenated for much of the period covered by Figure 3.6, because ice-caps and glaciers did not begin to develop until late in the Tertiary era. In the absence of ice-caps, there could be no regular supply of abundant cold, dense, well-oxygenated water to the deep oceans, as there is now. At the same time, the warm climatic conditions encouraged biological production, not only in the oceans themselves, but also on the now very extensive continental shelves and on land (the Cretaceous was a time not only of great inundation, but also of great increases in the number and diversity of land plants). The huge amounts of organic carbon supplied to the oceans were greater than the meagre supply of oxygenated water could cope with. There was

widespread depletion of dissolved oxygen throughout the world's oceans, extending from a few hundred metres below the surface to about 2000–3000m depth. Carbon-rich sediments were deposited where these anoxic waters intersected the sea-bed. The waters were anoxic because the oxygen had all been used up in respiration and converted to CO_2. This would in turn have made the water sufficiently acid to dissolve calcium carbonate sinking from the surface, thus maintaining the shallow CCD.

As sea-level began to fall again after the Cretaceous, the amount of organic matter supplied to the oceans decreased as the areas of continental shelf became smaller. The deep oceans began to be supplied with oxygenated water from polar regions, and the CCD began to deepen towards its present level, albeit with some fluctuations.

By way of a postscript to this tale, it is worth mentioning why the record in Figure 3.6 extends back only about 150Ma. There is hardly any ocean floor older than this left in the ocean basins (Section 1.1). The floors of older oceans have nearly all been subducted back down into the Earth's mantle (Figure 2.2).

3.2 THE PRESERVATION OF PELAGIC SILICEOUS REMAINS

Broadly speaking, similar factors affect the accumulation of siliceous sediments as affect the accumulation of carbonate sediments; the supply of skeletal debris, the extent to which dissolution is able to take place and whether or not the siliceous debris becomes diluted on the ocean floor by other types of sediment. There is also a fundamental difference affecting the preservation of the two types of sediments; seawater is everywhere undersaturated with respect to SiO_2, whereas only deep waters are undersaturated with respect to $CaCO_3$.

The solubility of amorphous (opaline) silica decreases by about 30% for a fall in temperature from 25 to 5°C, though this decrease is offset somewhat in the deep oceans, because high pressure acts to increase the solubility slightly. Inspection of samples from sediment traps suggests that most dissolution of opaline silica occurs at the sea-bed, although profiles such as Figure 2.9(c) testify to considerable dissolution and recycling in upper parts of the water column.

Siliceous skeletal material that reaches the sea-bed must be rapidly transported in large, fast-sinking particles (marine snow and faecal pellets). The greater the supply of skeletal debris, the more likely some of it is to reach the ocean floor. Supply is related to productivity, and siliceous sediments on the ocean floor thus underlie areas of high productivity (Figure 1.4). Even in these areas, however, only between 1 and 10% of siliceous material escapes dissolution, either in the upper parts of the water column or at the sea-bed, and accumulates to form sediments. This small proportion can be easily swamped, especially where there is a high input of terrigenous sediment, or where the sea-floor is above the CCD or lysocline.

As in the case of carbonate, the pore waters in the uppermost few millimetres of the sediment become saturated with respect to silica, and

undersaturation is only restored by exchange with bottom waters. Clearly, the greater the flux of siliceous debris, the more difficult it is for undersaturation to be restored and the better the chances of preservation of the siliceous remains.

Close to continental margins where inputs of terrigenous material are high, sediments can accumulate at rates as high as a few metres per *thousand* years, enough to obliterate any biogenic component. By contrast, the accumulation rate of a siliceous ooze is of the order of a few metres per *million* years; whereas accumulation rates of pelagic carbonates can reach several tens of metres per million years, which is also quite enough to dilute the siliceous skeletal content of sediments beneath regions of high productivity, where the CCD is depressed.

As recorded in Chapter 1, diatom oozes generally predominate below the CCD in high latitudes and in areas of coastal upwelling, whereas radiolarian oozes occur in tropical regions. The belt of siliceous sediments round the Antarctic (Figure 1.4) consists of diatom ooze, whereas that in the equatorial Pacific is of radiolarian ooze. Mixed radiolarian and foraminiferal oozes may occur in the most productive areas, where there has been some depression of the CCD.

3.3 BIOGENIC SEDIMENTS AND PALAEOCEANOGRAPHY

Sediments recovered in deep-sea drill cores contain a wealth of information about past climates and changing patterns of ocean circulation.

Calcareous sediments can provide information about more than past levels of the CCD (Section 3.1.3). Different species of organisms inhabit different water masses of contrasted temperature, salinity and other properties. For example, modern benthic foraminiferal assemblages show a correlation with present-day oceanic bottom water masses. Studies of similar assemblages of benthic Foraminifera in deep-sea sediment cores should therefore enable the past distribution and extent of bottom water masses to be mapped, *always assuming that the species concerned have not changed their environmental requirements with time.*

Figure 3.8 illustrates some results from one such investigation, which suggests that the influence of Antarctic Bottom Water (AABW) may have extended as far as the British Isles during mid- to late Miocene times, but no further than the latitude of Gibraltar since the late Pliocene. The southwards 'retreat' of the AABW appears to have been accompanied by intensified production of North Atlantic deep and bottom water masses in the Pliocene and Pleistocene. Correlation with data from other regions suggests that maximum build up of Antarctic ice occurred in the late Miocene, around 5Ma ago, while the development of major Arctic ice-sheets took place in the Pliocene, some 3–2.5Ma ago.

There is another way in which calcareous organisms can provide information about past conditions in the oceans. This is through the ratio of the two main isotopes of oxygen, ^{16}O and ^{18}O, in the calcite of their skeletons. ^{16}O is lighter than ^{18}O, so water molecules containing it

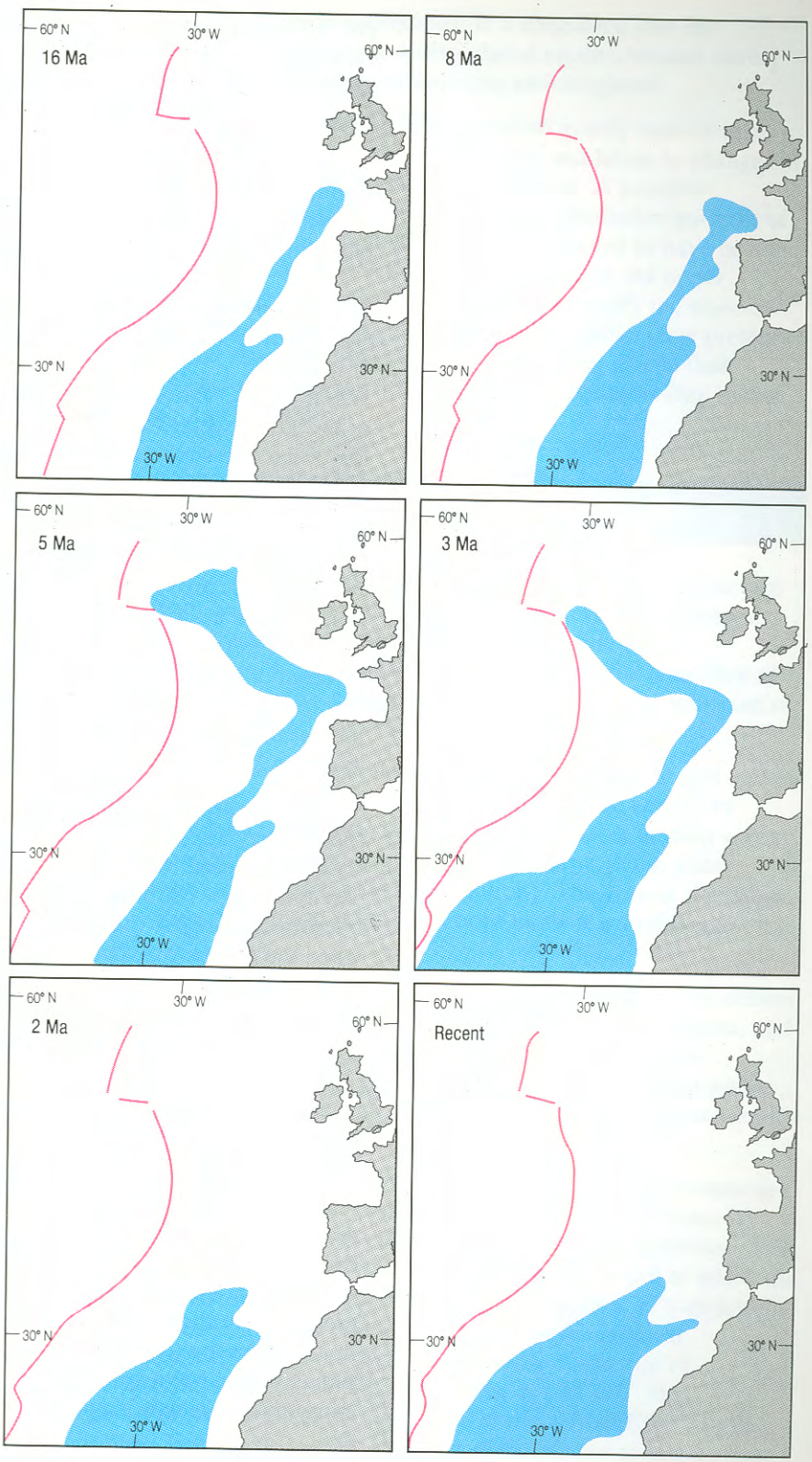

Figure 3.8 The extent of penetration of Antarctic Bottom Water (blue shaded area) into the eastern North Atlantic from the middle Miocene to the present, as inferred from the distribution of benthic foraminiferal assemblages.

($H_2{}^{16}O$) are preferentially removed by evaporation, leaving seawater relatively enriched in the heavier molecule ($H_2{}^{18}O$). As the water removed by evaporation is eventually precipitated in polar regions and becomes 'locked up' in ice-sheets, so the average ratio of ^{18}O:^{16}O in the oceans will increase.

The ratio of ^{18}O:^{16}O in calcite skeletal material varies according to that of the water in which the organisms live. It is higher when polar ice-caps are large, and lower when they are small.

Accordingly, would you expect high ^{18}O:^{16}O ratios to be correlated with high or low stands of global sea-level?

When ^{18}O:^{16}O ratios are high, the oceans have been relatively depleted of $H_2{}^{16}O$, by water frozen into ice-sheets. Water has been removed from the oceans, so sea-level should be lower. Detailed research has established a good correlation between variations of oxygen isotope ratios in (especially) foraminiferal skeletal material and sea-level fluctuations resulting from glacial oscillations of the Pleistocene.

In addition to providing information about sea-level, oxygen isotope ratios can be used together with species distributions to determine how water temperatures have changed (the ^{18}O:^{16}O ratio in calcite skeletal material of a given species is greater in cold than in warm water). In the eastern North Atlantic (Figure 3.8), for example, bottom water temperatures were about 5°C during the middle to late Miocene, falling to about 2.5°C during the Pleistocene.

Siliceous sediments can also provide palaeoceanographic information, and though they are perhaps not quite so versatile as calcareous sediments, they can be used to supplement information obtained from them. Thus, assemblages of benthic and planktonic Foraminifera and siliceous microfossils suggest that latitudinal temperature gradients were weak when the southern Atlantic was opening in Upper Cretaceous times; and that they remained so until about the middle to late Eocene, *c.*45–50Ma ago.

The Indian Ocean is particularly interesting because of the seasonal reversals of winds and currents that occur there (the monsoons). One of the more spectacular monsoonal reversals occurs in the north-west Indian Ocean, where the Somali Current flows north-eastwards for half the year (April to September), accompanied by strong upwelling and high biological productivity, and south-westwards for the other half of the year (October to March), with no upwelling. Drill cores have been obtained in this region in order to document the history of the Somali Current. Biogenic sediments rich in diatom and foraminiferal remains are good indicators of upwelling (Chapter 1), and such sediments become prominent in the record during the middle Miocene. The implication is that (seasonal) upwelling was not an important feature of the north-west Indian Ocean before about 10–12Ma ago, suggesting in turn that monsoonal reversals may have been weak or non-existent before that time.

In the upper part of the sedimentary record in this region, representing the glacial–interglacial alternations of the Pleistocene, the sediments show a strong cyclical character; they are alternately enriched and depleted in biogenic remains typical of upwelling and in land-derived pollen (brought from inland by south-westerly winds). The cycles are correlated with

glacial to interglacial climatic oscillations. It is concluded that the (seasonal) upwelling was stronger during glacial epochs, weaker during interglacials—the Earth is presently enjoying an interglacial.

These oscillations are considered to have resulted mainly from changes in configuration of the Earth's orbit round the Sun, and hence to changes in the intensity of solar radiation at the Earth's surface. A possible contributory factor was the effect on atmospheric circulation patterns of the uplift of the Himalayan mountains, which is believed to have become more rapid in the past 3Ma. By influencing the winds in the upper atmosphere, the rise of this great barrier acted to intensify the seasonal contrasts between the (winter) high pressure and (summer) low pressure systems over Asia; these contrasts were greater during glacial than interglacial epochs, and thus led to enhanced seasonal upwelling in the north-west Indian Ocean.

3.4 SUMMARY OF CHAPTER 3

1 Biogenic sediments are most abundant where productivity in surface waters is high and terrigenous sediments are scarce. The geographical separation of carbonate and siliceous sediments is related to the preservation potential of the planktonic organisms and the chemistry of the water column. Biological aggregation is important in the transport of planktonic skeletal remains to the sea-bed.

2 Carbon dioxide gas dissolves in seawater to form carbonic acid and its dissociation products. These ions are also supplied to the oceans by rivers. Total dissolved inorganic carbon (ΣCO_2) increases in deep water chiefly because of the decomposition of organic matter in the water column (liberating CO_2 which goes into solution). The greater the value of $[\Sigma CO_2]$, the more acid the water, the more likely it is to dissolve calcium carbonate.

3 The solubility of calcium carbonate increases with depth in the oceans. Surface waters are supersaturated with respect to calcium carbonate, and deep waters are undersaturated. The degree of saturation can be determined from measurements of ΣCO_2 and alkalinity, A, from which concentrations of CO_3^{2-} in the water can be calculated and compared with the concentration appropriate to $CaCO_3$ saturation.

4 The depth at which dissolution of carbonate is observed to commence is called the lysocline. It lies at or below the depth where the water is shown from measurements to be saturated with respect to carbonate. The carbonate compensation depth (CCD) is defined as the depth at which the carbonate content (usually calcite content) of sediments is 20% or less. It tends to be depressed (deeper) beneath areas of high biological productivity in the open oceans. Below the lysocline, the rate of carbonate dissolution is controlled by the value of $-\Delta CO_3^{2-}$, the difference between the saturation $[CO_3^{2-}]$ and the actual $[CO_3^{2-}]$ in the water column. Both lysocline and CCD are shallower for aragonite than for calcite.

5 Direct solution of atmospheric CO_2 makes seawater more acid, because negative charges on the bicarbonate and carbonate ions so produced are balanced by hydrogen ions (H^+). This process tends to

make the levels of the lysocline and CCD shallower. Bicarbonate and carbonate ions entering the ocean from rivers (and produced by weathering of rocks on land) are balanced by cations other than H^+ (i.e. Ca^{2+}, Na^+, K^+, etc.), and in general do not make seawater more acid (it is sometimes said that rivers add alkalinity to seawater). This process will in general not affect the levels of the lysocline and CCD.

6 The global level of the CCD was shallower in Cretaceous times than it is now, possibly: (a) because marine transgressions led to increased biological production and carbonate sedimentation on broad continental shelves; and (b) because widespread anoxia in ocean waters led to increased acidity.

7 Seawater at all depths is undersaturated with respect to silica, and the preservation of siliceous sediments depends upon the survival of siliceous skeletal debris as it descends the water column. The likelihood of preservation is greater once the remains have survived descent through surface waters. The chances of siliceous sediments accumulating are greatest where surface productivity is high, and where water depths are great, so that dilution by terrigenous or calcareous material is low. Siliceous sediments are most abundant at high latitudes in the Pacific Ocean, in the equatorial regions of both the Pacific and Indian Oceans, and in coastal upwelling areas.

8 Different marine organisms inhabit different water masses. Assuming that their ecological requirements do not change significantly over geological time, the remains of such organisms in biogenic sediments can be used to determine past distributions of water masses and patterns of ocean circulation—as well as fluctuations of the CCD.

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

QUESTION 3.5 Locate the Ninety-East Ridge in the Indian Ocean on Figure 1.5 (as the name implies, the ridge is near longitude 90° E and is aligned north–south). Now look back to Figure 1.7. From the nature of the sediments recovered in that core from the ridge, would you infer that the ridge has always been a relatively upstanding feature, or that it has only recently become one?

QUESTION 3.6 Explain briefly why neither calcite nor aragonite is likely to be accumulating to any significant extent on the sea-bed at the station represented by the profile in Figure 3.3.

QUESTION 3.7 Give two reasons why CO_2 will be released to the atmosphere if deep water upwells to the surface in tropical latitudes.