8.2.1 Marine carbon sinks and the conditions that sustained them

In Chapter 6 (Table 6.1), you saw that the two main geological sinks for carbon are carbonate rocks (containing ‘carbonate carbon’, or C_{carb}) and organic-rich deposits (containing ‘organic carbon’, or C_{org}), and that the ratio of their global reservoirs today is estimated to be about 4 : 1. Apart from the brief episodes of enhanced C_{org} burial during the OAEs (Section 5.2), the stratigraphical record suggests that marine C_{carb} burial likewise outstripped C_{org} burial by several times during the Cretaceous. Swiss geochemist Helmut Weissert and colleagues (1998) have estimated that the ratio of C_{carb} to C_{org} burial in marine deposits fell from 6 : 1 in the Late Jurassic to 4.7 : 1 in the Early Cretaceous, but then rose again to 7 : 1 in the Late Cretaceous.

- ○ Based on what you have read in earlier Chapters, what were the dominant sinks for C_{carb} in the Cretaceous seas?
- ● As discussed in Chapter 5, the main accumulations of C_{carb} in the Cretaceous were carbonate platforms at low latitudes and, in the late Cretaceous, the Chalk, especially at mid-latitudes.

Palaeogeographical maps of the carbonate platforms (e.g. Figure 2.16) allow estimation of their total areas. For example, French stratigrapher Jean Philip and his colleagues (1995) provided the following estimates for the Tethyan/Atlantic platforms: Early Aptian, about $7.4 \times 10^6\,km^2$; Late Cenomanian (Figure 2.16), $9.7 \times 10^6\,km^2$; and Late Maastrichtian, $5.1 \times 10^6\,km^2$ (plus part of $1.4 \times 10^6\,km^2$ of mixed siliciclastic/carbonate platforms). Using other estimates for the mean thickness of the platform successions in question, we can derive volumetric estimates of the platform carbonates for the corresponding time-slices, and hence calculate their contribution to C_{carb} burial rates.

Let us consider the platforms that developed in the Early Aptian. Different platform successions vary considerably in thickness because of variation in the provision of accommodation space for their accumulation, as discussed in Chapter 3. In fact, values of total thickness vary widely from tens to hundreds of metres. A preliminary survey of several Lower Aptian platform successions yields a mean thickness of about 130 m. Unfortunately, the duration in absolute time of the Early Aptian is not well constrained, but it is currently estimated at about 4.5 Ma, which would give a mean accumulation rate of 130 m/4.5 Ma = approximately 29 m/Ma. Hence the mean volumetric rate of accumulation of $CaCO_3$ in the Tethyan/Atlantic carbonate platforms (assuming deposition of virtually pure carbonate) can be estimated at $29 \times 7.4 \times 10^{12}\,m^3/Ma = 2.146 \times 10^{14}\,m^3/Ma$, or $2.146 \times 10^8\,m^3/year$.

Assuming a density of $2.71 \times 10^3\,kg/m^3$ for $CaCO_3$ (a slight overestimate, as such limestones may have porosities of up to about 10%), and a value of 0.12 as the mass proportion of carbon (C) in $CaCO_3$, the rate of C_{carb} burial can be calculated as $2.146 \times 2.71 \times 0.12 \times 10^{11}\,kgC/year = 0.07 \times 10^{12}\,kg\,C/year$. A similar calculation for the Late Cenomanian yields an estimate of $0.09 \times 10^{12}\,kg\,C/year$ (Skelton *et al*., 1997, Section 7.7.2). Given the many uncertainties involved in such calculations, these values should be considered only as rough approximations, although they do at least illustrate the order of magnitude concerned.

- ❍ Refer back to Figure 6.4 and determine how these values for C_{carb} burial rates in the Tethyan/Atlantic carbonate platforms of the Early Aptian and Late Cenomanian compare, in proportional terms, to the global flux into carbonate sinks today.
- ● According to Figure 6.4, the global rate of burial of C_{carb} today (in all sinks) is estimated to be about 0.24×10^{12} kg C/year. Thus, the Tethyan/Atlantic carbonate platforms buried C_{carb} at about 0.29, and 0.38, times the present global rate during the Early Aptian and the Late Cenomanian, respectively.

Hence, these platforms alone constituted a major carbon sink, and, indeed, the total contribution of carbonate platforms was even greater, as we have been considering only those that formed in or around the Tethys and Atlantic Oceans.

- ❍ What other major shallow carbonate platforms should also be considered?
- ● Those of the Pacific guyots, which were mentioned in Section 1.1.5.

Our knowledge of these now deeply sunken Pacific platforms is still too scanty for us to quantify their contribution to C_{carb} burial, although, judging from the size of the oceanic promontories on which they formed (Figure 7.21), it must also have been fairly large.

Given the relatively high levels of CO_2 that have been postulated for the Cretaceous atmosphere (Section 6.3), the rapid formation of such vast amounts of $CaCO_3$ poses an apparent chemical paradox, for which we now need to consider some aspects of ocean chemistry in a little more detail.

In natural waters, including seawater, the inorganic carbon (i.e. that which is not incorporated in organic compounds) is contained in four chemical species, namely dissolved CO_2 gas (aqueous CO_2, or $CO_2(aq)$), carbonic acid (H_2CO_3), and bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. Together, these four species make up what is referred to as total dissolved inorganic carbon, usually abbreviated to 'ΣCO_2' (the Greek letter Σ standing for 'sum of'). The balance between the different chemical species depends upon the pH of the seawater (i.e. how acid or alkaline it is, recorded as an inverse measure of the concentration of hydrogen ions, H^+) (Figure 8.10).

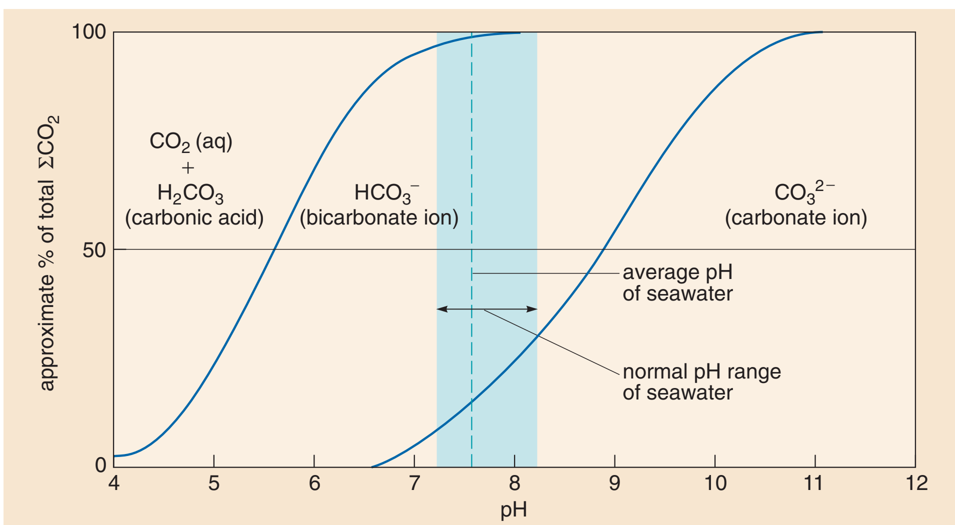

Figure 8.10 The approximate relative proportions of the main chemical species of dissolved inorganic carbon vary with pH in natural waters. Average pH of open seawater today is about 7.7 (dashed vertical line), but may range between 7.2 and 8.2. Note that the positions of the curved lines also vary with temperature, salinity and pressure.

❍ Which is the dominant chemical species in seawater?

● Bicarbonate (HCO_3^-) ions, which make up between 70% (at pH 8.2) and 88% (at pH 7.2) of the ΣCO_2 over the usual pH range of seawater.

Thus, in normal seawater, the content of $CO_2(aq)$ is very small, while that of H_2CO_3 is invariably negligible (regardless of pH). Hence, to a first approximation, ΣCO_2 consists largely of bicarbonate ions with a smaller component of carbonate ions. Nevertheless, the trace of $CO_2(aq)$ in surface waters is important to our concerns, because that is the reservoir that directly equilibrates over short time-scales with atmospheric CO_2. The chain of reactions relating atmospheric CO_2 to dissolved inorganic carbon is thus as follows:

$$\text{atm } CO_2 + H_2O \rightleftharpoons CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \quad (8.1)$$

As the atmospheric reservoir of CO_2 is tiny compared with the total dissolved inorganic carbon in the oceans (Table 6.1), relatively small changes to the latter can have a big impact on the former. A small reduction of pH (i.e. to more acid conditions, with more H^+ ions), for example, will push the equilibria in Equation 8.1 towards the left, so releasing CO_2 into the atmosphere.

The apparent paradox referred to above concerns the relationship between calcification and the atmospheric content of CO_2. Calcification in seawater today is almost entirely mediated by shell-producing organisms. From Figure 8.10, we see that most of the carbonate that ends up in the solid $CaCO_3$ must come from bicarbonate ions, involving a shift to the right in the following equation (which you previously encountered in Section 6.2.2):

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + CO_2(aq) + H_2O \quad (8.2)$$

In fact, the contribution to calcification from carbonate ions in seawater is even less than you might suppose from Figure 8.10. This is because a large proportion of the carbonate ions form electrostatic bonds with magnesium ions (Mg^{2+}), which are abundant in seawater, to form ion pairs that inhibit incorporation of the carbonate in the calcite lattice.

Equation 8.2 shows that for every molecule of $CaCO_3$ formed, a molecule of CO_2 is released. Thus, although you might intuitively have supposed that calcification should consume CO_2, and so draw it down from the atmosphere, in fact — in the short term at least — it does the opposite, pushing CO_2 back into the atmosphere. This has been termed the ‘coral reef hypothesis’, after the observation that the rapid growth of coral reefs that accompanied interglacial eustatic rises in sea-level during the Quaternary was matched by rising levels of atmospheric CO_2 (Figure 6.2). Direct measurements of sea/air fluxes over modern coral reefs have since confirmed the hypothesis, showing them to be net releasers of CO_2 to the atmosphere.

Turning now to atmospheric CO_2: in water of given temperature, pressure and salinity, at equilibrium with the atmosphere, the concentration of $CO_2(aq)$ correlates with the volumetric proportion of CO_2 in the atmosphere (which is equivalent to its proportional contribution to total pressure, termed ‘partial pressure’). Thus, as the partial pressure of atmospheric CO_2 increases, so does the concentration of $CO_2(aq)$, involving a shift towards the right in Equation 8.1 (with a decrease in pH because of the extra H^+ ions produced). This in turn leads to increased dissolution of $CaCO_3$, i.e. a shift to the left in Equation 8.2.

So it would appear that a high partial pressure of CO_2 and enhanced calcification should be incompatible, as they tend to shift the equilibrium in Equation 8.2 in opposite directions. While the calcification should push more CO_2 into the atmosphere, the high partial pressure of the latter should push it the other way, so dissolving $CaCO_3$. Yet, as this and previous Chapters have shown, the available evidence points to their co-existence in the Cretaceous. The solution to the problem must lie in the two processes having occurred in different places, under different conditions. To explore what these different conditions might have been, we must consider other aspects of the relationship between inorganic carbon and seawater.

❍ From your own general experience, how would you expect the solubility of CO_2 in water to vary with increasing temperature?

● As with any gas, its solubility decreases with increasing temperature. Common experience shows that when you heat water in a pan bubbles start to appear as the dissolved air comes out of solution (long before the water actually boils to give off steam).

To express this in quantitative terms, we need to consider how the solubility coefficient of CO_2 in seawater varies with temperature. The solubility coefficient is the concentration of the dissolved gas ($CO_2(aq)$), in moles per litre of seawater of given salinity, when at equilibrium with the pure gas at a pressure of 1 atmosphere (Table 8.1).

Table 8.1 Selected values of the solubility coefficient of CO_2 in seawater in equilibrium with the pure gas at 1 atm pressure, for given temperatures and salinities (10^{-2} moles/litre) (from Weiss, 1974).

	Salinity					
Temperature (°C)	30	34	35	36	38	40
0	6.635	6.498	6.465	6.431	6.364	6.298
10	4.621	4.529	4.507	4.485	4.440	4.396
20	3.400	3.337	3.322	3.306	3.275	3.245
30	2.627	2.583	2.572	2.561	2.540	2.518
40	2.121	2.090	2.082	2.074	2.059	2.044

Thus, for example, if seawater of salinity 35 is heated from 30 °C to 40 °C, it will lose approximately 19% of its $CO_2(aq)$.

❍ What influence would you expect this loss of $CO_2(aq)$ to have (a) on the equilibria shown in Equation 8.1, and (b) on the equilibrium in Equation 8.2?

● (a) By driving off $CO_2(aq)$ into the atmosphere, heating would shift the equilibria in Equation 8.2 towards the left. (b) At the same time, however, it would move the equilibrium in Equation 8.2 to the right, enhancing the precipitation of $CaCO_3$ (that is why you get ‘kettle fur’, especially with hard water, which has a high carbonate content).

Table 8.1 also shows that increasing salinity likewise reduces the solubility of CO_2, a process known as 'salting out'. If, as in our previous example of heating seawater from 30 °C to 40 °C, the salinity were also raised, from 35 to 40, the loss of $CO_2(aq)$ would amount to about 20.5%. Thus, where heating is accompanied by increased salinity through evaporation, there is a double impetus to calcification. Indeed, the strong shift to the left of the equilibria in Equation 8.1 translates into an increase in pH, because of the decreased concentration of H^+ ions.

○ What influence on the proportion of carbonate, relative to bicarbonate ions, should an increase in pH have?

● From Figure 8.10, we see that the proportion of carbonate ions increases with increasing pH.

Eventually, the concentration of CO_3^{2-} ions can cause the water to become so supersaturated with respect to $CaCO_3$ as to overcome the inhibiting effect of magnesium ion pair bonding, and clouds of minute $CaCO_3$ crystals start to form in the water. Such 'whitings', as they are called, have been observed in restricted waters in extremely hot, arid areas, such as the Bahama Banks and the Persian Gulf.

These facts suggest a possible solution to the apparent paradox of massive carbonate platform growth despite the inferred high partial pressure of CO_2 in the Cretaceous atmosphere (Figure 8.11). Given the intense heat and evaporation that the vast expanses of water overlying the shallow platforms and shelves are likely to have experienced during extreme greenhouse phases, it is probable that temperatures and salinities there rose relative to surrounding open waters. This inference, with respect to salinity at least, is confirmed in some instances by the presence of evaporites in the platform or shelf interiors (Section 5.4). By driving off the CO_2 resulting from calcification, such conditions could have shielded the carbonate factories from the contrary effect of the high levels of CO_2 in the atmosphere. Indeed, the return of CO_2 to the atmosphere arising from the calcification would have served as a positive feedback that maintained the extreme climatic conditions. By contrast, the cooler regions of the open oceans (Figure 5.11) would have borne the brunt of the high partial pressure of CO_2, with a compensatory rise in the level of the CCD (Box 6.1).

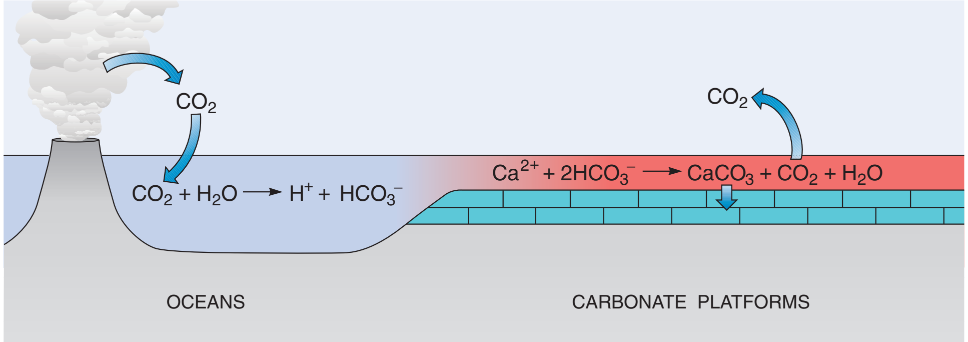

Figure 8.11 A model to explain the rapid growth of carbonate platforms despite high levels of CO_2 in the Cretaceous atmosphere, ultimately fuelled by increased volcanic emission (Section 7.2.6). CO_2 from calcification on the platform is pushed into the atmosphere because of the high temperature and salinity of the shallow water there (red), thereby both conserving the conditions favouring calcification and maintaining greenhouse warmth. Uptake of atmospheric CO_2 is essentially limited to cooler regions of the open oceans (blue), thereby lowering pH and raising the CCD.

However, a further chemical problem remains to be resolved — that of sustaining the supply of ions required for calcification. In seawater today, calcium ions (Ca^{2+}) are nearly four times as abundant as bicarbonate and carbonate ions together, while in the Late Cretaceous (as you will see in Section 8.2.3) the concentration of Ca^{2+} ions may have been even higher. Hence the problem essentially concerns the replenishment of bicarbonate and carbonate ions.

○ What was the most likely source for the bicarbonate and carbonate ions for the platforms?

● Ocean waters, where less extreme temperatures, as well as the dissolution of calcareous planktonic remains falling beyond the CCD, would have fostered higher concentrations of ΣCO_2, and hence of bicarbonate and carbonate ions (Figure 8.10).

The question thus becomes: how were the platforms supplied with ocean water? To some extent the loss of water volume through evaporation over the platforms would have led in any case to influx from the surrounding open sea (evaporative loss from the ocean itself being compensated for by meteoric influx in other, less arid regions). However, there is one further, more drastic possibility for seasonal replenishment. Given the fairly wide latitudinal distribution of platforms (e.g. Figure 2.16), some seasonal variation in temperature seems likely, especially for those around the northern Tethys, which extended beyond 30° N palaeolatitude.

○ Refer back to Figure 5.13 and decide what might have been the effect of cooling platform water to a temperature near that of the surrounding seawater, as far as relative density is concerned.

● If the salinity of the platform water had risen above that of the open seawater, cooling it to a similar temperature would then have made it relatively more dense.

In such circumstances, the platform water could thus have flowed off the platform, down into the neighbouring basin (as suggested in Section 5.4), to be replaced by surface waters from the open sea. At present, however, this model for seasonal overturn is merely informed speculation, which has yet to be tested.

The system described in Figure 8.11 requires the maintenance of extreme climatic warmth, implying that cooling could have had a deleterious effect on the carbonate factories of the platforms. Section 5.4 introduced the model of enhanced polar energy transport due to the latent heat of evaporation, but what would have driven the atmospheric convection cells to transport the moisture-laden air to high latitudes, if the latitudinal temperature gradient was no greater (and possibly less) than today? An ingenious twist to the water-vapour model of Hay and DeConto (1999) relies on the effect of water vapour on the density of air. Water has a lower molecular weight (approximately 18) than the main constituents of air (N_2, molecular weight 28, and O_2, molecular weight 32). Since equal volumes of gas at the same temperature and pressure contain the same number of atoms or molecules, air laden with water vapour is less dense than dry air. Conventional thermal convection from the equatorial belt could thus have been supplemented by the effect on air density of the additional water vapour content. The latitudinally extended warmth resulting from these effects would in turn have allowed the development of the carbonate platform systems well beyond the tropics. A picture thus begins to emerge of a distinctive greenhouse climate system sustained by positive feedbacks ensuing from the high carbon flux.