his model, a rain ratio of 0.5 leads to too strong preservation in the Atlantic, while a rain ratio of 1.0 leads to almost no preservation in the Pacific. A rain ratio of about 0.7 seems to best represent the observations. This value is in remarkably good agreement with the sediment trap–derived estimate of 0.8 ± 0.2 [*Klaas and Archer*, 2002]. *Archer* [1996a] also demonstrated that the main cause of the differences in the thickness of the transition zone between the Atlantic and Pacific is the rain of non-$CaCO_3$ material, with the Atlantic receiving much higher rates of such material than the Pacific.

CONCLUDING REMARKS

Before leaving this subject, we summarize the most important conclusions. The promotion of calcium carbonate dissolution by the degradation of organic matter plays a critical role in the dissolution of $CaCO_3$ in the sediments. Model results indicate that as one goes from supersaturated to undersaturated conditions in the overlying water column, already 40% to 70% of the $CaCO_3$ gets dissolved by this process when one reaches

saturation. This large dissolution percentage does not necessarily show up as a large drop in the percent dry weight $CaCO_3$ content of the sediments for reasons that are discussed next.

The relationship between $CaCO_3$ rain, dissolution, and final $CaCO_3$ content in the sediments can be illustrated by computing the final $CaCO_3$ content, f_{CaCO_3}, as a function of the proportion of $CaCO_3$ to inert (e.g. terrigenous) material arriving at the sediment, R, and of the fraction of the deposited $CaCO_3$ that dissolves in the sediments, f_{diss}. This gives $f_{CaCO_3} = (1 - f_{diss})/(1 - f_{diss} + 1/R)$. If $R = 9$ and $f_{diss} = 0$, then $f_{CaCO_3} = 90\%$. If 50% of the $CaCO_3$ dissolves, i.e., $f_{diss} = 0.5$, the $CaCO_3$ content in sediments is still very high at 82%. Even with $f_{diss} = 0.9$, the sediment $CaCO_3$ drops to just 47%. Only if 99% of all $CaCO_3$ arriving at the sediments dissolves, will the final $CaCO_3$ sediment content fall below 10%. Thus, the $CaCO_3$ content of sediments is not a sensitive indicator of $CaCO_3$ dissolution fluxes until dissolution is very high, which also makes it difficult to detect the onset of dissolution from the depth of the lysocline.

9.5 Calcium Carbonate Compensation

One of the most exciting aspects of the marine $CaCO_3$ cycle is its possible role as a homeostat for regulating the *DIC* and *Alk* budgets of the ocean on millennial and longer timescales. Since the ocean carbon cycle controls atmospheric CO_2 on these timescales, this homeostat is also of great importance for controlling atmospheric CO_2. Without negative feedbacks, slight imbalances between the input and loss of alkalinity to the ocean would over time lead to large changes in oceanic alkalinity and hence atmospheric CO_2 concentrations. Such large excursions in atmospheric CO_2 do not appear to have occurred over the last tens of millions of years [*Prentice et al.*, 2001]. In order to have a stabilizing effect on atmospheric CO_2, the $CaCO_3$ homeostat in the ocean must somehow link the input of alkalinity with the loss of alkalinity in order to maintain a balance between the two. As seen in figure 9.1.1, the major inputs of alkalinity into the open ocean are export from the margins (mainly river input of weathering-derived alkalinity) and input from hydrothermal vents. The only loss term is the burial of $CaCO_3$ at the sea floor.

At first view, the input and loss processes seem to be completely uncoupled, so the existence of a strong coupling between these processes seems surprising. However, we have seen that the preservation of $CaCO_3$ in the sea-floor sediments is determined by a number of factors and most importantly by the degree of undersaturation of the seawater with respect to calcite. As the saturation state is governed by the concentration of the CO_3^{2-} ion, any process that changes the concentration of CO_3^{2-} in

the deep ocean necessarily alters also the preservation pattern of $CaCO_3$ in the sediments. Because $[CO_3^{2-}] \approx Alk - DIC$, a change in the CO_3^{2-} ion content can be generated either by changes in the alkalinity supply to the open ocean or by changes in the ocean biological pumps that affect *DIC*. The first mechanism thus opens the possibility for maintaining a long-term "external" balance in the ocean between the input and loss of alkalinity. The second mechanism plays an important role in many scenarios that attempt to explain glacial-interglacial changes in atmospheric CO_2. It builds on the premise that any anomaly in the deep ocean CO_3^{2-} content generated by the processes that are invoked to explain the lower atmospheric CO_2 concentration needs to be removed in order to re-establish the balance between input and burial of *Alk*. This process, termed "$CaCO_3$ compensation" [*Broecker and Peng*, 1987], can either enhance or diminish the effect of the original process in changing atmospheric CO_2. We will first discuss the $CaCO_3$ homeostat and its role in maintaining the "external" balance between input and burial. We will discuss the second mechanism thereafter.

$CaCO_3$ HOMEOSTAT

In order to understand the mechanisms that link variations in the alkalinity input to variations in the burial of $CaCO_3$, let us turn to figure 9.5.1. In the present steady state, the alkalinity input by rivers and hydrothermal
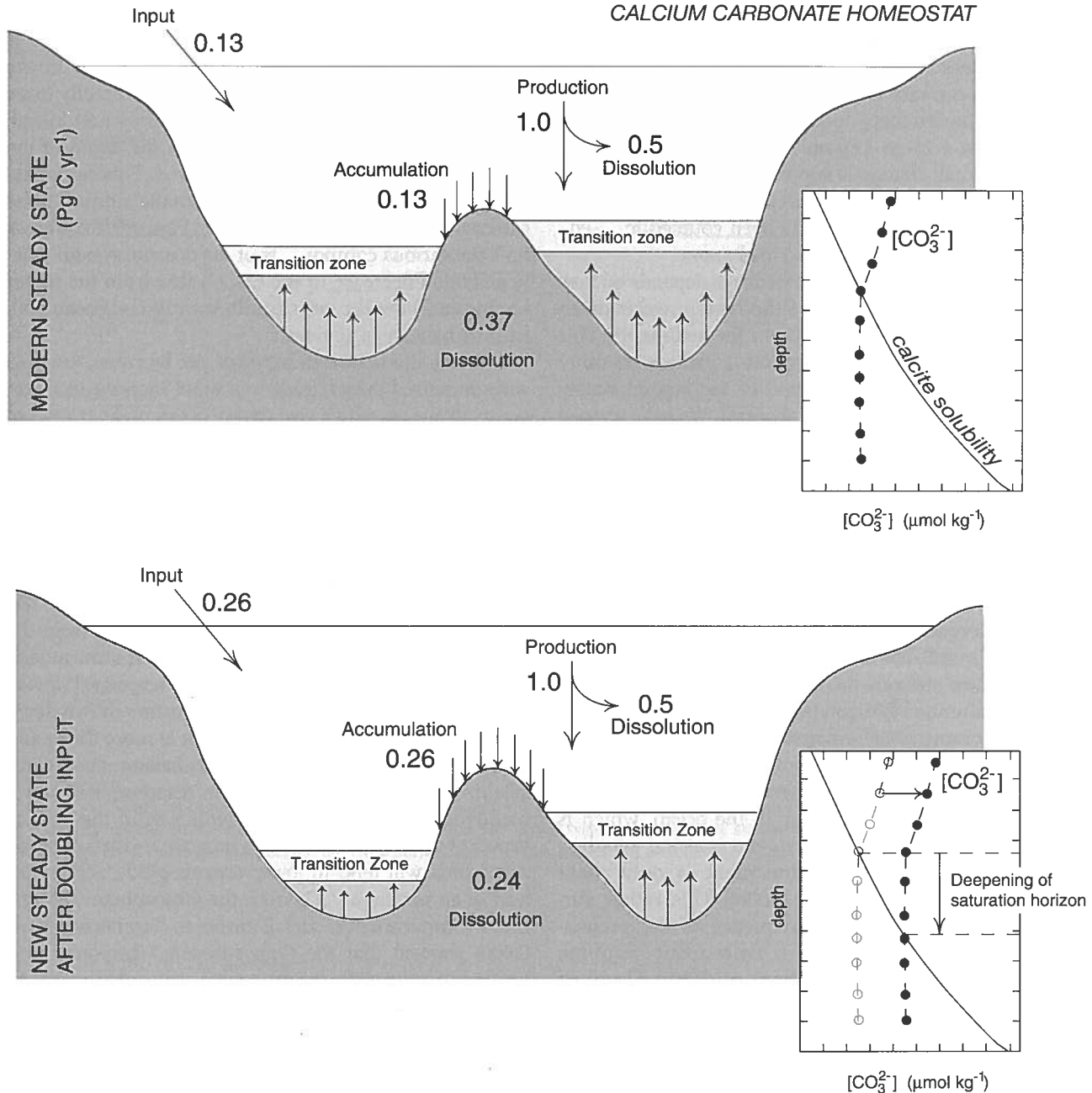
FIGURE 9.5.1: Illustration of the CaCO$_3$ homeostat. (a) Modern steady-state budget for CaCO$_3$ in the open ocean realm in units of Pg C yr^{-1} modified from [*Milliman et al.*, 1999]; see also figure 9.1.1). (b) New steady-state budget after the weathering input has been doubled from 10 Tmol C yr^{-1} to 20 Tmol C yr^{-1}. Insets show the CO$_3^{2-}$ ion concentrations as a function of depth. The increase in the input of alkalinity leads to an increase in the CO$_3^{2-}$ ion concentration in the entire ocean. This leads to a depression of the calcite saturation horizon, so that fewer sediments are exposed to undersaturated bottom waters. This process continues until the increased deposition of CaCO$_3$ in the supersaturated zone balances the input.

vents into the open ocean of about 0.13 Pg C yr^{-1} is balanced by deep sea burial (figure 9.5.1a). This balance is achieved by dissolving roughly 0.5 Pg C yr^{-1} of the surface CaCO$_3$ production of about 1.0 Pg C yr^{-1} in the water column and dissolving an additional 0.37 Pg C yr^{-1} in the sediments. If we now increase the input from terrestrial weathering, the CO$_3^{2-}$ content of the entire ocean starts to increase (figure 9.5.1b). This results in a signifi-

cant deepening of the saturation horizon, reducing the area of the sediments that are exposed to corrosive waters. The CO$_3^{2-}$ concentration continues to increase and the saturation horizon continues to deepen until the burial of CaCO$_3$ in the deep sea sediments has reached the magnitude of the new input. In case of a doubling of the input, the new steady state requires that about 0.26 Pg C yr^{-1} are buried and 0.24 Pg C yr^{-1} are

dissolved in the sediments. This is the feedback that keeps alkalinity in the ocean within rather tight bounds and hence provides a strong constraint on how much atmospheric CO_2 can vary over time. Using a multi-box model, Keir [1995] showed that a doubling of the weathering input leads to only a 25 to 35 ppm reduction in atmospheric CO_2. This small change is supported by the more recent results of Archer et al. [2000b] on the basis of a 3-D ocean biogeochemistry model that has been coupled to a sediment model similar to that described above.

The strength of this negative feedback depends on how strongly the saturation state of the bottom water determines the dissolution of $CaCO_3$ in the sediments. This $CaCO_3$ homeostat would be weaker if parameters other than the CO_3^{2-} ion concentration of the bottom waters were exerting a more dominant control. We have learned above that the remineralization of organic matter has a significant influence on the dissolution of $CaCO_3$ in the sediments. However, as long as the organic matter–to–$CaCO_3$ rain ratio arriving at the sediments is below 1:1, the saturation state of the bottom water remains the dominant factor. We have also seen that the efficiency of respiration-driven dissolution tends to decrease strongly if bottom waters are supersaturated, even in cases where the rain ratio is well above 1:1. There are thus substantial limits for how strongly the ocean's lysocline can deviate from the saturation horizon [Sigman et al., 1998].

An important note remains to be added regarding the timescale of the $CaCO_3$ homeostat. One might be tempted to argue that the timescale is of the order of the residence time of alkalinity in the ocean, which is about 100 kyr. However, it turns out that the e-folding timescale for the oceanic adjustment is only about 5–10 kyr [Archer et al., 1997, 2000b]. This rather surprising result is again a consequence of the peculiarities of the oceanic CO_2 system. Only about 5% of the DIC in the ocean is in the form of CO_3^{2-}. Thus the CO_3^{2-} content of seawater can adjust approximately 20 times faster than the 10^5 years it takes to change the entire DIC pool by the input from weathering processes and volcanic outgassing. The $CaCO_3$ homeostat is therefore able to interact with the global carbon cycle on timescales shorter than the 100 kyr cycle associated with the glacial-interglacial climate cycles of the last million years.

CaCO₃ COMPENSATION

The balance between river input of alkalinity and burial can also be changed by ocean internal changes, such as alterations of the marine production of $CaCO_3$, or changes in the oceanic distribution of ΔCO_3^{2-}. We have seen above that the latter is mainly controlled by the soft-tissue pump. Therefore any change of the ocean's biological pumps will upset the ocean's alkalinity balance and require an adjustment of the ocean's carbonate cycle.

However, the response of the latter to changes in the two biological pumps is fundamentally different.

In the case of the carbonate pump, a change in the production and export of $CaCO_3$ will lead directly to an imbalance between river input of alkalinity and burial, which is then adjusted by a change of the depth of the lysocline until a new balance is achieved. This carbonate compensation response is fundamentally similar to the external homeostat described above. Figure 9.5.2a shows how the various components of the oceanic system react to a sudden decrease in the $CaCO_3$ flux from the upper ocean, and how the new equlibrium of the ocean's alkalinity balance is achieved.

Initially, the unabated input of Alk by rivers, coupled with decreased burial, leads to a rapid increase in mean ocean alkalinity, which also causes ocean mean [CO_3^{2-}] to go up. As a result, the lysocline starts to deepen, so that a greater fraction of the produced $CaCO_3$ can be buried. The process continues until the lysocline has reached a depth at which burial of Alk is equal to the river input of Alk. The increase in ocean mean Alk also decreases the oceanic buffer factor, leading to an imbalance of inorganic carbon between the atmosphere and ocean. The balance is restored by the ocean taking up CO_2 from the atmosphere, hence causing a drawdown of atmospheric CO_2. In addition to this "open system" response [Sigman and Boyle, 2000], atmospheric CO_2 is further drawn down by a "closed system" response, which is more direct and exists even in the absence of a need to balance the ocean's alkalinity input. This closed system response is simply a consequence of the fact that a reduction in the surface export of $CaCO_3$ will lead to an increase in surface ocean Alk, which will tend to lower oceanic pCO_2, and hence lead to an uptake of CO_2 from the atmosphere. Using a multi-compartment model of the ocean, Sigman and Boyle [2000] showed that the "open system" response to a halving of the $CaCO_3$ export lowers atmospheric CO_2 by about 20 ppm, whereas the "closed system" response leads to a change in atmospheric CO_2 of about 30 ppm. The two changes are cumulative, so that the total atmospheric CO_2 change is about 50 ppm. However, as we will discuss in chapter 10 in more detail, the exact magnitude of the atmospheric CO_2 response depends quite sensitively on the ocean model being employed [Broecker et al., 1999a, Archer et al., 2000a]. The open and closed system responses are also associated with quite different timescales. The closed system response has a timescale of maximally a few hundred years, primarily determined by the whole ocean overturning timescale. By contrast, the open system response is quite slow, of the order of hundreds to thousands of years, primarily because of the low rates of $CaCO_3$ burial and the slow kinetics of sediment dissolution.

The response of the oceanic carbonate system to changes in the soft-tissue pump are quite different. In this case, and disregarding the potential role of a change
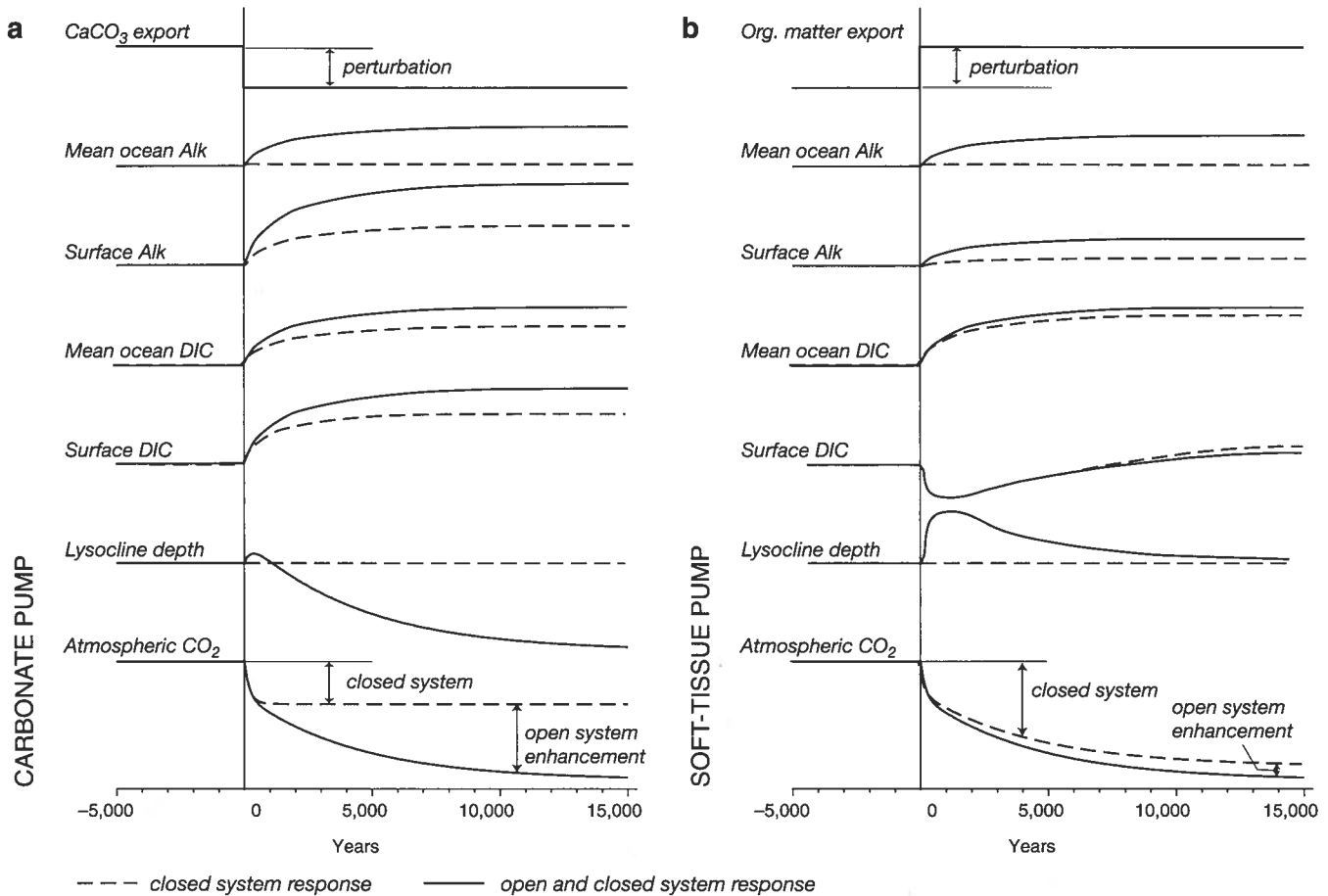
FIGURE 9.5.2: Response of the ocean carbon system and atmospheric CO_2 to (a) a sudden decrease in the surface export of $CaCO_3$, and (b) a sudden increase in the surface export of organic matter. The closed system responses are shown by the dashed lines, while the open system responses, i.e., those that include the river/burial balance of *Alk*, are shown as solid lines. The curves are approximate.

in the rain ratio on the decoupling of preservation from the saturation horizons, the main perturbation to the oceanic *Alk* balance consists of a change in the oceanic distribution of $[CO_3^{2-}]$, which changes the distribution of ΔCO_3^{2-}, and hence the depth of the saturation horizons. In the case of a sudden increase of the soft-tissue pump, the concentration of deep ocean CO_3^{2-} would fall quite strongly, leading to a rapid shoaling of the saturation horizon. Assuming that the depth of the saturation horizon is the main factor controlling preservation, this would lead to a large increase in $CaCO_3$ dissolution, which increases ocean mean *Alk* and hence $[CO_3^{2-}]$. As a consequence, the lysocline starts to deepen again until it has reached a level where the ocean's alkalinity balance is again met. This depth will be somewhat shallower than the original depth of the lysocline, with the exact location depending on the the intial $[CO_3^{2-}]$ distribution and where the additionally exported organic carbon gets remineralized in the water column.

As was the case for the carbonate pump, a change of the soft-tissue pump will lead to both open and closed system responses of atmospheric CO_2 (figure 9.5.2b). The closed system response is a result of the drawdown of surface ocean *DIC* induced by organic matter export, which will lead to an uptake of CO_2 from the atmosphere. The open system response is a consequence of the increase in ocean mean *Alk*, and will enhance the closed system response by removing additional CO_2 from the atmosphere. The exact magnitude of these two responses depends quite sensitively on the model being employed. For a 30% increase in the soft-tissue pump and using a multi-box model, *Sigman and Boyle* [2000] estimated a drawdown of 46 ppm, with the most of this being driven by the closed system response (43 ppm), and the open system response adding only 3 ppm.

In summary, the ocean's need for establishing a long-term *Alk* balance (i.e., the open system response) leads to a tendency for carbonate compensation to enhance the initial (i.e., closed system) response of atmospheric CO_2 to changes in the ocean's biological pumps, i.e., acting as a positive feedback in the system. This has important

consequences for discussing scenarios that attempt to explain the 80 ppm variations that occurred in atmospheric CO_2 between glacial and interglacial periods. We will return to this issue in chapter 10.

In chapter 10, we will also discuss a third type of $CaCO_3$ compensation, which occurs as a result of perturbations of atmospheric CO_2 external to the ocean, e.g., driven by imbalances in the terrestrial carbon cycle, or by the release of CO_2 from the burning of fossil fuel. In this case, the oceanic carbonate system acts as a negative feedback, neutralizing the carbon that has been added to the atmosphere-ocean-sediment system.