

Web Supplement 15.6

15.6.1 Carbonate Compensation: Glacial to Interglacial Transitions

An example of how carbonate compensation may have regulated atmospheric CO₂ levels during transitions from glacial to interglacial periods was first proposed by Broecker and Peng in 1987.¹ The following scenario provides a mechanism explaining why atmospheric P_{CO_2} levels have always increased at the end of Ice Ages. Toward the end of an Ice Age, sufficient time has elapsed for the ocean to have attained a steady state with respect to calcium carbonate. Thus, the rate of supply of Ca²⁺ and bicarbonate from rivers, volcanoes, and hydrothermal systems is exactly balanced by their removal via burial of CaCO₃. This causes the carbonate ion concentration and depth of the CCD to remain constant over time.

All glacial periods are characterized by low atmospheric P_{CO_2} as compared to interglacials. This is thought to reflect efficient uptake of carbon by marine plankton into POC and CaCO₃, followed by burial in sediments. To support this high level of biogenic production requires relatively high levels of nutrient supply, either in the form of river runoff, or as aeolian dust-borne iron. The resulting flux of detrital POC into the deep sea sets the depth of the CCD, as remineralization of sinking POC generates CO₂, which then reacts with CO₃²⁻. This determines the $\Omega_{calcite}$ in the deepwaters and, hence, the dissolution rate of PIC (Eq. 15.17).

In Broecker and Peng's scenario, the supply of nutrients to the ocean declined at the end of last Ice Age. Deprived of nutrients, plankton became less productive, so less CO₂ was converted to POC. With less POC raining into the deep ocean, the supply of remineralized CO₂ declined, causing [CO₃²⁻] to rise as rivers continued to supply HCO₃⁻ to the ocean (with less CO₂, there is more of a driving force to convert HCO₃⁻ to CO₃²⁻ as per Eq. 15.21). This makes the deep waters less corrosive to calcium carbonate. The CCD was shifted to deeper depths enhancing preservation and hence an increased

¹ Broecker, W. S., and T.-H. Peng (1987). The role of CaCO₃ in the glacial to interglacial atmospheric CO₂ change. *Global Biogeochemical Cycles* 1, 15–29.

burial of calcium carbonate. Given the overall stoichiometry shown in Figure 15.1, the burial of biogenic calcium carbonate leads to the production of CO_2 . This added CO_2 would eventually degas into the atmosphere, explaining the increase in P_{CO_2} , which occurred during the transition from glacial to interglacial conditions.

The rate of calcium carbonate burial (and CO_2 production) would have continued to increase until the removal rate of CO_3^{2-} matched its enhanced rate of supply. If the CaCO_3 deposition rate increases such that it exceeds the HCO_3^- and Ca^{2+} supply to the ocean, $[\text{CO}_3^{2-}]$ will eventually decline until the deep sea becomes undersaturated with respect to calcite. A decline in $[\text{CO}_3^{2-}]$ will cause the CCD to rise, thereby reducing the CaCO_3 deposition rate until a balance is reached with the HCO_3^- and Ca^{2+} supply to the ocean. This keeps the Ca^{2+} , alkalinity, and DIC concentrations within a narrow range dictated by their supply rates. Thus, the degree to which carbonate compensation can provide regulatory control is dependent on a fairly stable rate of supply of HCO_3^- and Ca^{2+} to the ocean via rivers and hydrothermal input.

Various possibilities have been suggested to explain why nutrient input to the ocean would decline at the end of an Ice Age. In one scenario, warming during the glacial to interglacial transition raises sea level and thereby reduces terrestrial weathering. This all begs the question as to what caused the warming that ended the last Ice Age. Likely causes are changes in insolation caused by periodic shifts in Earth's orientation and distance relative to the Sun. These are called *Milankovitch cycles*.

Other scenarios have been proposed, independent of nutrient changes, to explain why P_{CO_2} rises at the end of glacial times as Earth enters an interglacial period. For example, warming at the end of the last glaciation led to increased growth of boreal forests. The decline in atmospheric P_{CO_2} coincident with warming water temperatures would have driven CO_2 out of the ocean, thereby causing $[\text{CO}_3^{2-}]$ to rise at the expense of $[\text{HCO}_3^-]$ as follows:



As with the prior scenario, the increase in $[\text{CO}_3^{2-}]$ would cause the CCD to drop to deeper depths. With more of the seafloor lying above the CCD, the burial rate of CaCO_3 would increase. As CaCO_3 is deposited, the extracted CO_3^{2-} must be replaced by driving the equilibrium in Eq. W15.5 to the right, resulting in a decrease in HCO_3^- and an increase in P_{CO_2} . The CO_2 thus generated would eventually degas into the atmosphere, replacing what had been removed via uptake by the new boreal forests.

15.6.2 Carbonate Compensation: Interglacial to Glacial Transitions

In a last example, we explore how carbonate compensation could work during a transition from interglacial to glacial times. In this scenario, climate change leads to diminished terrestrial vegetation, thereby increasing soil erosion and the aeolian

dust flux of iron. This provides an increased supply of iron, the micronutrient that limits diatom growth. Iron fertilization enables the diatoms to outcompete the coccolithophorids causing a drop in biogenic calcite production. As per Eq. 15.1, a drop in calcite production lowers the marine production of CO_2 . Because of air-sea exchange, a diminished oceanic reservoir of CO_2 leads to a decrease in atmospheric P_{CO_2} . This lowers global temperatures, thereby intensifying the transition into a glacial climate.

The ability of the ocean to draw down atmospheric P_{CO_2} is enhanced by reaction with CO_3^{2-} whose availability is increased as a result of the reduction in coccolithophorid growth. Eventually reaction with CO_2 as per Eq. 15.21 will drive $[\text{CO}_3^{2-}]$ below saturation levels leading to the dissolution of calcium carbonate. This resupplies CO_3^{2-} , enabling further uptake of CO_2 . A further enhancement of CO_2 uptake by the oceans would be provided by the higher solubility of CO_2 in seawater at lower temperatures.

15.6.3 Carbonate Compensation: Key Regulatory Factors

Although the carbonate compensation mechanism operates over time scales of 5 to 10 ky, it is linked to the much slower deep carbon cycle because the latter controls weathering rates and, hence, the supply of bicarbonate in river water. As is discussed in Chapter 21, the rate of this bicarbonate supply is dependent on the weathering rates of silicate rocks, which is, in turn, influenced by P_{CO_2} content. The feedbacks associated with the deep carbon cycle operate over time scales on the order of millions of years. The oceanic carbonate compensation feedbacks occur over much shorter times scales because only small shifts in P_{CO_2} are required to have significant impacts on the relatively small reservoir of oceanic CO_3^{2-} .

The shifts in the carbonate reservoir responsible for the compensating effects are the ones that occur solely in the deep sea. In contrast, surface seawater remains super-saturated. This is crucial because the most important component of the carbonate compensation mechanism is the production of biogenic PIC by pelagic plankton in the surface waters. The settling of this PIC into the deep waters provides the means by which the CCD can adjust over time in response to changing P_{CO_2} , climate, nutrient, and bicarbonate supply. This adjustment mechanism is also influenced by the ratio of POC to CaCO_3 in sedimenting particles. Shifts in this ratio are likely to arise from changes in plankton speciation. The carbonate compensation mechanism also responds to changes in deep-water circulation and diapycnal mixing as both of these processes control the rate and degree to which the chemical adjustments in the deep sea are transmitted to the surface waters and thereby to the atmosphere.

15.6.4 Paleoceanographic Records of Change in the Inorganic Carbon Pump

The power of marine calcifiers is hard to overestimate. As noted earlier, the most prolific calcifying phytoplankton are the coccoliths, which first came to prominence about

200 to 250 mybp. Their great ecological success is recorded by the massive coccolith chalks deposited in the late Cretaceous (65 to 99 mybp). These are coincident with a significant decline in calcium ion concentrations in seawater and an increase in pH. This makes it particularly worrisome that anthropogenic increases in CO₂ are causing a global decline in the pH of seawater, 0.1 unit to date, with seawater becoming increasingly less saturated with respect to biogenic calcite and aragonite. This means that calcifiers must expend more energy to deposit their calcareous hard parts. Evidence already exists for changes in plankton viability and speciation as a consequence of this increased stress. Without pelagic calcifiers, we lose the carbonate compensation regulation in the crustal-ocean-atmosphere factory.

Given the importance of carbonate compensation in regulating atmospheric CO₂ and, hence, global climate, much research emphasis is currently directed toward understanding the marine carbonate cycle and its linkages to the biogeochemical cycling of nitrogen, phosphorus, and iron and to global oceanic circulation (see Chapter 25.4). Particular emphasis has been directed toward interpreting the paleoceanographic record provided by downcore variations in sedimentary calcium carbonate content. Corroborating evidence for past changes in P_{CO₂}, climate, and weathering has been obtained from other independent sources, such as polar ice cores and tree rings. Efforts are now underway to develop proxies for paleocarbonate ion concentrations, pH, and the degree of calcite saturation. Promising options include using the Zn-to-Ca ratio in benthic forams, the boron isotopic composition of corals, and indices of foram dissolution based on shell weight and fragmentation.