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The role of the global carbonate cycle in the regulation and evolution of the Earth system

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Abstract

We review one of the most ancient of all the global biogeochemical cycles and one which reflects the profound geochemical and biological changes that have occurred as the Earth system has evolved through time—that of calcium carbonate ($CaCO_3$). In particular, we highlight a Mid-Mesozoic Revolution in the nature and location of carbonate deposition in the marine environment, driven by the ecological success of calcareous plankton. This drove the creation of a responsive deep-sea sedimentary sink of $CaCO_3$. The result is that biologically driven carbonate deposition provides a significant buffering of ocean chemistry and of atmospheric CO_2 in the modern system. However, the same calcifying organisms that under-pin the deep-sea carbonate sink are now threatened by the continued atmospheric release of fossil fuel CO_2 and increasing acidity of the surface ocean. We are not yet in a position to predict what the impact on $CaCO_3$ production will be, or how the uptake of fossil fuel CO_2 by the ocean will be affected. This uncertainty in the future trajectory of atmospheric CO_2 that comes from incomplete understanding of the marine carbonate cycle is cause for concern.

Keywords: Earth system; carbon cycle; carbonate; calcifiers; ocean chemistry; CO_2; fossil fuel

1. Introduction

The geochemical or long-term carbon cycle primarily involves the exchange of carbon between the 'surficial' and 'geologic' reservoirs [1]. The former comprise atmosphere, oceans, biosphere, soils, and exchangeable sediments in the marine environment (Fig. 1) while the latter include crustal rocks and deeply buried sediments in addition to the underlying mantle. How carbon is partitioned between the various reservoirs of the surficial system and between surficial and geologic reservoirs is what sets the concentration of CO_2 in the atmosphere. Life, and the cycle of organic carbon, as well as its geological (and subsequent fossil fuel exhumation) is of particular importance in this regard. The cycle of

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Box 1
Carbonate chemistry ‘101’ and jargon buster

The mineral *calcium carbonate* ($CaCO_3$) has a crystal lattice motif comprising one calcium ion (Ca^{2+}) ionically bound to one carbonate ion (CO_3^{2-}), configured in different polymorphic forms; e.g., *calcite*, a trigonal structure, or *aragonite*, which is orthorhombic. Precipitation may be described by the following reaction: $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_{2(aq)} + H_2O$. Of the reactants required for this, Ca^{2+} is naturally abundant in sea-water and at one of the highest concentrations of all ionic species in the ocean. *Bicarbonate ions* (HCO_3^-) are also ubiquitous in sea-water and are formed through the dissolution of CO_2 gas. Under typical marine conditions, carbon dioxide will largely hydrate to form a proton (H^+) and a bicarbonate ion (HCO_3); $H_2O + CO_{2(aq)} \rightarrow H^+ + HCO_3^-$ (see Fig. 3), while true *carbonic acid* (H_2CO_3) is only present in very small concentrations. A fraction of HCO_3^- dissociates to form a *carbonate ion* (CO_3^{2-}); $HCO_3^- \rightarrow H^+ + CO_3^{2-}$. The sum total; $CO_{2(aq)}$ ($+H_2CO_3$)$+HCO_3^- + CO_3^{2-}$ is collectively termed *dissolved inorganic carbon* (‘DIC’).

The climatic importance of the $CaCO_3$ precipitation reaction arises because although the sum total of dissolved carbon species (DIC) is reduced, the remaining carbon is re-partitioned in favor of $CO_{2(aq)}$, resulting in a higher *partial pressure* of CO_2 (pCO_2) in the surface ocean. (Another way of thinking about this is in terms of removing CO_3^{2-} and shifting the aqueous carbonate equilibrium reaction $CO_{2(aq)} + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^-$ to the left to compensate.) The counter-intuitive and often confusing consequence of all this is that the precipitation of carbonate carbon drives an *increase* in ocean pCO_2, and with it, an increase in atmospheric CO_2 concentration. Conversely, dissolution of $CaCO_3$ drives a pCO_2 (and atmospheric CO_2) *decrease*.

Whether $CaCO_3$ precipitates or dissolves depends on the relative stability of its crystal structure. This can be directly related to the ambient concentrations (strictly, activities) of Ca^{2+} and CO_3^{2-} by the *saturation state* (also known as the *solubility ratio*) Ω of the solution, defined; $\Omega = [Ca^{2+}] \times [CO_3^{2-}]/K_{sp}$, where K_{sp} is a solubility constant [44]. The precipitation of calcium carbonate from sea-water is thermodynamically favorable when Ω is greater than unity and occurs at a rate taking the form of a proportionality with $(\Omega - 1)^n$ [100], where n is a measure of how strongly the precipitation rate responds to a change in CO_3^{2-}. Conversely, $CaCO_3$ will tend to dissolve at $\Omega < 1.0$, and at a rate proportional to $(1 - \Omega)^n$ [101].

As well as the concentrations of Ca^{2+} and CO_3^{2-}, depth in the ocean is also important because K_{sp} scales with increasing pressure. Since K_{sp} and Ω are inversely related, the greater the depth in the ocean the more likely the ambient environment is to be under-saturated (i.e., $\Omega < 1.0$). The depth at which $\Omega = 1.0$ occurs is termed the equilibrium *calcite saturation horizon* (CSH). (Similar terminology can be applied to the aragonite polymorph.) Although calcite becomes thermodynamically unstable just below this, dissolution proceeds only extremely slowly. The (greater) depth at which dissolution impacts become noticeable is termed the *calcite lysocline* [102]. In practice this is taken as the inflection point in the trend of sedimentary $CaCO_3$ content vs. water depth. For want of a more robust definition, a *chemical lysocline* is sometimes defined at $\Omega = 0.8$, a value which marks a distinct increase in dissolution rate [6]. Deeper still, and dissolution becomes sufficiently rapid for the dissolution flux back to the ocean to exactly balance the rain flux of calcite to the sediments. This is known as the *calcite* (or *carbonate*) *compensation depth* (CCD). Because in the real World the boundary in depth between sediments that have carbonate present and those in which it is completely absent is gradual rather than sharp, the CCD is operationally defined, and variously taken as the depth at which the $CaCO_3$ content is reduced to 2 or 10 wt.%.