

Not a source of atmospheric CO₂...

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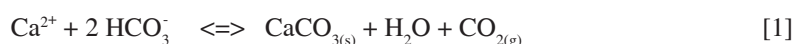
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Many authors refer to the precipitation of calcium carbonate from sea water expressed by equation [1], either by purely chemical mechanisms (e.g., an increase in sea surface temperature [SST]) or mediated by organisms such as coccolithophores (biomineralization) as a source of CO_{2(g)} degassing back to the atmosphere (e.g., Hutchins, 2011).



However, there are four reasons why the precipitation of calcium carbonate from seawater does not contribute to atmospheric CO_{2(g)}:

Reason #1 – The overall cycle. Equation [1] does not take into consideration the entire geochemical process, starting with the weathering (hydrolysis in acidic conditions) of crustal rocks rich in calcium silicates, such as a metamorphic rock rich in the inosilicate Wollastonite (CaSiO₃) or a magmatic mafic rock with plagioclase anorthite (CaAl₂Si₂O₈). In this last case, the hydrolysis of the feldspar occurs according to equation [2].



The main supplier of H⁺ is the CO_{2(g)}, according to equations [3] and [4]. To maintain the bivalent calcium in solution, two molecules of CO_{2(g)} are needed to produce the two negative bicarbonate ions on the left side of equation [1] promoting acidic conditions, i.e., with two protons (H⁺) in excess.



Thus, the overall balance of this mechanism ([3] + [4] + [2] + [1]) indicates that this mechanism is a sink and not a source of CO_{2(g)}. On the other hand, if instead of siliceous magmatic or metamorphic rocks, one considers the weathering (karstification) of sedimentary Ca-rich rocks such as limestone or marble, the overall process is neutral (neither a sink nor a source) for CO_{2(g)} because in this case the solubilization of the calcium only requires one molecule of carbon dioxide (equation [1] from right to left), which is “released” by the precipitation of calcium carbonate (equation [1] from left to right). Many may argue that these geological processes occur at much longer time scales, but we will present a study on weathering of monuments in Lisbon that demonstrates that this is not the case.

Reason #2 – There is no addition of [CO₂]. Equation [1], as in any other chemical balance equation, indicates that both sides are equivalent in terms of mass and so, the molecule CO₂ that appears on the right side is already in the medium, i.e., there is no addition of dissolved inorganic carbon (DIC) to the system due to precipitation of CaCO₃ itself.

Reason #3 – Part is used to produce sugars. Significant amounts of CO₂ are absorbed by coccolithophores and other photosynthetic organisms to produce carbohydrates and other forms of organic carbon. While some of this organic carbon may be remineralized in the water column or due to resuspension (Smeaton & Austin, 2022), for example, an estimated 266 Gt of organic carbon is incorporated only within the top 1 meter of sediment of the continental shelves

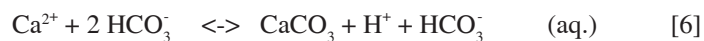
worldwide (Atwood et al., 2020).

Reason #4 – The pH factor. When the alkaline ion Ca^{2+} is incorporated into the seawater solution from river discharges, it increases the ocean's alkalinity, which in turn promotes the dissolved inorganic carbon (DIC) chemical species on the right side of equation [4], releasing H^+ and thus diminishing the ocean's pH.

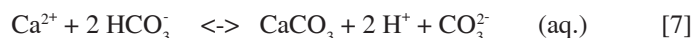


As with most calcifying organisms, coccolithophores preferentially uptake DIC in the form of HCO_3^- mainly because it is the dominant chemical species in current pH oceanic conditions (Glotter et al., 2014). In coccolithophores, the buildup of protons from equation [5] led to the appearance of mechanisms designed to eliminate H^+ in excess while promoting the uptake of the bivalent ion calcium via solute carrier 4 (SLC4) family, a $\text{Ca}^{2+}/\text{H}^+$ exchanger of the CAX family of exchangers and a vacuolar H^+ -ATPase (Mackinder et al., 2011; Brownlee et al., 2021).

Thus, for sea water with pH around 8, equation [1] should be rewritten as:



As well as, in lower concentrations:



We will present results from modeling the forced precipitation of CaCO_3 due to the (bio)mineralization of calcite as coccoliths from seawater at a pH of around 8, showing that the remaining DIC always tends to stay in solution according to equations [6] and [7] (Parkhurst & Appelo, 1999). Therefore, the precipitation of CaCO_3 does not serve as a source of CO_2 as a gas for the sea water and much less for the atmosphere.

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