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What is actually driving $CaCO_3$ dissolution in the ocean?

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The difference between glacial and interglacial periods reaching about 100 ppm for atmospheric carbon dioxide (CO_2) during the last 400.000 years remains one of the major unsolved question in climate research. One potential CO_2 sink is represented by the ocean, where it is buffered by $CaCO_3$ from the sediments.

In biogeochemical models $CaCO_3$ dissolution is usually calculated as $R = k * S^n$, where k is the dissolution rate constant transforming S, the degree of undersaturation of seawater with respect to $CaCO_3$, into a time-dependent rate R, and n is the reaction rate order. Generally, there are two definitions for the description of the saturation state of seawater with respect to $CaCO_3$:

(1) $\Delta[CO_3^{2-}]$, which reflects the difference between the in-situ carbonate ion concentration $[CO_3^{2-}]$ and the saturation concentration $[CO_3^{2-}]_{sat}$, and

(2) Ω, which can be approximated by the ratio of in-situ $[CO_3^{2-}]$ over $[CO_3^{2-}]_{sat}$,

where $[CO_3^{2-}]_{sat}$, the saturation concentration, is a function of temperature, salinity and pressure.

In contrast to $\Delta[CO_3^{2-}]$, Ω exhibits a vertical gradient in the sensitivity to changes in the $[CO_3^{2-}]$ concentration. This becomes clear when considering that a unity change in $[CO_3^{2-}]$ always equals the amount of change in $\Delta[CO_3^{2-}]$ (d$\Delta[CO_3^{2-}]$ / d$[CO_3^{2-}]$ = 1), whereas for Ω the change depends on the background $[CO_3^{2-}]_{sat}$ level (dΩ / d$[CO_3^{2-}]$ = 1 / $[CO_3^{2-}]_{sat}$). As a result of the increasing solubility of $CaCO_3$ ($[CO_3^{2-}]_{sat}$) with pressure the sensitivity of Ω to $[CO_3^{2-}]$ decreases over depth in the water column. When computing a time-dependent $CaCO_3$ dissolution rate by using the equation as described above, this has the counterintuitive effect that although solubility ($[CO_3^{2-}]_{sat}$) is vertically increasing the dissolution reaction in response to a unity $[CO_3^{2-}]$ change would be slower at greater depth. For a reaction rate order of $n = 1$ dissolution at depth is delayed by a factor of three (Archer et al., 1989), however, for $n = 4.5$ as reported by Keir (1980), this factor may rise up to 100.

Consequently, the two commonly used formulations to express the degree of undersaturation of seawater with respect to $CaCO_3$ are not equally applicable for the calculation of $CaCO_3$ dissolution in the ocean across pressure gradients. However, to assess the time scales of sediment buffering the appropriate formulation needs to be known.

In the present study we apply a marine biogeochemical model to test the sensitivity of the marine carbon cycle to the formulation of the saturation state of seawater with respect to $CaCO_3$.