Carbonate compensation dynamics

Bernard P. Boudreau,
Jack J. Middelburg,
Filip J. R. Meysman

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[1] Carbonate saturation (z_sat) and compensation (z_cc) depths change with deep-ocean acidification and basification. We present simple, explicit, mechanistic formulas for the positions of these two critical depths. In particular z_cc is expressed as a function of the mean dissolved carbonate ion concentration of the deep ocean, [CO_3]^2-, the supply of dissociable CaCO_3, F_c, and the dissolution rate constant at the sediment-water interface, k_w, which we show to be essentially mass-transfer controlled. Calculations reveal that z_sat and z_cc are today some ~0.9 km apart and will rise and separate by as much as 1.7 km with acidification; conversely, if [CO_3]^2- increases, z_sat and z_cc will deepen, but their separation will asymptote to ~0.7 km. Citation: Boudreau, B. P., J. J. Middelburg, and F. J. R. Meysman (2010), Carbonate compensation dynamics, Geophys. Res. Lett., 37, L03603, doi:10.1029/2009GL041847.

1. Introduction

[2] Carbonate compensation refers to self-induced adjustments in the deep-sea carbonic acid system via interaction with sedimentary carbonate, also termed the oceanic homeostat [Archer, 1996; Sarmiento and Gruber, 2006]. Three dynamic horizons in the ocean are crucial to compensation [Zeebe and Westbroek, 2003], i.e., the saturation horizon, the compensation depth, and the snow line, all defined later. The position and time evolution of these horizons is needed to predict the fate of CO_2, both natural and anthropogenic, in the oceans and to interpret the geological record in oceanic sediments [Broecker, 2009]. Forecast/hindcast of these positions has suffered from unclear or multiple meanings of these horizons; this paper provides clear definitions and simple formulas for these horizons for use in predictive models and for paleoceanographic studies.

2. Definitions and Formulas

[3] The calcite saturation depth, z_sat, occurs where the oceans first become undersaturated with respect to this mineral. (Aragonite is ignored, henceforth, as a minor complication.) z_cc is depth-dependent because the solubility of calcite increases with pressure and decreases with temperature. A simplified depth/pressure-dependent fit (Figure 1)

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of the solubility data for calcite from Mucci [1983], with pressure corrections from Millero [1995], produces the following formula for the carbonate ion concentration at saturation, C_sat,

\[ C_{sat} = \frac{K^0_{sp}}{K^0_{Ca}} \exp\left(\frac{p(z)}{p_c}\right) \] (1)

where p(z) is the gauge pressure (atm) at depth z (km), [Ca] is the dissolved calcium (Ca^{2+}) concentration, taken as 0.010828 M (moles dm^-3), K^0_{sp} = 4.35 \times 10^{-7} M^3 is the average solubility product of calcite at the ocean surface, and p_c = 511 atm, which is a characteristics pressure. If the deep-ocean carbonate ion concentration, [CO_3]^2-, is assumed constant below the pycnocline, as currently occurs in the oceans, then equation (1) can be inverted explicitly for z_sat, i.e.,

\[ z_{sat} = \frac{p_c}{\rho \rho} \ln \left(\frac{[Ca][CO_3]^2-}{K_{sp}^0}\right) \] (2)

where \( \rho \) is the mean seawater density and g is the acceleration due to gravity (\( \rho g \approx 100 \text{ atm/km} \)). In past models, z_sat has been calculated implicitly [e.g., Sundquist, 1990; Merico et al., 2008; Tyrrell, 2008]. Calculation of z_sat is also possible if [CO_3]^2- is a function of depth, but that dependence must be known and a more complex equation will result; furthermore, while our emphasis here is on a mean ocean, one could also generate a form of equation (2) for a specific basin by employing the local temperature profile and an appropriate [CO_3]^2- depth-function.

[4] The carbonate compensation depth is defined in two ways. The geochemical compensation depth, z_cc, is the depth where dissolution at the sediment-water interface exactly balances the rain of CaCO_3 from above, such that none accumulates [Schink and Guinasso, 1977; Takahashi and Broecker, 1977; Tyrrell, 2008]. The geological compensation depth, z_cc^geo, occurs where the CaCO_3 content of sediments drops to ~10% of solids, due again to dissolution [Kennett, 1982; Morse and Mackenzie, 1990; Broecker, 2009].

[5] Previously z_cc has been computed laboriously by modelling the calcite content of sediments with ocean depth using diagenetic models [e.g., Schink and Guinasso, 1977; Takahashi and Broecker, 1977; Sundquist, 1990; Archer and Maier-Reimer, 1994; Ridgwell and Hargreaves, 2007]. These models predict that the zone of dissolution in the sediment is on-the-order-of a few millimeters at most. This extreme attenuation indicates that dissolution could be well approximated as a reaction at the sediment-water interface alone. Consequently, to write a formula for z_cc, one balances input and dissolution at this interface. As a first step, if F_c is the net amount of CaCO_3 that falls into the deep sea and reaches the bottom, i.e., the CaCO_3 input below ~2000 m [Berelson et al., 2007], and A_D is the area of the deep ocean...
Figure 1. Plot of the solubility product, $K_{sp}$, of calcite as a function of pressure, adjusted to an idealized, mean ocean temperature profile. The solid curve is an exponential fit to the relationship found by [Mucci, 1983] and [Miller, 1995], given as the dotted line. The exponential provides an excellent fit, but there are small over-predictions below 100 atm and above 550 atm.

below this same depth, then the average input per unit area of seafloor (the rain) is simply the quotient $F_r/A_D$.

[6] Next, we need to specify the calcite dissolution rate, which has been modeled as a high-order function of the undersaturation [e.g., Keir, 1980]. [Hales and Emerson, 1997] have argued instead that the order is linear, if the correct solubility is employed. We also employ linear kinetics, but for a different reason.

[7] Most experimental studies of CaCO$_3$ dissolution, including [Keir, 1980], deal with dissolution of suspended calcite, which is not directly applicable to the seafloor because of vastly different mass-transfer characteristics. [Keir, 1983] dissolved beds of natural carbonate-bearing sediments in a reaction chamber with a rotating mixer, and he interpreted his data as consistent with high order of reaction. However, plots of the product $C_{sat}$ ($1 - \Omega$) $b$, where $\Omega = [\text{CO}_3]_D/C_{sat}$ and $b = \text{fraction of CaCO}_3$ in sediment, versus his rates of CO$_3$ release are decidedly linear (see Figure S1) except for two, which are simply scattered. This observed linearity applies to the seafloor.

[8] The balance of carbonate rain and dissolution at $z_{cc}$ is then given as

$$\frac{F_r}{A_D} - k_c((C_{sat}(z_{cc}) - [\text{CO}_3]_D) = 0$$  (3)

where $k_c$ is the heterogeneous rate constant for dissolution at the sediment-water interface, with units of length per unit time, and $C_{sat}(z_{cc})$ is the CO$_3$ saturation concentration at $z_{cc}$. Equation (1) can be substituted into equation (3) to obtain an explicit equation for $z_{cc}$:

$$z_{cc} = \frac{p_c}{pg} \ln \left( \frac{\frac{F_r}{A_D}}{K_{sp}^0 A_D k_c} \frac{[\text{Ca}][\text{CO}_3]_D}{K_{sp}^0} \right)$$  (4)

This expression shows that $z_{cc}$ is always larger than $z_{sat}$ because the first term within the logarithm is always positive. If $[\text{CO}_3]_D$ is a known function of depth, an expression for $z_{cc}$ can still be obtained, but of a different form. Equations (2) and (4) hold for both steady state and transient conditions.

[9] One consequence of equations (3) and (4) is that there is no “tailing” of the predicted CaCO$_3$ content of sediments with ocean depth [e.g., Broecker, 2009, Figure 6]; the tail results from either a small recalcitrant calcite component or the preserving effect of bioturbation [Schink and Guinasso, 1977]. However, the tail contains far less than 1% of the CaCO$_3$ flux and, as such, can be ignored when considering global, rather than local, carbonate dynamics.

[10] The snow line [Zeebe and Westbroek, 2003], $z_{snow}$ a third critical depth occurs where no solid calcite can be found in the sediment due to dissolution. $z_{cc}$ and $z_{snow}$ are identical at steady state. The position of a transient snow-line depends on the amount of calcite in the sediments and the history of $[\text{CO}_3]_D$. If deep-sea sediments are essentially well mixed with respect to CaCO$_3$ [e.g., Schink and Guinasso, 1977; Takahashi and Broecker, 1977], then $z_{snow}$ is obtained from calcite mass balance for the sediment, which is, at constant calcite rain,

$$b(z_{snow},t)L(z_{snow}) + \left( \frac{F_r}{A_D} - k_c C_{sat}(z_{snow}) \right) \tau \int_0^\tau b(z_{snow},t)C_{sat}(z_{snow})d\tau = 0$$  (5)

where $b(z, \tau)$ is the concentration of dissolvable CaCO$_3$ in the sediment at water depth $z$ after elapsed time $\tau$ (which is a function of water depth), $L(z)$ is the depth in the sediment over which PDC can ultimately be dissolved [Takahashi and Broecker, 1977]. The elapsed time $\tau$ is the time since $z_{cc}$ was at the chosen depth $z$. The product $b(z, \tau)L(z)$ is the standing stock of dissolvable calcite at ocean depth $z$. $L(z)$ is a function of the amount of CaCO$_3$ and clay in sediments [see Archer et al., 1998]. Equation (5) is contingent on knowing the chemical history, $[\text{CO}_3]_D(t)$, to resolve the integral. An equation similar to equation (5) can be written to calculate the geological compensation depth, $z_{cc}^{sed}$, again given an appropriate CO$_3$ history.

[11] Finally, another common term, the lysocline, was originally the subjective depth where dissolution of CaCO$_3$ became apparent in the sediment [Kennett, 1982]. Archer [1991] attempted to quantify this definition by stating that the lysocline occurs where the CaCO$_3$ content drops below 80%. Morse and Berner [1972] argued from dissolution experiments that the lysocline instead reflected a change in the mechanism of dissolution at some critical degree of undersaturation, but Figure S1 suggests no such change in mechanism. Broecker and Peng [1982] and Burdige [2006] believe that the lysocline is equal to $z_{sat}$, in which case equation (2) would be its predictor. However, it is possible, even likely, that the lysocline reflects (in part) the depth at which metabolically-driven dissolution of CaCO$_3$ within sediments [Emerson and Bender, 1981; Jahnke et al., 1994] produces visually obvious effects on tests. Metabolically-driven dissolution occurs when CO$_2$ from oxic organic matter decay causes the local state of saturation of pore-waters within sediments to drop below the solubility of CaCO$_3$. Auxiliary materials are available in the HTML. doi:10.1029/2009GL041847.
calcite. This process is largely independent of the saturation state of the overlying waters, and it, in no way, alters the formulas and dynamic depths discussed above.

3. Computation of Saturation and Compensation Depths

[12] We now examine $z_{cc}$ and $z_{sat}$ as functions of the controlling parameters, i.e., $[CO_3]_D$, $k_c$, and $F_c$. The current/pre-industrial $[CO_3]_D$ can be taken as constant below ~1500 m [Key et al., 2004] at a value of 0.09 mM [Broecker, 2003; B. P. Boudreau et al., Ongoing transients in carbonate compensation, submitted to Global Biogeochemical Cycles, 2009]. The total rain of calcite, $F_c$, is between 20–60 × 10^5 Gmol y$^{-1}$ [Archer, 1996; Sarmiento and Gruber, 2006; Berelson et al., 2007], and we will examine solutions within that range.

[13] The unknown parameter in equation (4) is $k_c$, and Broecker [2009] has recently bemoaned this uncertainty. A $k_c$ from on Keir [1983] is inappropriate because (1) the dependence of $k_c$ on circulation velocity is unknown for that experiment, (2) a cylindrical reactor with an impeller system does not simulate the seafloor because of secondary flows [Broström and Nilsson, 1999], and (3) Keir’s experiment simulates transient dissolution of a bed of pre-existing CaCO$_3$. In a separate contribution (i.e., Boudreau et al., submitted manuscript, 2009), we have coupled our equations to a box model of the oceans and extracted a value for $k_c$ of 700 cm y$^{-1}$ for steady state (pre-industrial) conditions at the seafloor.

[14] To provide context for this $k_c$ value, dissolution cannot occur faster than the limit placed by transport across the benthic boundary layer. A theoretical value of the mass-transfer coefficient is given by $k_T = 0.0671 u_*, Sc^{-1/3}$ [Boudreau, 2001], where $u_*$ is the mean shear velocity at the ocean bottom and $Sc$ is the Schmidt number, about 3900 for carbonate/calcium ions. Wimbush [1976] states that $u_*$ has a mean value of about 0.1 cm s$^{-1}$, which gives $k_T = 965$ cm y$^{-1}$. Consequently, $k_c$ from fitting the oceanic carbonate system and $k_T$ differ only by 38%, and this concurrence suggests that CaCO$_3$ dissolution at the seafloor is largely controlled by mass transfer, rather than intrinsic

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**Figure 2.** Dependence of $z_{cc}$ and $z_{sat}$ on the values of the parameters $[CO_3]_D$, $k_c$ and $F_c$. (a) The dependence on $[CO_3]_D$ for fixed $F_c$ and $k_c$. The separation distance of $z_{cc}$ and $z_{sat}$ increases with falling $[CO_3]_D$ from about 0.9 km under today’s conditions to about 1.7 km at 0.045 mM; the right hand axis is the ratio of $z_{sat}$ to $z_{cc}$; (b) The dependence of $z_{cc}$ on $k_c$. The line $\Omega = 1$ is the saturation horizon, $z_{sat}$. Results for three values of $F_c$ (10^5 Gmol y$^{-1}$) and the pre-industrial $[CO_3]_D$ [Broecker, 2003] are illustrated. The hatched area covers $k_c$ values that are not physically possible if the mean bottom shear velocity is 0.1 cm s$^{-1}$ [Wimbush, 1976]; this limit can shift if the mean bottom shear velocity is altered. The orange dotted vertical line indicates the value for $k_c$ calculated by Boudreau et al. (submitted manuscript, 2009). (c) The dependence of $z_{cc}$ on $F_c$ for two $k_c$ values (cm y$^{-1}$) and today’s $[CO_3]_D$. 

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kinetics. Schink and Guinasso [1977] and Takahashi and Broecker [1977] have previously advanced a role for mass transfer in controlling benthic CaCO₃ dissolution, but we go further and argue that mass transfer at the interface is the dominant factor.

[15] Figures 2a–2c plot zₕ and zₚ as functions of [CO₃]∕, Fₗ, and kₚ. Clearly, zₕ and zₚ are not at the same depth. With a present-day/pre-industrial [CO₃] of 0.09 mM, Figure 2a indicates a separation of ∼0.9 km. This distance increases rapidly as [CO₃] decreases, potentially reaching ∼1.7 km if [CO₃] is approximately 0.045 mM, which is anticipated within the next 2000 years [Ridgwell and Hargreaves, 2007]. If, however, [CO₃] increases, as in the geological past, the distance between zₕ and zₚ will asymptote to ∼0.68 km, or a ratio of about 0.9. Thus, the assumption of a constant separation when the zₚ is deepening from its present position is correct.

[16] Figure 2b illustrates the dependence of zₚ on kₚ. The position of zₚ is crucially dependent on the value of this parameter, i.e., small drops (bottom-water stagnation) will result in large increases in zₚ. However, if kₚ increases towards the pure mass-transfer value, zₚ will shift to the saturation horizon. Over the range of Fₗ values currently thought to apply in the oceans, Figure 2c shows that zₚ is a linear function of the rain rate, with a modest slope; thus, zₚ changes only in a limited way if the calcite rain remains with that range; that said, it should be realized that these calculations are made with [CO₃] fixed, while in reality zₚ can shallower, rather than deepen with increasing Fₗ because the compensation mechanism lowers [CO₃].

[17] The results in Figure 2 have implications not only to the current acidification of the oceans, but also to the interpretation of the geological record in terms of paleoceanographic conditions. The depths zₕ and zₚ are often equated in modeling and in reconstructions of past excursions of the carbonate compensation horizon [e.g. Merico et al., 2008; Roberts and Tripati, 2009], while our formulas predict that they are at least ∼0.7 km apart. At steady state, obtained on a 10⁷ y time scale [Archer et al., 1998], Zₚ and zₚ should be equal, and this then implies a separation between zₕ and zₚ of between ∼0.7 to ∼2 km (Figure 2), more than the ∼250 m uncertainty in global reconstructions of the zₚ record [Roberts and Tripati, 2009]. Moreover, the difference between zₕ and zₚ is highest during periods of rapidly increasing atmospheric carbon dioxide, such as the Anthropocene, the Paleocene-Eocene Thermal Maximum [Zeebe et al., 2009] and glacial to interglacial transitions, consistent with Minhoven [2007].

During periods of ocean de-acidification, such as the Eocene-Oligocene transition [Merico et al., 2008], zₕ and zₚ deepen and their separation asymptotes.

4. Conclusions

[18] Two horizons important to the mathematical/theoretical description of carbonate dynamics in the oceans, i.e., the saturation horizon, zₕ, and the geochemical carbonate compensation depth, zₚ, can be calculated via equations (2) and (4), respectively. At steady state, zₚ can be considered to be first-order predictor for the operational/data-defined geological compensation depth, zₚ.

[19] The distance between zₕ and zₚ is not fixed, but a function of the deep-water carbonate ion concentration, [CO₃]ᵢ/, the input of calcite, Fₗ, and the dissolution rate constant, kₚ. Acidification causes these horizons to rise and to separate, whereas, a higher carbonate ion concentration causes deepening and the difference between these depths to asymptote to about 0.68 km (or a ratio of 0.9). In transient situations, Zₚ will lag the movement of zₚ, but approach this latter depth as a steady state is established.

[20] Our analysis further indicates that CaCO₃ dissolution at the seafloor is (largely) mass-transfer controlled, based on the dissolution rate constant derived by Boudureau et al. (submitted manuscript, 2009).

References


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B. P. Boudreau, Department of Oceanography, Dalhousie University, Halifax, NS B3H4J1, Canada. (bernie.boudreau@dal.ca)

F. J. R. Meysman, NIOO-KNAW, Centre for Estuarine and Marine Ecology, N-4401 NT Yerseke, Netherlands. (f.meysman@nioo.knaw.nl)

J. J. Middelburg, Geochemistry, Faculty of Geosciences, University of Utrecht, Utrecht, Netherlands. (J.Middelburg@geo.uu.nl)
Rate (mol cm$^{-2}$ yr$^{-1}$)

$C_{sat}$ [1-$\Omega$] [b (mol cm$^{-3}$)]

$R^2 = 0.952$

$R^2 = 0.992$

$R^2 = 0.542$

$R^2 = 0.947$

$R^2 = 0.984$

$R^2 = 0.905$