

## Carbonate compensation dynamics

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[1] Carbonate saturation ( $z_{\text{sat}}$ ) and compensation ( $z_{\text{cc}}$ ) depths change with deep-ocean acidification and basification. We present simple, explicit, mechanistic formulas for the positions of these two critical depths. In particular  $z_{\text{cc}}$  is expressed as a function of the mean dissolved carbonate ion concentration of the deep ocean,  $[\text{CO}_3]_{\text{D}}$ , the supply of dissolvable  $\text{CaCO}_3$ ,  $F_{\text{c}}$ , and the dissolution rate constant at the sediment-water interface,  $k_{\text{c}}$ , which we show to be essentially mass-transfer controlled. Calculations reveal that  $z_{\text{sat}}$  and  $z_{\text{cc}}$  are today some  $\sim 0.9$  km apart and will rise and separate by as much as 1.7 km with acidification; conversely, if  $[\text{CO}_3]_{\text{D}}$  increases,  $z_{\text{sat}}$  and  $z_{\text{cc}}$  will deepen, but their separation will asymptote to  $\sim 0.7$  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  $\text{CO}_2$ , 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,  $z_{\text{sat}}$ , occurs where the oceans first become undersaturated with respect to this mineral. (Aragonite is ignored, henceforth, as a minor complication.)  $z_{\text{cc}}$  is depth-dependent because the solubility of calcite increases with pressure and decreases with temperature. A simplified depth/pressure-dependent fit (Figure 1)

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,  $C_{\text{sat}}$ ,

$$C_{\text{sat}} = \frac{K_{\text{sp}}^0}{[\text{Ca}]} \exp\left(\frac{p(z)}{p_{\text{c}}}\right) \quad (1)$$

where  $p(z)$  is the gauge pressure (atm) at depth  $z$  (km),  $[\text{Ca}]$  is the dissolved calcium ( $\text{Ca}^{2+}$ ) concentration, taken as  $0.010282$  M (moles  $\text{dm}^{-3}$ ),  $K_{\text{sp}}^0 = 4.35 \times 10^{-7} \text{ M}^2$  is the average solubility product of calcite at the ocean surface, and  $p_{\text{c}} = 511$  atm, which is a characteristics pressure. If the deep-ocean carbonate ion concentration,  $[\text{CO}_3]_{\text{D}}$ , is assumed constant below the pycnocline, as currently occurs in the oceans, then equation (1) can be inverted explicitly for  $z_{\text{sat}}$ , i.e.,

$$z_{\text{sat}} = \frac{p_{\text{c}}}{\rho g} \ln\left(\frac{[\text{Ca}][\text{CO}_3]_{\text{D}}}{K_{\text{sp}}^0}\right) \quad (2)$$

where  $\rho$  is the mean seawater density and  $g$  is the acceleration due to gravity ( $\rho g \simeq 100$  atm/km). In past models,  $z_{\text{sat}}$  has been calculated implicitly [e.g., Sundquist, 1990; Merico *et al.*, 2008; Tyrrell, 2008]. Calculation of  $z_{\text{sat}}$  is also possible if  $[\text{CO}_3]_{\text{D}}$  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  $[\text{CO}_3]_{\text{D}}$  depth-function.

[4] The carbonate compensation depth is defined in two ways. The geochemical compensation depth,  $z_{\text{cc}}$ , is the depth where dissolution at the sediment-water interface exactly balances the rain of  $\text{CaCO}_3$  from above, such that none accumulates [Schink and Guinasso, 1977; Takahashi and Broecker, 1977; Tyrrell, 2008]. The geological compensation depth,  $z_{\text{cc}}^{\text{sed}}$ , occurs where the  $\text{CaCO}_3$  content of sediments drops to  $\sim 10\%$  of solids, due again to dissolution [Kennett, 1982; Morse and Mackenzie, 1990; Broecker, 2009].

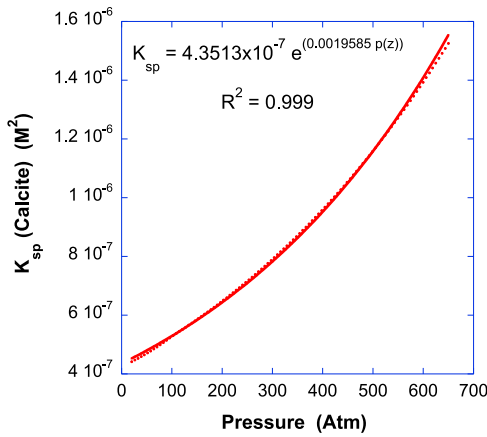
[5] Previously  $z_{\text{cc}}$  has been computed laboriously by modelling the calcite content of sediments with ocean depth using diagenetic models [e.g., Schink and Guinasso, 1977; Takahashi and Broecker, 1977; Sundquist, 1990; Archer and Maier-Reimer, 1994; Ridgwell and Hargreaves, 2007]. These models 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  $z_{\text{cc}}$ , one balances input and dissolution at this interface. As a first step, if  $F_{\text{c}}$  is the net amount of  $\text{CaCO}_3$  that falls into the deep sea and reaches the bottom, i.e., the  $\text{CaCO}_3$  input below  $\sim 2000$  m [Berelson *et al.*, 2007], and  $A_{\text{D}}$  is the area of the deep ocean

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**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 Millero [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  $F_c/A_D$ .

[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  $\text{CaCO}_3$  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  $b$  = fraction of  $\text{CaCO}_3$  in sediment, versus his rates of  $\text{CO}_3^{2-}$  release are decidedly linear (see Figure S1) except for two, which are simply scattered. This observed linearity applies to the seafloor.<sup>1</sup>

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

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

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  $\text{CO}_3^{2-}$  saturation concentration at  $z_{cc}$ . Equation (1) can be substituted into equation (3) to obtain an explicit equation for  $z_{cc}$ :

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

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  $\text{CaCO}_3$  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  $\text{CaCO}_3$  flux and, as such, can be ignored when considering global, rather than local, carbonate dynamics.

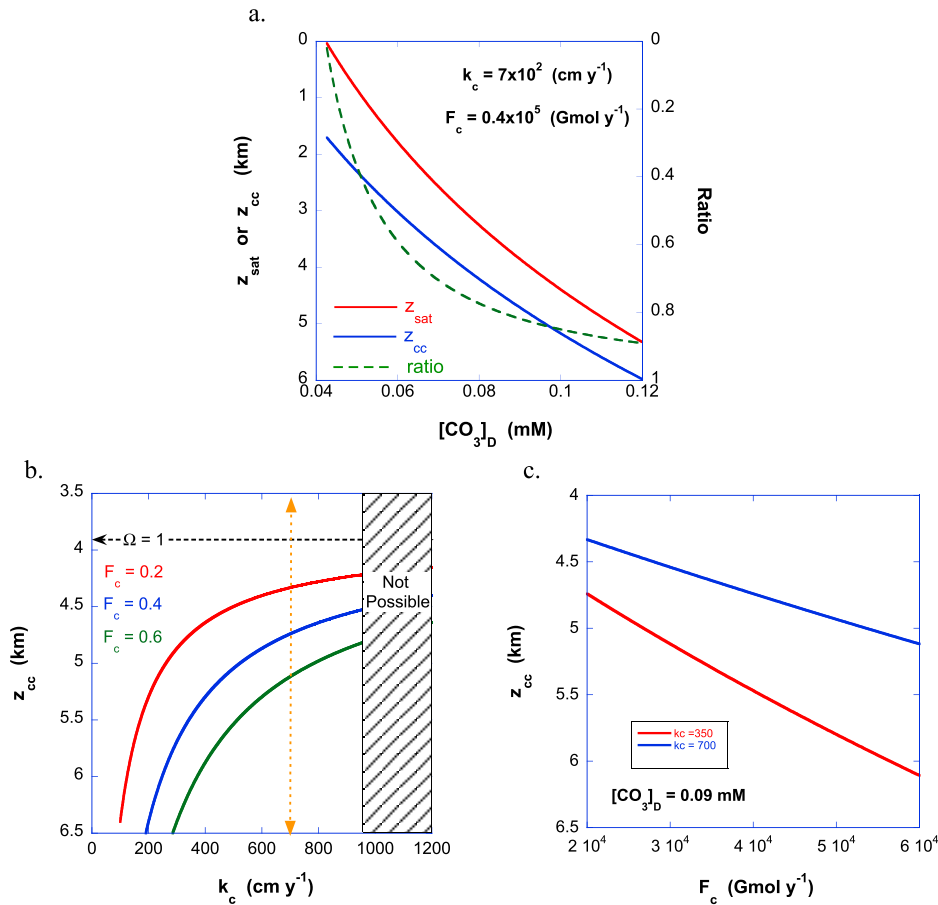
[10] The snow line [Zeebe and Westbroek, 2003],  $z_{snow}$ , a third critical depth occurs where no solid calcite can be found in the sediment due to dissolution.  $z_{cc}$  and  $z_{snow}$  are identical at steady state. The position of a transient snow-line depends on the amount of calcite in the sediments and the history of  $[\text{CO}_3]_D$ . If deep-sea sediments are essentially well mixed with respect to  $\text{CaCO}_3$  [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,

$$b(z_{snow}, 0)L(z_{snow}) + \left( \frac{F_c}{A_D} - k_c C_{sat}(z_{snow}) \right) \tau + k_c \int_0^\tau [\text{CO}_3]_D(t) dt = 0 \quad (5)$$

where  $b(z, \tau)$  is the concentration of dissolvable  $\text{CaCO}_3$  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  $\text{CaCO}_3$  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  $\text{CO}_3^{2-}$  history.

[11] Finally, another common term, the lysocline, was originally the subjective depth where dissolution of  $\text{CaCO}_3$  became apparent in the sediment [Kennett, 1982]. Archer [1991] attempted to quantify this definition by stating that the lysocline occurs where the  $\text{CaCO}_3$  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  $\text{CaCO}_3$  within sediments [Emerson and Bender, 1981; Jahnke et al., 1994] produces visually obvious effects on tests. Metabolically-driven dissolution occurs when  $\text{CO}_2$  from oxic organic matter decay causes the local state of saturation of pore-waters within sediments to drop below the solubility of

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2009GL041847.



**Figure 2.** Dependence of  $z_{\text{cc}}$  and  $z_{\text{sat}}$  on the values of the parameters  $[\text{CO}_3]_{\text{D}}$ ,  $k_c$  and  $F_c$ . (a) The dependence on  $[\text{CO}_3]_{\text{D}}$  for fixed  $F_c$  and  $k_c$ . The separation distance of  $z_{\text{cc}}$  and  $z_{\text{sat}}$  increases with falling  $[\text{CO}_3]_{\text{D}}$  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  $z_{\text{sat}}$  to  $z_{\text{cc}}$ . (b) The dependence of  $z_{\text{cc}}$  on  $k_c$ . The line  $\Omega = 1$  is the saturation horizon,  $z_{\text{sat}}$ . Results for three values of  $F_c$  ( $10^5 \text{ Gmol y}^{-1}$ ) and the pre-industrial  $[\text{CO}_3]_{\text{D}}$  [Broecker, 2003] are illustrated. The hatched area covers  $k_c$  values that are not physically possible if the mean bottom shear velocity is  $0.1 \text{ cm s}^{-1}$  [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  $z_{\text{cc}}$  on  $F_c$  for two  $k_c$  values ( $\text{cm y}^{-1}$ ) and today's  $[\text{CO}_3]_{\text{D}}$ .

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  $z_{\text{cc}}$  and  $z_{\text{sat}}$  as functions of the controlling parameters, i.e.,  $[\text{CO}_3]_{\text{D}}$ ,  $F_c$  and  $k_c$ . The current/pre-industrial  $[\text{CO}_3]_{\text{D}}$  can be taken as constant below  $\sim 1500 \text{ m}$  [Key et al., 2004] at a value of  $0.09 \text{ mM}$  [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  $20\text{--}60 \times 10^3 \text{ Gmol y}^{-1}$  [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  $\text{CaCO}_3$ . 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  $700 \text{ cm y}^{-1}$  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  $k_T = 0.0671 u_* \text{ Sc}^{-2/3}$  [Boudreau, 2001], where  $u_*$  is the mean shear velocity at the ocean bottom and  $\text{Sc}$  is the Schmidt number, about 3900 for carbonate/calcium ions. Wimbush [1976] states that  $u_*$  has a mean value of about  $0.1 \text{ cm s}^{-1}$ , which gives  $k_T = 965 \text{ cm y}^{-1}$ . Consequently,  $k_c$  from fitting the oceanic carbonate system and  $k_T$  differ only by 38%, and this concurrence suggests that  $\text{CaCO}_3$  dissolution at the seafloor is largely controlled by mass transfer, rather than intrinsic

kinetics. Schink and Guinasso [1977] and Takahashi and Broecker [1977] have previously advanced a role for mass transfer in controlling benthic  $\text{CaCO}_3$  dissolution, but we go further and argue that mass transfer at the interface is the dominant factor.

[15] Figures 2a–2c plot  $z_{\text{sat}}$  and  $z_{\text{cc}}$  as functions of  $[\text{CO}_3]_{\text{D}}$ ,  $F_c$  and  $k_c$ . Clearly,  $z_{\text{sat}}$  and  $z_{\text{cc}}$  are not at the same depth. With a present-day/pre-industrial  $[\text{CO}_3]_{\text{D}}$  of 0.09 mM, Figure 2a indicates a separation of  $\sim 0.9$  km. This distance increases rapidly as  $[\text{CO}_3]_{\text{D}}$  decreases, potentially reaching  $\sim 1.7$  km if  $[\text{CO}_3]_{\text{D}}$  is approximately 0.045 mM, which is anticipated within the next 2000 years [Ridgwell and Hargreaves, 2007]. If, however,  $[\text{CO}_3]_{\text{D}}$  increases, as in the geological past, the distance between  $z_{\text{sat}}$  and  $z_{\text{cc}}$  will asymptote to  $\sim 0.68$  km, or a ratio of about 0.9. Thus, the assumption of a constant separation when the  $z_{\text{cc}}$  is deepening from its present position is correct.

[16] Figure 2b illustrates the dependence of  $z_{\text{cc}}$  on  $k_c$ . The position of  $z_{\text{cc}}$  is crucially dependent on the value of this parameter, i.e., small drops (bottom-water stagnation) will result in large increases in  $z_{\text{cc}}$ . However, if  $k_c$  increases towards the pure mass-transfer value,  $z_{\text{cc}}$  will shift to the saturation horizon. Over the range of  $F_c$  values currently thought to apply in the oceans, Figure 2c shows that  $z_{\text{cc}}$  is a linear function of the rain rate, with a modest slope; thus,  $z_{\text{cc}}$  changes only in a limited way if the calcite rain remains within that range; that said, it should be realized that these calculations are made with  $[\text{CO}_3]_{\text{D}}$  fixed, while in reality  $z_{\text{cc}}$  can shallow, rather than deepen with increasing  $F_c$  because the compensation mechanism lowers  $[\text{CO}_3]_{\text{D}}$ .

[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  $z_{\text{sat}}$  and  $z_{\text{cc}}$  are often equated in modeling and in reconstructions of past excursions of the carbonate compensation horizon [e.g. Merico *et al.*, 2008; Roberts and Tripathi, 2009], while our formulas predict that they are at least  $\sim 0.7$  km apart. At steady state, obtained on a  $10^5$  y time scale [Archer *et al.*, 1998],  $z_{\text{cc}}$  and  $z_{\text{cc}}^{\text{sed}}$  should be equal, and this then implies a separation between  $z_{\text{sat}}$  and  $z_{\text{cc}}^{\text{sed}}$  of between  $\sim 0.7$  to  $\sim 2$  km (Figure 2), much greater than the  $\sim 250$  m uncertainty in global reconstructions of the  $z_{\text{cc}}^{\text{sed}}$  record [Roberts and Tripathi, 2009]. Moreover, the difference between  $z_{\text{sat}}$  and  $z_{\text{cc}}$  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 Munhoven [2007]. During periods of ocean de-acidification, such as the Eocene-Oligocene transition [Merico *et al.*, 2008],  $z_{\text{sat}}$  and  $z_{\text{cc}}$  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,  $z_{\text{sat}}$ , and the geochemical carbonate compensation depth,  $z_{\text{cc}}$ , can be calculated via equations (2) and (4), respectively. At steady state,  $z_{\text{cc}}$  can be considered to be first-order predictor for the operational/data-defined geological compensation depth,  $z_{\text{cc}}^{\text{sed}}$ .

[19] The distance between  $z_{\text{sat}}$  and  $z_{\text{cc}}$  is not fixed, but a function of the deep-water carbonate ion concentration,  $[\text{CO}_3]_{\text{D}}$ , the input of calcite,  $F_c$ , and the dissolution rate constant,  $k_c$ . 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,  $z_{\text{cc}}^{\text{sed}}$  will lag the movement of  $z_{\text{cc}}$ , but approach this latter depth as a steady state is established.

[20] Our analysis further indicates that  $\text{CaCO}_3$  dissolution at the seafloor is (largely) mass-transfer controlled, based on the dissolution rate constant derived by Boudreau *et al.* (submitted manuscript, 2009).

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