

The role of calcification in carbonate compensation

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The long-term recovery of the oceans from present and past acidification is possible due to neutralization by the dissolution of biogenic CaCO₃ in bottom sediments, that is, carbonate compensation. However, such chemical compensation is unable to account for all features of past acidification events, such as the enhanced accumulation of CaCO₃ at deeper depths after acidification. This overdeepening of CaCO₃ accumulation led to the idea that an increased supply of alkalinity to the oceans, via amplified weathering of continental rocks, must accompany chemical compensation. Here we discuss an alternative: that changes to calcification, a biological process dependent on environmental conditions, can enhance and modify chemical compensation and account for overdeepening. Using a simplified ocean box model with both constant and variable calcification, we show that even modest drops in calcification can lead to appreciable long-term alkalinity build-up in the oceans and, thus, create overdeepening; we term this latter effect biological compensation. The chemical and biological manifestations of compensation differ in terms of controls, timing and effects, which we illustrate with model results. To better predict oceanic evolution during the Anthropocene and improve the interpretation of the palaeoceanographic record, it is necessary to better understand biological compensation.

The oceans play a major role in the global carbon cycle because they contain ~37,400 Gt (10¹⁵ g) of inorganic carbon, or ~50 times more than is in the atmosphere and over 18 times that in the terrestrial realm¹. This large storage capacity results from the reaction of carbon dioxide with water to form carbonic acid, bicarbonate and carbonate ions. This carbonic acid system buffers seawater against moderate acidity/alkalinity changes by adjusting the distribution of dissolved carbonate species to a new equilibrium configuration, following Le Chatelier's principle, which is a process of homogenous buffering.

In addition, seawater is in contact with solid carbonate minerals in sediments or suspended in the water column. These minerals can also react to changes in the carbonate chemistry by dissolving in undersaturated conditions to generate carbonate species. Reactions between carbonate minerals and seawater are the basis for a heterogeneous form of buffering, known widely as carbonate compensation².

Marine carbonate minerals are overwhelmingly of biological origin² as tests of organisms, such as coccolithophorids, foraminifera and gastropods, in the open ocean, and additionally as corals and mollusks in shelf environments; this Perspective focuses on the pelagic/deep/blue ocean, but we will touch on the shelf. Carbonate minerals are, furthermore, not uniformly distributed in the oceans; they are far more abundant in shallow and surface waters, as living organisms, and even more so in sediments, as biogenic material.

Surface ocean waters are currently supersaturated with respect to biogenic aragonite, high-Mg calcite, and calcite; the latter is by far the most abundant CaCO₃ mineral in oceans and sediments, while aragonite and Mg calcites are common as tests, corals and sediments in shelf environments. Supersaturation must be reduced to undersaturation before carbonate mineral in surface waters can dissolve and help neutralize acidification, that is, via carbonate compensation, which constitutes another major difference with homogeneous buffering. In contrast, CaCO₃-rich pelagic sediments are in contact with deep waters that become progressively undersaturated with increasing depth and age, that is, time since contact with the atmosphere. Consequently, ocean bottom sediments can respond readily to changes in the dissolved carbonate chemistry, after these are

transmitted to the deep ocean. While homogeneous buffering may be faster, it has limited capacity for direct neutralization of added CO₂, whereas heterogeneous buffering, that is, carbonate compensation, while slower, has an immense capacity because of the enormous mass of CaCO₃ in sediments (>6 × 10⁷ Gt)¹.

Biological versus chemical compensation

Compensation is a process internal to the oceans, and the drivers of acidification, such as CO₂ release, or alkalization, such as additional weathering or geoengineering, are not part of compensation itself. We explore two ways to achieve carbonate compensation, and these two mechanisms can and do operate simultaneously.

Chemical carbonate compensation. This process centres on the dissolution or preservation of CaCO₃ at the seafloor (Fig. 1). CaCO₃ saturation in the surface ocean drops with depth because of increasing solubility and, to a lesser extent, decreasing carbonate ion concentration. The latter decrease is due to oxidation of exported organic matter, which releases CO₂ to deep waters, that is, the biological pump, and which reduces the saturation state of these waters. The depth where seawater first becomes undersaturated with respect to a carbonate mineral is known as the saturation depth (Z_{sat}) for that mineral³ (see Box 1). Dissolution rates for that mineral increase systematically thereafter with depth. At the compensation depth (Z_{cc}) for a particular mineral, the rain (flux) of those biogenic CaCO₃ tests to the sediment is matched by the depth-increasing dissolution rate at the seafloor (see Box 1). Meanwhile, the snowline (Z_{snow}) is the depth where, because of dissolution, there is (effectively) no CaCO₃ in the sediment^{3,4}. In a steady state, or in an alkalinizing ocean, Z_{cc} and Z_{snow} coincide; in an acidifying ocean, Z_{snow} lags Z_{cc} changes because previously deposited CaCO₃ must be removed from sediment to restore the equality and that takes time. The mineral content of the sediments diminishes progressively between Z_{sat} and Z_{cc} , a depth range we propose to define as the lysocline (see Box 2). All further discussion will refer to the horizons (Z_{sat} , Z_{cc} and Z_{snow}) for calcite only, as it is overwhelmingly the dominant carbonate mineral produced in the open/pelagic oceans. The horizons for aragonite and high-Mg calcite follow those of calcite

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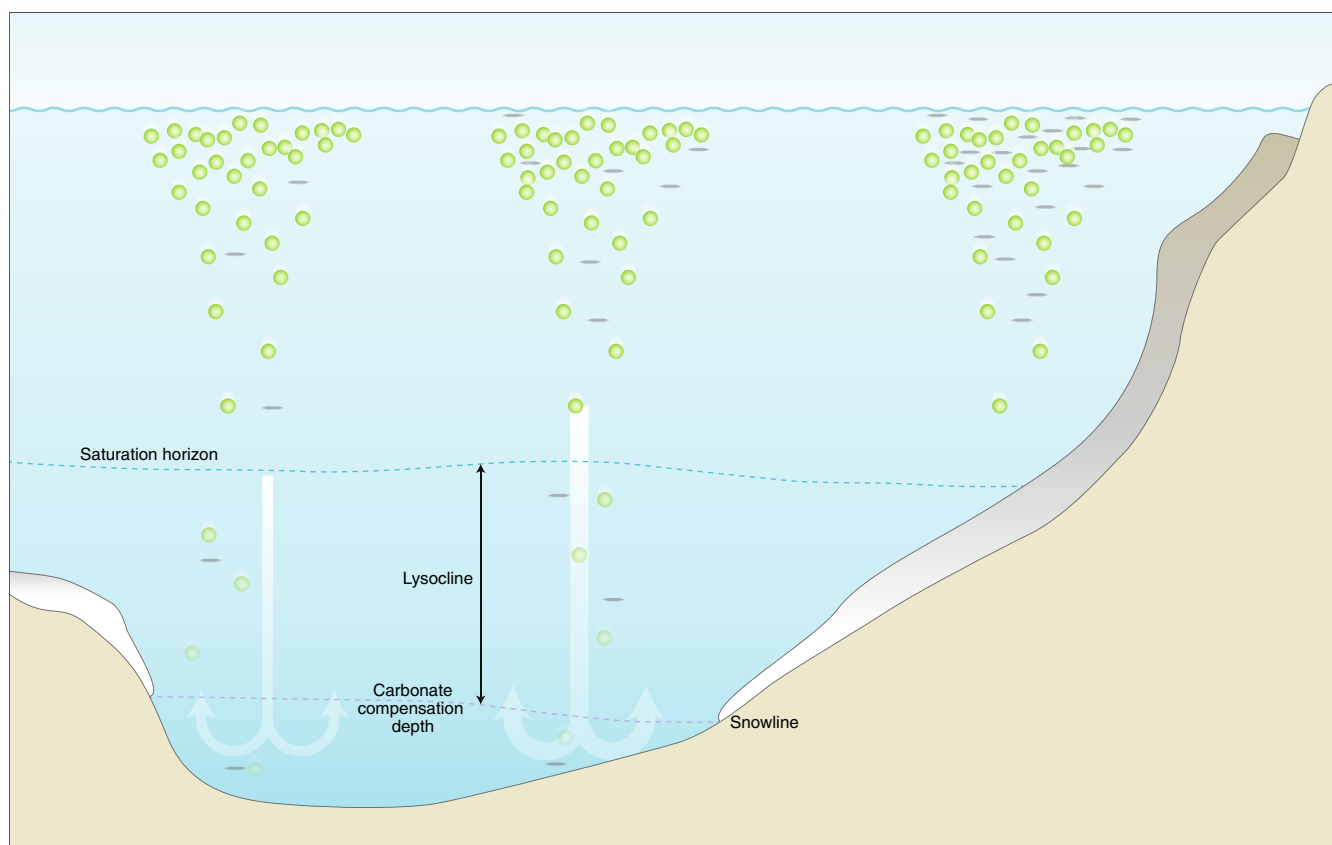


Fig. 1 | Schematic diagram of the critical horizons of open-ocean carbonate compensation. Biogenic CaCO_3 tests, produced in the photic zone of the oceans (green circles), sink towards the bottom, along with lithogenic materials (grey plates). Because of increasing solubility with depth and the release of CO_2 from organic matter decay, there exists a horizon in the oceans where the waters are exactly saturated with respect to CaCO_3 , that is, the saturation depth. At an even greater water depth, the rate of dissolution exactly matches the rate of supply of CaCO_3 from above, that is, Z_{cc} .

but are all shallower and dependent on their respective solubilities and the magnitude of their export fluxes.

As acidity from atmospheric CO_2 invasion enters the ocean, convection will transfer it into oceanic bottom waters and Z_{sat} will then rise, increasing the dissolution of CaCO_3 and thus raising Z_{cc} , all of which neutralizes the increased acidity. Similarly, if the oceans receive additional alkalinity, for example, from increased weathering, the saturation state of bottom waters will increase, deepening Z_{sat} , reducing the dissolution of CaCO_3 and lowering Z_{cc} , all of which counteracts the increased alkalinity. This constitutes the classical picture of chemical compensation for the deep oceans.

Chemical compensation, as a result of an atmospheric CO_2 perturbation, can also occur in shallow waters if the amount of added carbonic acid is sufficient to drop the surface saturation of the shelf waters below the solubility of aragonite and Mg calcite. Andersson et al.⁵ found that, while an Anthropocene-level CO_2 increase could drive additional dissolution in shelf sediments, this dissolution provided an “insignificant buffer” to changes in pH and the saturation state of shelf waters. Nevertheless, Morse et al.⁶ found that this dissolution could change the average mineralogical composition of shallow-water sediments.

Biological carbonate compensation. Chemical carbonate compensation implicitly assumes that the production of CaCO_3 remains the same. But what if it doesn't? Evidence has accumulated that calcifiers respond to changes in the chemistry of their surrounding waters, both at the physiological and ecological levels^{7,8}. For example, some short-term experiments suggest decreased production

with acidification^{9–11}, while others indicate mixed responses^{12–14}. Extensive field studies by Beauford et al.¹⁵ and Eyre et al.¹⁶ have found strong negative impacts on calcification, which meta-analysis⁷ supports. Reduced calcification need not be directly caused by changes in saturation, as it can result from associated stressors, such as warming^{7,17,18}. Boyce et al.¹⁹ have attributed a decline of phytoplankton biomass, including calcifiers, to the current global warming. On longer time scales, the geological record contains examples of decreases in the abundance/production of calcifiers following acidification^{20–24}.

Calcification is the primary mechanism for alkalinity removal from the oceans²⁵. If this rate falls, alkalinity will build up in the surface ocean on the time scale of the delivery of alkalinity to the oceans; likewise, if calcifiers increase their rates, surface alkalinity will fall. Ocean surface waters that become enriched/depleted in alkalinity due to falling/rising calcification will reach the deep sea due to deep convection, thus raising/lowering the alkalinity of deep waters; this, in turn, would cause Z_{sat} and consequently Z_{cc} to deepen/shallow^{26–30}. These are the elements of what we term ‘biological carbonate compensation’. A related compensation mechanism will operate if calcification in shelf environments falls, because more of the alkalinity delivered by rivers to the sea will then reach the open ocean, leading again to a rise in Z_{sat} and Z_{cc} , all else remaining constant. In what follows, we will highlight compensation in the open/deep ocean.

Compensation in the Anthropocene

Important response differences between biological and chemical compensation are revealed by considering the transient responses

Box 1 | Quantitative relations for Z_{sat} and Z_{cc}

By fitting an exponential^{43–45} to the temperature- and pressure-dependent stoichiometric solubility product (K_{sp}) for calcite⁴⁶, the saturation depth, Z_{sat} , is given by,

$$Z_{\text{sat}} = Z_{\text{ref}} \ln \left(\frac{[\text{Ca}^{2+}]_{\text{D}} [\text{CO}_3^{2-}]_{\text{D}}}{K_{\text{sp}}^1} \right) \quad (1)$$

where Z_{ref} is a reference depth (typically ~5,100 m in today's oceans), $[\text{Ca}^{2+}]_{\text{D}}$ and $[\text{CO}_3^{2-}]_{\text{D}}$ are the concentrations of the dissolved calcium and carbonate ions in the deep water of the ocean, respectively, and K_{sp}^1 is the stoichiometric solubility constant at 1 atm pressure in seawater. Boudreau et al.⁴⁵, Boudreau⁴⁷ and Sulpis et al.⁴⁸ have shown that the rate of dissolution of calcite of the seafloor is essentially controlled by the transport rate of carbonate ions across the benthic (diffusive) boundary layer at the seafloor. Balancing the flux (rain) of calcite to the sediment–water interface (B/A_{D}) with this rate of transport, the calcite compensation depth, Z_{cc} , is given by

$$Z_{\text{cc}} \approx Z_{\text{ref}} \ln \left(\frac{B [\text{Ca}^{2+}]}{\beta K_{\text{sp}}^1 A_{\text{D}}} + \frac{[\text{Ca}^{2+}]_{\text{D}} [\text{CO}_3^{2-}]_{\text{D}}}{K_{\text{sp}}^1} \right) \quad (2)$$

where B is the export of calcite that reaches the seafloor, A_{D} denotes the area of the bottom of the oceans, and β the mass transfer coefficient for carbonate ion across the diffusive boundary layer at the sediment–water interface of the oceans^{47,49}. Similar equations can be written for aragonite and high-Mg calcite but these occur at shallower depths.

of the carbonate horizons with and without biological compensation. To this end, we first examine the effects of a hypothetical acidification event similar to the current, with a ~400-year release time scale, as predicted by a simplified ocean box model (see Methods) with constant calcification^{28,29}, that is, chemical compensation alone (Fig. 2). CO_2 addition causes the surface-water saturation to fall; however, acidified surface water will intrude into the deep waters only on a time scale set by meridional/thermohaline overturning (~200 years), which we term 'convective lag'. Until this intrusion becomes significant, benthic dissolution is not appreciably increased. (We do not address here the effects of possible convective slowdown with ocean warming, which would increase the lag time.) Following convective lag, both Z_{sat} and Z_{cc} rise tangibly with chemical compensation, as illustrated in Fig. 2a. Z_{snow} rises no more than 100 m under these conditions (not shown).

Bottom-water alkalinity increases after ~1,000 years because of the loss of CO_2 forcing, elevated benthic dissolution and constant riverine alkalinity input over this time scale, which combine to deepen both Z_{sat} and Z_{cc} (Fig. 2a). With deeper Z_{sat} and Z_{cc} , and the resulting falling dissolution rate, both horizons monotonically approach their original positions, as does Z_{snow} . The additional alkalinity from all that dissolution in the deep waters is slowly removed by increasing CaCO_3 accumulation/burial, that is, textbook chemical compensation.

In contrast, biological carbonate compensation can produce a number of different outcomes with CO_2 emission changes. While the long-term ecological response of pelagic calcifiers to acidification is quantitatively unknown, we consider three possible responses, which we believe bracket the range of possibilities (see Methods): (1) rapid recovery, wherein calcification changes proportionally with emissions, which indicates no permanent or

Box 2 | Terminology of carbonate compensation

The terms surrounding carbonate compensation are copious, confused and confusing. The terms 'saturation depth' (Z_{sat}) and 'compensation depth' (Z_{cc}) for a given mineral are clearly defined in the main text and as mathematical formulae in Box 1. Kolla et al.⁵⁰ used the term 'carbonate critical depth' for the depth where the calcite content of sediments falls to <10%. A truly problematic term is the 'lysocline', which has been variously defined as the depth where carbonate tests in sediments first exhibit the effects of dissolution⁵¹, or the depth below which the rate of dissolution of suspended calcite exhibits a dramatic increase^{51–53}, or the depth "difference in overlying water carbonate saturation, ΔCO_3^{2-} , between high and low calcite sediments"⁵⁴. Yet, other papers have equated it with either the saturation or compensation depths³⁴. Still, at other times, the lysocline means a transition zone between high and low carbonate preservation or from slow to fast dissolution rates^{55,56}, rather than a depth. We advocate strongly that lysocline means the vertical distance between Z_{sat} and Z_{cc} , which can be expressed dynamically; this usage is consistent with the original Greek meaning of 'klinein', which signifies 'to slope', and the common use of 'cline' in oceanography, referring to a distance over which something changes. For example, pycnocline (density change), thermocline (temperature change), oxycline (oxygen change), and so on. Finally, the ' R_0 depth' is defined by Berger⁵⁷ as the depth at which the ratio of the number of 'soluble' to 'resistant' foraminiferal shells in sediments first changes significantly (~10%). The R_0 depth is superior to the term lysocline to denote the depth where dissolution first becomes apparent in the sediment, as the R_0 depth is associated with a quantitatively definable measure.

long-term effect on the calcifier ecology; (2) no recovery, wherein the production falls to a set minimum with rising emissions but does not increase again after emissions cease—this represents partial failure to regain an ecological niche; and (3) delayed recovery, wherein the reduced calcification does recover to original levels, but only after a 'long' lag.

While the description of these three scenarios was cloaked in geochemical terms, they do have ecological equivalents. Rapid recovery is equivalent to biological acclimation in direct response to the environmental forcing. No recovery denotes a 'permanent' reduction in the abundance of (pelagic) calcifiers due to unfavourable environmental chemistry; generally, this does not equate with extinction, but that is the logical end-member of this type of response. Finally, delayed recovery indicates long-term adaptation to the new conditions, with a probable reoccupation of an ecological niche.

The results of these scenarios are illustrated in Fig. 2b (Z_{cc}) and 2c (Z_{snow}). Rapid recovery of net CaCO_3 export (solid lines in these diagrams) generates a Z_{cc} evolution quantitatively comparable to that of pure chemical compensation. An equilibrium-like link between calcification and emissions means that net CaCO_3 export falls gradually over the first 200-year interval. With no sudden change in calcification, that is, B in equation (2) in Box 1, the effect of the loss of biology on Z_{cc} is not readily apparent. Emissions fade entirely after ~550 years, and biology is fully recovered in that same time with rapid recovery. The build-up of alkalinity has a time scale of >1,000 years, so this temporary loss of calcification does not alter significantly the long-term chemistry of the oceans.

The predicted evolution differs significantly if there is no recovery or delayed recovery (dashed red lines Fig. 2b,c). In both these cases, there is a ~150 m extra rise of the carbonate horizons beyond that predicted by chemical compensation alone as the emissions fade

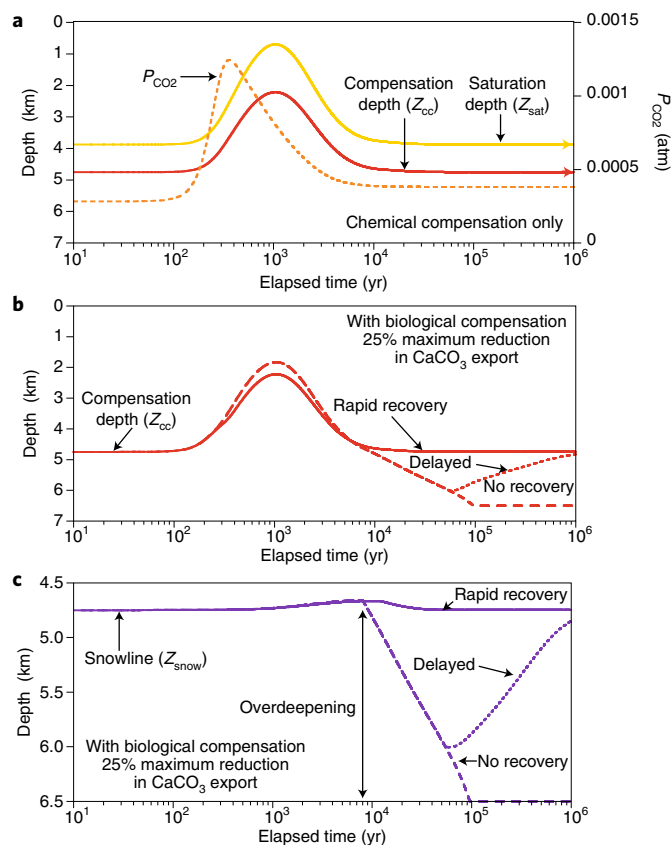


Fig. 2 | Predicted evolution of carbonate horizons as a result of different compensation mechanisms for Anthropocene-like conditions. **a**, Evolution of Z_{sat} , Z_{cc} and atmospheric P_{CO_2} , driven by an acidification event ($0 \leq t \leq 10^3$ years) with only chemical compensation. **b**, Z_{sat} and Z_{cc} driven by the same acidification event but with a 25% maximum reduction in calcification, that is, biological compensation, in addition to chemical compensation and three types of biological responses to acidification—rapid recovery, delayed recovery and no recovery. **c**, Z_{snow} change for the same conditions as **b** (note the change in y-axis scale).

appreciably after ~ 300 years elapsed time (ET). The additional rise is predicted by equation (2) in Box 1 if calcification does not readily return. Whereas this additional rise is certainly modest in these cases, this is not always true. As acidification fully wains, input of alkalinity restores the carbonate chemistry; but with unrecovered net export, that alkalinity builds up in the ocean after ~ 6 kyr ET, causing the deep waters to increase their saturation state with respect to calcite to levels greater than the pre-acidification situation; the latter drives all three carbonate horizons deeper than the pre-acidification depths (Fig. 2b,c). The accumulation of CaCO_3 below the pre-perturbation Z_{snow} has been termed ‘overdeepening’ or ‘overshooting’, and it has been recognized in the geological record^{31,32}.

After the overshooting, the horizons will remain at their new deeper positions—that is, no recovery—unless calcification is restored—that is, delayed recovery. If calcification returns to pre-perturbation rates, the increased CaCO_3 removal will act to extract more of the added alkalinity and return the horizons to their previous positions (Fig. 2b,c). Overshooting is entirely created by the internal, longer-term dynamics of calcifiers in the oceans.

The amount of calcification loss (25%) employed in Fig. 2 might be considered too generous. Consequently, we carried out calculations with a modest 10% drop in the maximum rate, as illustrated in Fig. 3. This essentially unmeasurable 10% decrease still generates a ~ 350 m deepening of Z_{snow} . The CaCO_3 compensation

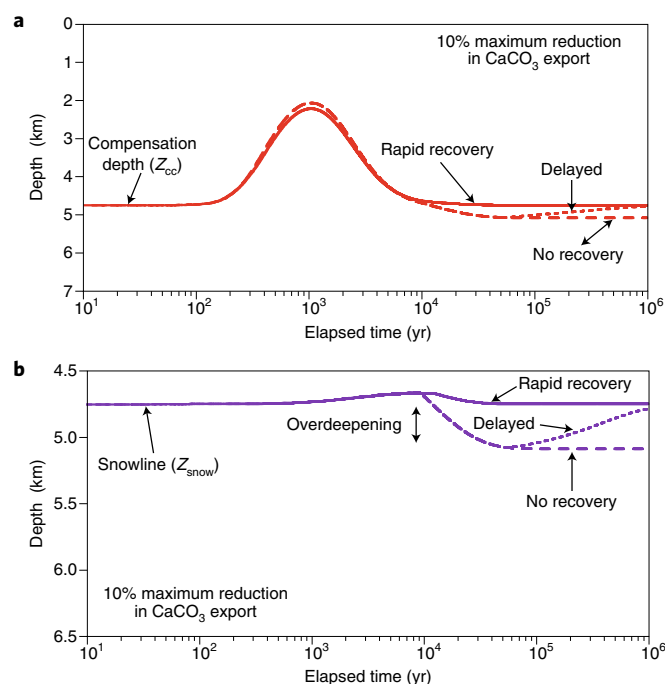


Fig. 3 | Predicted evolution of the carbonate horizons as a result of a 10% (maximum) drop in calcification for Anthropocene-like conditions.

a, Evolution of Z_{sat} and Z_{cc} driven by the same acidification event as in Fig. 2 with three types of biological responses to acidification that is, rapid recovery, delayed recovery and no recovery, as explained in the text. **b**, Evolution of Z_{snow} for the same conditions (note the change in y-axis scale).

and preservational mechanism is sensitive to the biological supply and thus the state of the carbonate-producing ecology.

Whereas our numerical results all focus on open-ocean production changes, as stated before, loss of calcification in shelf environments would also allow alkalinity to build-up in the ocean, as the rate of interception of riverine alkalinity delivery to the oceans would fall. A new model to quantify this effect is needed but, we feel, beyond the scope of this Perspective.

We would be remiss here not to mention that overshooting can be produced abiotically, but this requires an input of additional external alkalinity (see Fig. 4). Added atmospheric CO_2 may increase continental weathering rates and augment riverine delivery of alkalinity to the oceans³². This additional alkalinity input is not a separate form of compensation. If transmitted past shallow-water calcifiers (such as corals) to the pelagic oceans, that enhanced input can affect pelagic compensation by acting as a negative feedback to acidification on a time scale of weathering (10^3 – 10^5 years). As illustrated in Fig. 4, using the alkalinity input function from Lenton and Britton³³, Z_{sat} and Z_{cc} as well as Z_{snow} , deepen to depths beyond their pre-perturbation positions, which again is overshooting.

Both biological compensation and weathering-enhanced chemical compensation models predict a challenging chemical environment in the oceans for calcifying organisms over the next 1 Myr, which highlights our need to better understand both processes. For example, which has dominated in the past? Are their effects essentially identical? Can we distinguish them in the sedimentary record? One might expect biologically induced overshooting to recover faster, because the calcification rate can change more rapidly (\sim years) than the alkalinity supply from rivers/weathering ($\sim 1,000$ years), and this is suggested by the delayed recovery results in Fig. 2b,c. Next, what does this imply for the Anthropocene oceans? Most anthropogenic carbon enters the ocean in high-latitude

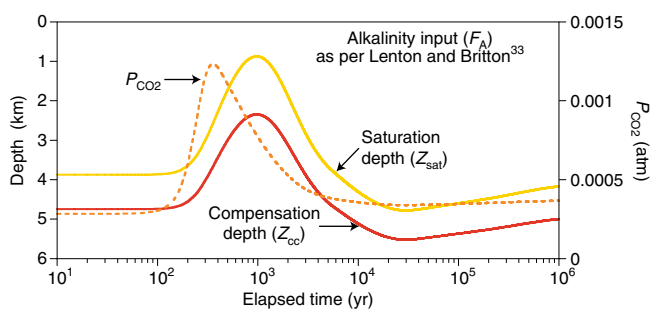


Fig. 4 | Predicted evolution of the carbonate horizons and P_{CO_2} as a result of added carbonate alkalinity input (F_A) for Anthropocene-like conditions. Curves and symbols are identical to those in Fig. 2.

systems where aragonitic pteropods are the main calcifiers. Biological compensation through diminished aragonite production in the high-latitude ocean might initially be a prominent feature of ocean carbonate compensation.

Discussions of the future carbonate chemistry of the oceans are primarily based on chemical compensation and thus do not consider the possibility of overshooting. (Those few models that included calcification feedback did not run long enough ($>10^4$ years) to capture that phenomena^{10,27,34}.) Moreover, the central role for calcifiers in carbonate compensation has additional implications. Other major stressors, such as warming²⁴ and hypoxia, can impact calcifying communities in the surface ocean, altering carbonate export and thus the pelagic carbonate horizons. Changes in food-web structure, community composition or evolutionary adaptations can impact carbonate preservation, for example as happened with the proliferation of coccoliths and the transfer of carbonate burial from the coastal domain to the deep ocean³⁵. Coastal calcifiers can also be affected³⁶ by ecological perturbations, altering the alkalinity supplied from the continents. Far more needs to be known.

Past compensation

Is there any evidence that biological compensation played a role in the carbonate chemistry of the oceans of the past? We describe briefly two examples.

The PETM. First, a biological compensation event possibly occurred during the Palaeocene–Eocene thermal maximum (PETM) at about 55 Ma. This period witnessed a serious rise in atmospheric CO_2 (though at a slower rate than today) and an overshooting-and-recovery event³⁷ in the Atlantic Ocean, over a ~ 200 kyr interval. The overshooting has commonly been attributed to weathering-enhanced chemical compensation^{38,39}. There is no incontrovertible evidence against enhanced weathering; however, Luo et al.²⁹ note that Fig. 4 in Gibbs et al.²³ could be interpreted as indicating an initial 20–25% drop in mass calcification at Site 690 in the far South Atlantic Ocean at the start of the acidification episode. Aze et al.²⁴ have argued for a virtual shutdown of planktonic calcification in tropical waters due to temperature effects. Luo et al.²⁹ estimated that net CaCO_3 export was initially reduced by $\sim 50\%$ over the Walvis Ridge sites in the central South Atlantic, only to recover completely as part of the recovery phase of the PETM (see Supplementary Figs 3 and 4).

The K–Pg mass extinction. Another palaeoceanographic event that certainly involves the effects of biological compensation is the CaCO_3 productivity crisis at the Cretaceous–Palaeogene (K–Pg) boundary (~ 65 Ma). That event saw a reduction in calcification^{26,40–42} by a factor greater than 3. This crisis appears to have been instigated by a meteorite/comet collision with Earth²³, rather than an

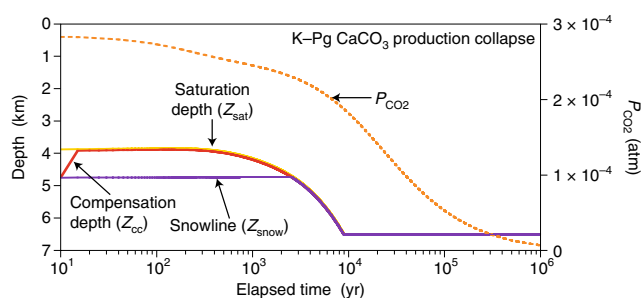


Fig. 5 | Simulation of the effects of a quasi-K-Pg calcification collapse. Predicted evolution of the carbonate horizons as a result of a calcification rate collapse to 5% of its pre-event level in a 10-year interval. Of particular interest is the very rapid rise in the compensation depth at the very early stages of the event, but the long-term development of a highly calcite-saturated ocean for times beyond ~ 3 kyr ET. See the text on the K–Pg mass extinction for further discussion.

acidification event⁴¹. This event caused the mass extinction of a vast array of CaCO_3 -secreting pelagic organisms, but had a much weaker repercussion on benthic calcifiers. Caldeira and Rampino²⁶ first simulated the carbonate system of this event, noting the existence of a slight reduction in “the area on which carbonate is accumulating”, which we equate with a rise in Z_{cc} and Z_{snow} in the first ~ 300 years after the impact. On time scales greater than 1 kyr, they predicted that the carbonate ion concentration of the deep oceans rose considerably and remained at this higher level for at least 10 Myr, with no recovery of productivity.

It is beyond the scope of the present Perspective to provide a detailed simulation of that event, and highly relevant results can be gleaned in Caldeira and Rampino²⁶ and Henehan et al.⁴². Nonetheless, a quasi-simulation is possible by imposing a short time-scale (10 year) collapse of net export of CaCO_3 in our present model, while leaving organic matter production unchanged and without introducing additional CO_2 emissions. These results are illustrated in Fig. 5 and show a nearly immediate rise in the compensation depth by ~ 800 m, as predicted by equation (2) in Box 1. The snowline does not shift upwards in tandem, as there has been insufficient time to dissolve a tangible amount of previously deposited CaCO_3 . Over the next ~ 600 years, the loss of alkalinity removal causes the compensation and saturation depths to deepen. These trends accelerate thereafter, so that by ~ 3 kyr ET these horizons have deepened to the snowline depth. All three horizons reach the bottom of the ocean (6.5 km) at ~ 9 kyr ET and stay there afterwards.

In our model, the atmospheric CO_2 content collapses over a ~ 200 kyr time scale because the build-up of carbonate alkalinity exceeds the increase in dissolved inorganic carbon (DIC) with a loss of calcification (see ref. 2):

$$P_{\text{CO}_2} \sim \frac{(2 \text{ DIC} - C_{\text{Alk}})}{C_{\text{Alk}} - \text{DIC}}$$

where P_{CO_2} is the CO_2 partial pressure in the atmosphere and C_{Alk} is the carbonate alkalinity of surface waters. Thus, if C_{Alk} increases more than DIC, as it does in our case, then P_{CO_2} must fall. Our CO_2 predictions are dissimilar to those in Caldeira and Rampino²⁶, but that is due to their contrasting assumption that all productivity fails, rather than calcification alone; nevertheless, our results are not dissimilar to those in Henehan et al.⁴². Beware, however, our results are not quantitatively accurate on longer time scales because of our neglect of volcanism, which replenishes atmospheric CO_2 , and weathering feedbacks.

Conclusion

Except with rapid-recovery-type events, biology is not simply a background player in compensation but instead alters the oceanic response to acidification on time scales ranging from 10^0 – 10^6 years. As the evolution of the oceans can be markedly different with and without strong biological compensation, more effort needs to be made to properly incorporate calcification dynamics into long-term predictive models. That goal cannot be achieved without better data on long-term biological responses. If we are to predict credibly the future state of the carbonate system during the Anthropocene and properly interpret the palaeoceanographic record, we must obtain a far better understanding of biological compensation—not just the attenuation of calcification during acidification, but the means and rate of its recovery thereafter.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, statements of data availability and associated accession codes are available at <https://doi.org/10.1038/s41561-018-0259-5>.

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Author contributions

B.P.B. provided the concept for the paper, ran the code and co-wrote the paper. J.J.M. researched various aspects of the problem and co-wrote the paper. Y.L. wrote the code and contributed to the writing of the paper. Address scientific requests and inquiries to B.P.B. (bernie.boudreau@dal.ca), and questions regarding the code can be directed to Y.L. (luoyiming@mail.sysu.edu.cn).

Competing interests

The authors declare no competing interests.

Additional information

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Methods

The model curves in Figs. 2–5 were produced with a three-box time-dependent model for the oceanic carbonate system, as detailed in refs^{28,29}. This model is highly simplified and cannot be considered to be an Earth systems model. It is more aptly described as a ‘toy model’, which does not rob it of its essential predictive power.

We did modify the model with respect to the functionality of the calcification rate, B , as dependent on the CO_2 emissions. One can reasonably argue that calcification should be linked to atmospheric CO_2 , surface saturation state, pH, or surface water temperature, and so on, or any combination, instead of emissions. We fully recognize such alternatives; however, in the absence of a quantitative model of the calcification rate, the emissions scenario is as good of a compromise as any.

Rapid recovery is simulated with:

$$B = f_x B_o \left(1 - \frac{E_m(T)}{E_{\max}} \right) + (1 - f_x) B_o$$

where f_x is the fractional maximum reduction in B , B_o is the pre-acidification calcification rate, $E_m(T)$ is the emissions function of CO_2 with time, T , and E_{\max} is the maximum value of $E_m(T)$. f_x values of 0.1 and 0.25 were investigated. In this equation, $E_m(T)$ is in the form of a Gaussian, as discussed in ref.²⁸.

No recovery was obtained by assuming that the above equation holds until the time when E_{\max} is obtained, and then:

$$B = (1 - f_x) B_o$$

for all times thereafter.

Delayed recovery was obtained by assuming that:

$$B = (1 - f_x) B_o + f_x B_o \frac{(T - T_D)}{T}$$

for all times $T > T_D$, where T_D is a delay time (50 kyr).

To model these three scenarios, we must provide a quantitative estimate of the maximum reduction in net CaCO_3 export during increased emissions, and as stated before, the long-term ecological response of calcifiers to acidification is not well known. However, meta-analysis of short-term experiments reveals mean reductions in calcification of 22–39% for corals, coccolithophores and mollusks⁷. We examined 10% and 25%, which are on the lower side of this range.

Code availability. We are unable to make the Fortran code that produced the results in this paper available at this time but it can be obtained from B.P.B. or Y.L. upon request.

Data availability

The authors declare that the data supporting the findings of this study are available within the article and its supplementary information files and further information are available from the corresponding author upon request.