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Key Points:
- Methane hydrate hydrates will dissociate with global warming
- This methane will oxidize to CO_2 and further acidify the oceans
- This will appreciably prolong anthropogenic ocean acidification

Supporting Information:
- Text S1 and Figures S1–S6

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Gas hydrate dissociation prolongs acidification of the Anthropocene oceans

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Abstract Anthropogenic warming of the oceans can release methane (CH_4) currently stored in sediments as gas hydrates. This CH_4 will be oxidized to CO_2, thus increasing the acidification of the oceans. We employ a biogeochemical model of the multimillennial carbon cycle to determine the evolution of the oceanic dissolved carbonate system over the next 13 kyr in response to CO_2 from gas hydrates, combined with a reasonable scenario for long-term anthropogenic CO_2 emissions. Hydrate-derived CO_2 will appreciably delay the neutralization of ocean acidity and the return to preindustrial-like conditions. This finding is the same with CH_4 release and oxidation in either the deep ocean or the atmosphere. A change in $CaCO_3$ export, coupled to CH_4 release, would intensify the transient rise of the carbonate compensation depth, without producing any changes to the long-term evolution of the carbonate system. Overall, gas hydrate destabilization implies a moderate additional perturbation to the carbonate system of the Anthropocene oceans.

1. Introduction

Gas hydrates, also known as clathrates, are solids that consist of gas molecules surrounded by cages of water molecules [*Sloan and Koh*, 2007]. Methane (CH_4) hydrates are stable at the relatively low temperatures and relatively high pressures that exist in much of the world's oceans, and they are found in sediments over large areas of the modern continental slopes and rises [*Kvenvolden*, 1993; *Beaudoin et al.*, 2014]. The total mass of carbon stored in present-day subseafloor gas hydrate systems remains the subject of debate, as obvious from the recent literature. For example, using geochemical modeling, *Piñero et al.* [2013] and *Kretschmer et al.* [2015] estimated 550 and 1146 gigatons of carbon (Gt C = 10^{15} g C), respectively, in oceanic gas hydrates. However, this work implies $<$60 kg of methane C m^{-2} of the seafloor, whereas measurements at multiple drill sites indicate $>$300 kg of methane C m^{-2} everywhere across the seafloor [*Dickens et al.*, 1997; *Milkov et al.*, 2003; *Malinverno et al.*, 2008], even after excluding underlying free methane gas. *Beaudoin et al.* [2014] note these issues in their extensive review, emphasizing that the gas hydrate standing stock in modern oceanic sediments is uncertain, but may be ~5000 Gt C. Our study employs a judicious mean value reported by *Yamamoto et al.* [2014], which was ~2680 Gt C.

Concerns exist that ongoing climate warming will increase the temperature of the oceans, thus causing presently stable hydrates to dissociate and release part of their total subseafloor CH_4 pool to the oceans and atmosphere [*Krey et al.*, 2009; *Mascarelli*, 2009; *Ruppel*, 2011; *Biastoch et al.*, 2011; *Hunter et al.*, 2013; *Kessler*, 2014; *Yamamoto et al.*, 2014]. *Archer* [2007] has argued not only that such destabilization is likely if current fossil fuel emission scenarios hold but also that CH_4 leakage from the seafloor will be chronic —taking place over hundreds to thousands of years. With chronic release, the CH_4 that escapes from the seafloor will most likely be rapidly and efficiently oxidized to CO_2 within the oceans, or perhaps partially in the atmosphere [*Dickens*, 2001; *McGinnis et al.*, 2006; *Kessler et al.*, 2011; *Zeebe and Ridgwell*, 2011; *Yamamoto et al.*, 2014]. Aerobic CH_4 oxidation produces CO_2,

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \tag{1}$$

which would enhance anthropogenic acidification of the oceans. (For those unfamiliar with CO_2-induced acidification of the oceans, we direct the reader to the highly readable expositions by *Feely et al.* [2009] and *Gattuso and Hansson*, [2011].) Methane hydrate-related acidification may have occurred during past episodes of global warming, most notably the Paleocene-Eocene Thermal Maximum, circa 56 Ma [*Dickens et al.*, 1995; *Zeebe et al.*, 2009].

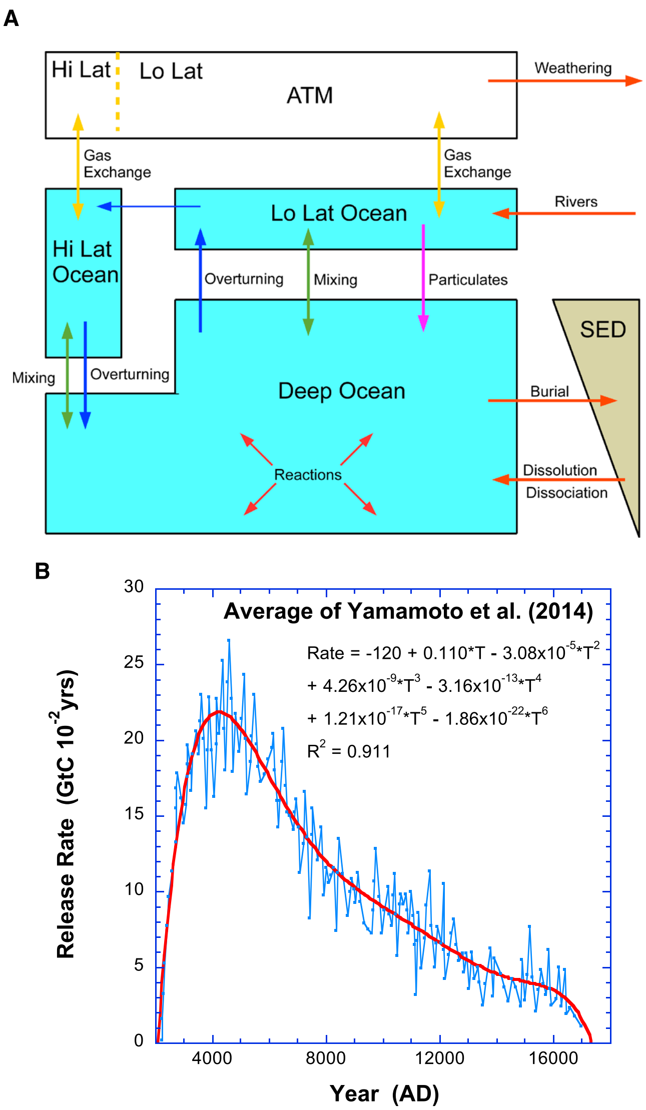

Figure 1. (a) Schematic of the box model used to model the average temperature, oxygen concentration, and carbonate system of the oceans. The boxes represent the atmosphere (ATM), a low-latitude ocean (Lo Lat Ocean), a high-latitude ocean (Hi Lat Ocean), a Deep Ocean, and the sediments. Four boxes are considered compositionally uniform, that is the atmosphere, and the three ocean boxes. The atmosphere is divided into high and low portions with respect to temperature only. The sediment box has a built-in depth dependency to allow for the observed decrease of $CaCO_3$ in sediments in the oceans. The arrows indicate mass or heat flows between the boxes. The equations that describe conservation of temperature (as a passive scalar), dissolved inorganic carbon, carbonate alkalinity and $CaCO_3$ are given in the supporting information. (b) The release rate of CH_4 from dissociating gas hydrates as predicted by *Yamamoto et al.* [2014] and a smooth polynomial fit (red line). This additional forcing, beyond the anthropogenic input, is used to drive the model in Figure 1a.

The potential effects of the release and oxidation of CH_4 from gas hydrates on the future carbonate chemistry of the global oceans have received only limited consideration [*Biastoch et al.*, 2011; *Zeebe and Ridgwell*, 2011]. Specifically, it is not known how much the pH and carbonate saturation state of the surface and deep waters will further fall with this additional CO_2. Moreover, the timing and duration of any such effects remains uncertain.

2. Model

This paper examines these questions using the biogeochemical model developed in *Boudreau et al.*, [2010a], which was designed to simulate the oceanic and atmospheric CO_2 system over millennial timescales. To this end, the model includes a simplified and computationally efficient description of the carbonate compensation feedback by seafloor sediments. The current version of this model differs somewhat from that in *Boudreau et al.* [2010a], as a result of an improved description of the dynamics of the snowline (the water depth where the sedimentary $CaCO_3$ falls to zero)—see the supporting information for details. Our model is capable of predicting the $CaCO_3$ content of seafloor sediments with oceanographic depth and the three critical carbonate horizons [*Boudreau et al.*, 2010b]: the *saturation horizon* (Z_{sat}) below which oceanic waters are undersaturated with respect to $CaCO_3$, the *carbonate compensation depth* (Z_{cc}), where seafloor dissolution just balances the downward rain of $CaCO_3$, and the depth at which the $CaCO_3$ content of the sediment falls to 10% (Z_{10}), as an operational surrogate for the *snowline*. Past results with this model are entirely consistent with those from more complex models, such as those presented by *Archer et al.* [1997, 2009b]—see discussion in *Boudreau et al.* [2010a].

To account for warming feedbacks, our model includes temperature as a variable for the atmosphere and each ocean reservoir—see Figure 1 and Figures S1–S5 in the supporting information. While the atmosphere is treated as compositionally homogeneous, this box was subdivided into high- and low-latitude domains for the purpose of temperature modeling (Figure 1a). The temperature, T (°C), in each of the atmospheric boxes at any given time was related to the partial pressure of CO_2, using the formula $T = c\ln(P/P_o) + T_o$ [*Scheffer et al.*, 2006], where T_o is the initial (preindustrial) year-averaged temperature in a chosen atmospheric subbox, P_o is the initial (preindustrial) P_{CO2}, P is the P_{CO2} at a subsequent time (atm), and c is a scaling coefficient. We employed values of $c = 1.7$ and 4.7 in different simulations, as these might represent "short-term climate" and "long-term Earth system" sensitivities. As it turns out, almost identical results are obtained with respect to the carbonate system with either c value (Figures S2–S5).

The anthropogenic component of the added CO_2 in our model follows the IS92a emissions scenario as extrapolated by *Boudreau et al.* [2010a]; this injection (their Figure 2) introduces ~4025 Gt C as CO_2 over ~600 years and closely resembles other estimates of this forcing [e.g., *Caldeira and Wickett*, 2003; *Feely et al.*, 2004]. Additional CO_2 release (Figure 1b) from methane hydrate dissociation and oxidation was provided by a smooth fit to the release-versus-time prediction in *Yamamoto et al.* [2014]. While the location of the oxidation of methane from marine sediments is most likely the oceans, we examined two end-member cases: a deep oceanic scenario, whereby all CH_4 oxidation occurred within the deep water column, and an atmospheric scenario, whereby all the marine-hydrate-generated CH_4 was oxidized within the atmosphere. The total CO_2 released from methane hydrate dissociation and oxidation (Figure 1b) is ~1600 Gt C over 13 kyr, which represents ~60% of the total gas hydrate reserves estimated by *Yamamoto et al.* [2014].

3. Results

The predicted CO_2 partial pressure in the atmosphere (P_{CO2}) is displayed for three "end-member" scenarios (Figure 2a): these are the prescribed IS92a CO_2 emissions with (i) no CH_4 release, (ii) seafloor CH_4 release, but immediate transfer to and oxidation in the atmosphere, and (iii) seafloor release of CH_4 and oxidation in the deep ocean. We recognize that scenario (ii) is highly unlikely given the rapid rates of bubble dissolution and CH_4 oxidation witnessed in the ocean water column, but it is included for completeness. All scenarios produce P_{CO2} peaks of 1240 ppmv to be reached in 2210 A.D., which is consistent with previous model predictions [e.g., *Archer*, 2005]. Methane-generated CO_2 does not noticeably affect this P_{CO2} maximum, either in timing or in magnitude, because the hydrate dissociation process has a built-in delay of about 1000 years [*Archer et al.*, 2009a; *Yamamoto et al.*, 2014], as a result of the need to transfer heat into the seafloor where the gas hydrates are located. After the maximum atmospheric P_{CO2} is reached, all scenarios follow a decline to attain a quasi steady state between years 8000 and 15000 A.D. This decline is slightly more gradual with the atmospheric release scenario, as CH_4-derived CO_2 needs to be adsorbed into surface waters and transferred into the deeper ocean. As expected, the quasi steady state P_{CO2} differs between scenarios. The IS92a quasi steady value is ~390 ppmv, while both methane-affected scenarios are ~94 ppmv greater, reflecting the additional carbon input.

The addition of CO_2 to seawater, either directly or via the atmosphere, causes short-term and long-term drops in both the pH and the carbonate saturation state of the oceans. IS92a-driven CO_2 release, with or without a contribution from CH_4 release and oxidation, decreases the pH of the low-latitude surface ocean by ~0.575 by 2210 AD (Figure 2b), which is consistent with predictions by *Caldeira and Wickett* [2003], *Feely et al.* [2004], and *Zeebe et al.* [2008]. However, pH values slowly recover thereafter, and the long-term pH value of the surface ocean, i.e., at 15000 A.D., is only ~0.05 lower under the IS92a scenario (Figure 2b) when compared to preindustrial times, but ~0.12 lower with the additional acidification from CH_4-derived CO_2.

The aragonite saturation index, Ω_a, will drop in the surface ocean in line with the P_{CO2} increase (Figure 2c), where $\Omega_a = [Ca^{2+}][CO_3^{\ 2-}]/K_a$ in which square brackets indicate dissolved concentrations, and K_a is the solubility product for the aragonite form of $CaCO_3$. If $\Omega_a > 1$, the water is supersaturated with respect to aragonite and it is thermodynamically favored to precipitate; if $\Omega_a < 1$, the water is undersaturated with respect to this mineral and it is thermodynamically favored to dissolve. Under the IS92a scenario alone, the surface oceans will approach saturation with respect to aragonite ($\Omega_a = 1$) by year 2200, before recovering steadily toward a value slightly below preacidification values (Figure 2c). *Orr et al.* [2005] previously predicted that southern ocean surface water could become undersaturated, whereas we find that, *on average*, ocean waters will remain marginally saturated. This does not mean that (locally) undersaturated waters do not currently exist

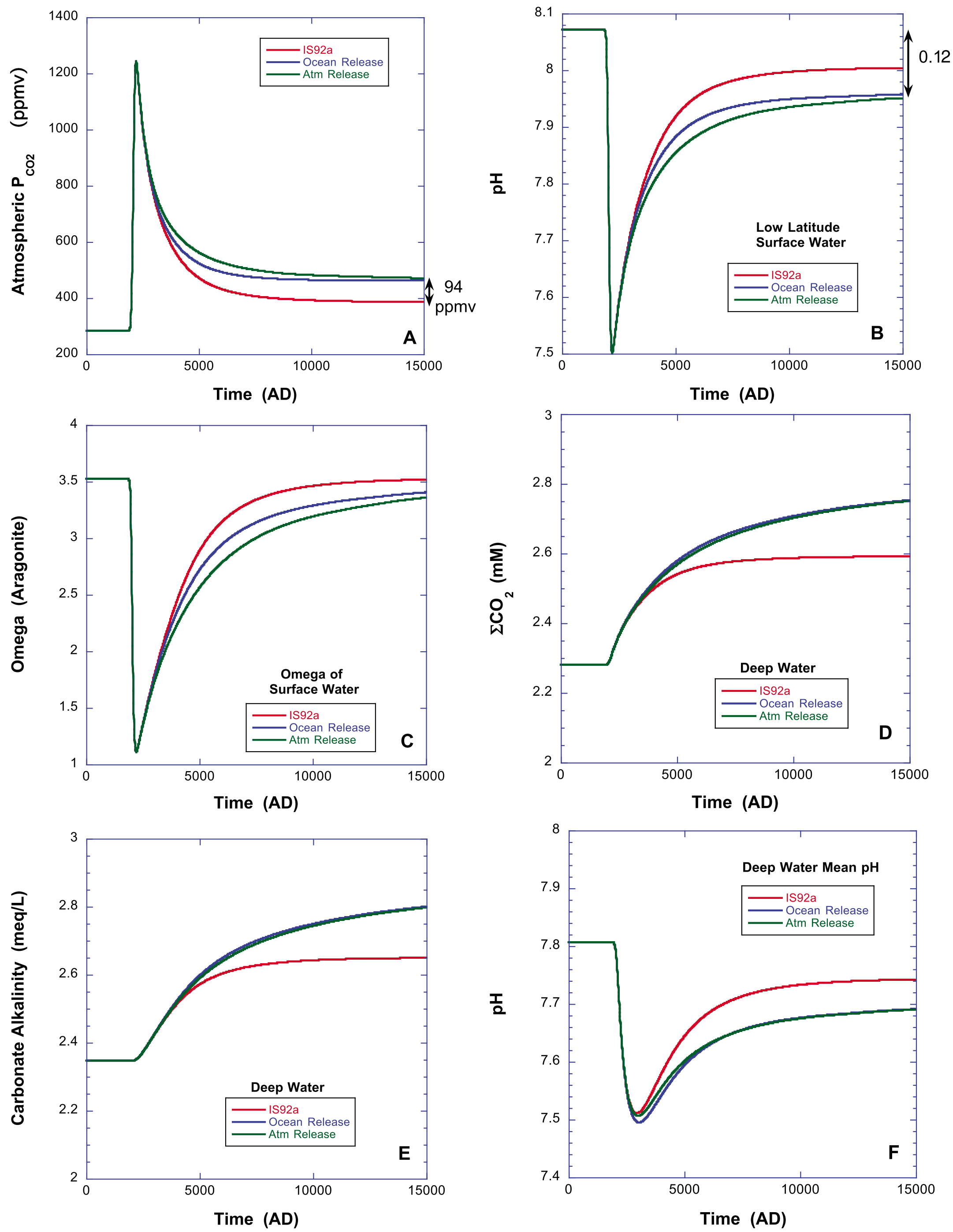

Figure 2. Model results for (a) P_{CO2} of the atmosphere as a result of CO_2 emissions that follow the IS92a scenario (red) and with additional release due to gas hydrate melting and oxidation in the deep ocean (blue) and atmosphere (green). (b) The pH of the low-latitude surface ocean with time, with the same CO_2 inputs as in Figure 2a. (c) Saturation state (omega) with respect to Aragonite (Ω_a in the text) of the low-latitude surface ocean as a function of time, under the same conditions. Evolution of (d) the total dissolved carbon dioxide (ΣCO_2), (e) the carbonate alkalinity, and (f) the pH of the deep ocean for the same conditions and time frame. Please note that each curve in all the figures starts as a constant given by a steady state set by the assumed preindustrial (1865) ocean and atmospheric chemistries [see *Boudreau et al.*, 2010a]. (Effects of previous perturbations in these chemistries are ignored.) All the curves tend to a quasi steady state (not an equilibrium) with time as the effects of the CO_2-induced perturbations decline and alkalinity input from rivers becomes balanced by $CaCO_3$ burial. The model lacks a complete geochemical cycle of CO_2, i.e., rock weathering, and so cannot return to exact preindustrial conditions.

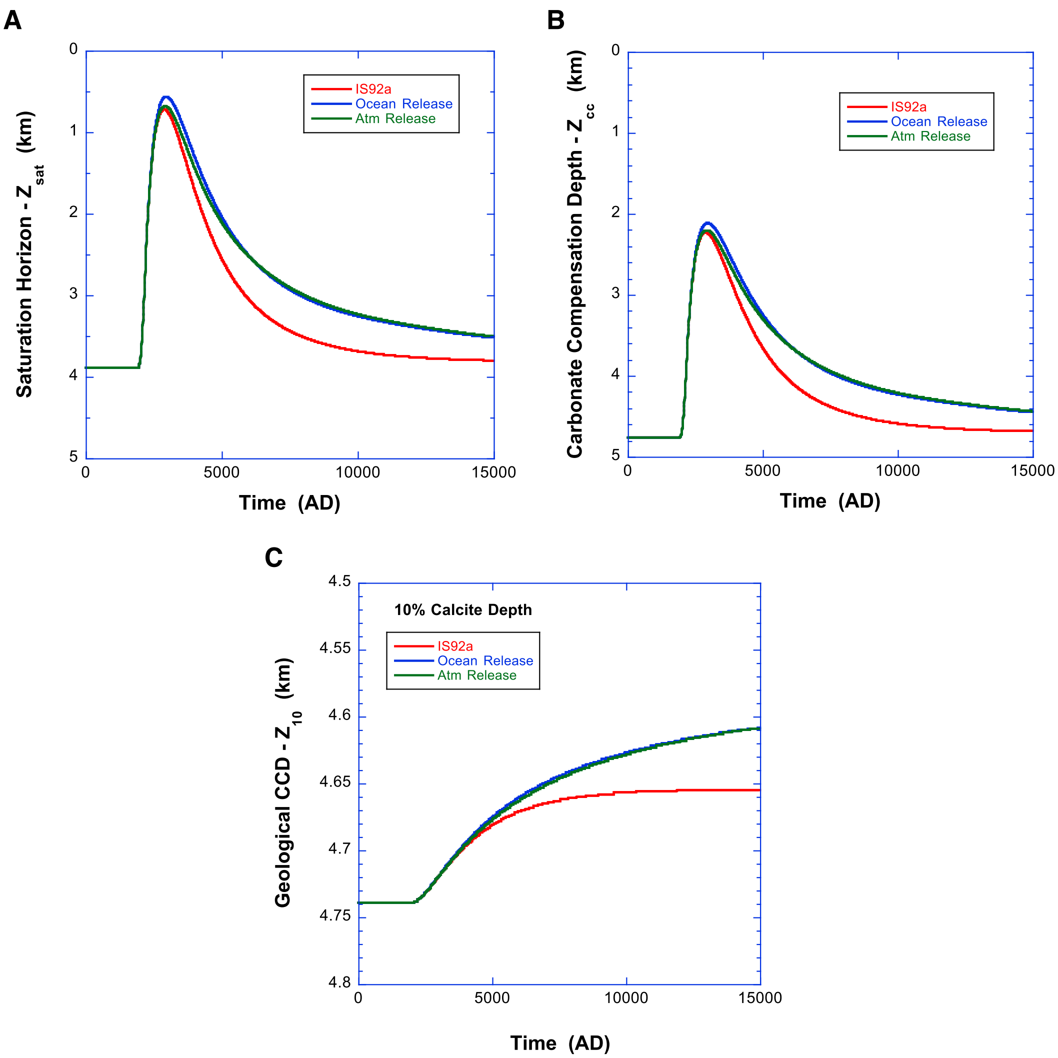

Figure 3. Positions of the critical carbonate horizons with time for the IS92a forcing alone (red) and with additional CO_2 input from gas hydrate melting and oxidation in the deep oceans (blue) and atmosphere (green). (a) Saturation horizon —Z_{sat}. (b) Carbonate compensation depth—Z_{cc}. (c) The 10% $CaCO_3$ horizon—Z_{10}.

(e.g., west coast of North America) or cannot be expected in the future, through the effects of upwelling or biogeochemistry; such spatial variation is not captured by the current box model. If gas hydrate dissociation is added to the IS92a emissions, the recovery is delayed and the long-term saturation index is ~0.025 units lower (Figure 2c).

Deep-ocean carbonate chemistry is also affected by both anthropogenic and hydrate-related CO_2 (Figures 2d–2f). With time, the hydrate-based CO_2 release increases ΣCO_2 of the deep oceans by ~0.15 m*M* over the IS92a source alone; similarly, carbonate alkalinity is some 0.15 meq L^{-1} higher, due to additional dissolution of seafloor carbonates. These changes in the chemistry of the deep ocean also affect the evolution of the positions of the critical carbonate horizons (Figure 3). The saturation horizon (Z_{sat}) rapidly rises, reaching a minimum depth of ~722 m by Year 2950 with IS92a forcing alone, deepening thereafter (Figure 3a). In the scenarios with methane release, Z_{sat} rises to a shallower depth of ~567 m on the same time frame, and deepens more slowly afterward. This Z_{sat} behavior is very similar whether CH_4 oxidation occurs in the atmosphere or in the oceans. Anthropogenic CO_2 release certainly dominates the upward migration of the saturation horizon; the deep ocean will be almost entirely undersaturated with respect to aragonite and calcite for a period of several millennia. Hydrate-based CO_2 will offset the return to the preindustrial position by ≥300 m at any selected time before year 15,000. Accordingly, the seafloor will become a more corrosive environment

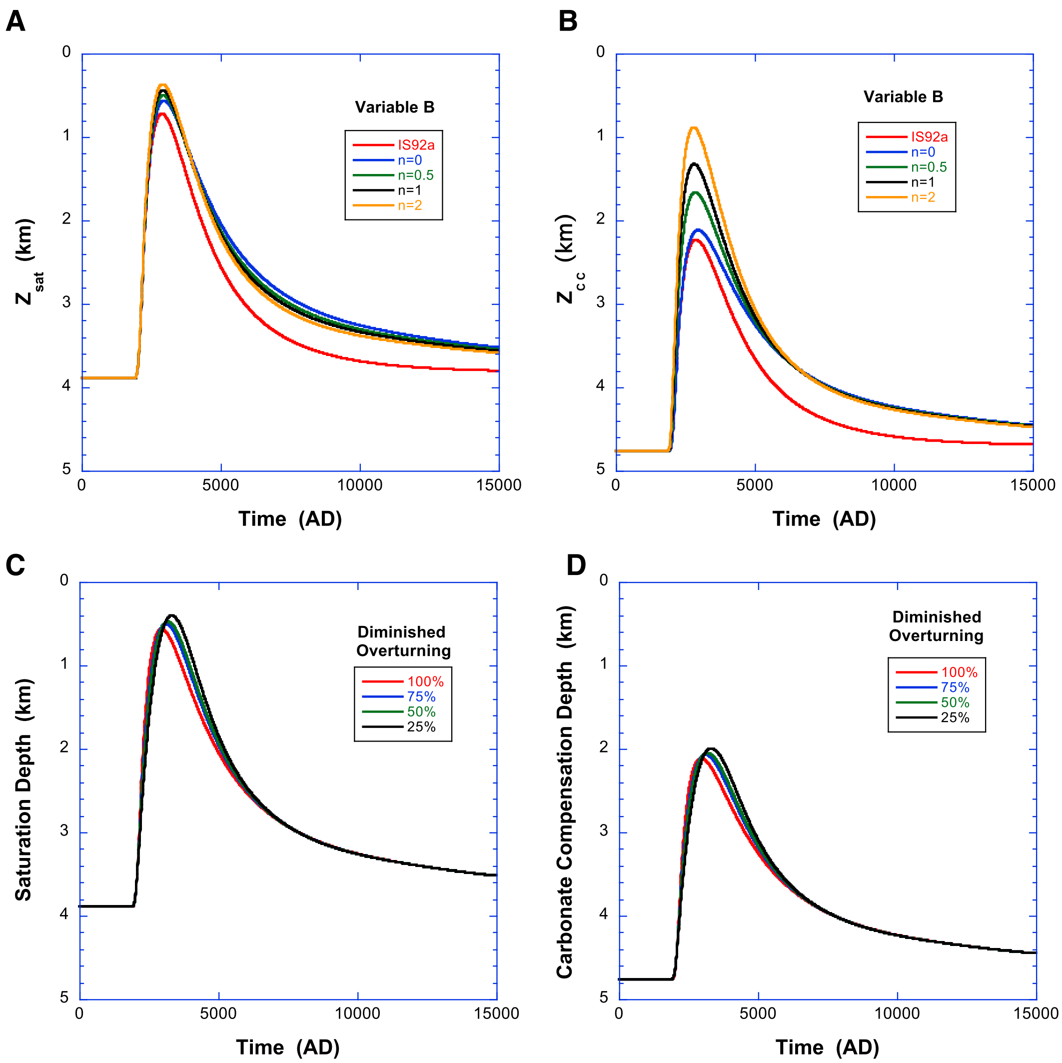

Figure 4. (a) Effect of allowing the export of $CaCO_3$, *B(t)*, to change with surface saturation as given by equation (2) of the text. Lines correspond to different values of the parameter *n*. (b) Change in the carbonate compensation depth for the same conditions as Figure 4a. (c) Effect of allowing the overturning circulation to decrease with time to 75% (blue), 50% (green), and 25% (black) of its current value as the oceans acidify. (d) Change in the carbonate compensation depth for the same conditions as Figure 4c.

for longer periods of time, to the detriment of $CaCO_3$-secreting benthic organisms, such as deep water corals [*Hall-Spencer et al.*, 2008; *Guinotte and Fabry*, 2008].

The carbonate compensation depth (Z_{cc} in Figure 3b) will rise to ~2.2 km by year 2950 in all release scenarios; however, CO_2 added from hydrates will again offset the subsequent return to initial conditions, amounting to ~300 m between the years 8000 and 15000 A.D. The increased undersaturation will lead to further dissolution of previously deposited $CaCO_3$ in seafloor sediments. As a result, the depth where the $CaCO_3$ content of the sediments is 10% (Z_{10} in Figure 3c) will be shallower by an additional ~50 m in year 15,000.

Other possible changes in ocean biogeochemistry could act, in concert with hydrate dissociation, to produce stronger changes, and we investigate two possibilities. First, experimental evidence indicates that the production of $CaCO_3$ in the surface ocean may decrease in response to ocean acidification [*Riebesell et al.*, 2000; *Orr et al.*, 2005; *Hall-Spencer et al.*, 2008; *Riebesell*, 2008; *Waldbusser et al.*, 2015]; such a drop in production should lead to diminished $CaCO_3$ export from the surface to the deep waters. *Boudreau et al.* [2010a] showed that lower $CaCO_3$ production/export could be an important factor in enhancing anthropogenic changes in the future oceans. To explore this effect further, we assume that $CaCO_3$ export from the surface waters to the deep sea, $B(t)$, scales as

$$\frac{B(t)}{B_o} = \left(\frac{\Omega_a(t)}{\Omega_o}\right)^n \tag{2}$$

where t is time, B_o is the preindustrial export (Gmol a^{-1}), $\Omega_a(t)$ is the aragonite saturation of the surface oceans at time t, Ω_o is the preindustrial value of Ω_a, and n is a constant that determines the degree of dependence of $B(t)$ on the surface saturation. Values of n are unknown; in fact, equation (2) is quite speculative, but it can capture a wide variety of possible responses. For the latter reason, we performed simulations with $n = 0$, 0.5, 1, and 2.

Figures 4a and 4b illustrates the effects of reduced $CaCO_3$ export on the evolution of the saturation horizon and the carbonate compensation depth for the three basic scenarios. The curves with $n = 0$ have $B(t)$ constant and correspond to the simulations in Figures 2 and 3. Changing n to 0.5, 1, or 2 modestly raises the position of the saturation horizon at the atmospheric P_{CO2} maximum; conversely, there is a dramatic rise in the carbonate compensation depth, such that it is shallower than 1 km with $n = 2$. Such a rise would induce dissolution of previously deposited carbonate at much shallower depths. On a longer timescale, the differences between curves with different n values in Figure 4 are generally small and do not enhance the effect of hydrate-derived CO_2 addition to the atmosphere-ocean system. This result indicates that the effects of anthropogenic acidification are sensitive to changes in $CaCO_3$ export (Figure 1a), as found in *Boudreau et al*. [2010a], but that this is not true for the effects of chronic CO_2 release from gas hydrates.

There has been speculation that meridional overturning (conveyor-belt circulation) of the oceans may decrease, at least temporarily, in a warming climate [*McPhaden and Zhang*, 2002; *Bryden et al*., 2005; *Srokosz et al*., 2012; *Ramstorf et al*., 2015]. We have added this effect to our model (Figures 4c and 4d) by dropping the rates of overturning and high-latitude deep-ocean mixing (see U_T and U_M in Figure S1) to 75%, 50%, and 25% of the present day value (via a linear function of sea surface temperature). Such changes lead to marginal shifts in the timing of the minimum depths for the saturation horizon and the carbonate compensation depth, but they do not enhance the effects of slow additional CO_2 from gas hydrate dissociation.

As stated above, our findings are based on the *Yamamoto et al*. [2014] estimate of the gas hydrate inventory, as well as their release scenario. If a smaller inventory of gas hydrates is instead correct [*Piñero et al*., 2013], then the effects will be decidedly smaller. Conversely, a doubling of *Yamamoto et al*. [2014] emissions, equivalent roughly to a doubling of the gas hydrate reservoir [*Beaudoin et al*., 2014], causes approximately a doubling of the long-term offsets in the deep and surface water pH values and the total CO_2 in the deep water (see Figure S6), such that these effects become an appreciably more important consideration.

4. Conclusions

We conclude that if anthropogenic warming induces dissociation of seafloor gas hydrates and significant release of CH_4 to the ocean or atmosphere [e.g., *Archer*, 2007; *Yamamoto et al*., 2014], ocean acidification will occur over a longer time interval; that is, such a release would add a long (time) tail to the acidification. Consequently, the deep ocean will remain more corrosive to calcifying organisms for several millennia. However, the additional effects upon carbonate saturation caused by hydrate-derived CO_2 generally pale in comparison to those predicted from anthropogenic CO_2 emissions. This is principally because of the difference in the duration of CO_2 injection. Notwithstanding these findings, three central uncertainties about future ocean acidification remain: first, the response of $CaCO_3$-secreting organisms to increasing acidification; second, the true mass of seafloor CH_4 susceptible to thermal perturbation; and third, despite the work of *Yamamoto et al*. [2014], the exact magnitude and timing of CH_4 escape.

Acknowledgments

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