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Short-term dissolution response of pelagic carbonate sediments to the invasion of anthropogenic CO₂: A model study

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[1] This study addresses the potential for and the quantification of dissolution of marine calcium carbonate (CaCO₃) sediments occurring on century timescales in response to the invasion of anthropogenic CO₂. It presents results obtained with the global biogeochemical model PISCES interactively coupled to a global sediment model. The latter represents the principal reactions involved in early diagenesis of biogenic opal, CaCO₃, and organic matter. The model reproduces observed distributions of core top CaCO₃ content and bottom water carbonate chemistry (e.g., [CO₃²⁻]). Starting from the climatological state, a model experiment is carried out according to the standard CMIP scenario of atmospheric pCO₂ increasing at a rate of 1% per year from 286 to 1144 ppm over a 140 year time period. The invasion of anthropogenic CO₂ results in a strong decrease in bottom water [CO₃²⁻] reaching -100 μM in areas of deep water formation in the North Atlantic and mode and intermediate water formation in the Southern Hemisphere. The concomitant decrease in calcite saturation state of bottom waters drives the dissolution of CaCO₃. The absolute CaCO₃ content averaged over the top first centimeter decreases by up to 6%, while the change in advection calculated at the base of the bioturbated layer (10 cm) is indicative of net erosion. The predicted changes in bottom water chemistry are discussed in terms of their potential impact on benthic communities.

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1. Introduction

[2] The importance of the dissolution of marine carbonate sediments in buffering anthropogenic CO₂ on geologic timescales has long been recognized [e.g., *Broecker and Takahashi*, 1977; *Sundquist*, 1990; *Archer et al.*, 1998; *Archer*, 2005]. The rate of uptake of anthropogenic CO₂ by the world oceans, as well as their maximal capacity for neutralization depends on ocean circulation and the chemistry of the carbonate system. According to *Sundquist* [1990], about 60% of the total buffering of an atmospheric CO₂ perturbation by ocean processes can be attributed to circulation with characteristic timescales between 280 and 570 years. The remaining 40% are assigned to the interaction with carbonate sediments on timescales exceeding 10,000 years. While mostly the long response time associated with carbonate compensation has been considered, it has been overlooked that there exists regionally also a short-term sedimentary dissolution response. This short-term response to changes in bottom water chemistry is the focus of this paper.

[3] Marine carbonate sediments are viewed as a slow reacting reservoir, connected to and interacting with the atmosphere over multiple turnover cycles of the large-scale ocean circulation. The calcium carbonate (CaCO₃) fraction of marine sediments is dominated by hard-shell remains of pelagic organisms. These organisms synthesize two polymorphs of CaCO₃: aragonite (pteropods) and calcite (foraminifera and coccolithophores). The combined effect of increasing pressure and decreasing temperature with depth translates into an increase of CaCO₃ solubility of with depth. Because of its higher solubility [*Mucci*, 1983], aragonite disappears from the sedimentary record at shallower depths than calcite. Accumulation and burial of CaCO₃ is favored in sediments in contact with supersaturated bottom waters. In these sediments, dissolution of CaCO₃ is exclusively induced by the release of CO₂ to the pore waters during organic matter respiration, a process referred to as “metabolic dissolution”. With increasing water depth, the corrosiveness of bottom waters increases until undersaturation is reached. Below this critical depth, the saturation horizon, the dissolution of CaCO₃ is driven by the undersaturation of the bottom waters in addition to metabolic dissolution. A shoaling of the saturation horizon in response to

anthropogenic CO₂ ventilation will expose a larger area of sediments to undersaturated waters. The resulting dissolution of CaCO₃ will contribute to the neutralization of anthropogenic CO₂ by the reaction $\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow 2 \text{HCO}_3^- + \text{Ca}^{2+}$.

[4] The shoaling of the saturation horizon of calcite and aragonite relative to preindustrial depth can already be quantified from global ocean data sets [e.g., *Feely et al.*, 2002; *Chung et al.*, 2003; *Sabine et al.*, 2002]. It goes along with an estimated decrease in average surface ocean pH by 0.1 units [*Brewer*, 1997]. Future projections [*Orr et al.*, 2005] predict large changes in carbonate chemistry under the IPCC “business as usual” scenario which extend well below the sea surface. *Orr et al.* [2005] focus in their discussion on changes in the saturation state with respect to aragonite. Since the aragonite and calcite solubility products are related by a constant factor $K_{\text{sp(arag)}}^*/K_{\text{sp(calc)}}^*$ of 1.5 [*Mucci*, 1983], a shoaling of the aragonite saturation horizon implies an upward migration of the calcite saturation horizon of the same order of magnitude. Thus as the signal of anthropogenic CO₂ penetrates deeper in the oceans, the location and extent of CaCO₃ dissolution will change. The aim of this study is to assess the amplitude of changes in bottom water carbonate chemistry in response an acidification scenario. We asses to potential for and quantify the extent of benthic CaCO₃ dissolution on century timescales. Predicted changes in bottom water chemistry are discussed in terms of their potential impact on benthic deep-sea fauna.

2. Model Description

[5] The biogeochemical model PISCES selected for this study is documented in detail by *Aumont and Bopp* [2006] and *Gehlen et al.* [2006]. It simulates the biogeochemical cycles of oxygen, carbon and of the main nutrients controlling marine phytoplankton growth: nitrate and ammonium, phosphate, silicate and iron. The model distinguishes two phytoplankton size classes nanophytoplankton and diatoms, and two zooplankton size classes which are microzooplankton and mesozooplankton. The production of CaCO₃ (calcite) is assigned to nanophytoplankton as a function of temperature, nutrient and light availability. The particulate detrital pools particulate organic carbon (POC), biogenic silica (BSi) and CaCO₃ are fueled by mortality, aggregation from nanophytoplankton and diatoms, fecal pellet production and grazing.

[6] The fluxes of POC, BSi and CaCO₃ reaching the sediment-water interface are incorporated to the bioturbated sediment layer and undergo early diagenesis as described by *Heinze et al.* [1999]. The model computes the distribution of 4 solid tracers (3 reactive tracers: POC, BSi, CaCO₃, and an inert clay fraction), along with the dissolved species O₂, Si(OH)₄, alkalinity, TCO₂ and NO₃. Particulate organic carbon is mineralized by oxygen reduction and denitrification, the dominant pathways of organic matter breakdown in pelagic sediments. The dissolution of BSi and CaCO₃ in bioturbated sediments is described as by *Heinze et al.* [1999]. The sediment model is restricted to the uppermost 10 cm of the sediment column, which reflects the global mean depth of mixed sediments of 9.8 ± 4.5 cm [*Boudreau*, 1998]. The vertical resolution decreases with depth from 0.3 cm at the sediment-water interface to 2.45 cm at depth. The porosity decreases with depth from 0.95 to 0.75 in line with observations of porosity profiles in marine sediments [e.g., *Ullman and Aller*, 1982]. The model is built on the assumption that at equilibrium accumulation equates deposition minus dissolution [*Archer et al.*, 1993]. It allows for net sediment accumulation if deposition exceeds losses to reaction (dissolution), but also net erosion if dissolution exceeds deposition. In that case the excess of material lost to dissolution is compensated by the inert clay fraction from deeper layers. The capability of the model to take into account net erosion in response to changes in deposition (e.g., shut down of deposition due to changes in ice cover) or bottom water chemistry (e.g., decrease of bottom water saturation state with respect to the CaCO₃ fraction) allows the investigation the impact of anthropogenic CO₂ invasion on surface sediments.

3. Methodology

3.1. Model Spin-up and Initial State

[7] The three-dimensional (3-D) global ocean general circulation model OPA with a horizontal resolution of $2^\circ \times 2^\circ \cos(\text{latitude})$ and 31 vertical layers [*Madec et al.*, 1998] provided the physical forcing fields for off-line tracer transport [*Aumont and Bopp*, 2006]. After 3000 years of integration, PISCES reached a quasi steady state with a mean state and seasonal variations similar to those observed for nutrients and chlorophyll [*Aumont and Bopp*, 2006]. This reference state is the starting point for our study. In order to initialize the sediment compartment, yearly mean fluxes of POC, BSi, CaCO₃ and clay (see *Tegen and Fung*

[1995] for clay deposition) were used together with yearly averaged bottom water compositions to equilibrate surface sediments in an off-line mode. After 50ky of integration, stable distributions of solid and dissolved sediment tracers were obtained. Modeled ocean biogeochemistry including productivity, dissolved properties, particle fluxes and surface sediment composition are fully documented and compared to observations of *Aumont and Bopp* [2006] and *Gehlen et al.* [2006]. Experiment STD3 from *Gehlen et al.* [2006] corresponds to the model configuration used in this study.

3.2. Acidification Scenario

[8] For the acidification experiment, the PISCES water column model and the sediment compartment were interactively coupled. The model was run for an additional 1600 years before the experiment was started. The model experiment was then performed according to the standard CMIP scenario (Coupled Model Intercomparison Project, <http://www-pcmdi.llnl.gov/projects/cmip/index.php>) of atmospheric pCO₂ increasing at a rate of 1% per year from 286 to 1144 ppm over a 140 year time period. In order to isolate the effect of anthropogenic CO₂ invasion and acidification of bottom waters on benthic CaCO₃ dissolution, we kept the circulation field constant and pelagic calcification independent of changes in the calcite saturation state of seawater. The experiment was completed by a control run at constant pCO₂ of 286 ppm.

4. Results and Discussion

4.1. Initial State

[9] Figure 1 compares the average carbonate content expressed in percent dry weight (%CaCO₃) in the bioturbated layer (0–10 cm) of modeled sediments (Figure 1a) to a gridded distribution of core-top %CaCO₃ values by *Archer* [1996] (Figure 1b). The model reproduces the general pattern of the large-scale %CaCO₃ distribution. The %CaCO₃ of marine sediments reflects at first-order carbonate production [e.g., *Milliman*, 1993], water depth and chemistry [e.g., *Archer*, 1996]. The effect of topography is due to the increase of calcite solubility [*Zeebe and Wolf-Gladrow*, 2001] with pressure. Sediments of topographic heights stand out with high %CaCO₃ compared to surrounding deep basins. Typical examples are the Mid-Atlantic Ridge, but also the Indian Ocean Ninety East Ridge surrounded by the Indian Basin to the west and the Wharton Basin to the east.

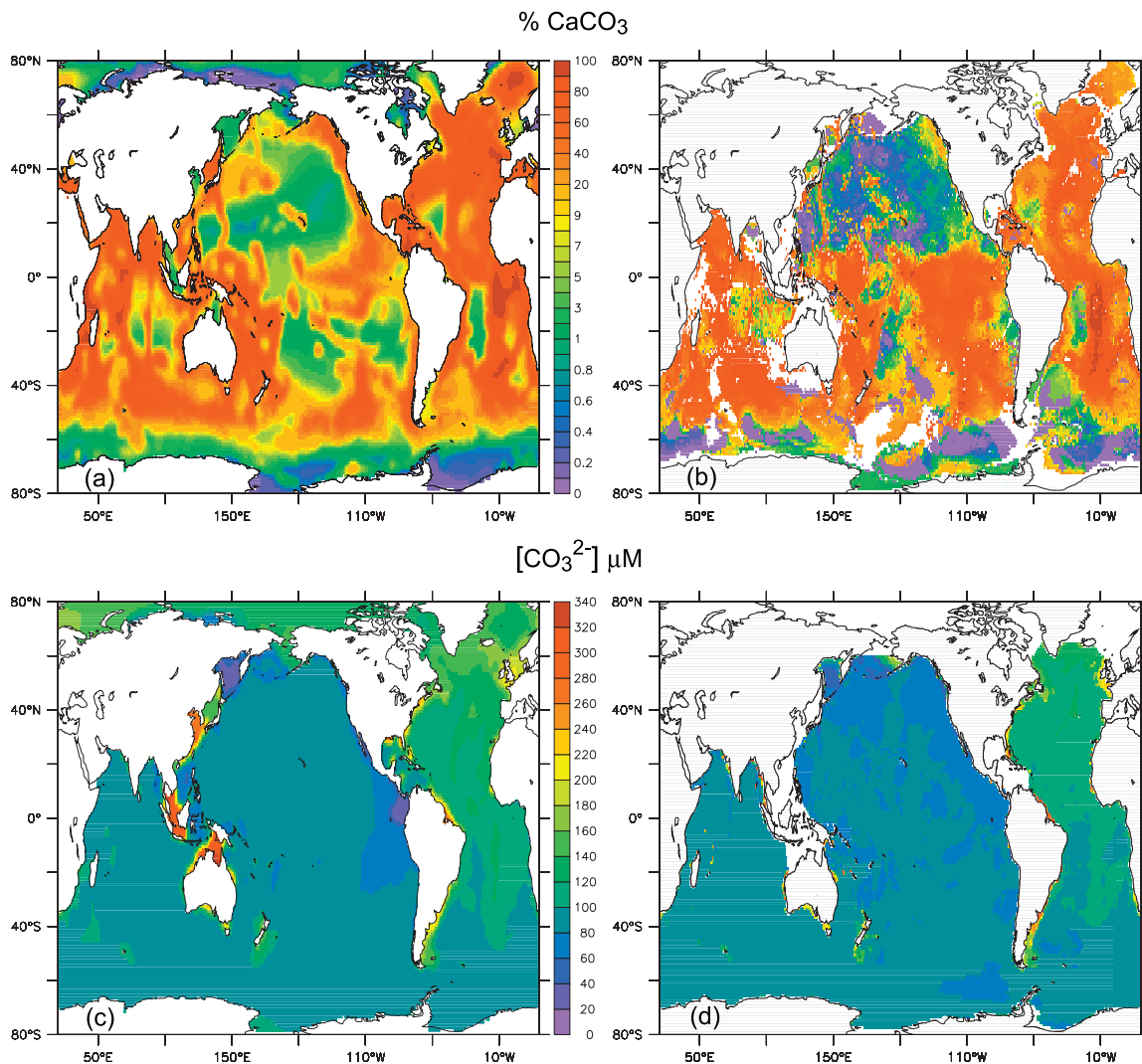


Figure 1. (a) Modeled CaCO₃ content in % dry weight averaged over the bioturbated layer (0–10 cm). (b) Gridded core top CaCO₃ levels in % dry weight after Archer [1996]. (c) Modeled [CO₃²⁻] of bottom waters in μM. (d) Preindustrial [CO₃²⁻] concentration of bottom waters in μM based on GLODAP preindustrial TCO₂ and alkalinity fields [Key *et al.*, 2004].

[10] Bottom water chemistry adds to the effect of topography. Water masses get increasingly enriched in TCO₂ produced by the mineralization of organic matter as they flow along the path of the large-scale meridional overturning circulation. This effect contributes to the contrast between high %CaCO₃ sediments in the North Atlantic and low %CaCO₃ sediments in the North Pacific. The carbonate ion content ([CO₃²⁻]) of model bottom waters (Figure 1c) reflects the evolution of their chemistry. The comparison to a reconstruction of preindustrial [CO₃²⁻] based on the GLODAP data set [Key *et al.*, 2004], reveals that the model overestimates [CO₃²⁻] in the North Atlantic and locally in the Pacific by ≤20 μmol/L. This offset falls within the range of uncertainty of [CO₃²⁻] concentrations computed

from total alkalinity (TALK) and TCO₂ measurements taking into account the associated analytical uncertainty. It should nevertheless be noted that it results in an overestimation of the bottom water saturation state.

[11] In addition to the chemistry of bottom waters, early diagenesis contributes to set the %CaCO₃ content of core top sediments. Oxidic organic matter decay acidifies pore waters and drives CaCO₃ dissolution above the saturation horizon. The relative importance of (1) metabolic CO₂ addition to pore waters by organic matter respiration, (2) the formulation of CaCO₃ dissolution kinetics, (3) the composition of particle rain, and (4) sediment mixing has been reviewed by Archer [1996] and

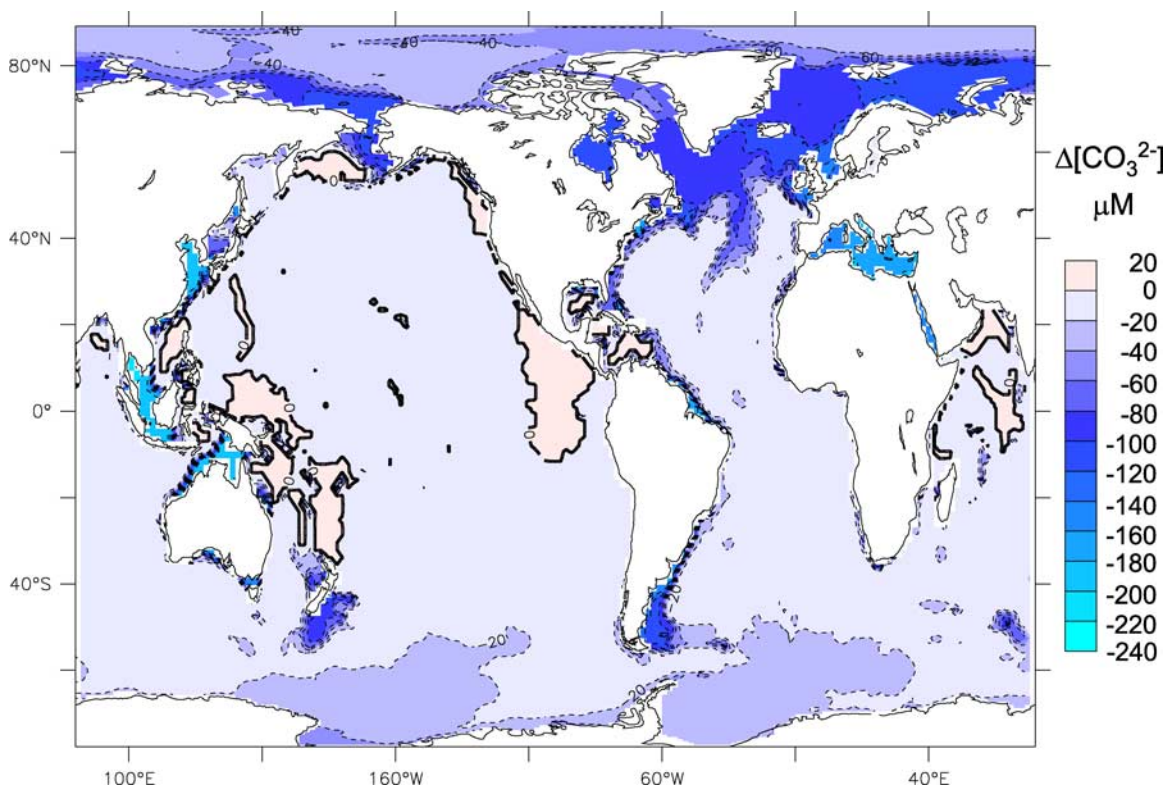


Figure 2. Absolute drift-corrected change in bottom water $[\text{CO}_3^{2-}]$ concentrations between $4 \times \text{CO}_2$ and $1 \times \text{CO}_2$ in μM .

Hales [2003]. Our model includes parameterizations of these processes and reactions [Heinze *et al.*, 1999]. The simulated distribution of %CaCO₃ in the bioturbated layer (Figure 1a) suggests that the primary controls on the CaCO₃ content of top sediments are reproduced by the model.

4.2. Acidification Scenario

[12] Figure 2 displays the drift-corrected change in bottom water carbonate ion concentration ($\Delta[\text{CO}_3^{2-}]_{\text{BW}}$) computed at the end of the simulation compared to the starting conditions. In large areas of the world ocean, $[\text{CO}_3^{2-}]_{\text{BW}}$ changes by $\pm 20 \mu\text{M}$. Areas for which a decrease is predicted largely dominate. At high latitudes, $\Delta[\text{CO}_3^{2-}]_{\text{BW}}$ up to $-100 \mu\text{M}$ are predicted by the model, with maximum values occurring in the North Atlantic and in a band between 30 and 50°S. Large decreases in $[\text{CO}_3^{2-}]_{\text{BW}}$ are associated with deep water formation in the North Atlantic and intermediate and mode water formation in the Southern Hemisphere (30°S to 50°S). These regions correspond to those for which the highest contemporary column inventories of anthropogenic CO₂ were estimated by Sabine *et al.* [2004].

[13] The saturation index with respect to calcite (Ω_c) of bottom waters is shown on Figure 3 at $1 \times \text{pCO}_2$ (Figure 3a) and $4 \times \text{pCO}_2$ (Figure 3b). We express the saturation state of bottom waters as the ratio of the in situ ion concentration product $[\text{CO}_3^{2-}] \times [\text{Ca}^{2+}]$ over the calcite stoichiometric solubility product computed after Mucci [1983] at the prevailing temperature, pressure and salinity. Figure 3 demonstrates a large increase of the seafloor area in contact with undersaturated bottom waters ($\Omega_c < 1$). At the end of our acidification scenario (Figure 3b) the area in contact with undersaturated bottom waters has increased by 58% compared to the situation prevailing at $1 \times \text{pCO}_2$ (Figure 3a). Transects of the calcite saturation state (not shown) computed after 140 years of simulations ($4 \times \text{pCO}_2$) compare qualitatively to the predictions by Orr *et al.* [2005] of an upward migration of the aragonite saturation horizon. As forecasted for aragonite, the largest shoaling is observed at high latitudes, where the calcite saturation horizon is predicted to outcrop around 60°N and 60°S.

[14] The decrease in bottom water calcite saturation state drives the dissolution of benthic CaCO₃ (Figure 4a). Dissolution removes up to 6% CaCO₃

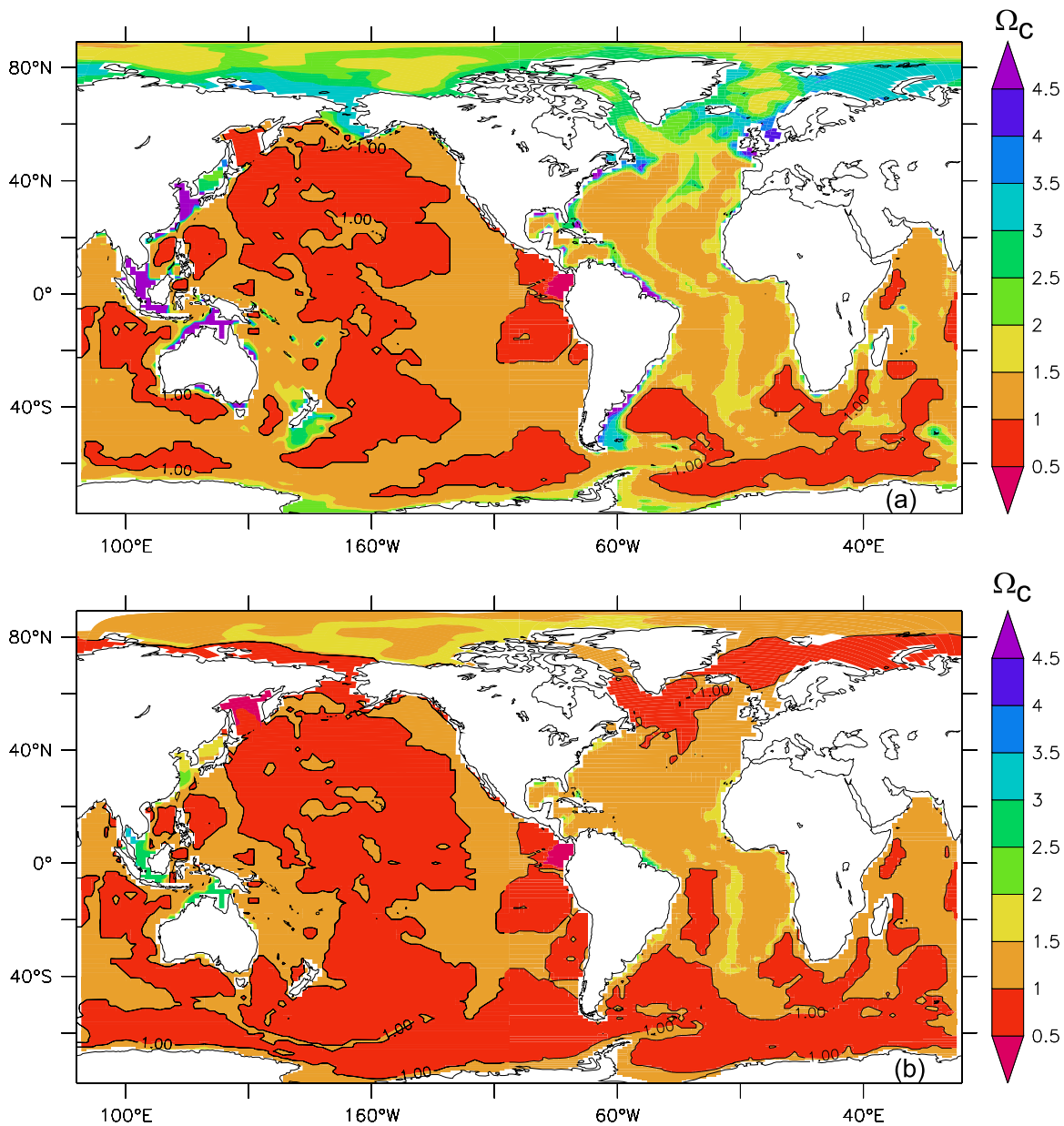


Figure 3. Calcite saturation state (Ω_c) of bottom waters at (a) $1 \times \text{CO}_2$ and (b) $4 \times \text{CO}_2$. Values < 1 indicate undersaturation.

in areas of deep water or intermediate and mode water formation. This large signal translates into a change in advection rate between -0.3 and -1.0 cm/100 years (Figure 4b) computed as the difference between rates at $4 \times \text{CO}_2$ and $1 \times \text{CO}_2$. The advection rate is computed at the lower boundary of the last sediment layer. Negative values indicate a change of direction of advection (positive indicates burial away from sediment-water interface; negative indicates upward movement toward the sediment-water interface). Negative values are indicative of net erosion and suggest that CaCO_3

dissolution affects the entire bioturbated layer (10 cm). In principle, net erosion might result from a change in any of the bulk constituents of modeled sediments taken individually or in combination: biogenic opal, clay, CaCO_3 and particulate organic carbon. The downward flux of particles did however not change over the 140 years of simulation, neither did bottom water concentrations of dissolved Si or O_2 . The carbonate chemistry, however, reacted to the increase of atmospheric pCO_2 . The acidification of water masses reaches the seafloor in areas of subduction of water masses and drives the dissolu-

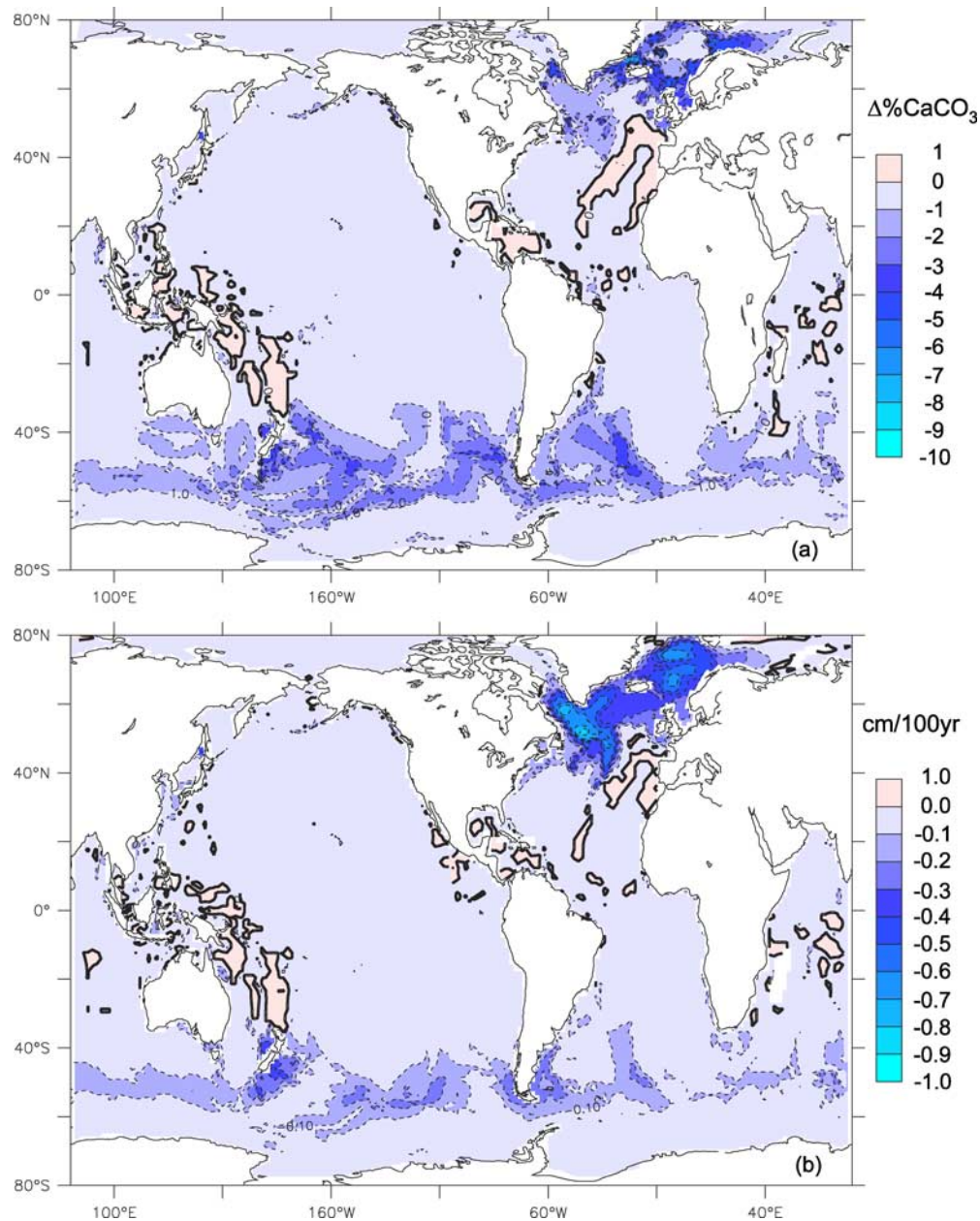


Figure 4. (a) Absolute drift-corrected change in $\% \text{CaCO}_3$ averaged over the top first centimeter: $4 \times \text{CO}_2 - 1 \times \text{CO}_2$; (b) Absolute change in sediment advection rate (cm/100 years) calculated at the base of the bioturbated layer. Negative values indicate net erosion.

tion of benthic CaCO_3 . A significant loss of CaCO_3 is predicted to occur over the time span of our experiment.

4.3. Geochemical Implications of Model Results

[15] The fate of anthropogenic CO_2 on geologic timescales, as well as the role of marine carbonate sediments in its neutralization has been highlighted in the past [e.g., Archer *et al.*, 1997, 1998; Archer,

2005]. In order to address timescales of several 10,000 years, these studies relied on coarse ocean models with a simplified description of ocean biogeochemistry. The impact of a range of emission scenarios and stabilization pathways on ocean chemistry on a 500 year time period was addressed by Caldeira and Wickett [2005] using an ocean general circulation model. In this context, our study contributes the first results of a state-of-the-art biogeochemical model coupled interactively to a sediment compartment. It is set up as a sensitivity

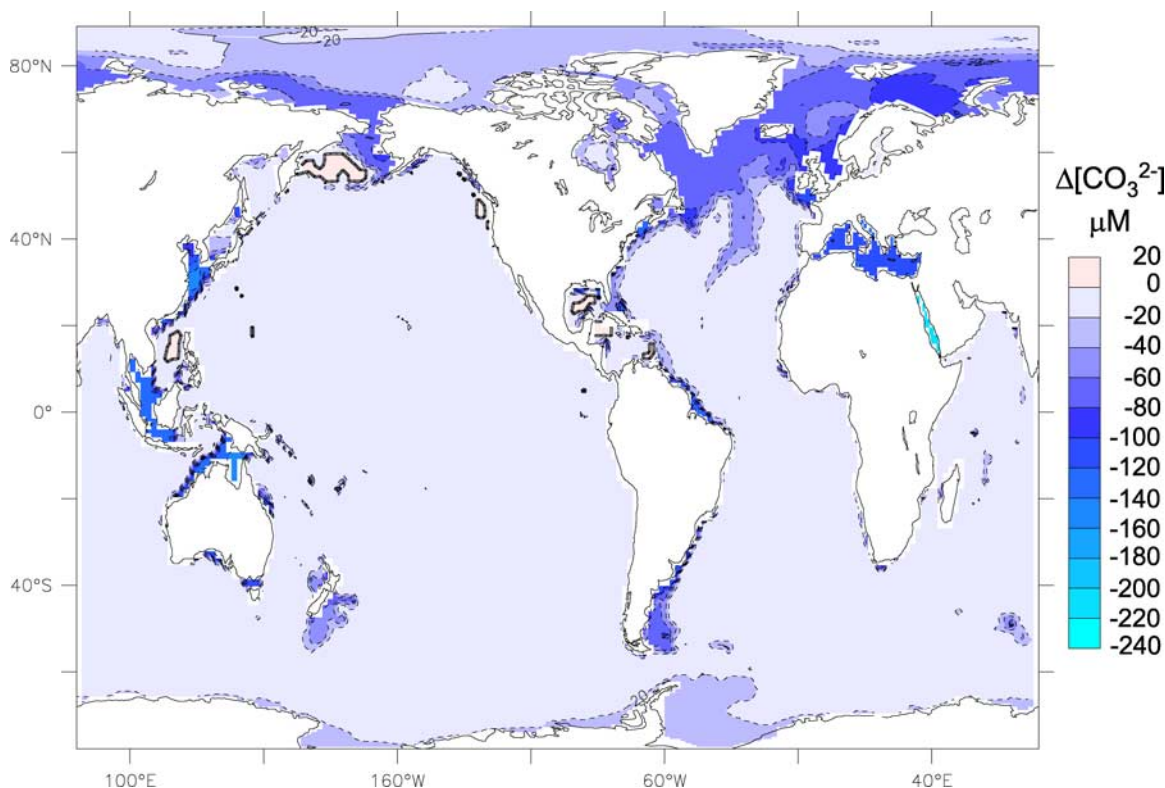


Figure 5. Absolute drift-corrected change in bottom water $[\text{CO}_3^{2-}]$ concentrations between final CO_2 and initial CO_2 in μM computed for the SRESA2 emission scenario.

study assessing the impact of anthropogenic CO_2 uptake by the ocean on bottom water chemistry. We focus on regional changes in bottom water carbonate chemistry occurring on IPCC timescales.

[16] A rate of 1% per year increasing atmospheric CO_2 over 140 years from 286 ppm to 1144 ppm is approximately twice as large as the anthropogenic forcing over the last decades [Keeling and Whorf, 2005]. While the use of the standard CMIP scenario is justified within the context of a sensitivity study, it raises the question of the representativeness of our results in terms of future changes in ocean chemistry. High computational costs are a drawback from using a model with a higher resolution and preclude at present repeating the model experiment with varying forcing conditions. Alternatively, we analyzed changes in bottom water $[\text{CO}_3^{2-}]$ computed for the IPCC emission scenario SRESA2 (Figure 5) using the same constant off-line forcing of PISCES derived from the OPA general circulation model, but without a sediment compartment. In this particular scenario, pCO_2 increases from 286 ppm to 836 ppm over a time span of 240 years (historical period: (1860 to 2000) + time span of SRESA2 pathway (2000 to 2100)). The comparison between Figure 2 which displays

changes in bottom water $[\text{CO}_3^{2-}]_{\text{BW}}$ computed for the CMIP forcing, and Figure 5 reveals a consistent pattern. In both simulations largest decreases in $[\text{CO}_3^{2-}]_{\text{BW}}$ are associated with deep water formation in the North Atlantic. They are of the same order of magnitude. The latter holds also for $\Delta[\text{CO}_3^{2-}]_{\text{BW}}$ computed for Southern Hemisphere areas of intermediate and mode water formation. The signal spreads however over a larger area in the case of a forcing by 1% per year increasing atmospheric CO_2 (CMIP). The lower rate of increase of atmospheric CO_2 in the SRESA2 pathway combined to the longer duration result in changes in bottom water carbonate chemistry that a comparable to results of the CMIP scenario. The acidification of bottom waters in areas of deep water formation appears thus as a robust feature driving the dissolution of benthic CaCO_3 on IPCC timescales. Both simulations were however executed assuming constant ocean circulation. We expect that changes in bottom water chemistry will be sensitive to the response of deep water formation to climate change.

[17] The geochemical effect of benthic CaCO_3 dissolution is to increase the buffer capacity of ocean waters. The overall change in alkalinity

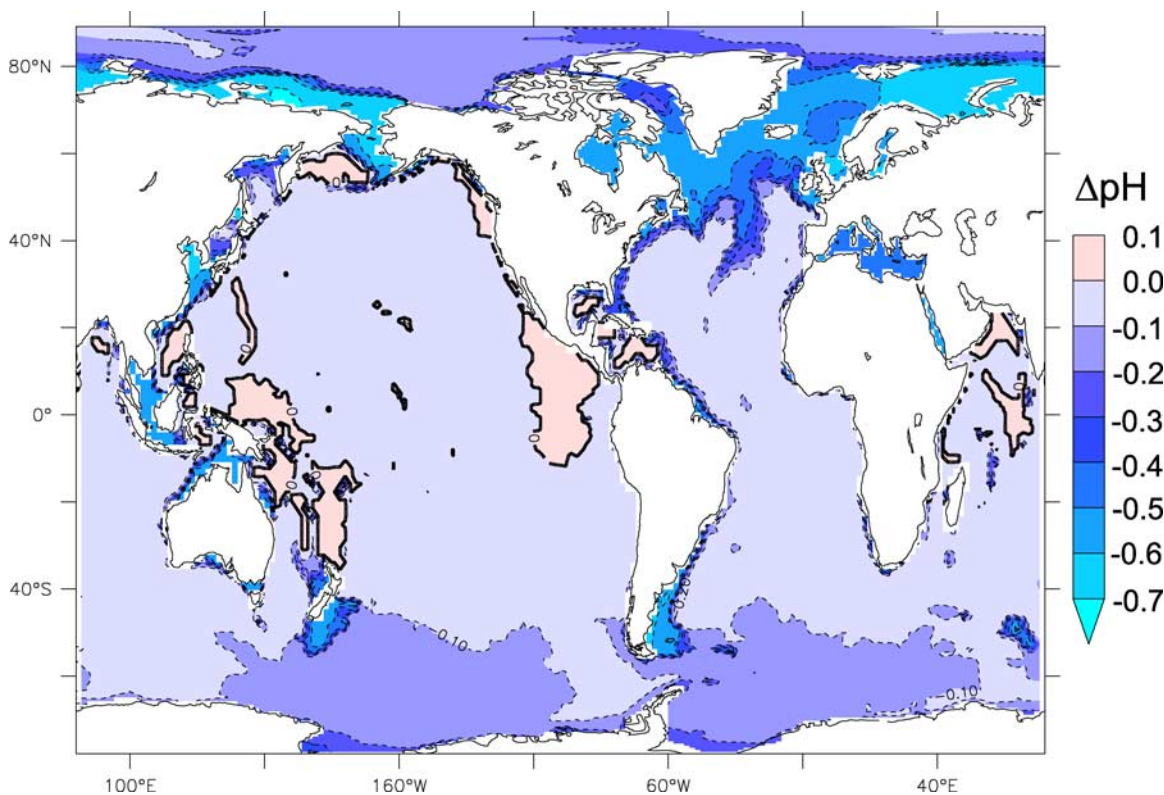


Figure 6. Absolute drift-corrected change in pH at the sediment-water interface (sediment layer 0–3 mm) between $4 \times \text{CO}_2$ and $1 \times \text{CO}_2$ in μM .

predicted by the model is however too small to be detected as a build-up in bottom water concentration in the model owing to the coarse resolution of the grid in the deep ocean (500 m). The increase in alkalinity will ultimately feed-back on atmospheric CO_2 on the timescale of the thermohaline circulation [Archer, 2005]. While our study does not modify our understanding of the timescales involved in neutralizing anthropogenic CO_2 by ocean uptake and interaction with carbonate sediments, it highlights the potential for drastic changes in bottom water chemistry on IPCC timescales.

4.4. Biological Implications of Model Results

[18] Potential impacts on benthic biota have been reviewed recently in comprehensive reports addressing ocean acidification [e.g., Royal Society, 2005; Haugan et al., 2006; Kleypas et al., 2006]. Today there is little experimental evidence to document the effects of CO_2 on benthic community with most studies focusing on shallow water biota [e.g., Shirayama and Thornton, 2005; Turley et al., 2006]. In contrast to shallow water benthic organisms which are adapted to a highly dynamic

environment with large changes in temperature and water chemistry, the deep benthos has evolved in a rather stable environmental setting [Childress and Seibel, 1998]. Past studies of the physiology of deep sea organisms have highlighted several particularities that combine to make deep sea biota highly sensitive to even moderate changes in pH (refer to Seibel and Walsh [2001] for an in depth discussion). Experimental studies of the effects of exposure of benthic organisms to elevated CO_2 were conducted as part of the evaluation of impacts of deep sea CO_2 sequestration [Shirayama, 1998; Seibel and Walsh, 2003; Barry et al., 2004; Carman et al., 2004; Barry et al., 2005; Thistle et al., 2005]. While the pH excursion during these experiments are often much greater and occur on shorter timescales than pH changes predicted by our model scenario (Figure 6), a careful analysis of experimental results provides a first insight in the sensitivity of deep sea organisms. This approach was taken by Barry et al. [2005], who reported a lower survival of meiofauna after exposure to pH levels ~ 0.2 units lower than normal. We computed pH changes at the sediment-water interface ≥ 0.2 units below initial values at the end of the acidification scenario in the North Atlantic. These values sug-

gest that meiofauna in these areas is likely to experience the detrimental effects of pH over the coming 2 centuries.

[19] The saturation state with respect to calcite (Figure 3) decreases with the acidification of bottom waters in areas of deep water formation. Calcifying organisms such as benthic foraminifera are expected to be sensitive to the saturation state of bottom waters. A dependency of calcification on [CO₃²⁻] has been recognized for planktonic foraminifera [Bijma *et al.*, 1999]. It is unlikely that communities of calcifying benthic foraminifera will be maintained in areas of undersaturated bottom waters. We expect a progressive replacement of the latter by agglutinated species.

[20] Our model sensitivity study highlights the potential for changes in bottom water carbonate chemistry in response to an acidification scenario of magnitude sufficient to trigger changes in benthic communities. While we use available experimental data to back up our conclusions, the cascading effects on deep sea ecosystems remain undocumented.

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