

## Detection and projection of carbonate dissolution in the water column and deep-sea sediments due to ocean acidification

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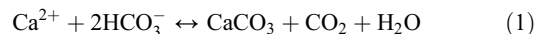
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[1] Dissolution of fossil fuel CO<sub>2</sub> in seawater results in decreasing carbonate ion concentration and lowering of seawater pH with likely negative impacts for many marine organisms. We project detectable changes in carbonate dissolution and evaluate their potential to mitigate atmospheric CO<sub>2</sub> and ocean acidification with a global biogeochemistry model HAMOCC forced by different CO<sub>2</sub> emission scenarios. Our results suggest that as the anthropogenic CO<sub>2</sub> signal penetrates into ocean interior, the saturation state of carbonate minerals will drop drastically – with undersaturation extending from the ocean floor up to 100–150 m depth in the next century. This will induce massive dissolution of CaCO<sub>3</sub> in the water column as well as the sediment, increasing the Total Alkalinity (TA) by up to 180 μmol kg<sup>-1</sup> at the surface and in the ocean interior over the next 2500 years. Model results indicate an inhomogeneous response among different ocean basins: Atlantic carbonate chemistry responds faster and starts recovering two millennia after CO<sub>2</sub> emissions cease, which is not the case in the Pacific. CaCO<sub>3</sub> rain stops in the Pacific Ocean around 2230. Using an observation-derived detection threshold for TA, we project detectable dissolution-driven changes only by the year 2070 in the surface ocean and after 2230 and 2500 in the deep Atlantic and Pacific respectively. We show that different model assumptions regarding dissolution and calcification rates have little impact on future projections. Instead, anthropogenic CO<sub>2</sub> emissions overwhelmingly control the degree of perturbation in ocean chemistry. In conclusion, ocean carbonate dissolution has insignificant potential in mitigating atmospheric CO<sub>2</sub> and ocean acidification in the next millennia. **Citation:** Ilyina, T., and R. E. Zeebe (2012), Detection and projection of carbonate dissolution in the water column and deep-sea sediments due to ocean acidification, *Geophys. Res. Lett.*, 39, L06606, doi:10.1029/2012GL051272.

### 1. Introduction

[2] Ocean acidification as a result of seawater invasion by anthropogenic CO<sub>2</sub> has already reduced the pH by 0.1 units and decreased carbonate ion concentrations [Intergovernmental Panel on Climate Change (IPCC), 2007]. Reduction in saturation state of ocean waters with respect to carbonate minerals such as calcite and aragonite on a short time scale is likely to have potentially negative effects on many pelagic calcareous organisms (as summarized by Gattuso and Hansson [2011]). On longer time

scales, as anthropogenic CO<sub>2</sub> penetrates into the subsurface ocean, it will be neutralized by dissolution of carbonates in the water column and in the sediments, thereby mitigating atmospheric CO<sub>2</sub> and ocean acidification [e.g., Broecker and Takahashi, 1977]. In fact, previous studies, e.g., by Sundquist [1990], Archer *et al.* [1997] and Ridgwell and Hargreaves [2007] show that given enough time (i.e., a few millennia), deep-sea carbonate sediments have the potential to remove up to 80% of anthropogenic CO<sub>2</sub>. If carbonate dissolution will counteract ocean acidification and mitigate atmospheric CO<sub>2</sub>, can we detect dissolution in observations and if so, when? Shifts in carbonate dissolution can be detected via changes in the vertical distribution of total alkalinity (TA) in seawater: TA is consumed during production (equation (1); forward reaction) and released during dissolution (CO<sub>2</sub> neutralization given by backward reaction in equation (1)) of calcium carbonate (CaCO<sub>3</sub>).



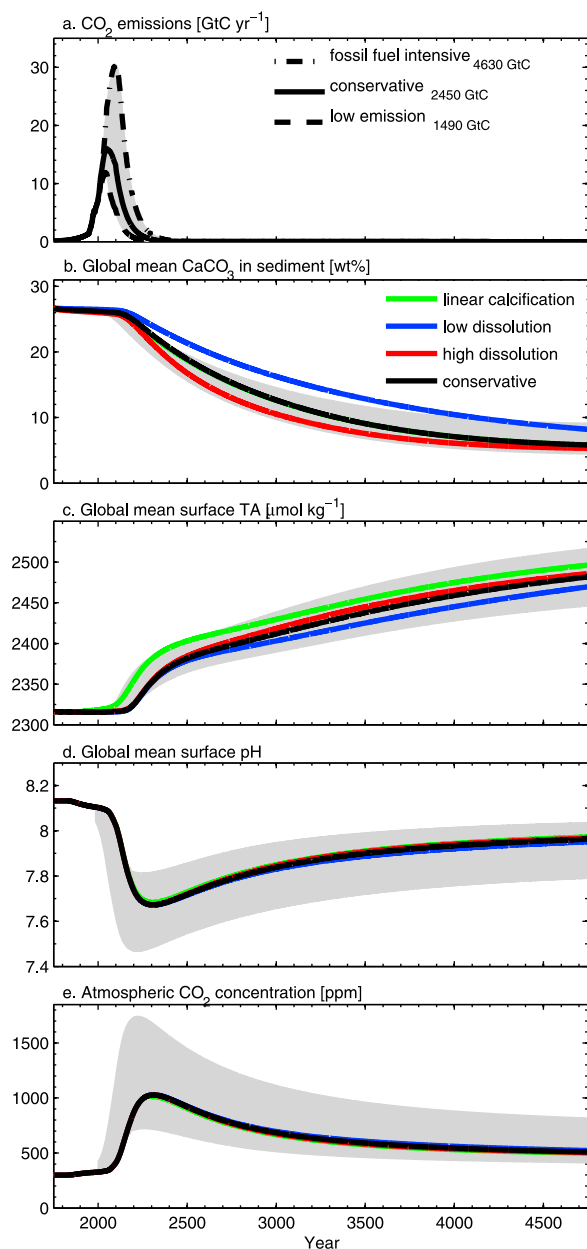
Taking into account the natural variability in ocean TA derived from observations in a previous study [Ilyina *et al.*, 2009], we project time-scales of detectable changes in ocean chemistry due to fossil fuel neutralization by carbonate dissolution using the global biogeochemical model HAMOCC. The rates of carbonate dissolution are immeasurable on the global scale and previous experimental- and model-based studies [e.g., Hales and Emerson, 1997; Archer *et al.*, 1998; Heinze *et al.*, 1999; Gehlen *et al.*, 2005; Ridgwell *et al.*, 2007; Zeebe, 2007; Andersson *et al.*, 2003] suggest both first order and higher order dissolution kinetics. Therefore, another question is how robust are model projections of future ocean acidification? We address this question by running model scenarios with different assumptions for carbonate dissolution rates and CO<sub>2</sub> emission pathways. Note that our model projections do not include potential climate feedbacks on ocean circulation and carbon cycle [IPCC, 2007], nor can they consider processes that are not included in the model, e.g., CaCO<sub>3</sub> ballasting of organic matter [Klaas and Archer, 2002]. Here we compare the differences in ocean carbonate chemistry projections over the next millennia simulated in different dissolution and emission scenarios.

### 2. Global Ocean Biogeochemical Model and Model Scenarios

[3] The global ocean biogeochemistry model HAMOCC (Hamburg Model of Ocean Carbon Cycle) simulates inorganic carbon chemistry (given by Maier-Reimer and Hasselmann [1987]) and ecosystem dynamics (following Six and Maier-Reimer [1996]) in the water column and upper sediments (described by Heinze *et al.* [1999]). The carbonate system is given by two prognostic variables – TA

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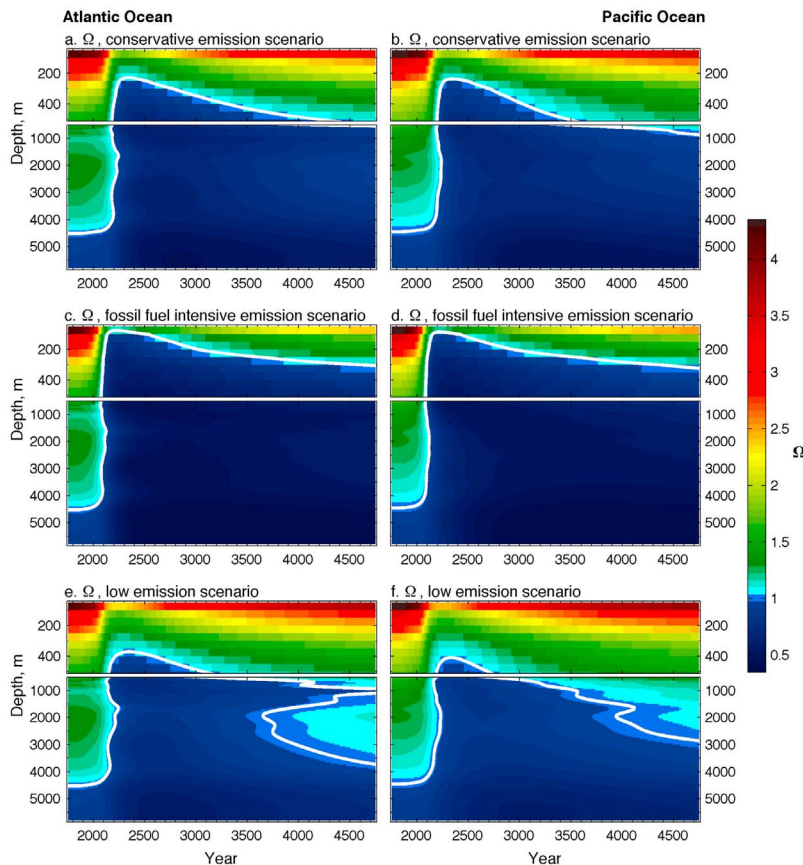
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**Figure 1.** (a) Fossil fuel  $\text{CO}_2$  emissions under three scenarios with cumulative amount of carbon emitted over the simulation period given for each scenario line. Temporal evolution of (b) wt% of  $\text{CaCO}_3$  content in sediment, (c) global surface TA, (d) global surface seawater pH, and (e) atmospheric  $\text{CO}_2$  were calculated under the conservative emissions (black), linear dependence of calcification on the saturation state  $\Omega$  (green), low (halved) and high (doubled) dissolution rates (blue and red lines respectively). The grey-shaded area brackets the range of the change calculated in the different emission scenarios shown in Figure 1a: upper border in Figures 1b and 1d corresponds to low emission scenario, lower to fossil fuel intensive scenario. Reversed in Figures 1c and 1e – upper range is fossil fuel intensive scenario, lower is low emission scenario.

and dissolved inorganic carbon ( $\text{TCO}_2$ ), with other components treated diagnostically. TA in the model is the sum of carbonate, borate alkalinity, and water dissociation products. Carbonate alkalinity is altered during production and dissolution of  $\text{CaCO}_3$  according to equation (1). Only calcite is considered in the model. Parameterization of the dissolution of  $\text{CaCO}_3$  (backward reaction given in equation (1)) in the water column and sediment is conceptually similar to approaches used in other studies [e.g., Archer *et al.*, 1998; Andersson *et al.*, 2003; Zeebe, 2007] with a different numerical formulation (see Heinze *et al.* [1999] for detailed description). Dissolution is a function of the carbonate ion  $\text{CO}_3^{2-}$  and the calcium ion  $\text{Ca}^{2+}$  concentrations, as well as temperature and pressure dependent stoichiometric constant  $K_{\text{sp}}^*$ , and is driven by the deviation from the saturation state:  $\Omega = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]/K_{\text{sp}}^*$ . Biogenic calcite particles, produced in the euphotic zone, precipitate if seawater is supersaturated with respect to  $\text{CaCO}_3$  (i.e.,  $\Omega > 1$ ) and start dissolving if the water column or the sediment pore-water is undersaturated with respect to  $\text{CaCO}_3$  (i.e.,  $\Omega < 1$ ). At every integration time step, a maximum dissolvable amount of  $\text{CaCO}_3$  is brought into solution in seawater (water column dissolution) or pore-water (sediment dissolution). Dissolution-driven changes in  $\text{CaCO}_3$  content are determined by the degree of carbonate undersaturation  $U_{\text{CO}_3^{2-}} = \max(0, [\text{CO}_3^{2-}]_{\text{sat}} - [\text{CO}_3^{2-}])$  multiplied by a dissolution rate constant  $r_{\text{CaCO}_3}^{\text{sed}}$  or  $r_{\text{CaCO}_3}^{\text{water}}$  in sediment or seawater respectively and an in-situ  $\text{CaCO}_3$  concentration. Values of  $r_{\text{CaCO}_3}^{\text{sed}}$  and  $r_{\text{CaCO}_3}^{\text{water}}$  being  $0.012 \text{ year}^{-1}$  and  $0.455 \text{ year}^{-1}$  are chosen to reproduce the water column and sedimentary calcite in accordance with the exponential e-folding depth formulation as used by Heinze *et al.* [1999];  $[\text{CO}_3^{2-}]_{\text{sat}}$  is the carbonate ion concentration at saturation. All model tracers are transported by a flow field provided by the Large-Scale Geostrophic Ocean General Circulation Model [Maier-Reimer *et al.*, 1993] tuned to represent the modern ocean. The flow field remained invariant over the simulation period. The model uses a relatively coarse horizontal discretization of about 3.5 degrees and has 22 vertical layers of varying depth (25 m in the surface layers and up to 700 m in the deep ocean). Such assumptions permit time-efficient long-term simulations in which we start the model runs in the preindustrial steady state and run it for about 3000 years into the future. Model results were evaluated in earlier studies [e.g., Ilyina *et al.*, 2009; Six and Maier-Reimer, 1996] and showed good agreement with the observed present day ocean chemistry.

[4] We ran three groups of model scenarios. In the first group, different fossil fuel  $\text{CO}_2$  emissions have been prescribed. Emissions of anthropogenic  $\text{CO}_2$  used to force the model followed historic fossil fuel emissions and the IPCC scenarios until the year 2100 [IPCC, 2007]. Model calculations have been performed under three different IPCC scenarios: the A1B scenario, referred to as conservative, a low emission scenario B1, and a fossil fuel intensive scenario A1FI (Figure 1a). After the year 2100,  $\text{CO}_2$  emissions gradually declined following a logistic function. As a result, cumulative carbon emissions over the simulation period are about 4600 GtC in the fossil fuel intensive scenario, 2450 GtC under the conservative scenario, and about 1500 GtC in the low emission scenario. In the second scenario group, we evaluated the effect of changes in  $\text{CaCO}_3$  production. We ran a linear calcification scenario, in which  $\text{CaCO}_3$



**Figure 2.** Temporal evolution of the basin averaged vertical profile of the saturation state of calcite ( $\Omega$ ) averaged over the (a, c, e) Atlantic and (b, d, f) Pacific basins for the three  $\text{CO}_2$  emission scenarios. White color represents  $\Omega = 1$  which serves as a threshold for dissolution or precipitation of  $\text{CaCO}_3$  in the model. Note the different vertical axes for the upper 500 m and below.

production decreases with the saturation state as described by *Ilyina et al.* [2009]. In all other scenarios, it was independent of  $\Omega$  following the constant calcification scenario. The third group of scenarios aims at studying the effect of model parameters on carbonate dissolution. First, either carbonate dissolution in the sediment or in the water column was switched off in order to separately estimate the contribution of these two processes to TA changes. Finally, the efficiency of carbonate dissolution kinetics has been tested in the scenarios, in which the dissolution rate was doubled ( $2 \times r_{\text{CaCO}_3}^{\text{sed}}$ ; high dissolution scenario) or halved ( $0.5 \times r_{\text{CaCO}_3}^{\text{sed}}$ ; low dissolution scenario). These scenarios ran with conservative emissions and constant calcification.

### 3. Changes in Subsurface Carbonate Chemistry in Response to Anthropogenic $\text{CO}_2$ Invasion

[5] In line with previous long-term modeling studies [e.g., *Archer et al.*, 1998; *Caldeira and Wickett*, 2003; *Boudreau et al.*, 2010; *Ridgwell and Hargreaves*, 2007], our results show that ongoing fossil fuel  $\text{CO}_2$  emissions will perturb ocean carbonate chemistry for many millennia to come. The saturation state of calcite ( $\Omega$ ) decreases significantly in all emission scenarios compared to the preindustrial state throughout the simulation period (Figure 2). The saturation state continues to decrease long after the peak in  $\text{CO}_2$

emissions had been reached. On average, the global surface ocean remains supersaturated with respect to calcite throughout the 3000 years of simulation regardless of the emission scenario. Undersaturation of ocean surface waters occurs locally in high latitudes. Recent observations [*Feely et al.*, 2008] found waters with low  $\Omega$  values in the surface ocean in regions of coastal upwelling. The Atlantic Ocean basin responds somewhat earlier than the Pacific due to faster penetration of anthropogenic  $\text{CO}_2$  into the deep Atlantic Ocean. The subsurface ocean at depths below about 250–300 m becomes undersaturated with respect to calcite ( $\Omega < 1$ ) by the year 2260 in the Atlantic Ocean and by the year 2275 in the Pacific Ocean (Figures 2a and 2b) responding to the 2450 GtC emitted under the business as usual scenario. Emission of >4600 GtC into the atmosphere in the fossil fuel intensive scenario (Figures 2c and 2d) drives the saturation horizon (i.e.,  $\Omega = 1$ ) to about 100 m depth in the Atlantic and Pacific Ocean already by the years 2150 and 2190, respectively. Ocean waters remain undersaturated with respect to calcite at depths of 400–500 m in the low emission scenario after the years 2220 and 2270 in the Atlantic and Pacific respectively (Figures 2e and 2f). Ultimately,  $\Omega$  starts to increase while approaching a new steady state in all scenarios. Our model projections indicate that as a result of ocean acidification, the ocean at depths below about 100–600 m depending on the emission

scenario, will stay largely undersaturated over the next millennia, promoting dissolution of carbonate in the water column and in the sediments.

[6] Biogenic  $\text{CaCO}_3$  produced in the upper ocean slowly rains to the bottom and in supersaturated conditions (i.e.,  $\Omega > 1$ ) it forms a standing stock of calcite in the water column (not shown). Water column dissolution (where  $\Omega < 1$ ) depletes this  $\text{CaCO}_3$  inventory so that only about 80% and 36% reaches the sediment in the modern Atlantic and Pacific Ocean, respectively. As ocean acidification continues, seawater becomes undersaturated with respect to  $\text{CaCO}_3$  (Figure 2) and the water column inventory is dissolved almost entirely. Our projections indicate no calcite rain after the year 2230 in the Pacific Ocean. In the Atlantic Ocean basin, only 1% of the produced  $\text{CaCO}_3$  will reach the sediment. The  $\text{CaCO}_3$  inventory starts to recover about 1,000 years after the peak in  $\text{CO}_2$  emissions, but does not reach its preindustrial distribution in the course of the simulation period because corrosive conditions still persist in the water column.

[7] In addition to enhanced dissolution in the water column, production of  $\text{CaCO}_3$  by calcifying organisms is likely to change due to ocean acidification. Laboratory and mesocosm studies predict a wide range of responses in different pelagic organisms to changes in carbonate chemistry, with a prevailing decrease in calcification (as summarized by *Riebesell and Tortell* [2011]). In a previous study [*Ilyina et al.*, 2009] we showed that given a linear dependence of calcification on  $\Omega$ , pelagic production of  $\text{CaCO}_3$  drops by about 65% by the year 2100. As indicated by previous studies [i.e., *Boudreau et al.*, 2010], shoaling of the saturation horizon during this century might occur faster than prospective changes in calcification. However, as the water column is corrosive to calcite after the year  $\sim 2070$  (cf. conservative scenario in Figures 2a and 2b), potential changes in production will only have marginal effects ( $< 1\%$ ) for future water column and sediment  $\text{CaCO}_3$  inventories. Thus model assumption regarding calcification will most likely be irrelevant for future projections of carbonate chemistry and atmospheric  $\text{CO}_2$  on longer time scales [*Ridgwell et al.*, 2007]. The sediment inventory of  $\text{CaCO}_3$  (Figure 1b) responds slower to perturbations in seawater carbonate chemistry with the Atlantic basin being somewhat faster than the Pacific Ocean. In accordance with the general circulation pattern, carbonate content in the Atlantic sediments starts to decline already in the year 2150 – about 300 years earlier than in the Pacific Ocean (not shown). Atlantic sediments regain their carbonate content in the shallower regions after having reached its minimum about 2 millennia later, whereas a downward trend remains on average for the whole basin. Pacific sediments lose their carbonates continuously from the year 2470 onwards. Sedimentary carbonates continue to decrease after the water column starts to restore its  $\text{CaCO}_3$  inventory without an indication of a new steady-state even 2.5 millennia after the emissions have ceased.

#### 4. Total Alkalinity as a Tracer for Changes in Carbonate Dissolution

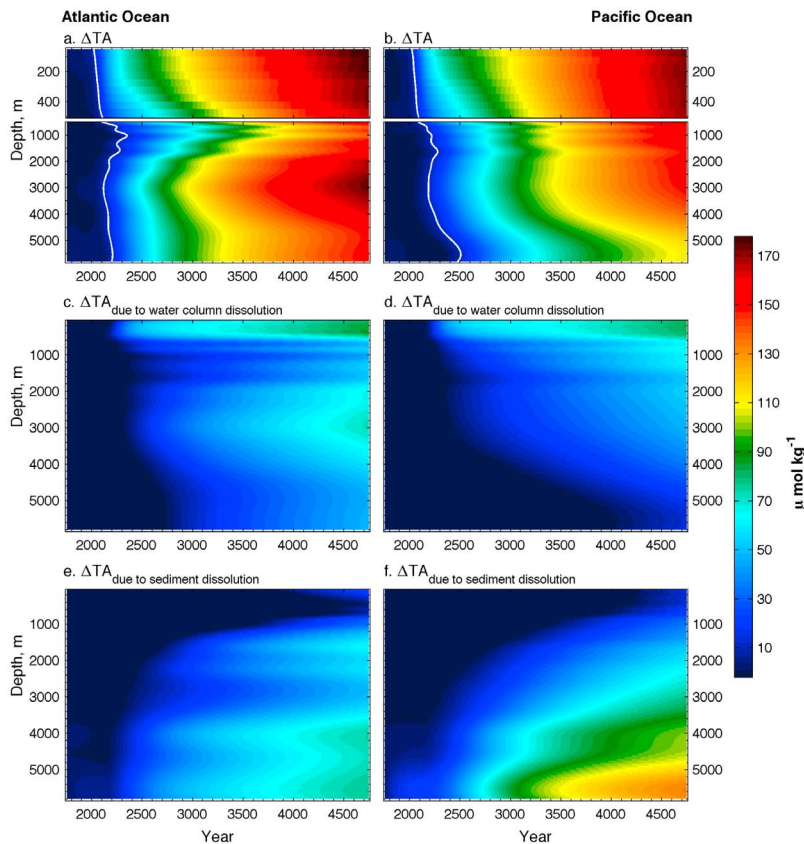
[8] Dissolution and production of  $\text{CaCO}_3$  result in the following changes in seawater carbonate chemistry:

Production by pelagic calcifiers decreases TA and  $\text{TCO}_2$ , whereas carbonate dissolution increases TA and  $\text{TCO}_2$  in a ratio 2:1. In the modern ocean, biogenically produced  $\text{CaCO}_3$  in the supersaturated surface waters can seasonally deplete TA by about  $25\text{--}30 \mu\text{mol kg}^{-1}$  [*Bates et al.*, 1996]. In the deep ocean, the TA budget is conserved by  $\text{CaCO}_3$  precipitation and dissolution. Thus, any shift in dissolution regime and thereby in carbonate chemistry due to ocean acidification — which is otherwise immeasurable on the global scale — can be detected through changes in TA. Our model simulation show that future changes will be accompanied by massive dissolution of carbonate both in the water column and in the sediments. As a result, global mean surface TA will increase by up to  $180 \mu\text{mol kg}^{-1}$  by year 4500 compared to its (annually averaged) preindustrial value (Figure 1c). TA increases continuously until the end of the simulation period, even after  $\Omega$  and the water column  $\text{CaCO}_3$  stock start to recover. Changes in TA driven by dissolution are of the same magnitude in the Atlantic and Pacific basins (Figures 3a and 3b). The earliest changes are projected to occur in the Atlantic Ocean consistent with a faster response to fossil fuel  $\text{CO}_2$  invasion (cf.  $\Omega$  in Figure 2). Additionally, there are large deposits of carbonate sediments in the North Atlantic at depths of about 3000 m which start to dissolve and thereby increase the TA with only a short time lag compared to the surface ocean.

[9] In a previous study [*Ilyina et al.*, 2009], we gave a detection threshold for changes in calcification that are statistically significant in terms of alkalinity of  $\Delta\text{TA} = \pm 9.8 \mu\text{mol kg}^{-1}$ , based on a simple statistical analysis of the available observational data. Application of this detection threshold to  $\Delta\text{TA}$  calculated here suggests that changes in TA due to carbonate dissolution in the water column and in the sediment will not be detectable in observations before the year 2250 in the deep Atlantic (Figure 3a) and in the year 2500 in the deep Pacific Ocean (Figure 3b) under a conservative emission scenario. In the surface waters of both basins, detectable changes in TA are projected already in the current century. Our previous calculations showed that reductions in pelagic calcification alone are responsible for about  $50 \mu\text{mol kg}^{-1}$  increase in TA in the surface ocean by the year 2100 [*Ilyina et al.*, 2009]. Contribution of carbonate dissolution in TA changes by the year 2100 is about  $20 \mu\text{mol kg}^{-1}$ . Further in time, the dissolution-driven  $\Delta\text{TA}$  exceeds the one driven by changes in calcification by more than a factor of three being insensible to assumptions regarding future changes in  $\text{CaCO}_3$  production (not shown).

[10] Both carbonate dissolution in the water column and in the sediment contribute to the projected increase in TA. In order to separate the contribution of these two dissolution processes, we ran two further model scenarios. In one scenario, the sediment dissolution has been disabled (Figures 3c and 3d). In the other, the water column dissolution has been switched off (Figures 3e and 3f). All other model parameters and assumptions remained unchanged. Note that switching off the water column dissolution will affect the sediment processes and vice versa so that such partitioning scenarios provide only a qualitative insight into the role of the two dissolution mechanisms. On the timescale of a few hundred years, contribution of water column dissolution is largest in the upper ocean, whereas sediment dissolution controls the deep  $\Delta\text{TA}$ . On millennial timescales, however, both





**Figure 3.** Temporal evolution of basin averaged vertical distribution of changes in TA calculated as the difference between the in-situ and the preindustrial values in the (left) Atlantic and (right) Pacific Ocean modeled under conservative emission scenario using constant calcification rates shown on different vertical axes for the upper 500 m and below. (a, b)  $\Delta\text{TA}$  due to carbonate dissolution in the water column and the sediment; (c, d)  $\Delta\text{TA}$  due to water column dissolution only; (e, f)  $\Delta\text{TA}$  due to sediment dissolution only.

processes are equally responsible for changes in TA in the subsurface ocean.

### 5. Relevance of Model Parameters Versus the $\text{CO}_2$ Emission Pathways

[11] Increased oceanic TA due to dissolution promotes the uptake of atmospheric  $\text{CO}_2$  and on longer time scales will contribute to natural carbon sequestration [Broecker and Peng, 1982; Sundquist, 1990; Archer et al., 1997; Ridgwell and Hargreaves, 2007]. Enhanced dissolution driven by fossil fuel neutralization (equation (1)) will ultimately increase the seawater pH, thereby mitigating the impacts of ocean acidification. We have shown that given the large fossil fuel  $\text{CO}_2$  emissions, model parameters will play a minor role in projecting the future efficiency of carbonates to neutralize fossil fuel  $\text{CO}_2$  and buffer ocean acidification. We have tested the influence of model parameters by running scenarios with halved (low dissolution) or doubled (high dissolution) carbonate dissolution rate and compared them to the “unperturbed” conservative emissions scenario. The production rate of  $\text{CaCO}_3$  in these scenarios did not change with time in contrast to the scenario with linear dependency of calcification on  $\Omega$ .

[12] Sediment content of  $\text{CaCO}_3$  (Figure 1b) declines significantly in response to fossil fuel  $\text{CO}_2$  invasion.

Temporal evolution of carbonate dissolution varies throughout the next millennia in different model setups. Carbonate sediment content is projected to drop from about 27 wt% (globally averaged estimate) to 5 wt% in the conservative, fossil fuel intensive, and high dissolution scenarios. In the low dissolution and the low emission scenarios, carbonate depletion progresses somewhat slower, but ultimately drops to about 8 wt%. On longer time scales (i.e., >2500 years), it is less sensitive to assumptions regarding dissolution kinetics than to the amount of  $\text{CO}_2$  emitted, which is consistent with the results of Archer et al. [1998]. The difference between the dissolution scenarios decreases with time, whereas the difference between the low emission and the fossil fuel intensive scenarios remains the same. Likewise, surface TA is practically insensitive to the choice of model parameters used to compute  $\text{CaCO}_3$  dissolution and production (Figure 1c). TA of the global ocean responds rapidly to a decrease in pelagic calcification, and in the next 600 years it increases almost at the same rate as in the fossil fuel intensive scenario. Changes in TA driven by different sediment dissolution parameterizations are discernible only after the year 2500 globally. Analogous to sediments, the difference in TA calculated in different dissolution and calcification scenarios decreases with time, whereas TA projected in the different emission scenarios continues to diverge from each other. The two dissolution scenarios are

indistinguishable from each other in their effect on seawater pH (Figure 1d). Zeebe *et al.* [2008] gave a range of pH decline as a function of emitted CO<sub>2</sub>. Analogously, we show that the CO<sub>2</sub> emission pathway will determine the degree of future ocean acidification, even many centuries after the emissions cease. Model parameterizations tested in this study have a small effect (<10 ppm) on atmospheric CO<sub>2</sub> (Figure 1e), which is negligible compared to the impact of different emission scenarios. According to our projections, carbonate dissolution will only have little potential to mitigate ocean acidification and atmospheric CO<sub>2</sub> over the next two to three millennia.

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