Effects of carbon dioxide and climate change on ocean acidification and carbonate mineral saturation

Long Cao,[1] Ken Caldeira,[2] and Atul K. Jain[1]

[1] We use an earth system model of intermediate complexity to show how consideration of climate change affects predicted changes in ocean pH and calcium carbonate saturation state. Our results indicate that consideration of climate change produces second-order modifications to ocean chemistry predictions made with constant climate; these modifications occur primarily as a result of changes in sea surface temperature, and climate-induced changes in dissolved inorganic carbon concentrations. Under a CO_2 emission scenario derived from the WRE1000 CO_2 stabilization concentration pathway and a constant climate, we predict a 0.47 unit reduction in surface ocean pH relative to a pre-industrial value of 8.17, and a reduction in the degree of saturation with respect to aragonite from a pre-industrial value of 3.34 to 1.39 by year 2500. With the same CO_2 emissions but the consideration of climate change under a climate sensitivity of 2.5°C the reduction in projected global mean surface pH is about 0.48 and the saturation state of aragonite decreases to 1.50. With a climate sensitivity of 4.5°C, these values are 0.51 and 1.62, respectively. Our study therefore suggests that future changes in ocean acidification caused by emissions of CO_2 to the atmosphere are largely independent of the amounts of climate change. **Citation:** Cao, L., K. Caldeira, and A. K. Jain (2007), Effects of carbon dioxide and climate change on ocean acidification and carbonate mineral saturation, *Geophys. Res. Lett.*, *34*, L05607, doi:10.1029/2006GL028605.

1. Introduction

[2] The ocean plays a major role in the uptake of anthropogenic CO_2 emitted from fossil fuel burning, helping to moderate future climate change. However, the addition of CO_2 into the ocean affects the carbonate system, posing a threat to marine biota. When CO_2 dissolves in the seawater it increases concentrations of hydrogen ion [H^+], lowering ocean pH. This reduction in ocean pH has some direct effect on marine organisms [*Seibel and Walsh*, 2001; *Ishimatsu et al.*, 2005]. Furthermore, some of this additional [H^+] reacts with carbonate ions [CO_3^{2-}] to form [HCO_3^-]. The decrease in carbonate ion decreases the saturation state of calcium carbonate minerals, making it more difficult for calcifying marine organisms to form their shells and skeletons [*Riebesell et al.*, 2000; *Zondervan et al.*, 2001; *Feely*

et al., 2004; *Orr et al.*, 2005]. The effect of reduction in the available carbonate ions has been most studied in coral, which form their skeletons from aragonite, a metastable form of calcium carbonate [*Kleypas et al.*, 1999; *Langdon et al.*, 2003; *Hoegh-Guldberg*, 2005].

[3] Several modeling studies have looked at the possible future change in ocean chemistry under various CO_2 concentration and/or emission scenarios [e.g., *Caldeira and Wickett*, 2003, 2005; *Harvey*, 2003; *Orr et al.*, 2005; *McNeil and Matear*, 2006]. These studies predicted a reduction in ocean pH and a lowering of the saturation state of seawater with respect to the calcium carbonate minerals (i.e., calcite and/or aragonite) as a consequence of the increase in atmospheric CO_2 concentrations. Here we investigate future changes in ocean chemistry as a result of both increased CO_2 concentrations and climate change. Our main goal is to quantify the effect of climate change on ocean pH and the saturation state of calcium carbonate minerals.

2. Effect of Temperature and CO_2 on Marine Carbonate Chemistry

[4] Before discussing model simulated ocean chemistry in the context of climate change, it is illustrative to examine the effect of changes in carbon and temperature on ocean chemistry. We used the chemistry routine from the OCMIP project (available at http://www.ipsl.jussieu.fr/OCMIP/phase3/simulations/NOCES/HOWTO-NOCES.html) to calculate ocean pH and the state of aragonite saturation ($\Omega_{aragonite}$) as a function of surface CO_2 pressure (pCO_2), the concentration of dissolved inorganic carbon (DIC), and sea surface temperature (SST). It is shown that at constant pCO_2 both pH and $\Omega_{aragonite}$ increase with increased temperature, but their dependences on temperature are weaker than on pCO_2 for the range of typical ocean surface temperature (-2 to 32°C) and atmospheric CO_2 concentrations (200 to 1200 ppm) experienced in the past and likely to be seen in the future (Figures 1a and 1b). This is especially true for pH. Our calculations show that at present-day conditions with a global sea surface temperature of about 16°C and atmospheric CO_2 concentration of about 380 ppm (corresponding to a DIC concentration of 2066 μmole kg^{-1}), the surface ocean has a globally averaged pH and $\Omega_{aragonite}$ of 8.07 and 2.68, respectively. With a doubling of atmospheric CO_2 and a climate sensitivity (ΔT_{2x}, global mean temperature change as a result of doubling of atmospheric CO_2) of 2.5°C and 4.5°C (corresponding to a DIC concentration of 2168 and 2158 μmole kg^{-1}), the pH decreases by 0.27 and 0.26 respectively, with almost all effects originating from increased CO_2 concentration. The $\Omega_{aragonite}$ decreases from 2.68 to 1.75 and 1.87 respectively (increased temperature increases $\Omega_{aragonite}$ by 0.23 and 0.44 for $\Delta T_{2x} = 2.5$°C

[1]Department of Atmospheric Sciences, University of Illinois, Urbana, Illinois, USA.
[2]Department of Global Ecology, Carnegie Institution, Stanford, California, USA.
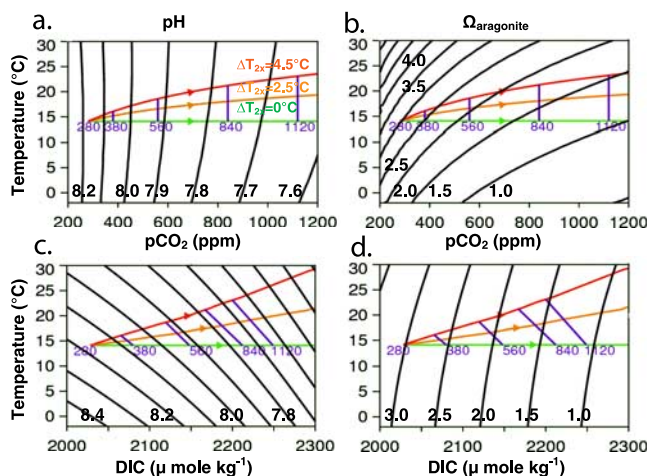
Figure 1. (a and c) Ocean pH and (b and d) aragonite saturation state, $\Omega_{\mathrm{aragonite}}$, as a function of surface pCO_2 and temperature (Figures 1a and 1b), and dissolved inorganic carbon (DIC) and temperature (Figures 1c and 1d). The carbonate chemistry is calculated based on the chemistry routine from the OCMIP project. Here, we show only the saturation state of aragonite, which is defined as $\Omega_{\mathrm{aragonite}} = [Ca^{2+}] \ [CO_3^{2-}]/\kappa^*_{sp}$, where κ^*_{sp} is the stoichiometric solubility product of aragonite determined based on the work of *Mucci* [1983]. The effect of temperature on the saturation state of calcite is similar to that of aragonite, but with higher saturation state. The trajectories of equilibrium-state pH and $\Omega_{\mathrm{aragonite}}$ are overlaid in Figures 1a and 1b for pCO_2 between 280 and 1200 ppm and corresponding temperature change for three different climate sensitivities: ΔT_{2x} = 0.0°C, 2.5°C and 4.5°C. The trajectories for corresponding DIC concentrations and climate sensitivities are shown in Figures 1c and 1d. The points where CO_2 concentrations are equal to the level of pre-industrial time (280 ppm), present-day (380 ppm), two (560 ppm), three (840 ppm), and four times (1120 ppm) of pre-industrial CO_2 concentrations are marked in these trajectories.

and 4.5°C, respectively, while increased CO_2 concentration decreases $\Omega_{\mathrm{aragonite}}$ by 1.09 in both cases. The difference between the sum of these effects and the total change in $\Omega_{\mathrm{aragonite}}$ is due to nonlinearity in the carbonate system).

[5] Temperature change affects ocean chemistry in two primary ways: (1) the carbonate acid dissociation constants vary with temperature and (2) CO_2 solubility and hence total DIC concentrations vary with temperature. At constant DIC, an increase in temperature reduces ocean pH and slightly increases $\Omega_{\mathrm{aragonite}}$ (Figures 1c and 1d) solely due to changes in dissociation constants, which change the partitioning of total DIC among the various carbon species (CO_2, CO_3^{2-}, and HCO_3^-). However, at constant pCO_2, an increase in temperature reduces the solubility of CO_2, leading to lower DIC concentrations and thus increases ocean pH and $\Omega_{\mathrm{aragonite}}$. The effect of temperature on the Henry's law constant governing CO_2 solubility (and thus DIC concentrations) affects ocean chemistry more than the effect of temperature on the carbonate dissociation constants. In Figure 1, changes in pH and $\Omega_{\mathrm{aragonite}}$ as a function

of temperature and pCO_2 are shown for specified atmospheric CO_2 concentrations. However, CO_2 emissions drive changes in atmospheric CO_2 concentrations and climate. Therefore, a more realistic boundary condition in the study of climatic effects on ocean chemistry is prescribed CO_2 emissions. In addition to temperature change, changes in ocean circulation, salinity, and marine biology associated with climate change will affect ocean chemistry. We now describe and apply a model to examine these effects on ocean chemistry.

3. Model Description

[6] The modeling framework we use in this study is the ISAM-2.5D (Integrated Science Assessment Model-2.5D) earth system model of intermediate complexity [*Cao and Jain*, 2005]. The ISAM-2.5D model couples key components of the earth system including atmosphere, ocean, sea ice, land surface, and marine biogeochemical cycles. The ocean is represented by a zonally averaged multi-basin ocean model [*Wright and Stocker*, 1992] that resolves the thermohaline circulation in the Atlantic, Pacific, Indian, and Southern Ocean with isopycnal mixing and a parameterization of the effect of eddy-induced tracer transport [*Gent et al.*, 1995]. The ocean module is coupled to an energy-moisture balance model of the atmosphere and land surface [*Weaver et al.*, 2001] and a thermodynamic-dynamic sea-ice model [*Semtner*, 1976]. The ocean model was tested [*Cao and Jain*, 2005] using an abiotic carbon cycle module simulating dissolved inorganic carbon (DIC) and radiocarbon (in terms of $\Delta^{14}C$) based on the OCMIP protocol (available athttp://www.ipsl.jussieu.fr/OCMIP). A marine ecosystem model (Dynamic Green Ocean Model, DGOM) that represents multiple nutrients and different types of phytoplankton and zooplankton [*Le Quéré et al.*, 2005] has been incorporated into the ISAM-2.5D model [*Cao*, 2007]. The coupled model has the ability to realistically simulate the concurrent uptake of heat, freshwater, CO_2, natural and bomb ^{14}C, and nutrients, and has been applied to studies related to effects of climate change and marine biology on the uptake of carbon over a time scale of hundreds to thousands of years [*Cao and Jain*, 2005; *Cao*, 2007].

4. Experiment Configuration

[7] The model was spun up with a pre-industrial (year 1765) atmospheric CO_2 concentration of 278 ppm for several thousands of years to reach an approximate stationary state. Between year 1765 and 1990 the model was integrated with the observed CO_2 concentrations [*Keeling and Whorf*, 2000]. Then the model was integrated from year 1991 to 2500 with prescribed CO_2 emissions. The emission pathway (Figure 2a) was derived from oceanic CO_2 uptake predicted by our model in the absence of climate change and with atmospheric CO_2 changes under the WRE1000 CO_2 concentration pathway [*Wigley et al.*, 1996]. For the purpose of this study CO_2 uptake by the terrestrial biosphere was not explicitly taken into account, and thus our estimates of CO_2 emissions include both fossil-fuel CO_2 emissions and net CO_2 emissions from the terrestrial biosphere. To compare climatic effects on ocean chemistry between pre-
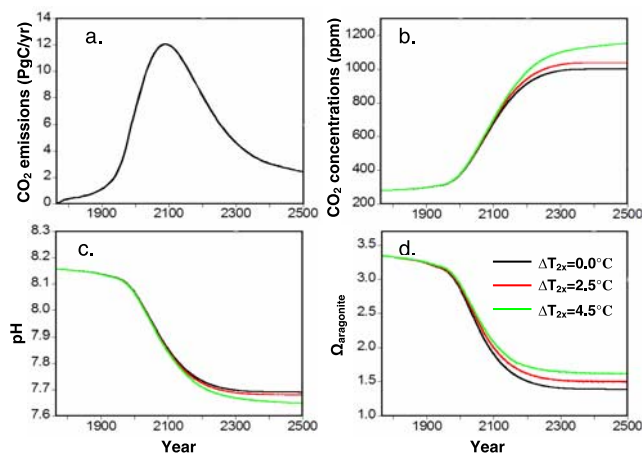
Figure 2. (a) Model predicted CO_2 emissions under the WRE1000 CO_2 concentration pathway in the absence of climate change (i.e., $\Delta T_{2x} = 0.0°C$). (b) Model predicted atmospheric CO_2 concentrations under this emission pathway for simulations with different climate sensitivities: $\Delta T_{2x} = 0.0°C$, $2.5°C$ and $4.5°C$. Model predicted temporal evolution of (c) global mean surface ocean pH and (d) global mean surface ocean aragonite saturation state ($\Omega_{aragonite}$) with different climate sensitivities: $\Delta T_{2x} = 0.0°C$, $2.5°C$, and $4.5°C$.

scribed CO_2 emission and concentration cases, we also performed sets of experiments in which atmospheric CO_2 concentrations are specified following the WRE1000 stabilization pathway. To investigate the effect of climate change on ocean chemistry, three different climate sensitivities were used for the perturbation simulations of the period 1765-2500, i.e., $\Delta T_{2x} = 0.0°C$, $2.5°C$, and $4.5°C$ warming for each doubling of atmospheric CO_2 concentration. In the simulation with $\Delta T_{2x} = 0.0°C$ ocean chemistry is only influenced by increased atmospheric CO_2, whereas in the simulations with $\Delta T_{2x} = 2.5°C$ and $4.5°C$, ocean chemistry is affected by changes in atmospheric CO_2 and climate.

5. Results

[8] Model simulated atmospheric CO_2 concentrations based on the specified CO_2 emissions for the simulations with different climate sensitivities are shown in Figure 2b. Model predicted CO_2 concentrations for the simulation with $\Delta T_{2x} = 0.0°C$ are the same as that for the WRE1000 CO_2 concentration pathway. The simulations with $\Delta T_{2x} = 2.5°C$ and $\Delta T_{2x} = 4.5°C$ predict higher CO_2 concentrations than that of $\Delta T_{2x} = 0.0°C$, i.e., concentrations of 1040 and 1150 ppm respectively in year 2500. The increased atmospheric CO_2 concentrations are a result of reduced oceanic CO_2 uptake associated with increased temperature, enhanced ocean stratification, and reduced North Atlantic overturning circulation. With a climate sensitivity of $4.5°C$ under prescribed CO_2 emissions, our model predicts an increase in average sea surface temperature of $5.3°C$ and a reduction in sea surface salinity of 2.1 per mil by year 2500 relative to year 1765. At the same time, the maximum intensity of the North Atlantic overturning circulation decreases by about 46%. The global mean vertical density gradient at the base of

the first model layer (50 m) decreases by about 30%, indicating increased stratification of the upper ocean. Associated with these changes, simulated biogenic carbon export is decreased by about 32% in year 2500 relative to year 1765.

[9] Projected ocean surface pH and $\Omega_{aragonite}$ decrease with increasing CO_2 concentrations. The rate of decrease largely follows the rate of CO_2 increase (Figures 2c and 2d). From a pre-industrial ocean mean pH value of 8.17, our simulations predict a reduction in surface ocean pH of 0.31 and 0.47 units by year 2100 and 2500 respectively without the inclusion of climate change. From pre-industrial time to year 2100, $\Omega_{aragonite}$ decreases from 3.34 to 1.91, and then to 1.39 by year 2500. Consideration of climate change does not alter the trend of changes in pH and $\Omega_{aragonite}$, but modestly modifies their magnitudes. Inclusion of climate change amplifies the decrease in projected pH (Figure 2c) and diminishes the decrease in predicted $\Omega_{aragonite}$ (Figure 2d). In the simulation with $\Delta T_{2x} = 4.5°C$ with prescribed CO_2 emissions, the global mean surface ocean pH is reduced by 0.51 by year 2500, compared with a reduction of 0.47 predicted without considering climate change. At the same time, the global mean surface ocean $\Omega_{aragonite}$ is reduced from the pre-industrial value of 3.34 to 1.62, compared with a value of 1.39 in the case without climate change (Table 1). These changes in ocean chemistry predicted by our model are comparable with other relevant studies. For example, *Harvey* [2003], by taking into account the effect of increased CO_2 and temperature in a 1D ocean model, predicted a reduction in surface pH and $\Omega_{calcite}$ of 0.6 and 3.2 respectively by year 2500 when atmospheric CO_2 reaches about 1600 ppm in his model. *Caldeira and Wickett* [2005], by accounting for the CO_2 effect only in a 3D ocean model, projected a reduction in surface pH and $\Omega_{aragonite}$ of 0.48 and 2.1 respectively by year 2500 under the WRE1000 CO_2 concentration scenario.

[10] To investigate the relative importance of different climate change effects in ocean chemistry, sensitivity experiments were performed to quantify the time-dependent contribution of individual factors to changes in pH and $\Omega_{aragonite}$ as a result of climate change. Figure 3 shows the direct effects on pH and $\Omega_{aragonite}$ of changes in sea surface temperature (SST) and sea surface salinity (SSS) (through changes in the carbonate dissociation constants), and indirect effects through changes in alkalinity (ALK) and DIC induced by changes in temperature, ocean circulation, and marine biology. As shown in Figure 3, direct temperature effects and changes in DIC play a dominate role in affecting pH and $\Omega_{aragonite}$, while the effect of changes in salinity and alkalinity is much smaller. The direct SST effect is to reduce pH and increase $\Omega_{aragonite}$, while the indirect DIC effect is to cause a smaller decrease in pH and $\Omega_{aragonite}$, which appears as a net increase as shown in Figure 3. These dependencies of pH and $\Omega_{aragonite}$ on SST and DIC can be readily understood with the aid of Figures 1c and 1d. In the case of $\Omega_{aragonite}$, the SST and DIC effect reinforce each other, leading to a net increase in $\Omega_{aragonite}$, while for pH the SST effect dominates the DIC effect, resulting in a net reduction in pH. By year 2500 the DIC effect increases pH by 0.03 for a climate sensitivity of $4.5°C$, whereas the SST effect reduces pH by 0.07, leading to a net reduction in ocean pH of 0.04.

Table 1. Model Predicted Global Mean Surface Ocean pH Change and Aragonite Saturation State for Simulations With Prescribed CO_2 Emissions and Concentrations With Different Climate Sensitivities[a]

	Specified Emissions			Specified Concentrations		
Year	0°C	2.5°C	4.5°C	0°C	2.5°C	4.5°C
			ΔpH			
1765	0.0	0.0	0.0	0.0	0.0	0.0
2000	−0.09	−0.09	−0.09	−0.09	−0.09	−0.09
2100	−0.31	−0.32	−0.32	−0.31	−0.30	−0.30
2500	−0.47	−0.48	−0.51	−0.47	−0.46	−0.46
			$\Omega_{aragonite}$			
1765	3.34	3.34	3.34	3.34	3.34	3.34
2000	2.86	2.90	2.93	2.86	2.91	2.95
2100	1.91	2.00	2.09	1.91	2.03	2.13
2500	1.39	1.50	1.62	1.39	1.54	1.77

[a]Ocean pH change, ΔpH; aragonite saturation state, $\Omega_{aragonite}$; climate sensitivities, ΔT_{2x}.

[11] Climate change also affects predicted ocean pH and carbonate mineral saturation state in the deep ocean as shown in Figure 4. Relative to the simulation with $\Delta T_{2x} = 0.0°C$, the simulation with $\Delta T_{2x} = 4.5°C$ predicts a greater reduction of pH near ocean surface (as previously noted), but a smaller reduction in the deep ocean. The diminished reduction of pH in the deep ocean is due to increased ocean stratification and reduced North Atlantic overturning, both of which lead to reduced transport of anthropogenic CO_2 from the surface ocean to ocean depth. The reduced ocean mixing and circulation also lead to larger $\Omega_{aragonite}$ in the deep ocean.

6. Discussion and Conclusions

[12] In this study we predict future changes in ocean chemistry as a result of increased CO_2 concentrations and accompanying climate change. With prescribed CO_2 emissions calculated from the WRE1000 CO_2 concentration pathway and a constant climate, we predict a 0.47 unit

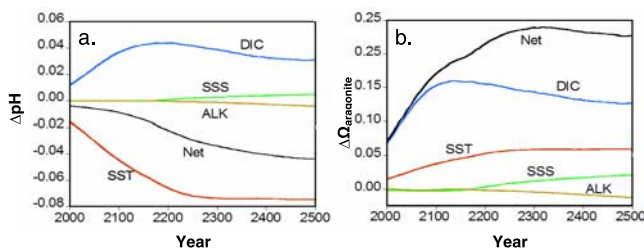**Figure 3.** Changes in (a) pH and (b) $\Omega_{aragonite}$ as a result of changes in sea surface temperature (SST), sea surface salinity (SSS) (through changes in the carbonate dissociation constants), alkalinity (ALK), and dissolved inorganic carbon (DIC) (through changes in temperature, circulation, and marine biology), as well as the combined effect of changes in SST, SSS, ALK, and DIC (Net). These changes are plotted for the simulation with $\Delta T_{2x} = 4.5°C$ relative to the simulation with constant climate ($\Delta T_{2x} = 0.0°C$). Negative values represent a reduction in pH and $\Omega_{aragonite}$, while positive values represent an increase in pH and $\Omega_{aragonite}$.
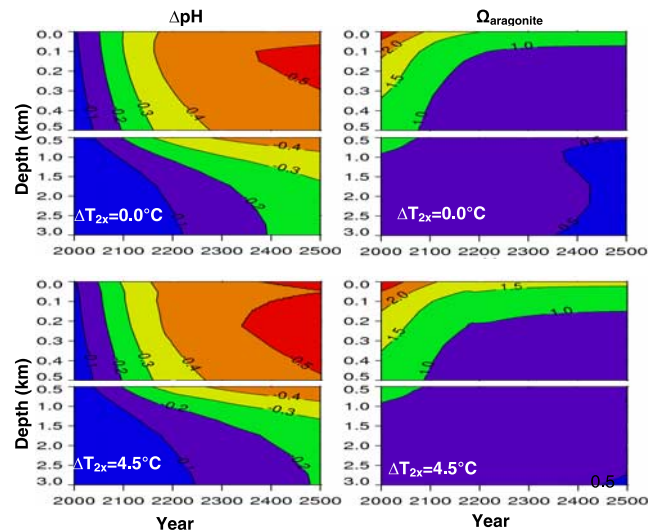

Figure 4. Model predicted horizontal mean ocean pH change (ΔpH) and aragonite saturation state ($\Omega_{aragonite}$) as a function of depth and time for the simulation with $\Delta T_{2x} = 0.0°C$ and $\Delta T_{2x} = 4.5°C$.

reduction in surface ocean pH relative to a pre-industrial value of 8.17, and a reduction in the degree of saturation with respect to aragonite from a pre-industrial value of 3.34 to 1.39 by year 2500. Ocean acidification (lowering of pH and carbonate saturation state) will almost certainly adversely impact marine biota through a variety of mechanisms [e.g., *Seibel and Walsh*, 2001; *Ishimatsu et al.*, 2005]. In particular, it will likely pose a great threat to the survival of calcifying organisms such as corals and foraminifera [e.g., *Kleypas et al.*, 1999; *Langdon et al.*, 2003; *Hoegh-Guldberg*, 2005]. The consideration of climate change produces a modest modification to the predicted ocean chemistry mainly through changes in sea surface temperature and climate-induced DIC concentrations. With a climate sensitivity of 2.5°C and 4.5°C our simulations show that relative to constant climate simulations, the inclusion of climate change further reduces projected global mean surface pH by 0.01 and 0.04, and increases projected saturation state of aragonite by 0.11 and 0.23 respectively by year 2500.

[13] *McNeil and Matear* [2006] reports that the effects of climate change on surface ocean pH are negligible from a coupled climate-carbon cycle simulation driven by the IS92a atmospheric CO_2 concentration pathway. With prescribed CO_2 concentrations we project negligible climatic effects on surface pH (Table 1), consistent with their study. In this case, the indirect DIC effect almost cancels the direct temperature effect (not shown), leading to a negligible net climatic effect on pH. However, with prescribed CO_2 emissions, we find that consideration of climate change has a pronounced effect on surface pH (namely, to cause a greater decrease in pH, as seen from Figure 2c); the direct temperature effect dominates the indirect DIC effect (as explained above) (Figure 3a).

[14] We also show that climate change results in less reduction in ocean pH and aragonite saturation state in the deep ocean due to reduced North Atlantic overturning circulation and increased ocean stratification. The reduced acidification in the deep ocean is of interest since the deep

ocean biota may be more sensitive to pH changes than surface biota [*Seibel and Walsh*, 2001]. Nevertheless, we conclude, based on our simulation results, that climate change exerts a second order control on ocean chemistry. The changes in ocean acidification and saturation state of calcium carbonate minerals caused by CO_2 emissions, and the resulting increases in atmospheric CO_2 concentration, are insensitive to the amounts of climate change.

References

Cao, L. (2007), An integrated modeling study of ocean circulation, the ocean carbon cycle, marine ecosystems, and climate change, Ph.D. thesis, Univ. of Ill., Urbana.

Cao, L., and A. Jain (2005), An Earth system model of intermediate complexity: Simulation of the role of ocean mixing parameterizations and climate change in estimated uptake for natural and bomb radiocarbon and anthropogenic CO_2, *J. Geophys. Res.*, *110*, C09002, doi:10.1029/2005JC002919.

Caldeira, K., and M. E. Wickett (2003), Anthropogenic carbon and ocean pH, *Nature*, *425*, 365.

Caldeira, K., and M. E. Wickett (2005), Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean, *J. Geophys. Res.*, *110*, C09S04, doi:10.1029/2004JC002671.

Feely, R. A., C. L. Sabine, K. Lee, W. Berelson, J. Kleypas, V. J. Fabry, and F. J. Millero (2004), Impact of anthropogenic CO_2 on the CaCO3 system in the oceans, *Science*, *305*, 362–366.

Gent, P. R., J. Willebrand, T. J. McDougall, and J. C. McWilliams (1995), Parameterizing eddy-induced tracer transports in ocean circulation models, *J. Phys. Oceanogr.*, *25*, 463–474.

Harvey, L. D. D. (2003), Impact of deep-ocean carbon sequestration on atmospheric CO_2 and on surface-water chemistry, *Geophys. Res. Lett.*, *30*(5), 1237, doi:10.1029/2002GL016224.

Hoegh-Guldberg, O. (2005), Low coral cover in a high-CO_2 world, *J. Geophys. Res.*, *110*, C09S06, doi:10.1029/2004JC002528.

Ishimatsu, A., M. Hayashi, K.-S. Lee, T. Kikkawa, and J. Kita (2005), Physiological effects on fishes in a high-CO_2 world, *J. Geophys. Res.*, 110, C09S09, doi:10.1029/2004JC002564.

Keeling, C. D., and T. P. Whorf (2000), Atmospheric CO_2 records from sites in the SIO air sampling network, in Trends: A compendium of data on global change, report, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn.

Kleypas, J. A., R. W. Buddemeier, D. Archer, J.-P. Gattuso, C. Langdon, and B. N. Opdyke (1999), Geochemical consequences of increased atmospheric CO_2 on coral reefs, *Science*, *284*, 118–120.

Langdon, C., W. S. Broecker, D. E. Hammond, E. Glenn, K. Fitzsimmons, S. G. Nelson, T.-S. Peng, I. Hajdas, and G. Bonani (2003), Effect of elevated CO_2 on the community metabolism of an experimental coral reef, *Global Biogeochem. Cycles*, *17*(1), 1011, doi:10.1029/2002GB001941.

Le Quéré, C., et al. (2005), Ecosystem dynamics based on plankton functional types for global ocean biogeochemistry models, *Global Change Biol.*, *11*, 1–25.

McNeil, B., and R. Matear (2006), Projected climate change impact on oceanic acidification, *Carbon Balance and Manage.*, *1*(2), doi:10.1186/1750-0680-1-2.

Mucci, A. (1983), The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure, *Am. J. Sci.*, *283*, 780–799.

Orr, J. C., et al. (2005), Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, *Nature*, *437*, 681–686.

Riebesell, U., I. Zondervan, B. Rost, P. D. Tortell, R. E. Zeebe, and F. M. M. Morel (2000), Reduced calcification of marine plankton in response to increased atmospheric CO_2, *Nature*, *407*, 364–367.

Seibel, B. A., and P. J. Walsh (2001), Potential impacts of CO_2 injections on deep-sea biota, *Science*, *294*, 319–320.

Semtner, A. J. (1976), A model for the thermodynamic growth of sea ice in numerical investigations of the climate, *J. Phys. Oceanogr.*, *6*, 379–389.

Weaver, A. J., et al. (2001), The UVic Earth System Climate Model: Model description, climatology, and application to past, present, and future climates, *Atmos. Ocean*, *38*, 271–301.

Wigley, T. M. L., R. Richels, and J. A. Edmonds (1996), Economic and environmental choices in the stabilization of atmospheric CO_2 concentrations, *Nature*, *379*, 240–243.

Wright, D. G., and T. F. Stocker (1992), Sensitivities of a zonally average global ocean circulation model, *J. Geophys. Res.*, *97*, 12,707–12,730.

Zondervan, I., R. E. Zeebe, B. Rost, and U. Riebesell (2001), Decreasing marine biogenic calcification: A negative feedback on rising atmospheric pCO_2, *Global Biogeochem. Cycles*, *15*, 507–516.

————————————
K. Caldeira, Department of Global Ecology, Carnegie Institution, 260 Panama Street, Stanford, CA 94305, USA.

L. Cao and A. K. Jain, Department of Atmospheric Sciences, University of Illinois, 105 South Gregory Street, Urbana, IL 61801, USA. (jain@atmos.uiuc.edu)