Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean

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[1] We present ocean chemistry calculations based on ocean general circulation model simulations of atmospheric CO_2 emission, stabilization of atmospheric CO_2 content, and stabilization of atmospheric CO_2 achieved in total or in part by injection of CO_2 to the deep ocean interior. Our goal is to provide first-order results from various CO_2 pathways, allowing correspondence with studies of marine biological effects of added CO_2. Parts of the Southern Ocean become undersaturated with respect to aragonite under the Intergovernmental Panel on Climate Change Special Report on Emissions Scenarios (SRES) A1, A2, B1, and B2 emission pathways and the WRE pathways that stabilize CO_2 at 650 ppm or above. Cumulative atmospheric emission of 5000 Pg C produces aragonite undersaturation in most of the surface ocean; 10,000 Pg C also produces calcite undersaturation in most of the surface ocean. Stabilization of atmospheric CO_2 at 450 ppm produces both calcite and aragonite undersaturation in most of the deep ocean. The simulated SRES pathways produce global surface pH reductions of $\sim$0.3–0.5 units by year 2100. Approximately this same reduction is produced by WRE650 and WRE1000 stabilization scenarios and by the 1250 Pg C emission scenario by year 2300. Atmospheric emissions of 5000 Pg C and 20,000 Pg C produce global surface pH reductions of 0.8 and 1.4 units, respectively, by year 2300. Simulations of deep ocean CO_2 injection as an alternative to atmospheric release show greater chemical impact on the deep ocean as the price for having less impact on the surface ocean and climate. Changes in ocean chemistry of the magnitude shown are likely to be biologically significant.

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1. Introduction

[2] Adding CO_2 to the ocean, either passively or actively, affects the ocean carbonate system, resulting in decreases in pH and carbonate-ion concentration [*Zeebe and Wolf-Gladrow*, 2001; *Bolin and Eriksson*, 1959]. These changes have the potential to have strong impacts on marine biota [*Kurihara et al.*, 2004; *Pörtner et al.*, 2004; *Langdon et al.*, 2003; *Seibel and Walsh*, 2001; *Riebesell et al.*, 2000; *Gattuso et al.*, 1999; *Kleypas et al.*, 1999]. Here we predict ocean chemistry changes for a range of cases of atmospheric CO_2 emissions, atmospheric CO_2 stabilization, and ocean CO_2 injection using a stand-alone ocean general circulation model forced with changing carbon dioxide concentrations or emissions, but no changing climate. The range of cases is wide enough such that it may span actual future atmospheric CO_2 concentrations and emission rates, and thus could provide a context for marine biological studies relative to atmospheric CO_2 emission or stabilization pathways.

[3] It has been suggested that continued release of CO_2 to the atmosphere may result in undersaturation of the surface ocean with respect to the calcium carbonate minerals (i.e., calcite and/or aragonite) and that this could potentially have catastrophic biological consequences [*Bacastow and Keeling*, 1973; *Fairhall*, 1973; *Broecker et al.*, 1971]. *Whitfield* [1974] suggested this undersaturation would not occur in the foreseeable future: a conclusion at odds with the results presented here. *Haugan and Drange* [1996] compared paleo-pH, geographical and seasonal pH variation, and projections from atmospheric invasion and direct injection cases. *Brewer* [1997] discussed ocean chemistry changes that might occur to year 2100 under an Intergovernmental Panel on Climate Change (IPCC) "business-as-usual" pathway. *Wolf-Gladrow et al.* [1999] attempted a preliminary assessment of direct effects of anthropogenic CO_2 increase on marine biota growth rates and carbon isotope fractionation. *Kleypas et al.* [1999] predicted changes in calcification in corals to year 2100 under an IPCC business-as-usual pathway. *Zondervan et al.* [2001] looked at the consequences of anthropogenic CO_2 for calcification by marine plankton.

[4] Aragonite and calcite are the two common CaCO$_3$ mineral forms and are generally precipitated in the ocean in highly saturated microenvironments created by marine organisms. The degree of saturation of with respect to aragonite and calcite ($\Omega_{Aragonite}$ or $\Omega_{Calcite}$) is the ion product of the concentrations of calcium and carbonate ions divided by the stoichiometric solubility product [*Feely et al.*, 2004]. *Caldeira and Wickett* [2003] compared estimates of paleo-CO$_2$ change with ocean pH anticipated under a multicentury 5000 Pg C (= 18,300 Pg CO$_2$) atmospheric emission pathway. *Feely et al.* [2004] predicted aragonite undersaturation for the entire ocean surface for this 5000 Pg C emission pathway.

[5] We performed several sets of simulations to look at chemical effects of CO$_2$ emission and stabilization pathways. From year 2000 to 2100, we consider the single-century IPCC Special Report on Emissions Scenarios (SRES) A1, A2, B1, and B2 marker emission pathways [*Intergovernmental Panel on Climate Change (IPCC)*, 2000] (available at http://www.grida.no/climate/ipcc/emission/index.htm). From year 2000 to 2500, we consider the WRE450 through WRE1000 atmospheric CO$_2$ stabilization pathways [*Wigley et al.*, 1996] and a range of emission pathways with total cumulative future emissions ranging from 1250 to 20,000 Pg C according to a smooth logistic curve [*Marchetti*, 1991; *Caldeira and Wickett*, 2003].

[6] We performed several simulations to look at chemical effects of possible large-scale deployment of engineered ocean carbon storage [*Herzog et al.*, 2001]. Many CO$_2$ stabilization pathways (e.g., WRE550) require lower emissions than "business-as-usual" emission pathways. This CO$_2$ emission avoidance can be attained through increased efficiency, by carbon emission–free energy sources, or by sequestration of CO$_2$ [*Hoffert et al.*, 1998, 2002; *Pacala and Socolow*, 2004]. We perform simulations in which all, 10%, and none of this CO$_2$ emission avoidance is accomplished by directly injecting CO$_2$ into the ocean. These simulations show the chemical impact of this method of emission avoidance and demonstrate, in principal, whether the method has the capacity to store the amount of CO$_2$ needed to stabilize atmospheric CO$_2$ under various assumptions of atmospheric CO$_2$ stabilization target and total amount of ultimately recoverable fossil fuel resources.

[7] Since the goal of this paper is to set out basic results for a wide range of cases, we perform first-order calculations without consideration of climate, circulation, marine biological, land-biosphere, or dust feedbacks. Accurately predicting ocean chemistry involves accurately predicting climate sensitivity, hydrological cycle, and wind changes, and the response of both the land biosphere and the ocean to such forcings. These factors could modify ocean chemistry in ways that are just beginning to be understood [e.g., *Sarmiento et al.*, 1998]. Here, we consider the changes in ocean chemistry for up to a 500 year time period. On longer timescales, one would need to consider interactions with the carbonate sedimentary system [*Archer et al.*, 1997, 1998].

[8] We would expect well-calibrated schematic model results [e.g., *Hoffert et al.*, 1979; *Völker et al.*, 2002; *Caldeira et al.*, 2002] to produce results similar to the spatially averaged results obtained from three-dimensional models [e.g., *Heinze*, 2004; *Orr et al.*, 2004; *Caldeira and Wickett*, 2003]. However, the use of a three-dimensional model allows for both better representation of physics and prediction of spatial variation. We would expect three-dimensional models run at higher, but still non-eddy-resolving, resolutions to produce similar results on the scales that we resolve [*Wickett et al.*, 2003].

2. Experimental Configuration

2.1. Ocean Model

[9] We use a configuration of the Lawrence Livermore National Laboratory (LLNL) ocean general circulation model [*Caldeira and Wickett*, 2003; *Caldeira et al.*, 2002; *Caldeira and Duffy*, 2000] to predict future changes in dissolved inorganic carbon (DIC) and then calculate the effect of these changes on marine chemistry.

[10] The model configuration is identical to that used by *Caldeira and Wickett* [2003], with a global domain having horizontal resolution of 4° longitude by 2° latitude, 24 levels in the vertical, and realistic but lightly smoothed topography. Isopycnal and Gent-McWilliams diffusion coefficients are 10^7 cm^2 s^{-1}. Vertical mixing is proportional to the inverse of the Brunt-Vaisala frequency with a coefficient of 10^{-3} cm^2 s^{-2}, chosen to approximately recover deep North Pacific Δ^{14}C values. All surface forcings are obtained by linear interpolation in time between monthly mean climatological data. Wind forcing (i.e., momentum fluxes) is from an NCEP reanalysis [*Kalnay et al.*, 1996]. Surface salinities over open ocean are restored to *Levitus et al.* [1994] data with a time constant of 58 days. Under sea ice, the sea ice model calculates fluxes of fresh water, and no restoring is used. Sensible, latent, longwave, and short-wave components of the surface heat flux are calculated independently using climatological atmospheric data, calculated sea surface temperatures, and bulk parameterizations. The data and algorithms used in the heat flux calculations are described by *Oberhuber* [1993]. No restoring of sea surface temperature to prescribed values is used.

[11] The model uses the abiotic carbon protocols from the OCMIP-2 project (http://www.ipsl.jussieu.fr/OCMIP/phase2/simulations/Abiotic/HOWTO-Abiotic.html), under which ocean carbon is assumed to be a conservative tracer in the ocean interior and global ocean carbon inventory is affected only by air-sea fluxes and directly injected carbon. The model was integrated for several thousand years with preindustrial atmospheric forcing to a near-stationary state and was then integrated for the period 1750 to 2000 to achieve an initial state for the cases we present here. This model configuration takes up 1.86 Pg C yr^{-1} for years 1980–1989 and 2.16 Pg C yr^{-1} for years 1990–1999. This compares with 1.8 ± 0.8 Pg C yr^{-1} for years 1980–1989 and 1.9 ± 0.7 Pg C yr^{-1} for years 1990–1999 estimated by *Le Quéré et al.* [2003] and 1.7 ± 0.6 Pg C yr^{-1} for years 1980–1989 and 2.4 ± 0.7 Pg C yr^{-1} for years 1990–1999 estimated by *Plattner et al.* [2002].

[12] Ocean carbon uptake and sequestration results for configurations of this model have been presented by *Orr et al.* [2004], *Caldeira and Wickett* [2003], *Wickett et al.* [2003], *Caldeira et al.* [2002], and *Caldeira and Duffy* [2000]. In carbon sequestration simulations, our model behaves like a generic coarse-resolution z coordinate ocean general circulation model [*Orr et al.*, 2004]. It simulates

tracers in the Southern Ocean [*Caldeira and Duffy*, 2000] fairly well and has reasonable predictions for global ocean carbon uptake in the 1980s and 1990s, but tends to get a relatively shallow North Atlantic thermohaline circulation, with much of the deep North Atlantic filling up with Antarctic Bottom Water. Nevertheless, it does a fairly good job of simulating the radiocarbon content of the deep North Pacific [*Caldeira et al.*, 2002], indicative of reasonable overall ocean turnover rates.

[13] To compute ocean chemistry, unless specified otherwise, we use the chemistry routines from the OCMIP-3/ NOCES project (http://www.ipsl.jussieu.fr/OCMIP/phase3/ simulations/NOCES/HOWTO-NOCES.html). The original versions of these routines were based on a code by *Dickson* [1994], but they have been modified by A. Mouchet and others (J. Orr, personal communication, 2004). In all cases, we add changes predicted by the model to preindustrial concentrations inferred from observations by the GLODAP project [*Key et al.*, 2004]. In reporting pH changes and other results, we report results relative to the preindustrial conditions (i.e., a pH change of 0.2 means a pH change of 0.2 relative to the preindustrial concentrations inferred by *Key et al.* [2004]).

[14] The calculations performed here assume a neutral biosphere. In the future, if the land-biosphere were to take up significant amounts of carbon released to the atmosphere, atmospheric CO$_2$ and ocean chemistry changes would be less than predicted here (for emission cases) or allowable emissions would be greater than predicted here (for concentration stabilization cases).

2.2. Application of CO$_2$ Boundary Conditions

[15] The model was configured to run cases of three types: (1) emission (specify CO$_2$ emissions to the atmosphere, calculate atmospheric CO$_2$ concentration); (2) stabilization (specify atmospheric CO$_2$ concentration, calculate allowable CO$_2$ emissions); and (3) deep ocean injection (specify atmospheric CO$_2$ concentration and CO$_2$ emissions, calculate amount of emission avoidance needed to attain stabilization target; inject all or some fraction of this amount into the ocean interior).

[16] The relations considered in these modes can be summarized as follows:

$$M_{atm} \frac{d}{dt}(x\mathrm{CO}_2) = F_{atm} - F_{ocean}, \quad (1)$$

where M_{atm} is the molar mass of the atmosphere, $x\mathrm{CO}_2$ is the CO$_2$ concentration in the atmosphere, F_{atm} is the emission to the atmosphere and F_{ocean} is the flux of CO$_2$ from the atmosphere to the ocean. For emission cases (i.e., SRES and logistic emission), F_{atm} is prescribed, the ocean model computes F_{ocean}, and atmospheric CO$_2$ concentration is predicted. For stabilization cases, atmospheric CO$_2$ concentration is prescribed, the ocean model computes F_{ocean}, and F_{atm} is predicted.

[17] For the deep ocean injection cases, we specify both an emission pathway and a stabilization pathway and define

$$\mathrm{Gap} = F_{atm}^{emission} - F_{atm}^{stabilization}, \quad (2)$$

where $F_{atm}^{emission}$ is the emission specified in the emission pathway and $F_{atm}^{stabilization}$ is the amount allowed under the stabilization pathway from equation (1). If Gap is positive, some fraction, k, is then injected to the ocean. Setting k to zero is equivalent to the stabilization cases. Experiments with k equal to 1.0 have the property that total emissions (atmosphere plus ocean) are the same as in the corresponding pure emission cases (e.g., 5000 Pg C over several centuries) but achieve the atmospheric stabilization targets of the stabilization cases (e.g., WRE550). We also perform experiments in which k is set to 0.1, which assumes that 90% of the emission reduction is derived from approaches other than direct injection of CO$_2$ into the ocean. Note that in these injection cases, F_{ocean} from equation (1) includes any outgassing to the atmosphere of CO$_2$ previously injected into the ocean.

3. Ocean Chemistry Consequences of Release of CO$_2$ to the Atmosphere

3.1. Emission Cases

[18] We consider two sets of emission pathways: century-scale SRES pathways and pathways that emit some specified amount of CO$_2$ over several centuries.

3.1.1. Century-Scale SRES Pathways

[19] The first set of cases (Figure 1b) is CO$_2$ emissions from the IPCC SRES A1, A2, B1, and B2 marker pathways for years 2000 to 2100 [*IPCC*, 2000]. These CO$_2$ emission pathways were developed based on different assumptions regarding global development over the rest of this century. The A1 storyline foresees rapid economic development in both developing and developed countries with convergence between poor and rich countries. The A2 storyline has the largest CO$_2$ emissions, envisioning a world that has large regional differences in rates of technological change, energy technologies, approaches to agriculture, and access to mineral resources. In contrast, the B1 storyline has the least CO$_2$ emissions, assuming a world with a globally coherent approach to sustainable development with a high level of environmental and social consciousness. The B2 world is like a less successful B1, with less technological advancement and greater regional differences in rates of development. The CO$_2$ emissions in these pathways include net CO$_2$ emissions from land use change.

[20] We used the model to simulate 100 years for each of the SRES pathways. Predicted atmospheric CO$_2$ concentrations are shown in Figure 1d and Table 1. Predicted changes in surface ocean pH and calcite and aragonite saturation state are shown in Figure 2 (horizontal means), and Figure 3 (zonal means). The lowest emission SRES pathway considered here (B1) produces global surface pH reductions of about 0.3 pH units by year 2100, whereas the highest emission pathway considered (A2) produces global surface pH reductions approaching 0.5 pH units by year 2100 (Figures 2 and 3). In our simulations, all of the SRES pathways produced aragonite undersaturation in the surface Southern Ocean by year 2100 (Figure 3).

3.1.2. Multicentury "Logistic" Emission Pathways

[21] For the second set of emission pathways, we develop a set of smooth CO$_2$ emission curves releasing specified amounts of CO$_2$ to the atmosphere over the next several centuries. In this set of emission pathways, start-
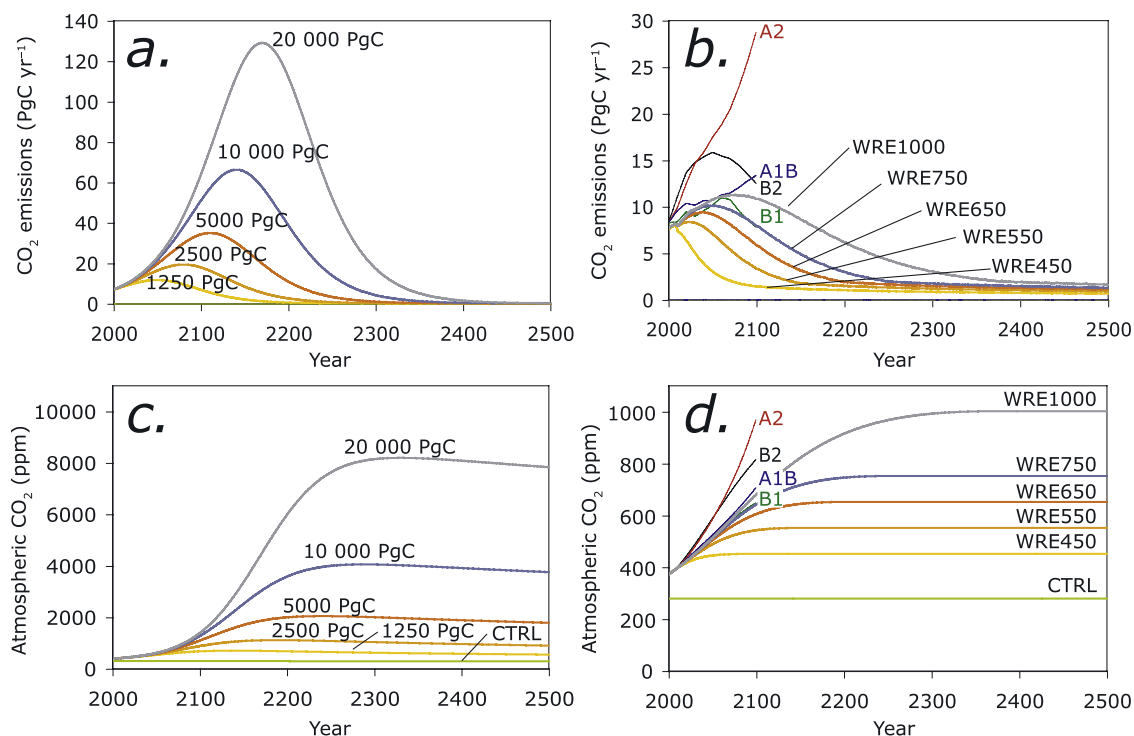
Figure 1. (a) CO$_2$ emissions scenarios releasing from 1250 to 20,000 Pg C (4580–73,300 Pg CO$_2$) to the atmosphere after year 2000 according to a smooth curve described by equation (3). (b) CO$_2$ emissions specified for the Special Report on Emissions Scenarios (SRES) A1, A2, B1, and B2 pathways and allowable emissions calculated with our ocean model from WRE CO$_2$ stabilization scenarios. (c) Atmospheric CO$_2$ contents predicted by our model for the emission pathways shown in Figure 1a. (d) Atmospheric CO$_2$ predicted for the SRES emission pathways and specified for the WRE stabilization scenarios.

ing in year 2000, CO$_2$ emissions (dF/dt) and fossil fuel resources (F) are assumed to follow the logistic equation

$$\frac{dF}{dt} = aF(t)[F(1750) - F(t)]. \qquad (3)$$

We examine cases varying the value of the amount of CO$_2$ emitted to the atmosphere after year 2000, $F(2000)$. We assume $F(1750) = F(2000) + 270$ Pg C (= 990 Pg CO$_2$) (G. Marland et al., unpublished data, 2002) (available at http://cdiac.esd.ornl.gov/trends/emis/tre_glob.htm), and adjust a

Table 1. Mean Surface Ocean Results for Simulated Years 2100 and 2300

| Case	Atmospheric CO$_2$ Concentration, ppm	Surface Ocean ΔpH	$\Omega_{Calcite}$	$\Omega_{Aragonite}$
Preindustrial	280	...	5.2	3.4
Year 2000	370	−0.09	4.4	2.9
	IPCC SRES Pathways, Year 2100			
B2	820	−0.39	2.5	1.6
A2	970	−0.46	2.1	1.4
B1	650	−0.30	3.0	1.9
A1	710	−0.34	2.8	1.8
	"Logistic" Pathways, Years 2100/2300			
1250 Pg C	660/600	−0.31/−0.28	2.9/3.1	1.9/2.0
2500 Pg C	860/1020	−0.41/−0.49	2.4/2.0	1.5/1.3
5000 Pg C	1070/1980	−0.50/−0.77	2.0/1.1	1.3/0.7
10,000 Pg C	1240/4030	−0.56/−1.07	1.7/0.6	1.1/0.4
20,000 Pg C	1350/8110	−0.60/−1.37	1.6/0.3	1.0/0.2
	Stabilization Pathways, Years 2100/2300			
WRE450	450/450	−0.17/−0.17	3.8/2.5	2.5/2.5
WRE550	540/550	−0.23/−0.24	3.4/2.2	2.2/2.2
WRE650	600/650	−0.27/−0.31	3.1/2.0	2.0/1.9
WRE750	640/750	−0.29/−0.36	3.0/2.0	2.0/1.7
WRE1000	680/990	−0.32/−0.47	2.9/1.9	1.9/1.4
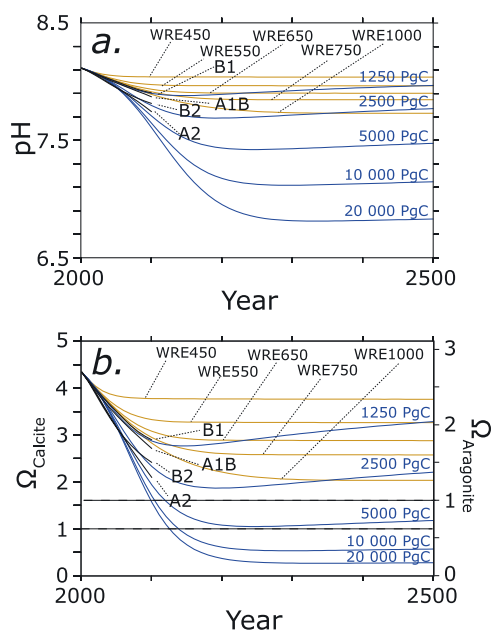
Figure 2. (a) Surface ocean pH and (b) calcite (Ω_{Calcite}) and aragonite ($\Omega_{\text{Aragonite}}$) saturation state starting from horizontal mean observed concentrations [*Key et al.*, 2004] with concentration changes applied from the three-dimensional ocean model simulations. Dashed lines show calcite and aragonite saturation.

such that $dF/dt = 6.8$ Pg C in year 2000. The *IPCC* [2001] estimates global fossil fuel resources to be roughly 5000 Pg C. Therefore we consider our base case to be 5000 Pg C (= 18,300 Pg CO$_2$) released to the atmosphere as CO$_2$ over several centuries. Given that typically only half of the reduced carbon is recovered in fossil fuel mining operations and there is a continuum of lower-grade carbon-rich shales, it is conceivable, given changing technology and economics, eventual fossil fuel recovery on land could reach 10,000 Pg C. Methane hydrates on continental shelves have been estimated to contain another 10,000 Pg C; if this were recovered, then total amounts of fossil fuel carbon would reach 20,000 Pg C. On the other hand, climate concerns could result in diminished release of fossil fuel carbon to the atmosphere, with the remainder of the fossil fuel resources permanently isolated from the atmosphere. Thus we examine cases in which from 1/4 to 4 times currently estimated fossil fuel carbon is released to the atmosphere as CO$_2$ over the next several centuries. We refer to these as "logistic" CO$_2$ emission pathways.

[22] Figure 1 shows the "logistic" CO$_2$ emission pathways with integrated emissions after year 2000 ranging from 1250 to 20,000 Pg C. We used our ocean model to simulate changes in ocean chemistry during 500 years of emissions under these pathways. Emission of 1250 Pg C produces an average surface ocean pH decrease of nearly 0.3 units by year 2300, whereas emission of 20,000 Pg C decreases surface pH by about 1.4 units. Emission of 5000 Pg C according to this scenario decreases surface ocean pH by about 0.8 pH units by 2300. Carbon absorbed by the ocean from the atmosphere initially affects the upper ocean, but is then mixed down into the ocean interior.
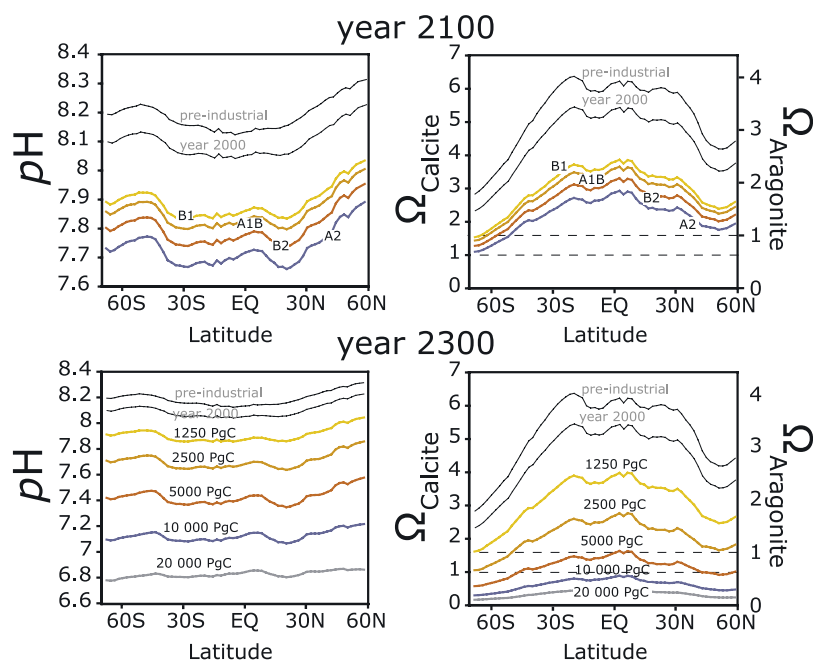
Figure 3. Predicted surface ocean pH change and calcite (Ω_{Calcite}) and aragonite ($\Omega_{\text{Aragonite}}$) saturation state in (top) year 2100 for the SRES emission pathways and (bottom) year 2300 for the "logistic" emission pathways. Preindustrial and year 2000 values are calculated from *Key et al.* [2004]. Chemistry changes are computed from zonal mean average concentrations in the three-dimensional ocean model. Dashed lines show calcite and aragonite saturation.
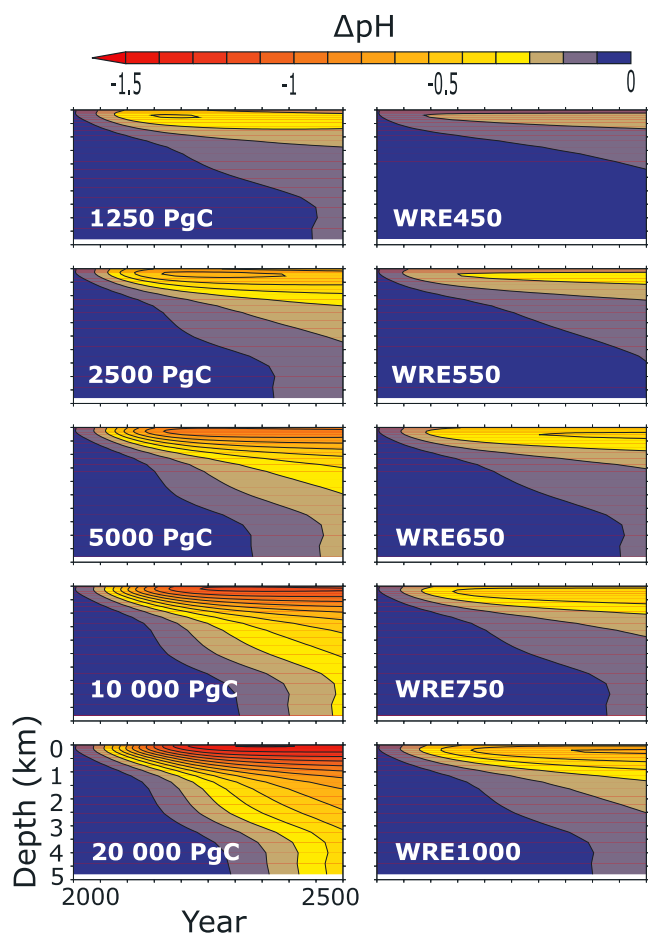
Figure 4. Predicted horizontal mean ocean pH as a function of depth and time for the "logistic" CO_2 emission pathways and WRE stabilization pathways. Chemistry changes starting from *Key et al.* [2004] are computed from horizontal mean concentrations in the three-dimensional ocean model simulations.

Because the pH of the upper thermocline is naturally lower than that of the surface waters, it is more sensitive to added carbon. Thus the greatest change in pH over the course of the simulation occurs several hundred meters below the ocean surface (Figure 4), even though the highest anthropogenic carbon concentrations are at the surface.

[23] By year 2300, the cases in which 10,000 Pg C and 20,000 Pg C are released to the atmosphere result in undersaturation of the surface ocean with respect to both calcite and aragonite. Emission of 1250 Pg C and 2500 Pg C produce surface waters that are saturated (on average) with respect to calcite but undersaturated with respect to aragonite (Figure 2). Emission of 5000 Pg C produces surface ocean waters that are saturated with respect to aragonite only near the equator and undersaturated with respect to calcite at high latitudes (Figure 3).

[24] Today, horizontally averaged seawater composition is saturated with respect to calcite from the surface of the ocean to a depth greater than 3 km (Figure 5). In all of the "logistic" emission cases considered here, the calcite lysocline shoals from deeper than 3 km to shallower than 1 km. For cases that cumulatively emit 2500 Pg C or more, the

calcite lysocline shoals to within a few hundred meters of the surface. In the transition, four layers can form from the top to the bottom that alternate with respect to calcite saturation, i.e., a surface layer that is calcite-saturated overlying a calcite-undersaturated layer in the thermocline, which in turn overlies a calcite-saturated layer centered at about 1.5 km depth overlying an undersaturated deep ocean (Figure 5a; see, for example, the 1250 Pg C case at year 2200).

3.2. Stabilization Cases

[25] Figure 1 shows the WRE450, WRE550, WRE650, WRE750, and WRE1000 atmospheric CO_2 stabilization pathways [*Wigley et al.*, 1996]. These pathways are designed to follow a "business-as-usual" trajectory prior to transition to stable atmospheric CO_2 concentrations. We use these pathways to address the question of ocean chemical consequences of atmospheric CO_2 stabilization.

[26] We used the model to simulate 500 years for each of the WRE450 through WRE1000 stabilization pathways. Computed atmospheric CO_2 emissions consistent with these stabilization pathways are shown in Figure 1. Changes in ocean pH and calcite and aragonite saturations states, based on mean changes in surface ocean chemistry, are shown in Figure 2. On a global mean basis, the WRE650 pathway produces a surface ocean with a pH more than 0.3 units lower than the preindustrial value. The WRE1000 pathway depresses surface ocean pH by about 0.5 pH units. On a global mean basis, surface waters remain saturated with respect to both calcite and aragonite in these simulations. However, the Southern Ocean eventually becomes undersaturated with respect to aragonite in the Southern Ocean in the WRE650, WRE750, and WRE1000 simulations. Predicted changes in surface ocean pH and calcite and
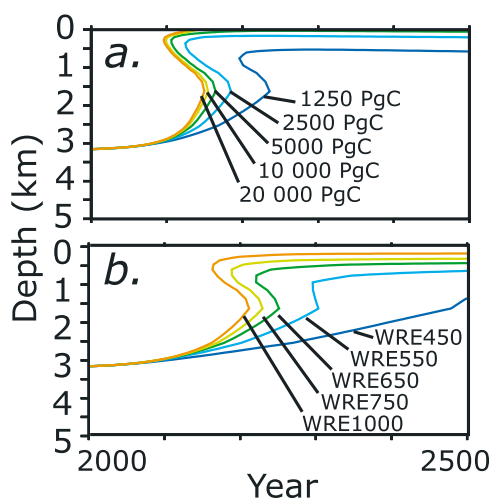
Figure 5. Changes in the depth of the calcite lysocline for (a) "logistic" emission pathways and (b) WRE stabilization pathways. The calcite lysocline represents the boundary between water that is saturated with respect to calcite and water that is undersaturated with respect to calcite. Today, the upper ocean is calcite saturated. Chemistry changes, starting from *Key et al.* [2004], are calculated from horizontal mean concentrations in the three-dimensional ocean model simulation.
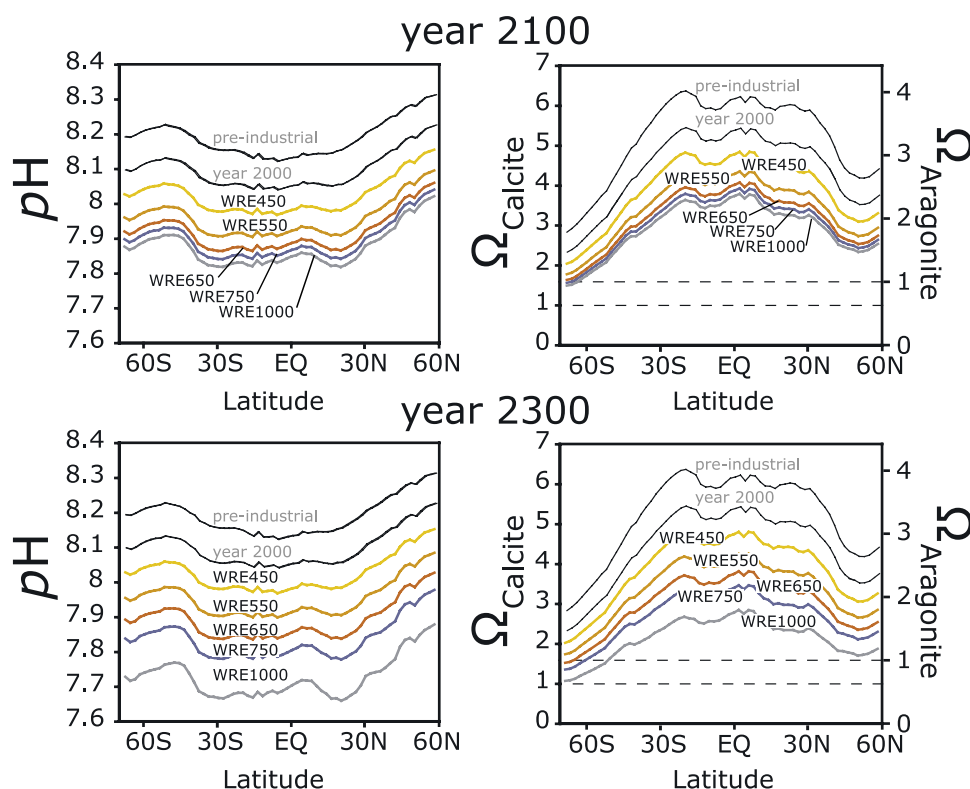
Figure 6. Predicted surface ocean pH change and calcite ($\Omega_{Calcite}$) and aragonite ($\Omega_{Aragonite}$) saturation state in (top) year 2100 and (bottom) year 2300 for WRE atmospheric CO_2 concentration stabilization pathways. Chemistry calculations are based on zonal mean concentrations from three-dimensional ocean model simulations described in the text. Preindustrial and year 2000 values are calculated from *Key et al.* [2004].

aragonite saturation states, based on zonal mean changes in dissolved inorganic carbon, are shown for year 2100 and year 2300 in Figure 6. Changes in ocean pH in depth and time, based on horizontal mean changes in dissolved inorganic carbon, are shown in Figure 4. In the WRE stabilization pathways that stabilize at 550 ppm, the calcite lysocline, computed from horizontal mean concentration changes, shoals from deeper than 3 km to shallower than 1 km (Figure 5b). Even with 450 ppm stabilization, most of the ocean volume becomes undersaturated with respect to calcite.

4. Mitigation

4.1. Deep Ocean CO₂ Injection

[27] The difference between a given emission pathway and the emissions allowable under an atmospheric CO_2 stabilization pathway could be thought of as a carbon gap that would need to be made up by increased carbon storage in biologic, geologic, or oceanic reservoirs (and/or by renewables, improved efficiency, nuclear, etc.) [*Hoffert et al.*, 1998, 2002; *Pacala and Socolow*, 2004]. We performed simulations in which the allowable CO_2 emissions to the atmosphere take into consideration the stabilization targets and the degassing to the atmosphere of some carbon earlier injected to the deep ocean (see section 2.2). When CO_2 is injected into the ocean in our simulations, we use the seven sites specified in OCMIP (Figure 7) and a nominal depth of 3 km. (Owing to limitation of the model grid, it is effec-

tively distributed uniformly between 2708 m and 3060 m.) We do not consider energy penalties associated with deep ocean CO_2 injection; thus, in the cases presented here, because energy would be needed for deep ocean injection, less energy would be available for other services in the injection cases than in the atmospheric release case.

[28] We consider the 5000 Pg C emission pathway and the WRE550 stabilization pathway (Figure 1) to be our central cases. We consider cases in which deep ocean CO_2 injection provides 100% or 10% of the mitigation effort needed to stabilize CO_2 at 550 ppm, assuming that the 5000 Pg C emission pathway represents a "business-as-usual" trajectory. If ever deployed, intentional ocean carbon storage would probably play a role as a part of a broader portfolio of approaches to climate mitigations [*Caldeira et al.*, 2004]. Thus the case in which ocean carbon storage provides 10% of the total mitigation effort required might be considered a "realistic" case in which intentional ocean carbon storage plays a significant, but not dominant, role in climate stabilization. The 100% oceanic injection case allows direct comparison of the effects of atmospheric release versus oceanic release.

[29] Using equations (1)–(3) above, we calculated the rate of ocean carbon injection needed to stabilize CO_2 according to the WRE550 pathway (Figure 8). In the case where ocean injection provides 100% of the mitigation effort ($k = 1$; see section 2.2), the total amount of carbon introduced to the ocean plus atmosphere equal to that of the 5000 Pg C emission pathway.). In the case where ocean
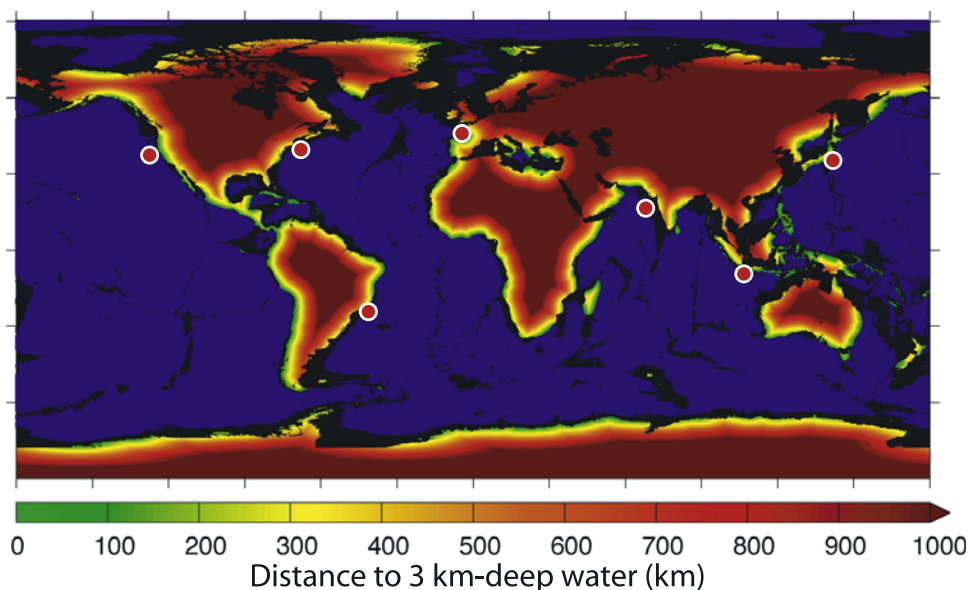
Figure 7. Injection locations. Blue represents ocean seafloor deeper than 3 km [*Smith and Sandwell*, 1997]. Colors on land represent distance to water deeper than 3 km. Coastal areas near deep water and CO$_2$ sources likely would be preferred locations for direct injection of CO$_2$ into the deep ocean.

injection provides 10% of the mitigation effort ($k = 0.1$), the total amount of carbon introduced to the ocean plus atmosphere is less that of the 5000 Pg C emission pathway because other approaches are assumed to provide 90% of the required mitigation. In these cases, deep ocean injection rates reach a maximum early in the 22nd century.

[30] For the 100% deep ocean injection case, allowable atmospheric emissions become negative by year 2200 (Figure 8). This is because CO$_2$ that had been injected into the deep ocean is escaping to the atmosphere at a rate that exceeds the atmospheric CO$_2$ emission rate allowed under the WRE550 stabilization pathway. This indicates that, even in principal, direct injection of CO$_2$ into the deep ocean would not be able to provide 100% of the required mitigation effort, but would need to be combined with some form of removal of CO$_2$ from the atmosphere [*Keith and Ha-Duong*, 2003]. In contrast, in the case where deep ocean injection provides 10% of the mitigation effort, in year 2500, atmospheric evasion of previously injected CO$_2$ is 0.3 Pg C yr^{-1}, less than the 0.9 Pg C yr^{-1} allowed under the WRE550 stabilization pathway. Thus degassing of previously injected CO$_2$ would diminish future CO$_2$ emissions allowed from other sources, but would not require active removal of CO$_2$ from the atmosphere.

[31] Direct injection of CO$_2$ into the ocean interior can produce regions with higher dissolved inorganic carbon concentrations than would occur with atmospheric release. CO$_2$ injected into the ocean interior is retained in the poorly ventilated isopycnal layers of the deep ocean but is lost to the atmosphere from the well-ventilated layers of the upper thermocline. Changes in ocean pH, based on horizontal mean ocean composition, are shown in Figure 9 for the cases described here. For the simulation in which deep ocean injection provides 100% of the mitigation effort, deep ocean pH values are much lower than in the WRE550 simulation, however, surface ocean pH values are nearly the same as in the WRE550 simulation.

[32] Volumes of water undergoing different changes in ocean pH, for years 2100 and 2300, are shown if Figure 10. If ocean injection were to provide 10% of the total abatement required, by year 2100, on the order of 1% of the ocean would have a large pH change relative to pH changes produced by the WRE550 pathway; by year 2300, this signal would spread out, so that most of the ocean would be roughly 0.1 pH unit lower than had the CO$_2$ emissions been abated without the use of the oceans. If ocean injection were to provide 100% of the total abatement required, on the order of 10% of the ocean would have a large pH change relative to pH changes produced by the WRE550 pathway; by year 2300, this signal would spread out, and most of the ocean would have a pH more than 0.5 unit lower than had the CO$_2$ emissions been abated without the use of the oceans. Ocean CO$_2$ injection could be engineered to disperse the carbon through a large range of depths in the deep ocean, and this would reduce the maximum change in horizontal mean ocean chemistry.

4.2. Dissolution of Carbonate Minerals

[33] It has been suggested [*Kheshgi*, 1995; *Rau and Caldeira*, 1999; *Caldeira and Rau*, 2000] that chemical effects of CO$_2$ addition to the ocean could be mitigated by the introduction of alkalinity to the oceans. Because of its abundance, CaCO$_3$ is the most likely source of this alkalinity. Figure 11 shows how surface ocean pCO$_2$, pH, and [COB$_3^{2-}$] would change for different amounts of added CO$_2$ and different amounts of dissolved CaCO$_3$ per unit added CO$_2$. It can be seen that the chemical mitigation provided by the dissolution of carbonate minerals is substantial, but partial. To maintain a constant carbonate-ion concentration in a closed system, somewhat less than 1 mol CaCO$_3$ would need to be added per mol of CO$_2$. To do this on a large scale implies massive amounts of carbonate mineral [*Rau and Caldeira*, 1999]. Furthermore, this would not completely mitigate the
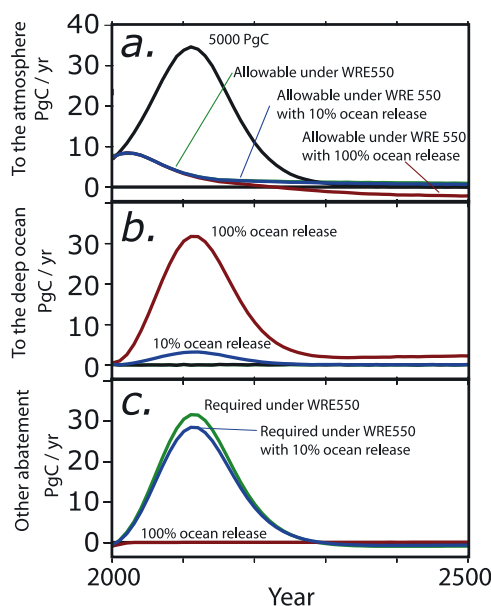
Figure 8. Emissions and abatement associated with achieving WRE550 atmospheric CO_2 stabilization starting from a 5000 Pg C (= 18,300 Pg CO_2) atmospheric CO_2 emission scenario: (a) emission to the atmosphere, (b) injection to the deep ocean, and (c) emissions abatement assumed to be provided by approaches other than direct CO_2 injection in the deep ocean. In each panel the black line represents a trajectory to emit 5000 Pg C of fossil fuel carbon over several centuries according to a smooth logistic curve described in the text; the green line represents emissions for CO_2 stabilization at 550 ppm according to the *Wigley et al.* [1995] pathway (this line is often hidden behind the blue line); the red line represents emissions changes that would be needed if ocean injection made up 100% of the carbon emissions avoidance; and the blue line represents emissions changes that would be needed if ocean injection made up 10% of emission avoidance, with 90% of avoidance coming from other means.

change in pH or pCO₂. If enough $CaCO_3$ were dissolved to mitigate the change in pCO₂, ocean pH and carbonate-ion concentrations would be higher than in their natural state. Nevertheless, addition of $CaCO_3$ with CO_2 brings ocean pCO₂, pH, and $[COB_3^{2-}]$ closer to their natural state than they would be with the addition of CO_2 alone. Thus there is potential to diminish chemical perturbation from added CO_2, perhaps locally, through the dissolution of carbonate minerals.

5. Discussion and Conclusions

[34] It is the goal of this study to allow a first-order correspondence to be made between studies of marine biological effects of added CO_2 and various CO_2 emissions and stabilization pathways. A wide range of biological studies suggests a sensitivity of marine biological systems to added CO_2 through a variety of mechanisms [e.g., *Kurihara et al.*, 2004; *Pörtner et al.*, 2004; *Langdon et al.*, 2003; *Seibel and Walsh*, 2001; *Riebesell et al.*, 2000].

[35] We have performed several sets of model simulations to address two questions: (1) what changes in ocean

chemistry would be expected on the century and multi-century timescale for a range of atmospheric CO_2 emission and atmospheric CO_2 stabilization pathways?; (2) what changes in ocean chemistry would be expected if direct injection of CO_2 into the deep ocean were to be a significant contributor to atmospheric CO_2 stabilization?

[36] Our simulations indicate that the SRES B1, A1, B2, and A2 pathways all lead to aragonite undersaturation in the surface Southern Ocean by year 2100. This is somewhat surprising, since the B1 pathway is often looked upon as a relatively benign "spontaneous stabilization" pathway. The WRE650, WRE750, and WRE1000 stabilization pathways eventually produce aragonite undersaturation in all or parts of the Southern Ocean. The WRE550, WRE650, WRE750, and WRE1000 pathways result in the calcite lysocline shoaling from a mean depth of greater than 3 km to a mean depth less than 1 km. Even relatively modest increases in atmospheric CO_2 (e.g., to 450 ppm) cause the deep ocean to
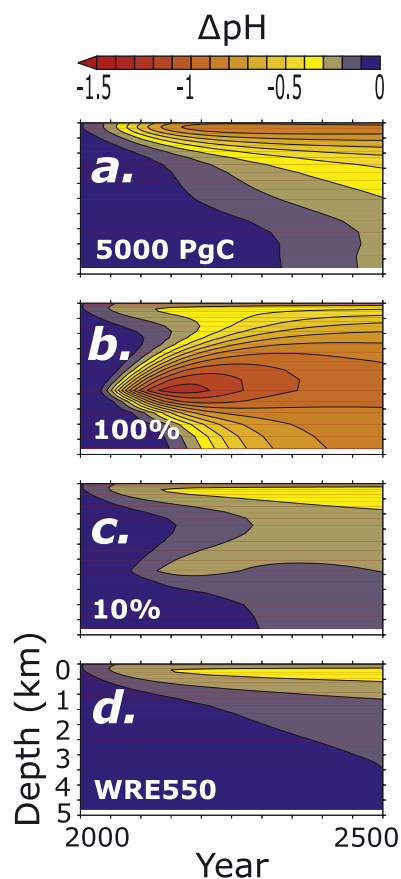
Figure 9. Changes in ocean pH predicted to occur if ocean carbon storage is used to stabilize CO_2 according to the WRE550 stabilization trajectory given total CO_2 emissions from the "logistic" 5000 Pg C (= 18,300 Pg CO_2) scenario. Ocean pH changes resulting from (a) atmospheric emission of 5000 Pg C (see Figure 4); (b) WRE550 atmospheric CO_2 pathway with injection at 3 km at 100% of the rate required to maintain total CO_2 release rate equal to that in Figure 9a; (c) WRE550 atmospheric CO_2 pathway with injection at 3 km at 10% of the rate required to maintaining total CO_2 release rate equal to that in Figure 9a; and (d) the WRE550 atmospheric CO_2 pathway (see Figure 4).
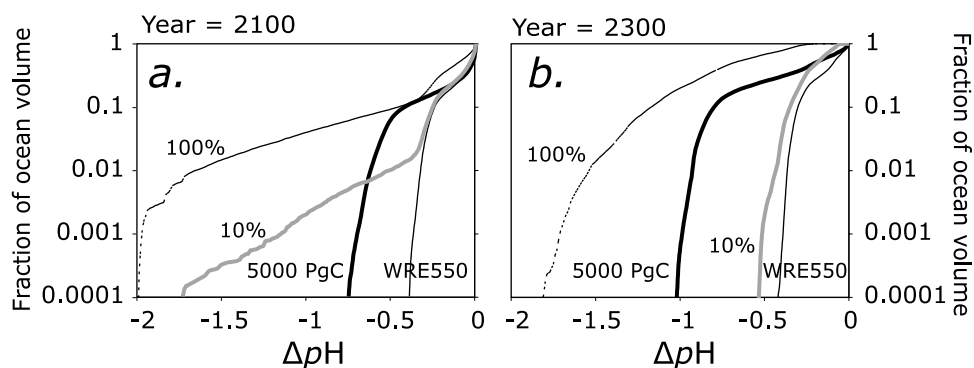
Figure 10. Fraction of ocean volume (between 60°N and 60°S) with a pH change greater than some specified amount in (a) year 2100 and (b) year 2300 for the cases shown in Figures 8 and 9. Lines are as follows: "5000 Pg C" shows predicted pH consequences of releasing 5000 Pg C of fossil fuel carbon to the atmosphere over several centuries according to a smooth curve described in the text; "WRE550" shows ocean pH changes predicted to result from CO2 stabilization at 550 ppm according to the WRE550 pathway; "100%" shows ocean pH changes that would be expected if ocean injection made up 100% of the carbon emissions avoidance; and "10%" shows ocean pH changes that would be expected if ocean injection made up 10% of emission avoidance, with 90% of avoidance coming from other means.

make a transition from being predominately saturated with respect to calcite to predominately undersaturated with respect to calcite.

[37] A pathway that releases 5000 Pg C (= estimated fossil fuel resources) to the atmosphere over the next several centuries causes the ocean to become undersaturated with respect to aragonite over nearly the entire surface. If organic-carbon rich shales or methane hydrates should prove minable, ultimate emissions could exceed 5000 Pg C. A pathway that emits 10,000 Pg C of CO2 to the atmosphere is predicted to produce surface ocean conditions that are undersaturated with respect to calcite nearly everywhere. Even if only one quarter of currently estimated fossil fuel resources are ultimately emitted to the atmosphere (= 1250 Pg C) as CO2, the ocean below 1 km is predicted to make a transition from being mostly saturated with respect to calcite to mostly undersaturated with respect to calcite.

[38] The SRES pathways considered here produce global surface pH reductions of about 0.3 to 0.5 pH units by year 2100. This is roughly the same reduction as produced by the WRE650 and WRE1000 stabilization scenarios and by the 1250 Pg C emission scenario by year 2300. Atmospheric emissions of 5000 Pg C and 20,000 Pg C produce global surface pH reductions of 0.8 and 1.4 pH units, respectively by year 2300.

[39] For the simulation in which deep ocean injection provides 100% of the mitigation effort, deep ocean pH values are much lower than in the WRE550 simulation; however, surface ocean pH values are nearly the same as in the WRE550 simulation. There is potential to diminish chemical perturbation from added CO2, perhaps locally, through the dissolution of carbonate minerals.

[40] In our simulations, the SRES B1 results are similar to those of WRE750 and the SRES A1 results are similar to that of WRE1000. Furthermore, the 1250 Pg C emission scenario lies between the WRE550 and WRE650. This suggests that if we are to stabilize atmospheric CO2 at twice the preindustrial value, and use 5000 Pg C in fossil fuel resources, three quarters of that fossil fuel will need to

be used with carbon capture and storage. Atmospheric results for the 2500 Pg C emission pathway are similar to those from the WRE1000 stabilization pathway. Thus stabilization at 1000 ppm might require carbon capture and storage for roughly half of the carbon in remaining fossil fuel resources.

[41] We did not simulate effects of changes in climate, circulation, and marine biology. In the simulations of *Sarmiento et al.* [1998], these feedbacks produced second-order effects on carbon uptake. Carbonate dissolution effects are thought to be small on the timescales considered here [*Heinze*, 2004; *Zondervan et al.*, 2001; *Archer et al.*, 1997, 1998], but would operate to lessen the magnitude of our results. We conjecture, but have not proved, that consideration of these feedbacks would produce second-order modifications to our basic results.

[42] Using a 5000 Pg C emission pathway and a 550 ppm atmospheric stabilization target, our simulations indicate that injection of CO2 into the deep ocean alone could not fill the entire carbon emission−free energy gap in the absence of CO2 removal from air. After several centuries of deep sea injection, the flux of previously injected carbon dioxide degassing to the atmosphere would exceed the total allowable CO2 emissions under the stabilization pathway. Without atmospheric removal, atmospheric CO2 content would increase. In contrast, when ocean injection fills 10% of the CO2 emission avoidance "gap," degassing of injected carbon is generally far slower than the CO2 emission rate allowed under the stabilization pathway. So, from the point of view of effectiveness of storage, ocean injection could potentially solve 10% of the problem, but could not solve 100% of the problem in the absence of active CO2 removal from air several centuries into the future. Deep ocean CO2 injection as an alternative to atmospheric release makes a greater chemical impact on the deep ocean as the price for having less of an impact on the surface ocean and climate.

[43] Our results indicate that atmospheric release of CO2 will produce changes in ocean chemistry that could
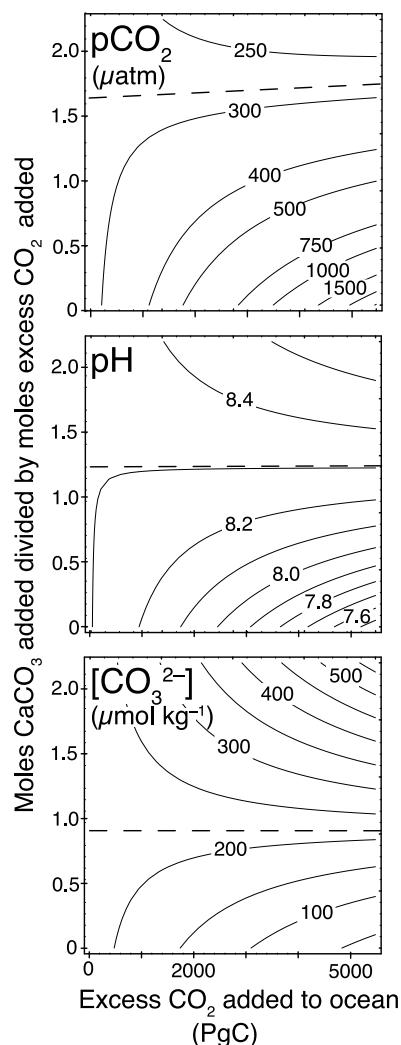
Figure 11. Effects of adding CO_2 and dissolved $CaCO_3$ on mean surface ocean chemistry, assuming uniform distribution in the ocean. $CaCO_3$ dissolution can mitigate much, but not all, of the chemical effects of CO_2 addition. The dashed lines indicate no change in the chemical parameter (pCO_2, pH, or $[CO_3^{2-}]$). For example, a uniform addition of 2000 Pg C as CO_2 and 8800 Pg $CaCO_3$ to a preindustrial ocean with a pCO_2 of 280 μatm (molar ratio = 1.2) would produce roughly 340 μatm pCO_2, almost no change in pH, and a carbonate-ion concentration roughly 20 μmol kg^{-1} higher than present.

affect marine ecosystems significantly, even under future pathways in which most of the remaining fossil fuel CO_2 is never released. Thus chemical effects of CO_2 on the marine environment may be as great a cause for concern as the radiative effects of CO_2 on Earth's climate.

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