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Glacial – interglacial atmospheric CO$_2$ change: a simple "hypsometric effect" on deep-ocean carbon sequestration? [*]

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Abstract

Given the magnitude and dynamism of the deep marine carbon reservoir, it is almost
certain that past glacial – interglacial fluctuations in atmospheric CO$_2$ have relied at
least in part on changes in the carbon storage capacity of the deep sea. To date,
5 physical ocean circulation mechanisms that have been proposed as viable explana-
tions for glacial – interglacial CO$_2$ change have focussed almost exclusively on dynam-
ical or kinetic processes. Here, a simple mechanism is proposed for increasing the
carbon storage capacity of the deep sea that operates via changes in the volume of
southern-sourced deep-water filling the ocean basins, as dictated by the hypsometry
10 of the ocean floor. It is proposed that a water-mass that occupies more than the bottom
3 km of the ocean will essentially determine the carbon content of the marine reservoir.
Hence by filling this interval with southern-sourced deep-water (enriched in dissolved
CO$_2$ due to its particular mode of formation) the amount of carbon sequestered in the
deep sea may be greatly increased. A simple box-model is used to test this hypothesis,
15 and to investigate its implications. It is suggested that up to 70% of the observed glacial
– interglacial CO$_2$ change might be explained by the replacement of northern-sourced
deep-water below 2.5 km water depth by its southern counterpart. Most importantly, it
is found that an increase in the volume of southern-sourced deep-water allows glacial
CO$_2$ levels to be simulated easily with only modest changes in Southern Ocean biolog-
20 ical export or overturning. If incorporated into the list of contributing factors to marine
carbon sequestration, this mechanism may help to significantly reduce the "deficit" of
explained glacial – interglacial CO$_2$ change.

1 Explaining glacial – interglacial CO$_2$ change

Although it is clear that changes in atmospheric CO$_2$ have remained tightly coupled
25 with global climate change throughout the past ~730 000 years (Siegenthaler et al.,
2005), the mechanisms responsible for pacing and moderating CO$_2$ change remain a

mystery. The magnitude of the marine carbon reservoir, and its inevitable response to changes in atmospheric CO_2 (Broecker, 1982a), guarantees a significant role for the ocean in glacial – interglacial CO_2 change. Based on thermodynamic considerations, glacial atmospheric CO_2 would be reduced by up to ~30 ppm simply due to the increased solubility of CO_2 in a colder glacial ocean; however this reduction would be counteracted by the reduced solubility of CO_2 in a more saline glacial ocean and by a large reduction in the terrestrial biosphere under glacial conditions (which would release carbon to the other global reservoirs) (Broecker and Peng, 1989; Sigman and Boyle, 2000). The bulk of the glacial – interglacial CO_2 change therefore remains to be explained by more complex inter-reservoir exchange mechanisms, and the most viable proposals involve either the biological- or the physical "carbon pumps" of the ocean. Indeed it appears that whichever mechanism is invoked to explain glacial – interglacial CO_2 change must involve changes in the sequestration of CO_2 in the deepest marine reservoir (Broecker, 1982a; Boyle, 1988, 1992; Broecker and Peng, 1989).

To date, three main types of conceptual model have been advanced in order to explain glacial – interglacial atmospheric CO_2 change: 1) those involving an increase in the export of organic carbon to the deep sea, either via increased nutrient availability at low latitudes or via increased efficiency of nutrient usage at high latitudes (Broecker, 1982a, b; Knox and McElroy, 1984); 2) those involving a reduction in the ventilation of water exported to the deep Southern Ocean (Siegenthaler and Wenk, 1984; Toggweiler and Sarmiento, 1985), either via sea-ice "capping" (Keeling and Stephens, 2001) or a change in ocean interior mixing efficiency (Toggweiler, 1999; Gildor and Tziperman, 2001); and 3) those involving changes in ocean chemistry and the "carbonate compensation" mechanism, possibly involving changes in the ratio of organic carbon and carbonate fluxes to the deep sea (Archer and Maier-Reimer, 1994). Each of these conceptual models has its own set of difficulties in explaining the pattern and magnitude of past glacial – interglacial CO_2 change (Archer et al., 2000b; Sigman and Boyle, 2000), and none is likely to have operated in isolation. However, one aspect of all of the proposed models that emerges as being fundamental to any mechanism propos-

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ing to explain glacial – interglacial CO_2 change is the balance between carbon export from the surface-ocean and carbon "reflux" by the overturning circulation of the ocean. These two processes, one biological and one physical, essentially determine the balance of carbon input into and output from (and therefore the carbon concentration of) the deepest marine reservoirs.

The regions of deep-water formation in the North Atlantic and especially in the Southern Ocean play a key role in setting the "physical side" of this balance, with which this study is primarily concerned. In the North Atlantic, carbon uptake via the "solubility pump" is enhanced by the large temperature change that surface water must undergo before being exported into the ocean interior. The formation of North Atlantic deep-water therefore represents an efficient mechanism for mixing CO_2 deep into the ocean interior (Sabine et al., 2004); though only to the extent that it is not completely compensated for (or indeed over-compensated for) by the eventual return flow of carbon-enriched deep-water back to the surface. It is in controlling the extent to which the return flow of deep-water to the surface (which occurs primarily in the Southern Ocean) represents a net "reflux" of carbon to the atmosphere that the formation of deep-water in the Southern Ocean plays a pivotal role in controlling the overall efficiency of the ocean's physical carbon pump. The key point here, as pointed out by Broecker (1999), is that up-welled (cold, carbon-rich) deep-water will only yield up its dissolved CO_2 if it is able to equilibrate with the atmosphere, and hence if the residence time of any up-welled water that actually reaches the surface-ocean is sufficiently long with respect to the gas-exchange rate, and the rate of biological export.

Today, the bulk of the deep ocean (although not the deep Atlantic) is "ventilated" from the Southern Ocean, by Circumpolar Deep Water (CDW) that is exported northwards into the various ocean basins from the eastward circulating Antarctic Circumpolar Current (ACC) (Orsi et al., 1999). This deep-water remains relatively poorly equilibrated with the atmosphere, and therefore maintains an elevated CO_2 content (TCO_2). In part this is because the rate of ocean – atmosphere CO_2 exchange cannot keep up with the rate of overturning in the uppermost Southern Ocean (Bard, 1988); however

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it is primarily because the bulk of southern sourced deep- and bottom-water is either produced via a combination of brine rejection below sea-ice and entrainment from the sub-surface, or else converted from "aged" northern-sourced deep-waters that are up-welled in the Southern Ocean (Orsi et al., 1999; Speer et al., 2000; Webb and Suginohara, 2001). Intense turbulent vertical mixing around topographic features in the deep Southern Ocean helps to enhance the amount of "carbon rich" sub-surface water that is incorporated into the CDW (from above and from below), and subsequently exported northwards to the Atlantic and Indo-Pacific (Orsi et al., 1999; Naviera Garabato et al., 2004). The process of deep-water export in the Southern Ocean may therefore be viewed as a mechanism for "recycling" carbon-rich water within the ocean interior, circumventing ocean – atmosphere exchange, and eventual CO_2 leakage to the atmosphere. Given these considerations, it is clear that investigations of the mechanisms of CO_2 draw-down by the physical ocean circulation will depend sensitively on the exact flow scheme that is either posited (in box-models) or simulated (in general circulation models; GCMs), particularly for the Southern Ocean.

The first investigation into the potential importance of the overturning circulation in setting the atmospheric CO_2 concentration was performed by Broecker and Peng (1989), who made use of the 10-box PANDORA box-model in order to assess the impact of variations in the export of North Atlantic Deep Water (NADW) on the alkalinity at the surface of the Southern Ocean, the pCO_2 of which was proposed to control that of the atmosphere. In this study it was suggested that a reduced export of low-alkalinity NADW, eventually reaching the surface Southern Ocean (via the deep Atlantic), might account for approximately half of the observed glacial – interglacial atmospheric CO_2 change. In a subsequent study, Toggweiler (1999) made use of a hierarchy of box-model experiments to illustrate the specific importance of deep-water ventilation (vertical mixing) locally in the Southern Ocean in setting atmospheric CO_2, indicating that ~25% of the glacial – interglacial CO_2 difference could be achieved, given a prescribed "biological pump" efficiency, by simply changing the net rate of export of carbon-rich water to the deep Southern Ocean. A similar effect, "bottling up" CO_2 in the deep

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Southern Ocean, has been obtained by changing the density, and therefore the up-welling efficiency, of carbon-rich deep-water in the Southern Ocean (Gildor and Tziperman, 2001), and by "capping" the Southern Ocean with sea-ice (Keeling and Stephens, 2001). The differences between these last three physical mechanisms are rather subtle, amounting to a shift in focus from the rate of deep-water export from the Southern Ocean (Toggweiler, 1999); to the rate of deep-water up-welling in the Southern Ocean (Gildor and Tziperman, 2001); to the modulation of the extent of equilibration of the surface Southern Ocean with the atmosphere (Keeling and Stephens, 2001). A more recent proposal (Watson and Naveira Garabato, 2006) for how Southern Ocean circulation and mixing might control atmospheric CO_2 levels has synthesised some of the main premises of the earlier hypotheses to provide a coherent mechanism that involves both a reduction in the overturning rate of the whole ocean (attributed to increased density stratification) and a suppression of up-welling (hence vertical mixing) in the uppermost Southern Ocean.

It is notable that all of the "physical pump" mechanisms that have been proposed as significant controls on glacial – interglacial CO_2 change have referred to dynamical (ocean mixing rate) or kinetic (ocean – atmosphere exchange rate) effects. Consideration of changes in the geometry, and therefore the volumes, of different intra-oceanic carbon reservoirs (i.e. different deep-water "masses") has largely escaped explicit treatment. One recent box-model simulation did include volumetric changes in the deep-water masses filling the ocean basins (Watson and Naveira Garabato, 2006), but did not examine their effects on CO_2 sequestration explicitly. The purpose of the present study is to address this specific issue, by advancing the simple hypothesis that changes in the volumes of different glacial deep-water masses, prior to their overturning or mixing rates, may significantly affect the amount of carbon that can be "bottled up" in the deep ocean. In this hypothesis, particular emphasis is placed on how the hypsometry of the ocean basins (the area distribution at different water depths) may affect the efficiency of volumetric water-mass changes that are caused by the vertical shoaling/deepening of water-mass mixing boundaries. A notable fact in this regard is that

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~56% of the sea-floor lies between 6000 and 3000 m (Menard and Smith, 1966), thus accounting for a majority increment in the ocean's volume. If a water mass that once occupied the >5 km interval in the Atlantic comes to occupy the >2 km interval, it will have increased its volume in this basin almost four-fold.

2 A thought experiment: a "southern flavour ocean"

One of the least ambiguous aspects of the palaeoclimate archive is the record of glacial – interglacial change in $\delta^{13}C$ recorded by benthic foraminifera from the Atlantic Ocean (Duplessy et al., 1988; Curry and Oppo, 2005). The data suggest a very positive $\delta^{13}C$ of dissolved inorganic carbon (DIC) in the upper ~2 km of the Atlantic, and a very negative $\delta^{13}C$ of DIC below this in the deepest Atlantic. The most widespread and well-supported interpretation of these data is that they represent a redistribution of glacial northern – and southern sourced deep- and intermediate water-masses, including in particular an incursion of glacial southern-sourced deep-water (rich in re-mineralised nutrients, and hence low $\delta^{13}C$ carbon) into the deep North Atlantic, up to a water depth of ~2–3 km (Curry et al., 1988; Duplessy et al., 1988; Oppo and Fairbanks, 1990; Oppo et al., 1990; Boyle, 1992). This interpretation draws implicit support from glacial benthic Cd/Ca and Zn/Ca ratios from the North Atlantic (Boyle, 1992; Keigwin and Lehmann, 1994; Marchitto et al., 2002), benthic radiocarbon measurements from the North Atlantic (Keigwin, 2004; Skinner and Shackleton, 2004; Robinson et al., 2005), neodymium isotope measurements (ε_{Nd}) from the Southern Ocean (Rutberg et al., 2000; Piotrowski et al., 2004, 2005), as well as an elegant box-model investigation of the possible causes of glacial deep-ocean chemistry (Michel et al., 1995).

Given this one apparently robust constraint on the deep-water geometry near the height of the last glaciation, one question immediately arises: how much must the volume of southern-sourced deep-water have increased in order to accomplish this change (i.e. filling the deep Atlantic, and dominating the deep-water export to the Indian and Pacific basins), and what would have been the immediate effect on deep-

water CO_2 sequestration? Answering the first part of this question is straightforward enough: as noted above, based on the hypsometry of the Atlantic basin (Menard and Smith, 1966), raising the upper boundary of southern-sourced deep-water (assumed for the sake of argument to be flat) from 5 km to 2.5 km in the Atlantic requires this water-mass to increase its Atlantic volume from just under ~20 million km^3 to nearly ~70 million km^3 (almost a 4-fold increase). In order to determine the eventual impact of this volumetric change on the carbon-storage capacity of the ocean we would require a great deal more information, including knowledge of the chemistry of the various deep-water masses in the ocean as well as their turnover and "ventilation" (atmosphere equilibration) rates, and the flux of dissolved carbon that they eventually incorporate via biological export. However, if we assume simplistically that nothing in the ocean changes except the volume occupied by southern-sourced deep-water (i.e. the chemistry and flow-rates of all water-masses stays the same, but not their volumetric contribution to the ocean's total budget) – and that ocean volume is constant – then we can infer that for a 4-fold increase in the volume of AABW at the expense of NADW (having average TCO$_2$ concentrations of ~2280 μmol kg^{-1} and ~2180 μmol kg^{-1}, respectively (Broecker and Peng, 1989)) the ocean would need to gain ~63 Gt of carbon. If we ignore all carbon exchanges with the ocean except from the atmosphere, our thought experiment implies that pre-industrial atmospheric pCO$_2$ would be reduced by ~20 ppm. This is equivalent to ~25% of the total observed glacial – interglacial CO$_2$ change (Siegenthaler et al., 2005).

Clearly many of the assumptions made in this thought experiment are not entirely valid: the chemistry and dynamics, not to mention the character and rate of biological export, of the glacial ocean will not have remained constant. Nevertheless, palaeo-ceanographic proxy evidence holds that the basic premise of the experiment is robust: the volume of southern-sourced deep-water did indeed increase significantly during the last glaciation. It seems important therefore to evaluate the impacts of this premise in a slightly more sophisticated way. Below, a simple box model is used to this end.

3 A box-model experiment

Figure 1 illustrates a simple box-model that has been constructed in order to explore in more detail the implications of deep-water mass geometry (and overturning rate) changes for glacial – interglacial CO_2 variability. This model comprises an atmosphere and six ocean boxes (Southern Ocean, low-latitude, North Atlantic, northern deep-water, intermediate-water and southern deep-water), and involves two coupled circulation cells driven by down welling in the southern- and northern high latitudes. Particle fluxes are treated as directly exported dissolved matter, with carbon, phosphate, and nitrogen being exported in fixed proportions, as defined by the Redfield Ratios (C:N:P=106:16:1), and carbonate being exported in fixed proportion to the total dissolved CO_2 of the water. The thermodynamics of the carbonate system are defined according to Millero (1995). The calculated components of the model include phosphate, alkalinity, total dissolved CO_2 (TCO_2) and pCO_2. Although the flow scheme of the box model essentially represents an Atlantic Ocean only, it is scaled to global proportions so that the volumes and concentrations of the atmosphere and the ocean balance with global budgets (all of which are fixed input parameters). This scaling is expected to increase the sensitivity of the model atmosphere to changes in ocean-box parameters, and should be borne in mind. The model is initiated with the concentrations of all boxes set to the global average, except for the pCO_2 of the surface boxes and the atmosphere, which are set to zero. In all model runs, for 'modern' or 'glacial' conditions, temperatures and salinities are kept constant, under the premise that the effects of these changes, combined with the estimated changes in the terrestrial biosphere, will have approximately cancelled out (Sigman and Boyle, 2000).

Particle fluxes in the model are defined as "export productivity" values and therefore represent the net amount of organic carbon exported from the surface to the deep Southern Ocean (P_s), to the intermediate ocean (P_I) and to the deep North Atlantic (P_n). Exchange fluxes (mixing rates) are defined between boxes where net thermohaline circulation fluxes do not exist, providing a mechanism for mixing: 1) the low-latitude

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and intermediate boxes; 2) the northern- and intermediate boxes; and 3) the northern- and southern deep-water boxes. The addition of mixing fluxes across other box boundaries (where unidirectional flow is prescribed) would tend to damp contrasts between box concentrations, much like a "diffusivity" term. The resulting model is broadly similar to that of Toggweiler (1999), though it makes use of a rather different circulation set-up, devised in order to emphasise the bi-polar character of the Atlantic deep circulation and in order to more effectively decouple the average deep-sea chemistry from "vertical mixing rates", as opposed to deep water-mass geometry and overturning rates. Arguably, only a box-model that includes the export of deep-water from the southern ocean (currently the volumetrically largest body of deep-water formed) may represent a realistic depiction of the physical carbon pump. It is important to stress that this box model can only include a highly simplified representation of the ocean circulation system (which is described today only with great difficulty; see Ganachaud and Wunsch, 2000), such that the utility of such a model ultimately lies in providing a testing ground for geologically founded premises that are held in parallel, and in providing test criteria that may eventually be sought in or refuted by the geological record, or indeed more complex general circulation models. It should be stressed that the motivation of this study is not to provide a full explanation of glacial – interglacial atmospheric CO_2 change, but rather to advance a simple hypothesis that appears to have been overlooked, and to test its conceptual merit.

The model will be explored in two stages. First, a "base-line" model parameterisation using modern input estimates will be defined, allowing the sensitivity and "skill" of the model to be evaluated. After this, the model will be applied to a "southern flavour" glacial scenario, where the deep ocean is dominated by southern-sourced deep-water, and where deep-water export rates are varied. This will provide an opportunity to test the capacity for changes in deep water-mass distributions (as well as their overturning rates) to significantly affect atmospheric CO_2. Finally, the results of the model runs will be summarised and the implications of this study for millennial and glacial – interglacial changes in the carbon cycle will be drawn.

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4 Model parameterisation and inputs

The majority of the input parameters of the model (including chemical ratios, global masses, ocean volumes and areas, net flow rates, temperatures and salinities) are reasonably well constrained by modern measurements and estimates. Of less certainty are the magnitudes of the particle fluxes (i.e. the export productivity to the intermediate and deep ocean) and the mixing rates in the ocean interior, both of which are absolutely critical in determining the partitioning of carbon between the ocean and the atmosphere. As noted above, the particle fluxes P_s, P_l and P_n represent the export of organic carbon to the deep Southern Ocean, the intermediate low-latitude ocean and the deep North Atlantic respectively.

Given that organic carbon is readily re-mineralised in the marine environment, with only ~1% reaching the deepest ocean (Martin et al., 1987; Santos et al., 1994; Chester, 2003), P_n and P_s will be only a fraction of P_l, the export productivity of the low-latitude surface ocean (100 m depth). Estimates summarised in Chester (2003) indicate an average export productivity (from 100 m water depth) of ~2 mol C m^{-2} yr^{-1} for both low-latitude/equatorial and North Atlantic waters. The total global primary productivity is estimated to be ~11.9 mol C m^{-2} yr^{-1} (Chester, 2003), and ~12% of this should equal the net export of organic matter from the global surface ocean. Provided that a maximum of ~2% of primary production will reach a depth of ~2000 m (and thus enter the deep boxes in the model presented here), and given that there is approximately twice as much primary production in the northern- versus the southern high-latitude Atlantic sectors (Longhurst et al., 1995), the particle fluxes P_s, P_l and P_n can be estimated to be ~0.2, ~2 and ~0.4 mol C m^{-2} yr^{-1} respectively. Due to the longer residence time of organic matter in the intermediate box than in the northern and southern down-welling boxes, the export of organic matter from the intermediate box to the deep boxes is set to 10 % of P_l, or ~1% of the primary productivity, in line with modern estimates (Chester, 2003). This export flux is partitioned between the northern and southern deep boxes in proportion to their respective volumes.

In order to avoid the unrealistic situation of continued carbon export from the surface boxes when nutrient concentrations drop to zero, variable particulate fluxes are defined using a "Michaelis-Menton" type parameterisation, such that:

$$P = P_{\text{max}} - \frac{P_{\text{max}}}{1 + e^{(C_P - 0.01)/0.05}} \tag{1}$$

where P indicates the instantaneous particle flux, P_{max} represents the maximum particle flux (as defined for each surface box above), and C_P indicates the instantaneous "dissolved particle" concentration in the surface box. Numerical values in the exponential denominator of this function are arbitrarily chosen in order to produce a rapid tailing off of particle export only at very low nutrient concentrations.

Defining the mixing rates of the ocean interior, as represented in a simplified box-model, is most problematic. For this reason, these parameters have been treated initially as "free variables" and hence estimated on the basis of sensitivity tests and model skill in reproducing modern atmospheric CO_2. Other model outputs (total dissolved CO_2, phosphate and alkalinity) are then used to evaluate the overall skill of the box-model, once is has been "tuned" to modern atmospheric CO_2 in this way. The flow rates for the northern- and southern thermohaline circulation cells, F_n and F_s, respectively, are defined based on the estimates of Ganachaud and Wunsch (2003), with ~15 Sv of deep-water being exported southward from the North Atlantic and ~6 Sv being exported northward into the Atlantic from the Southern Ocean (giving a total of ~21 Sv of overturning in the ocean). The modern parameterisation outlined above, which represents a pre-industrial Holocene scenario, is summarised in Table 1. This parameterisation has been used as a basis for sensitivity tests, carried out by varying the main "tuning parameters" of the model: the particle fluxes, and the mixing rates.

4.1 Model sensitivity

The sensitivity of modelled atmospheric pCO_2 is illustrated in Figs. 2 and 3 (above) with respect to variable mixing rates (f_{li}, f_{ns} and f_{ni}), and in Figs. 4 and 5 with respect to

variable particle fluxes (P_s, P_l and P_n). Thus in Figs. 2 and 3 it is evident that modelled atmospheric pCO_2 is highly dependent on the magnitude of low latitude vertical mixing (f_{li}) (i.e. stratification), moderately dependent on the mixing of intermediate- and North Atlantic water (f_{ni}) (i.e. intermediate-water up-welling in the North Atlantic), and
5   essentially insensitive to the mixing of northern- and southern deep-water (f_{ns}).

Based on the results illustrated in Figs. 2 and 3 (and the expectation that $f_{ns} \ll f_{ni} < f_{li}$) the magnitudes of the mixing rates used for the Holocene model parameterisation have been estimated to yield modern atmospheric $pCO_2 \sim 280$ ppm. It is notable that the viable range of values for f_{li} is bi-modal and relatively narrow (either ~ 5–10 or ~ 30–
10   40 Sv), and that atmospheric pCO_2 is not particularly sensitive to f_{ns}. The northern vertical mixing term, f_{ni}, essentially determines whether the low-latitude vertical mixing term, f_{li}, should be high (~ 30–40 Sv) or low (~ 5–10 Sv). This means that modern atmospheric pCO_2 provides a strong constraint for setting the low-latitude vertical mixing (f_{li}), in conjunction with the northern vertical mixing (f_{ni}) (assumed to be small relative
15   to f_{li}), while the deep mixing (f_{ns}) may be set freely so as to produce realistic contrasts in the chemical composition (i.e. phosphate, alkalinity and TCO_2) of the various boxes it affects.

In Figs. 4 and 5, atmospheric pCO_2 is shown to exhibit a strong sensitivity to changing particle fluxes, and in particular to changes in the Southern Ocean export produc-
20   tivity (P_s). This observation has two main implications: first, that large changes in pCO_2 may be efficiently obtained by arbitrarily changing the particle fluxes (as observed in previous box models); and second, that the modern pCO_2 provides a rigid constraint for the combined parameterisation of the model's particle fluxes and vertical mixing rates (f_{li} in particular). It is encouraging that the particle fluxes chosen on the basis
25   of independent export productivity estimates (outlined above) can easily be made to yield modern atmospheric pCO_2 in conjunction with a reasonable and narrow range of vertical mixing rates.

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4.2   Model realism

The "skill" of the model in recreating modern conditions (given a choice of suitable parameters as outlined above) is illustrated in Fig. 6, where a comparison is made between modelled and observed estimates of phosphate, alkalinity and TCO_2 for each
5   box. Modern estimates for Atlantic chemistry have been drawn from Broecker and Peng (1989) (based on the GEOSECS dataset) and from (Levitus, 1994). Although there is a tendency for the model to slightly overestimate the TCO_2 of all boxes (believed to be a result of using a global carbon budget in a purely "Atlantic" flow-scheme), and to significantly overestimate the phosphate of northern- and southern deep-water, the
10   relationship between all modelled and modern values is satisfactory, and essentially indistinguishable from unity (at the 95% confidence interval). Of course, this comparison does not demonstrate that the box-model is a complete depiction of the global climate system. However, given that the main "tuning parameter" values have not been arbitrarily chosen, it does provide some confidence that the model design is realistic enough
15   to be applied to an initial test of the "southern flavour" CO_2 sequestration hypothesis outlined above.

5   Atmospheric pCO_2 for a "southern flavour" ocean

5.1   The "hypsometric effect"

In Table 1, one of the input parameters is the volume ratio of northern- to southern
20   sourced deep-water. This ratio has been calculated as being ~ 8.9 today, on the basis of the Atlantic hypsometric curve (Menard and Smith, 1966), by assuming that North Atlantic sourced deep-water currently fills the depth interval ~ 2–5 km, and that Antarctic-sourced water fills the abyssal Atlantic >5 km (McCartney, 1992). It is notable that the largest volumetric increment in the Atlantic is the 4–5 km section (closely fol-
25   lowed by the 5–6 km section). This is illustrated in Fig. 7, where the volume ratio of two

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water-masses that occupy horizontally stratified intervals in the deep Atlantic (>2 km) is plotted against the depth of the horizontal boundary between the two water-masses. This plot suggests that the water-mass that occupies more than the 4–5 km depth interval will essentially define the chemistry of the average deep marine reservoir, via a "hypsometric effect".

5.2 Atmospheric CO_2 linked to deep-water mass geometry and overturning

Figure 8 illustrates the effect of changing the relative volumes of the northern- and southern deep-water boxes in the model, expressed in terms of the ratio (R_{ns}) of northern- to southern deep-water box volumes, as defined in Fig. 7. As described above, the modern situation (North Atlantic deep-water filling the basin ~2–5 km depth) corresponds to R_{ns}~8.9, while that inferred for the last glacial maximum, with southern-sourced deep-water filling the Atlantic basin up to 2.5 km depth, corresponds to R_{ns}~0.3. When this value for R_{ns} is used in the box model (with all other parameters kept constant), CO_2 in the atmospheric box drops by ~55 ppm (Fig. 8), which is equivalent to nearly 70% of the total glacial – interglacial CO_2 change. The observed "hypsometric effect" on carbon sequestration in the deep sea only becomes significant (and then increases rapidly) once the volumes of the southern and northern deep-water boxes are roughly equal. This would represent a situation where southern-sourced deep water has shoaled above ~3.5 km water depth in the Atlantic. For a shoaling of southern sourced deep-water to only ~3 km, CO_2 in the model drops by ~45 ppm; while for a near complete elimination of northern-sourced deep-water below 2 km water depth (i.e. a direct transfer of northern deep-water into the intermediate-depth ocean), CO_2 drops by ~68 ppm.

A significant "hypsometric" effect on atmospheric CO_2 is thus confirmed in the box model, as suggested by the initial "southern flavour" thought experiment. However, as found in previous box-model simulations, atmospheric CO_2 is also (indeed primarily) sensitive to the turnover rate of the ocean (in this case F_n and F_s), as well as the maximum "particle" export rate from the surface ocean. What this means is that sig-

nificant changes in carbon sequestration in the deep sea may be achieved by either changing the rate at which carbon in the deep-sea is "flushed out" by the overturning circulation and replenished by biological export (e.g. Sarmiento and Toggweiler, 1984; Toggweiler, 1999), or by filling the deep-sea with a particularly carbon-rich deep-water mass analogous to modern Antarctic Bottom Water (AABW), or by some additive combination of these. A "target" glacial atmospheric CO_2 level of ~200 ppm can therefore be easily reproduced in the box-model by using a variety of combinations of: 1) increased southern deep-water volume; 2) reduced overturning rates, of either southern (F_s) or northern (F_n) deep-water; and 3) increased particle export rates, especially in the Southern Ocean.

In previous box model investigations of marine carbon sequestration it was found that changes in the biological export of carbon to the deep sea or in the turnover rate of the ocean that were large enough to reproduce glacial atmospheric CO_2 levels, also tended to produce unrealistically dysoxic deep-waters (Toggweiler, 1999). In the box-model described here, a significant increase in the volume of southern sourced deep-water allows this to be avoided (based on changes in phosphate concentration, southern/northern deep-water oxygenation levels drop/increase by ~20%), primarily by decreasing the need to appeal to extreme changes in overturning- or biological export rates. This is illustrated in Fig. 9, where an increase in the budget of southern deep-water filling the box-model ocean is shown to reduce the need to invoke large changes in ocean overturning or biological export in order to reproduce a glacial CO_2 levels. By filling the deep ocean with southern sourced deep-water, atmospheric CO_2 drops and becomes less sensitive to changes in the northern overturning cell, while also becoming more sensitive to biological export- and overturning circulation changes in the Southern Ocean. The carbon content of the deep ocean may thus become highly dependent on its dominant overturning circulation route, as distinct from its overturning circulation rate.

In the real ocean, a large increase in the volume of southern-sourced deep-water exported to the Atlantic and Indo-Pacific basins would require an increase in the amount

of water that has been converted from deep- and abyssal waters in the Southern Ocean (Orsi et al., 1999). This could be achieved via both thermohaline- and wind forcing; by: 1) increasing the density gradient between southern- and northern deep-water so as to stabilise the southern component over a broader density range of the deep ocean
5 (Cox, 1989; Hughes and Weaver, 1994; Brix and Gerdes, 2003); and/or 2) reducing the "Ekman suction" in the Southern Ocean by winding down the Antarctic Circumpolar Current (ACC), either via a reduced westerly wind stress (Toggweiler and Samuels, 1998), or via a reduced density gradient (and buoyancy flux) across this current (Cox, 1989; Karsten and Marshall, 2002). The mechanisms responsible for increasing the
10 budget of deep-water exported northwards from deep within the ACC could therefore closely overlap with those outlined by Watson and Naviera Garabato (2006) for reducing the up-welling rate in the upper Southern Ocean (thus causing deep- and intermediate water to be re-circulated internally instead). If, as proposed by Watson and Naviera Garabato (2006), this mechanism relied in part on an increase in the vertical density
15 gradient in the Southern Ocean, this would also ensure that turbulent vertical diffusive mixing (which may have been enhanced in a shallower glacial ocean (Wunsch, 2002)) would only serve to homogenise the deepest ocean carbon reservoir, without causing it to "leak" into the surface-ocean and atmosphere.

Note that the rate at which southern-sourced deep-water is exported need not in-
20 crease in these scenarios as long as the standing volume of southern sourced deep-water has stabilised. For a constant overturning rate of this (poorly "CO_2 ventilated") southern sourced deep-sea reservoir, an increase in its volume equates to a proportionate increase in the residence time of carbon in that reservoir. Unless the rate of biological export of carbon from the surface ocean into this deep-sea reservoir de-
25 creases significantly at the same time, this will necessitate a net increase in the amount of carbon that is stored in the deep-sea.

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6   Closing the deficit of explained CO_2 change

The main purpose of the present study is not to attempt a complete simulation or explanation of last glacial maximum atmospheric CO_2 levels, but rather to investigate the plausibility and possible implications of a "hypsometric effect" on CO_2 sequestration,
5 which would arise due to large changes in the volume of southern-sourced deep-water filling the ocean basins. The "southern flavour ocean" theory proposed here has the advantage of being relatively parsimonious in its premises (i.e. it requires few changes to the ocean system in order to operate), and of being based on premises that should be easily refutable by proxy evidence, yet nonetheless are well supported by available
10 data and modelling studies (Duplessy et al., 1988; Michel et al., 1995; Rutberg et al., 2000; Kim et al., 2003; Shin et al., 2003; Piotrowski et al., 2004, 2005; Curry and Oppo, 2005). Furthermore, the proposed changes in the volumetric dominance of southern-sourced deep-water might be expected to be controlled by its density, and therefore to vary inversely to changes in its temperature. This may suggest a mechanism that
15 could explain the proposed links between atmospheric CO_2 and those components of the deep-water temperature and global ice-volume records that cannot be explained by linear insolation forcing (Shackleton, 2000; Parrenin and Paillard, 2003).

It is worth noting that the operation of the hypsometric effect in the box-model described here is not primarily dependent on an exaggeration of the efficiency of gas
20 exchange at high latitudes (Archer et al., 2000a; Toggweiler et al., 2003a, b) since it operates via changes in the relative magnitudes of different intra-oceanic carbon reservoirs, rather than changes in their extent of equilibration with the atmosphere. Indeed, the hypothesis proposed here essentially functions through an expansion of a "glacial analogue of AABW" to the majority of the deep ocean. What the proposed mechanism
25 does require is that glacial deep-water formation in the southern ocean operated in a broadly similar fashion to today, with a significant amount of water-mass conversion occurring away from the air-sea interface, and that vertical diffusivity was not so large (Archer et al., 2000a, b), or could not operate so efficiently against density gradients in

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the glacial ocean, that it was able to erode vertical gradients in carbon content more efficiently than they could be replaced by the physical and biological export mechanisms posited here.

Further studies, using more complete and complex model simulations, will be required in order to determine more securely the veracity and magnitude of the proposed hypsometric effect. Nevertheless, if this simple mechanism for enhancing deep-sea carbon sequestration is incorporated explicitly into the list of "ingredients" that have contributed to glacial – interglacial CO_2 change (Archer et al., 2000b; Sigman and Boyle, 2000), it may help to reduce the "CO_2 deficit" that remains to be explained by appealing to more "extreme" or controversial processes. Although, as previously, the mystery of glacial – interglacial CO_2 change still eludes us (Archer et al., 2000b), perhaps it is not quite as distant as we might have believed?

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Table 1. Input parameterisation for modern model scenario.

| Parameter	Parameter label	Value	Parameter	Parameter label	Values
Fluxes			Temperature, salinity		
Northern overturning	F_n	15 Sv	Southern temperature	T_s	5°C
Southern overturning	F_s	6 Sv	Low lat. temperature	T_l	21.5°C
Low lat. vertical mixing	f_{li}	35 Sv	Northern temperature	T_n	8°C
Northern vertical mixing	f_{ni}	8 Sv	Southern salinity	S_s	34.7‰
Deep mixing	f_{ns}	5 Sv	Low lat. salinity	S_l	36.0
Gas exchange – south	G_s	5 m day^{-1}	Northern salinity	S_n	35.0‰
Gas exchange – low lat.	G_l	3 m day^{-1}	Particle fluxes		
Gas exchange – north	G_n	5 m day^{-1}	Southern export	P_s	0.2 mol Cm^{-2} yr^{-1}
Volumes, areas			Low lat. export	P_l	2.0 mol Cm^{-2} yr^{-1}
Total volume ocean	V_o	1.3×10^{18} m^3	Northern export	P_n	0.4 mol Cm^{-2} yr^{-1}
Total area ocean	A_o	3.5×10^{14} m^3	Redfield ratios		
Volume atmosphere	V_{atm}	1.773×10^{20} moles	Carbon/phosphorus	C/P	106
N. Atlantic area/total area	A_n/A_o	0.2	Nitrogen/phosphorus	N/P	16
S. Atlantic area/total area	A_s/A_o	0.35	Southern CaCO$_3$/TCO$_2$	S-CaCO$_3$/CO$_2$	0.10
Vol. NADW/Vol. AABW	RV_{ns}	0.5	Low lat. CaCO$_3$/TCO$_2$	L-CaCO$_3$/CO$_2$	0.20
Global masses			Northern CaCO$_3$/TCO$_2$	N-CaCO$_3$/CO$_2$	0.25
Total phosphate	P_{glob}	2.769×10^{15} mol			
Total alkalinity	A_{glob}	3.14×10^{18} mol			
Total CO$_2$	TCO_{2glob}	3.0379×10^{18} mol			
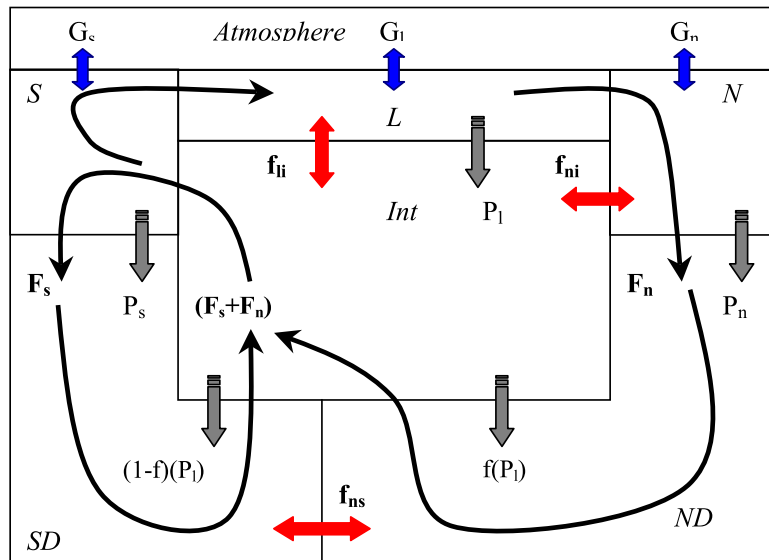
Fig. 1. Box-model schematic (S, southern surface; L, low-latitude surface; N, northern surface; ND, north deep; Int, intermediate; SD, south deep). Heavy black lines indicate thermohaline circulation (F_n = northern overturning; F_s = southern overturning). Red arrows indicate two-way exchange (i.e. mixing) terms. Blue arrows indicate gas exchange. Grey arrows indicate particle fluxes. The particle fluxes to the deep boxes are partitioned according to the relative volumes of the ND and SD boxes (see text).

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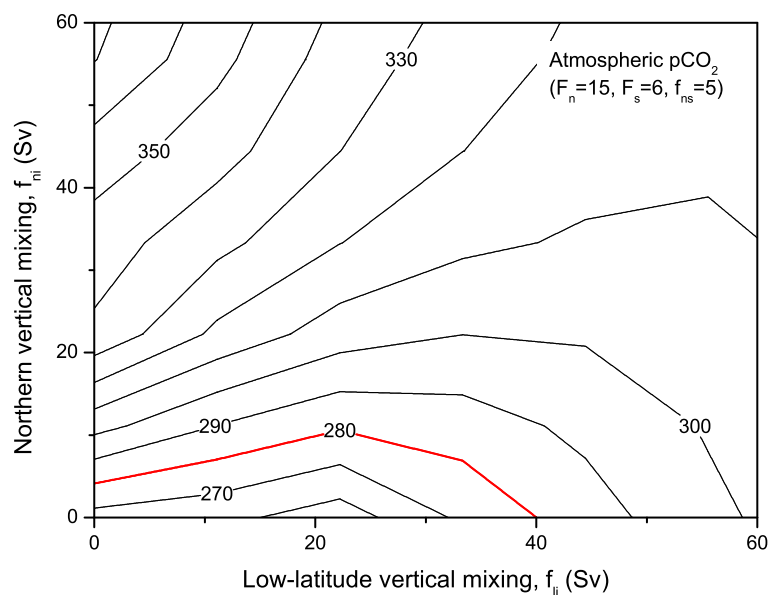
Fig. 2. Sensitivity of modelled atmospheric pCO_2 (μatm) to variable low-latitude (f_{li}) and northern (f_{ni}) vertical mixing rates. Other model parameters are as listed in Table 1.

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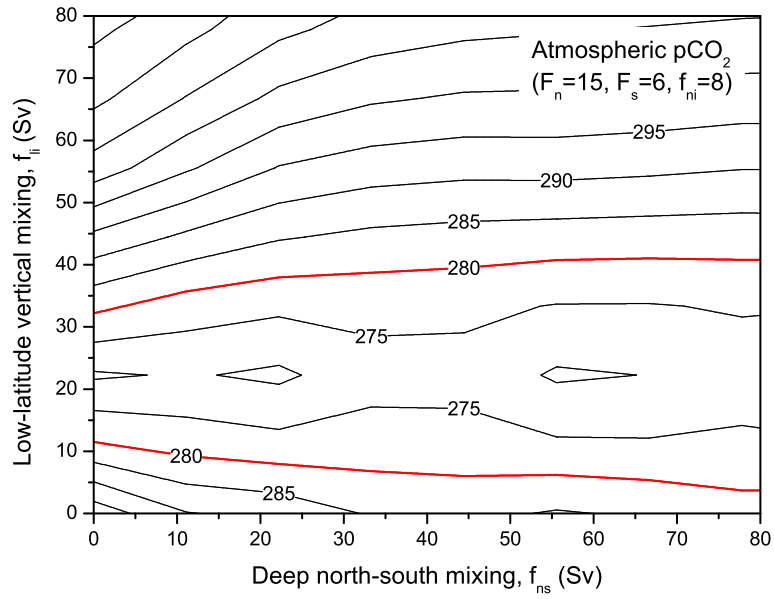
Fig. 3. Sensitivity of modelled atmospheric pCO_2 (μatm) to low-latitude (f_{li}) and deep (f_{ns}) mixing rates. Other model parameters are as listed in Table 1.
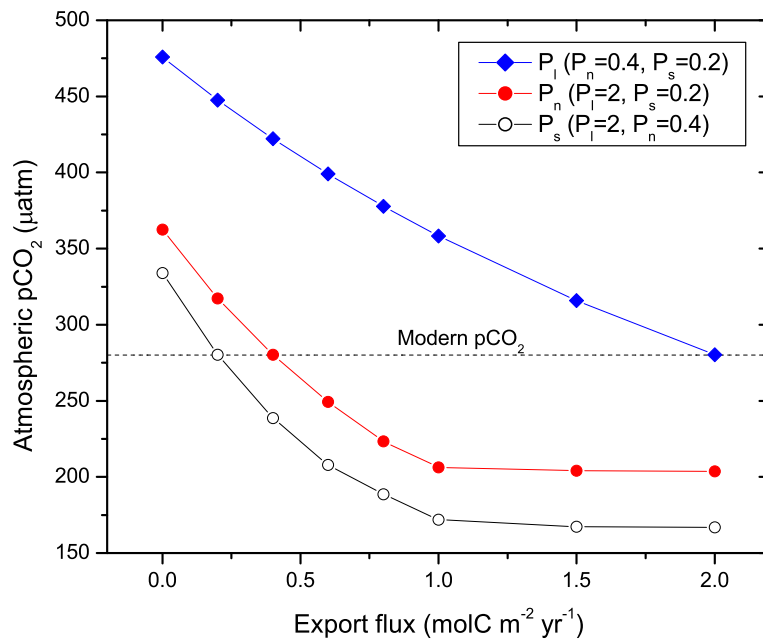
Fig. 4. Sensitivity of modelled atmospheric pCO_2 (μatm) to variable particle export fluxes (North Atlantic, P_n; South Atlantic, P_s; Low-latitude, P_l). Other model parameters are as listed in Table 1.
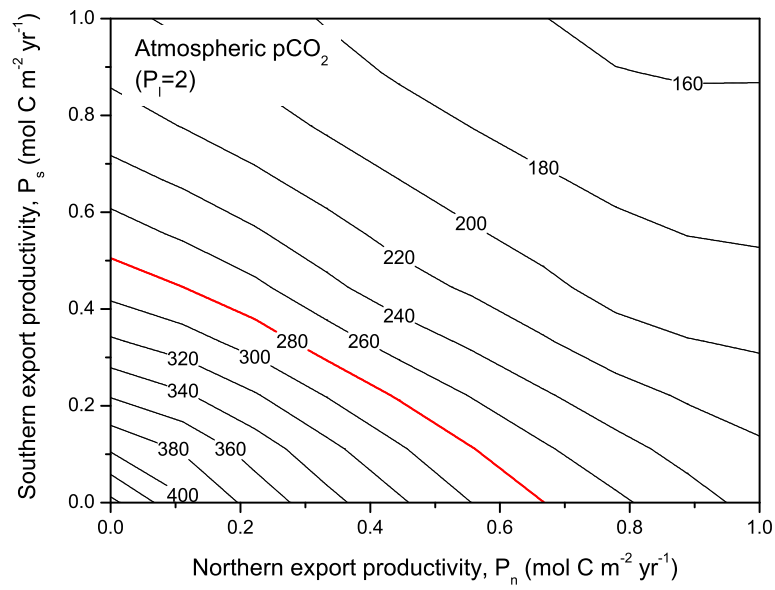
Fig. 5. Sensitivity of modelled atmospheric pCO$_2$ (μatm) to variable northern- and southern particle fluxes. Other model parameters are as listed in Table 1.
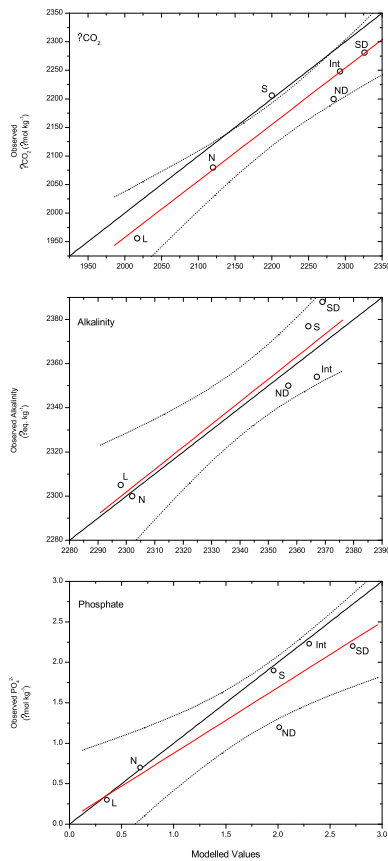
Fig. 6. Model skill, for modern reconstruction of phosphate, alkalinity and total dissolved CO$_2$ (ΣCO$_2$). Data labels indicate boxes: L, Low-latitude surface; N, North surface; S, South surface; Int, Intermediate; ND, North deep; SD, South deep. Model parameters are listed in Table 1. Solid red lines and dotted black lines indicate least squares regression onto the data and 95% confidence intervals respectively. Solid black lines indicate 1:1 relationship.

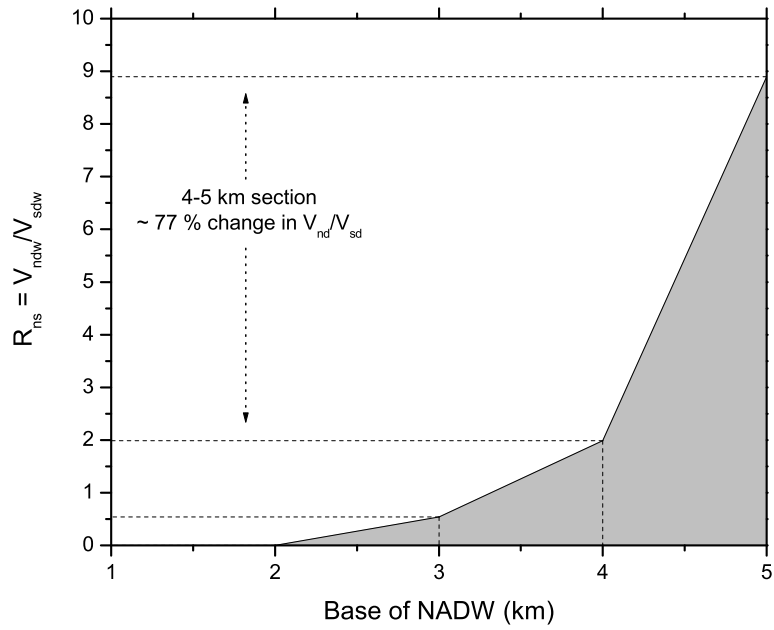**Fig. 7.** Volume ratio of northern (upper) deep-water to southern (lower) deep-water plotted against the depth of the base of the upper deep-water layer, as defined by the hypsometry of the Atlantic basin (Menard and Smith, 1966).
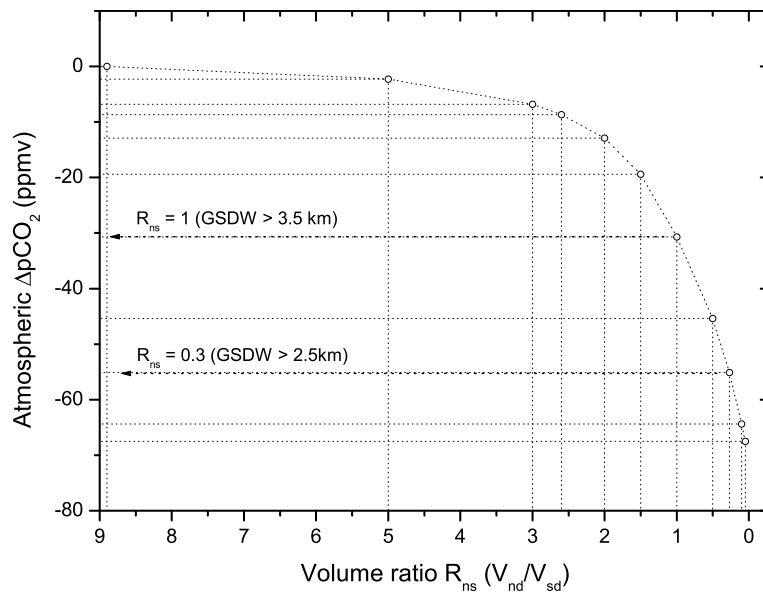
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Fig. 8. Simulated changes in atmospheric CO_2, with respect to modern (280 ppm) caused by varying the ratio of northern- to southern sourced deep-water (V_n/V_s) filling the Atlantic. GSDW refers to "glacial southern sourced deep water", the glacial analogue for modern AABW.
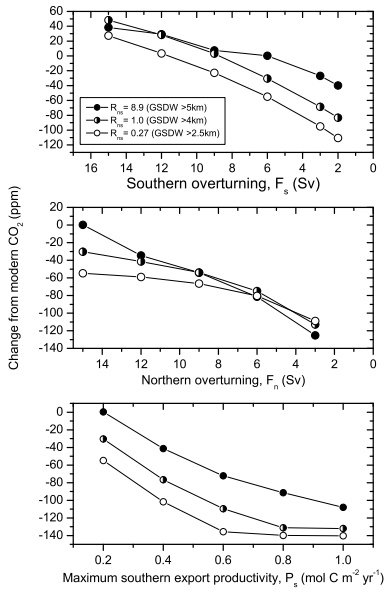
Fig. 9. Changes in atmospheric CO_2, from modern (280 ppm), produced in the box-model for different volume ratios of northern- versus southern deep-water (R_{ns}), in conjunction with: 1) changes in southern overturning; 2) changes in northern overturning; and 3) changes in the maximum level of southern ocean export productivity.

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