GLACIAL- INTERGLACIAL MECHANISMS

How can we explain the observed 80-100ppm difference between warm (high CO_2) interglacials and cold (low CO_2) glacials?

Bibliography by Irina Marinov (Oct 2011)

Atmospheric pCO$_2$ has varied in step with glacial/interglacial cycles, with values around 280 ppmv during interglacials, and values of 180-200 ppmv during during peak glacial times. Below is a literature review of the main mechanisms proposed to explain this variation. Sections I-IV review the observational (and simple box model) literature, Section V reviews some of the most recent Earth System modeling studies.

CONTENTS:

I. Ice core evidence for glacial-interglacial cycles:
Hays et al 1976, Barnola et al. 1987, Petit et al 1999, EPICA 2004

II. Terrestrial mechanisms: Shackleton et al 1978, Bird et al. 1994, Adams et al. 1990

III. Oceanic mechanisms:

1. Ocean temperature and salinity: CLIMAP 1976; Marchal et al. 1998, Zeebe et al 2001
2. Carbonate pump, alkalinity related mechanisms:

Alkalinity in general: Chapter 2 in Tracers in the Sea; Peterson et al. 2001
Coral reef hypothesis: Berger et al 1982, Opdyke and Walker 1982
Carbonate compensation mechanism: Broecker 1982, Broecker and Peng 1987, Boyle 1988, Farrell and Prell, 1989, Peterson and Prell, 1985
Rain ratio hypothesis: Archer and Maier-Raimer, 1994.

3. Oceanic Soft tissue or organic carbon pump mechanisms
   3.1 Low latitude mechanisms:

Pedersen 1983, Broecker 1982, Farrell et al. 1995, Ganeshram et al. 1995, Falkowski et al 1997, Sigman et al. 1998, Altabet et al. 2002, Ganeshram et al 2002.

   3.2 High latitude mechanisms:

Sarmiento and Toggweiler 1984, Siegenthaler and Wenk 1984, Knox and McElroy 1984.
a. The Iron hypothesis: Martin et al. 1991, 1990
Increase or decrease in Southern Ocean production?: Mortlock 1991, Kohfeld et al 2005
b. Nitrate utilization mechanism: Francois et al 1997, Sigma et al. 1999
c. The silica hypothesis: Harrison et al 2000, Brezinski et al 2002
d. Sea ice mechanism: Stephens and Keeling 2000

4. Oceanic circulation mechanisms: Toggweiler 1999, Toggweiler et al. 2006, Watson et al 2006, McManus et al 2004, Anderson et al. 2009, Oppo et al. 1993, Lynch-Stieglitz et al. 2007.

IV. Modeling of glacial-interglacial cycles using complex Earth System models: Cane et al. 2006, Rahmstorf 2002, Braconnot et al. 2007, Weber et al. 2007, Rojas et al. 2009, d'Orgeville 2010.

V. Good Review Papers: Broecker and Peng (1982; 1998), Sigman and Boyle 2000, Ridgwell and Zeebe 2005, Kohfeld and Ridgewell 2009, Sigman et al. 2010.

I. Ice core evidence for glacial-interglacial cycles: (very brief)

· *Hays J. D., Imbrie J., and Shackleton N. J., Variations in the Earth's orbit: Pacemaker of the Ice Ages. Science 194, 1121-1132 (1976).*
· *Barnola J. M., Raynaud D., Korotkevich Y. S., and Lorius C., Vostok ice core provides 160,000-year record of atmospheric CO_2. Nature 329, 408414 (1987).*

· *Petit, J. R. et al. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. Nature 399, 429–436 (1999)*
Data on $p\mathrm{CO}_2^{\mathrm{atm}}$ for the last four glacial cycles are reported and interpreted in the context of other ice core data.
· *EPICA Community Members. Eight glacial cycles from an Antarctic ice core. Nature 429:623-628 (2004).*

II. Terrestrial mechanisms:

· *Shackleton, N. J., Carbon-13 in Uvigerina: Tropical Rain- forest History and the Equatorial Pacific Carbonate Dissolution Cycles., in The Fate of Fossil Fuel CO2 in the Oceans., edited by N. R. Andersen and A. Malahoff, pp. 401–427, Springer, NY (1978)*
Shackleton estimated that some ~1000 PgC of carbon must have been removed from the ocean since the LGM. Shackleton's hypothesis was consistent with the idea that carbon storage increased in terrestrial ecosys- tems between glacial and interglacial times, through the CO2 fertilization of primary productivity together with afforestation of high northern latitudes.

· *Bird M. I., Lloyd J., and Farquhar G. D,. Terrestrial carbon storage at the LGM. Nature 371, 566 (1994).*
From an isotopic mass balance of δ^{13}C, the authors calculate the terrestrial carbon storage at LGM, which they claim to be 270 to 720PgC lower than the present terrestrial carbon storage.

· *Adams, J. M. , Faure, H. , Faure-Denard, L. , McGlade, J. M. & Woodward, F. I. Increases in terrestrial carbon storage from the Last Glacial Maximum to the present. Nature 348, 711–714 (1990).*
With forested or vegetated regions under kilometres of ice, an increase in the extent of deserts, apparent conversion of tropical forest to grassland, and exposure of organic-rich sediments on continental shelves, the continental reservoir of organic carbon likely decreased during the last ice age, contributing CO_2 to the ocean/atmosphere system (ref. above and references therein). Terrestrial carbon represents a source of CO_2 to the atmosphere, not a sink, during ice ages.

III. Oceanic mechanisms:

1. Ocean temperature and salinity

· *CLIMAP. The surface of the ice-age earth. Science* ***191****, 1131– 1144 (1976).*
· CLIMAP Project Members (1981), Seasonal reconstructions of the Earth's surface at the last glacial maximum, *Geol. Soc. Am. Map Chart Ser.*, *MC-36*, 1–18.
The CLIMAP project estimated that the tropical and subtropical sea surface was cooler by 3 °C or less during the last ice age. The lower temperatures of the glacial ocean would have reduced the concentration of CO_2 in the atmosphere by drawing more of it into the ocean (lower temperatures increase the solubility of CO_2 into the ocean). Since most of the ocean interior is ventilated in polar

environments, a given temperature change in polar surface waters has a greater influence on atmospheric CO_2 than the same temperature change in the low-latitude surface.

· *Marchal, O., et al., A latitude-depth circulation-biogeochemical ocean model for paleoclimate studies, Tellus, Ser. B, B50, 290–316 (1998).*
When glacial SST reconstructions [*CLIMAP*, 1981] are used and an additional 2°C cooling in the tropics are assumed, ocean general circulation models (GCM) which include carbon cycle models (as well as more highly resolved box models) produce an estimate for the atmospheric CO2 increase due to ocean surface warming across the glacial-to-interglacial transition with a central value of 26 ppm (CO2 range: 21 to 30 ppm).

· *Zeebe, R. E., and D. Wolf-Gladrow, CO_2 in Seawater: Equilibrium, Kinetics, Isotopes, 346 pp., Amsterdam (2001).*
An opposing effect on atmospheric CO_2 to that of glacial/interglacial temperature change is provided by the increased salinity of the glacial ocean, due to the storage of fresh water on land in extensive Northern Hemisphere ice sheets. Based on the approximately 120 m depression of sea level during the last ice age, the whole ocean was about 3% saltier than it is today. All else being constant, this increase would have reduced the solubility of CO_2 in sea-water and raised atmospheric CO_2 by about 6 p.p.m.v.

In conclusion, it seems that most of the 80–100 p.p.m.v. CO_2 change across the last glacial/interglacial transition must be explained by other processes other than terrestrial/ocean temperature/ocean salinity.

2. "Carbonate pump" or alkalinity related mechanisms:

· *Peterson L. C. Calcium carbonates. In Encyclopedia of Ocean Sciences, Vol. 1 (ed. J. H. Steele, K. K. Turekian, and S. A. Thorpe), pp. 359-368. Academic Press (2001)*
· *Chapter 2 in Broecker's Tracers in the Sea*
These are good general introductions to carbonate cycling.

Coral reef growth hypothesis

· *Berger, W. H. Increase of carbon dioxide in the atmosphere during deglaciation: The coral reef hypothesis. Naturwissenschaften **69**, 87–88 (1982).*
· *Opdyke, B. N. & Walker, J. C. G. Return of the coral reef hypothesis: Basin to shelf partitioning of $CaCO_3$ and its effect on atmospheric CO_2. Geology 20, 733– 736 (1982).*

The production of $CaCO_3$ coral reefs serves as an additional source of carbon dioxide to the atmosphere. As the glacial interval ends and sea level rises, flooding the continental shelves. In the tropics, reef growth resumes and CO_2 is released to the atmosphere. Conversely, as sea level begins to fall at the end of an interglacial, reefs become exposed to the atmosphere, get dissolved and CO_2 falls. This is a positive feedback on the atmosphere.

Carbonate Compensation mechanism/Carbonate preservation

· *Broecker, W. S. Glacial to interglacial changes in ocean chemistry. Prog. Oceanogr. 2, 151–197 (1982)*
A framework is proposed for the causes of glacial/interglacial pCO_2^{atm} change, and the biological pump and its interaction with seafloor calcium carbonate burial are implicated for the first time.

· *Broecker, W. S. & Peng, T.-H. The role of $CaCO_3$ compensation in the glacial to interglacial atmospheric CO_2 change. Glob. Biogeochem. Cycles* ***1***, *15– 29 (1987).*
At steady state, the flux of solutes such as Ca^{2+} and HCO_3^- to the ocean will equal the burial flux of $CaCO_3$ in marine sediments. However, when the ocean's distribution of dissolved carbon and/or ALK is altered, the carbonate ion (CO_3^{2-}) concentration of the deep ocean is also changed and, with it, the stability of $CaCO_3$ and its rate of dissolution in deep-sea sediments. In the absence of any concurrent increase in weathering or hydro- thermal inputs, the amount of $CaCO_3$ preservation and burial in marine sediments and hence the deep-sea CO_3^{2-} content must ultimately be restored to that required for steady state to be re-established. The changes to ocean chemistry brought about by a transitory imbalance between sources and sinks of DIC and ALK creates a lasting change in atmospheric CO_2. This process of adjustment of ocean chemistry and atmospheric CO_2 as a result of an initial imbalance induced between weathering input to the ocean and burial in deep-sea sediments, is called "carbonate compensation"

· *Boyle, E. A. Vertical oceanic nutrient fractionation and glacial/interglacial CO_2 cycles. Nature 331, 55–56 (1988)*
Motivated by his palaeoceanographic data, this author recognized that at the onset of ice ages shifting regenerated nutrients and CO_2 from the mid-depth to abyssal ocean drove a deep sea $CaCO_3$ dissolution event, helping to lower pCO_2^{atm}. This happens because CO_2 induced acidity in the deep ocean lowers deep ocean carbonate ion concentration and temporarily increases carbonate dissolution rates. Oceanic alkalinity then rises until the deep ocean carbonate ion is restored to its steady state value; the increase in alkalinity draws further CO_2 out of the atmosphere. This is a positive feedback.

· *Farrell J. W. and Prell W. L., Climate change and $CaCO_3$ preservation: an 800,000 year bathymetric reconstruction from the central equatorial Pacific Ocean. Paleoceanography* ***4***, *447-466 (1989).*
During the nine major glacial stages of the last 800 kyr, sediments show good preservation of $CaCO_3$ in sediments (relative to the modern ocean) due to the lysocline deepening by at least 400 to 800 m. This deepening indicates an increase in the abyssal carbonate ion concentration [CO_3=] and a depression of the calcite saturation horizon explained by the authors by a deeper presence of a more carbonate-saturated water mass during glacials.

· *Peterson L. C. and Prell W. L., Carbonate preservation and rates of climate change: An 800 kyr record from the Indian Ocean. In The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present, Vol. 32 (ed. E. T. Sundquist and W. S. Broecker). A.G.U. (1985)*

Rain ratio hypothesis:

· *Archer, D., and E. Maier-Reimer, Effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentration, Nature, 367(6460), 260–263 (1994).*

Changes in ecosystem structure, specifically the balance between siliceous and nonsiliceous phytoplankton, may affect the ratio of $CaCO_3$ to POC exported from the euphotic zone and reaching the sediments. The CO_2 released to sediment pore waters due to aerobic oxidation of organic carbon within sediments results in additional dissolution of $CaCO_3$ (via respiratory calcite dissolution). Thus, changes in the $CaCO_3$:POC rain ratio reaching the ocean floor will exert an important influence upon the preservation and burial of $CaCO_3$, ultimately affecting ocean chemistry and atmospheric CO_2. *Archer and Maier-Reimer* used a coupled ocean and sediment carbon cycle model to show that a 40% decrease in $CaCO_3$:POC rain ratio (to the sediments) was sufficient to reduce atmospheric CO_2 by ~90 ppm.

3. Oceanic Soft tissue or organic carbon pump mechanisms

3.1 Low latitude mechanisms:

- *Pedersen, T. F. Increased productivity in the eastern equatorial Pacific during the last glacial maximum (19,000 to 14,000 yr B. P.). Geology 11, 16–19 (1983).*

A number of palaeoceanographic studies suggest that export production was greater in low-latitude regions during ice ages. Could this have resulted in lower atmospheric $p\mathrm{CO}_2$?

· *Broecker, W. S. Ocean chemistry during glacial time. Geochim. Cosmochim. Acta **46**, 1689–1706 (1982).* Broecker first hypothesized a glacial increase in the strength of the biological pump as the driver of lower glacial CO_2 levels.

Phosphate and nitrate limit biological productivity. Broecker and McElroy described possible mechanisms by which the reservoirs of phosphate and nitrate might increase during glacial times, which would allow enhanced low-latitude biological production to lower atmospheric CO_2.

Since phosphate has a long residence time of 16kyr, it is unlikely that changes in oceanic phosphate could explain changes in atmospheric CO_2. However, it has been suggested that changes in the nitrate reservoir could lead to significantly higher export production in the ocean ocean during glacial periods, potentially explaining some of the glacial/interglacial atmospheric CO_2 changes:

· *Farrell J. W., Pedersen T. F., Calvert S. E., and Nielsen B., Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean. Nature 377 (6549), 514-517 (1995).*

The authors interpret a down-core decline in the $^{15}\mathrm{N}/^{14}\mathrm{N}$ ratio (in sedimentary marine organic matter) through the Last Glacial Maximum (12-24 kyr ago) as a decrease in relative nitrate utilization; the increase in nitrate supply to surface waters due to upwelling during this period was thus greater than the apparent increase in nitrogen removal by organic matter export out of surface waters. This is consistent with a higher CO_2 flux to the atmosphere (in the equatorial Pacific) during the LGM, indicating that these surface waters remained enriched in nutrients at the LGM, and did not act as a net sink for CO_2 at the LGM.

· *Ganeshram, R. S. , Pedersen, T. F. , Calvert, S. E. & Murray, J. W. Large changes in oceanic nutrient inventories from glacial to interglacial periods. Nature 376, 755– 758 (1995)*

Nitrogen isotope studies in currently active regions of denitrification indicate that water column denitrification was reduced in these regions during glacial periods.

· *Falkowski, P. G. Evolution of the nitrogen cycle and its influence on the biological sequestration of CO_2 in the ocean. Nature 387, 272–275 (1997)*

An increase in the nitrate reservoir during ice ages could come about because of increases in N_2 fixation rate driven by increased airborne supply of iron-bearing dust.

· *Haug G. H., Pedersen T. F., Sigman D. M., Calvert S. E., Nielsen B., and Peterson L. C. Glacial/interglacial variations in productivity and nitrogen fixation in the Cariaco Basin during the last 550 ka. Paleoceanography 13(5), 427-432 (1998).*

· *Sigman, D. M., McCorkle, D. C. & Martin, W. R. The calcite lysocline as a constraint on glacial/interglacial low-latitude production changes. Glob. Biogeochem. Cycles 12, 409–427 (1998)*

Box model calculations indicate that the immediate effect of 30% increase in the oceanic nutrient reservoir, enhanced extraction of CO_2 from the surface ocean and its sequestration in the deep sea, might lower atmospheric CO_2 by as much as 30–45 p.p.m.v.

· *Ganeshram R. S., Pedersen T. F., Calvert S. E., and Francois R., Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorus inventories. Nature 415 (2002).*

This paper questions the iron hypothesis. From a sediment core off the (oxygen-deficient) northwestern continental margin of Mexico, the authors show a decline in denitrification and phosphorite formation-processes in glacial period suggesting increases in marine inventories of nitrogen and phosphorus. Smaller and less rapid increases in phosphorus, led to increased N/P ratios in the oceans. Since phytoplankton require nitrogen and phosphorus in constant proportions and N/P ratios greater than the Redfield ratio are likely to suppress nitrogen fixation, they suggest therefore that marine productivity did not increase in glacial periods in response to either increased nutrient inventories or greater iron supply.

· *Altabet M. A., Higginson M. J., and Murray D. W., The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO_2. Nature 415(6868), 159-162 (2002).*

Marine denitrification-the reduction of nitrate to gaseous nitrogen- affects greenhouse gas concentrations directly through the incidental production of nitrous oxide, and indirectly through modification of the marine nitrogen inventory and hence the biological pump for CO_2. From nitrogen isotope ratios in sediment cores the authors show millennial-scale variability in Arabian Sea denitrification and productivity during the last glacial period, corresponding to the Dansgaard-Oeschger events recorded in Greenland ice cores. Such changes in turn likely impacted global marine productivity.

3.2 High latitude mechanisms:

· *Sarmiento, J. L. & Toggweiler, J. R. A new model for the role of the oceans in determining atmospheric pCO_2 . Nature 308, 621–624 (1984)*
· *Siegenthaler, U. & Wenk, T. Rapid atmospheric CO_2 variations and ocean circulation. Nature 308, 624–626 (1984)*
· *Knox, F. & McElroy, M. Changes in atmospheric CO_2 influence of the marine biota at high latitude. J. Geophys. Res. 89, 4629–4637 (1984)*
The modern Southern Ocean releases deeply sequestered CO_2 to the atmosphere. These three box model studies first identified the Southern Ocean as a major leak of CO_2 to the atmosphere in the modern biological pump and posited that a reduction in this leak was responsible for lower atmospheric pCO_2 during ice ages. An increase in nutrient utilization in the high latitudes (performed in these models by depleting nutrients in the high latitude box) results in increased biological productivity and increased storage of carbon in the ocean, hence less CO_2 in the atmosphere. This early research led to two important ideas: high latitude regions are more important in determining atmospheric pCO_2 than low latitudes, despite their much smaller area, and nutrient utilization and atmospheric pCO_2 are tightly linked. Stronger nutrient utilization, especially in high latitudes, increases the efficiency of the carbon pump and lowers atmospheric pCO_2.

a. The "Iron Hypothesis": Increased nutrient uptake in high latitudes due to increased Iron

· *Martin, J.H., " Glacial-interglacial CO_2 change: The iron hypothesis", Paleoceanography, 5(1), 1–13, 1990.*
In this all time classic paper, it is suggested that an increase in the input of dust and its associated trace metals (iron in particular) in the HNLC regions of the ocean drove an increase in the rate of nutrient and carbon uptake by phytoplankton and contributed to lower atmospheric pCO_2 during glacial times.

· *Martin, J. H., R. M. Gordon and S. E. Fitzwater, "The case for iron", Limnology and Oceanography, vol 36, 1991 {36}(8), 1793—1802, 1991*
Equatorial Pacific, North Pacific and Southern Ocean are all characterized by low chlorophyll relative to the large amounts of macronutrients present; these are the so-called high nutrient low chlorophyll or HNLC regions. It is proposed that this is due to the fact that these areas are far from Fe-rich terrestrial sources and therefore lack Fe. The addition of nanomole quantities of Fe increased these doubling rates by factors of 2-3, suggesting that Fe availability is a critical limitation for phytoplankton production here.

Increase or decrease in Southern Ocean export production?

The iron hypothesis above suggests that in the modern ocean nutrients are underutilized/unused because phytoplankton are limited by the lack of Fe. More efficient use of the nutrients by organisms (due to enhanced Fe addition) would lower the pCO_2, lower the surface nutrients, and cause respired CO_2 to build up in the deep ocean. This would imply that during glacials there was an increase in biological production. However, the predicted increase in productivity at the last glacial maximum (associated with the hypothesized iron increase) is not uniformly observed in paleoceanographic data from the Southern Ocean. The Antarctic and Subantarctic have responded very differently to glacial/interglacial cycles. In the modern Antarctic, export production is dominated by diatoms, a group of phytoplankton that is well preserved in sediments because of their silica shells. The accumulation of diatomaceous sediments in the Antarctic was lower during the last ice age, and indicators also suggest that the biological export of carbon was lower in general. However, it is possible that export due to other phytoplankton (not preserved in sediments) might have increased in the Antarctic during glacials.

· *Mortlock, R. A. et al. Evidence for lower productivity in the Antarctic during the last glaciation. Nature 351, 220–223 (1991)*
In this first large-scale reconstruction of Southern Ocean productivity during the last ice age, the Antarctic was found to be less productive than today, but the Subantarctic was found to be more productive.

· *Kohfeld, K. E., Le Quere, C., Harrison, S. P. & Anderson, R. F. Role of marine biology in glacial-interglacial CO_2 cycles. Science 308, 74–78 (2005)*
In the subantarctic, there is very strong evidence for higher export production during glacial times and an associated increase in the relative importance of diatom production.

b. Nitrate utilization increased during glacials:

· *Francois et al 1997 "Contribution of Southern Ocean surface-water stratification to low atmospheric CO_2 concentrations during the last glacial period"*
Palaeoceanographic evidence is reported that the ice-age Antarctic Ocean was characterized by less exchange between the surface and the deep ocean and by an associated increase in the completeness with which Antarctic phytoplankton consumed the available nutrient supply, both of which would have lowered pCO_2^{atm}. It is suggested that increased surface-water stratification south

of the Polar Front made a greater contribution to the lowering of atmospheric CO_2 concentration during the Last Glacial Maximum than did the increased export of organic carbon from surface to deep waters occurring further north.

· *Sigman, D. M. , Altabet, M. A. , Francois, R. , McCorkle, D. C. & Gaillard, J.-F. The isotopic composition of diatom-bound nitrogen in Southern Ocean sediments. Paleoceanography 14, 118–134 (1999).*
A box model calculation predicts that 25–40% higher nitrate utilization (that is, 50–65% during the last ice age compared to 25% during the present interglacial) could lower atmospheric CO_2 by the full glacial/interglacial amplitude.

The above papers seem to suggest that nutrient utilization changes in the Antarctic waters are a fundamental driver of glacial-interglacial changes in atmospheric pCO_2. Because palaeoceanographic proxy data suggest that Antarctic export production was lower during the last ice age, we infer that more complete nitrate utilization in the Antarctic was due to a lower rate of nitrate supply from the subsurface, implying that the fundamental driver of the CO_2 change was an ice age decrease in the ventilation of deep waters at the surface of the Antarctic, as suggested by Francois et al. (1997).

c. The silica hypothesis:

Dissolved silicate is a major nutrient for diatom growth because of the silica tests that these phytoplankton precipitate. Much like nitrate and phosphate, silicate is nearly completely depleted in the low-latitude surface ocean but is found at higher concentrations in the Antarctic. Changes in the supply of dissolved silica to the ocean should affect the relative contribution of export production derived from diatoms relative to that derived from phytoplankton that do not make opal frustules. In turn, such ecosystem shifts might affect the $CaCO_3$:POC rain ratio and thus atmospheric CO_2 via a cascade of mechanisms. Silicate from dust accounts for ~10% of the total new supply to the ocean, with riverine supply accounting for much of the remainder. Since the residence time of H_4SiO_4 in the ocean is of similar order to the observed lag, the aeolian input of dissolved Si to the ocean might play an important role in driving atmospheric CO_2 changes.

· *Harrison, K. G., Role of increased marine silica input on paleo-pCO_2 levels, Paleoceanography, 15(3), 292–298 (2000).*

Harrison proposed a "Silica Hypothesis," whereby higher aeolian Si supply to the surface ocean during glacial times enhances diatom productivity at the expense of calcium carbonate shell-forming species, producing a substantial second-order effect on atmospheric CO_2 through the rain ratio. Taken together, changes in the supply of dissolved silica to the open ocean since the last glacial, both via decreased dust and by enhanced burial of opal in coastal and shelf sediments, may be responsible for 1-8 ppm.

· Brzezinski M. A., Pride C. J., Franck V. M., Sigman D. M., Sarmiento J. L., Matsumoto K., Gruber N., Rau G. H., and Coale K. H., A switch from Si(OH)4 to NO3- depletion in the glacial Southern Ocean. *Geophysical Research Letters* 29(12) (2002).

This paper is known as the **"Silica leakage mechanism":** Addition of iron lowers diatom $Si(OH)_4$:NO_3^- uptake ratios. Higher iron supply during glacial times would thus drive the Antarctic towards NO_3^- depletion with excess $Si(OH)_4$ remaining in surface waters. Isotope records from Antarctic sediments confirm diminished $Si(OH)_4$ use and enhanced NO_3^- depletion during the last three glaciations. The authors suggest that the glacial high $Si(OH)_4$ water was transported poleward to the subtropics and beyond, causing diatoms to displace coccolithophores at low latitudes, weakening the carbonate pump and increasing the depth of organic matter remineralization. These effects may have lowered glacial atmospheric pCO_2 by as much as 60 ppm.

d. Sea Ice mechanism:

· *Stephens and Keeling, The influence of Antarctic sea ice on glacial–interglacial CO_2 variations, Nature 404, 171-174 (2000)*

A glacial increase in wintertime sea ice coverage may have contributed to lower atmospheric CO_2 by preventing gas exchange during winter, when Antarctic surface water is more likely to be supersaturated with CO_2. While it is unlikely that this mechanism contributed to the 67ppm reduction in CO_2 proposed by this too simplistic model, it is likely that this mechanism did contribute a modest amount to the drop in atmospheric $p$$CO_2$.

5. Oceanic Circulation mechanisms.

Evidence from $^{13}C/^{12}C$ ratios and Cd/Ca ratios in foraminifera suggest that the predominant meridional overturning circulation occurred at intermediate water depths during glacial periods and shifted to deeper water depths during the interglacial periods [for review of this paleoceanographic evidence, see *Boyle*, 1995]. Paleo-observations so far suggest that the glacial ocean was highly stratified compared to modern interglacial conditions. How could have this change in stratification come about?

· *Toggweiler, J. R. Variations in atmospheric CO_2 driven by ventilation of the ocean's deepest water. Paleoceanography **14**, 571– 588 (1999).*

One of the first studies to suggest that less ventilation of the Southern Ocean (via decreased UCDW) results in lower atmospheric $p$$CO_2$.

· *Toggweiler, J., J. L. Russell, and S. R. Carson, Midlatitude westerlies, atmospheric CO2, and climate change during the ice ages, Paleoceanography, 21, PA2005, doi:10.1029/ 2005PA001154 (2006).*

Reduced Southern Hemisphere westerly winds are proposed as the driver of reduced Antarctic overturning during ice ages. A positive feedback loop that propels transitions between warm and cold states of the climate system is proposed. Imagine a cooling trend that leads to an equatorward shift in the westerlies (characteristic for the cold last glacial maximum). This shift causes less deep water to upwell close to Antarctica, causing more respired CO_2 to accumulate in the deep ocean and flushing less CO_2 to the atmosphere. Lower CO_2 leads to cooler temperatures and an additional equatorward shift in the westerlies, etc.

· *Watson, A. J., and A. C. N. Garabato, The role of Southern Ocean mixing and upwelling in glacial-interglacial atmospheric CO_2 change, Tellus, Ser. B, 58, 73–87 (2006)*

Suggests that a combination of more extensive sea ice formation and reduced air-sea buoyancy fluxes resulted in weaker mixing and less upwelling in the Southern Ocean. Note that the consequences of this mechanism for CO_2 are similar to the Toggweiler et al. 2006 mechanism.

· *Toggweiler J. R., Shifting Westerlies , Science 323 (5920), p.1434-1435, doi: 10.1126/science.1169823, (2009).*

Easier read than the 2006 paper, more general.

· *Anderson R. F.; Ali S.; Bradtmiller L. I.; et al., Wind-Driven Upwelling in the Southern Ocean and the Deglacial Rise in Atmospheric CO_2, Science 323 (5920), p. 1443-1448, doi:10.1126/science.1167441, (2009).*

Highly cited paper. Diatom productivity south of the Antarctic Polar Front and the resulting burial of biogenic opal in sediments are limited by silicon supply from the deep ocean. New sediment cores show that opal burial rates, and thus upwelling, were enhanced during the termination of the last ice age in the Southern Ocean. Episodes of rising atmospheric CO_2 during deglaciation seem to correspond to intervals of enhanced upwelling and increased ventilation of deep water, in agreement with the Toggweiler 2006 theory.

· *Oppo, D. W. & Lehman, S. J. Mid-depth circulation of the subpolar North Atlantic during the last glacial maximum. Science* ***259****, 1148–1152 (1993).*
Since North Atlantic Deep Water formation and Antarctic upwelling are coupled in the modern ocean, a glacial reduction in Antarctic upwelling is consistent with the evidence for less North Atlantic Deep Water formation during the last ice age. The proposed upwelling of intermediate-depth waters into the glacial subantarctic surface is akin to a shoaling of modern Southern Ocean overturning, with new intermediate-depth waters being supplied from the North Atlantic and/or North Pacific.

· *McManus, J. F., François, R., Gherardi, J. M., Keigwin, L. D. & Brown-Leger, S. Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes. Nature 428, 834–837 (2004)*
One of a number of important studies showing that ventilation of the deep ocean by the North Atlantic decreased abruptly in response to Heinrich Event 1, coincident with the first major step in Antarctic warming.

· *Lynch-Stieglitz, J. et al. Atlantic meridional overturning circulation during the Last Glacial Maximum. Science 316, 66–69 (2007)*
A literature review and an attempt at community consensus regarding the nature of North Atlantic deep ocean circulation during the last ice age.

IV. Modeling of glacial-interglacial cycles using complex Earth System models

A few papers I have found relevant in this fast growing field

· *S. Rahmstorf, Ocean circulation and climate during the past 120,000 years, Nature 419, p. 207-214, (2002).*
Review paper discusses the role of ocean circulation in abrupt climate shifts such as sudden temperature changes in Greenland on the order of 5–10 C and massive surges of icebergs into the North Atlantic Ocean — events that have occurred repeatedly during the last glacial cycle. Contains good references for the nonlinear, bi-stability theories of ocean circulation and large-scale LGM climate modeling prior to 2002.

· *Cane Mark A.; Braconnot Pascale; Clement Amy; et al. Progress in paleoclimate modeling , Journal of Climate 19(20), p. 5031-5057, doi: 10.1175/JCLI3899.1, (2006).*
A review of the latest paleoclimate modeling advances, including the success of GCMs in simulating the onset of glaciations and the variation in ENSO cycles.

· *Braconnot P.; Otto-Bliesner B.; Harrison S.; et al., Results of PMIP2 coupled simulations of the Mid-Holocene and Last Glacial Maximum - Part 1: experiments and large-scale features, Climate of the Past 3 (2), p. 261-277, (2007).*
· *Braconnot P.; Otto-Bliesner B.; Harrison S.; et al., Results of PMIP2 coupled simulations of the Mid-Holocene and Last Glacial Maximum - Part 2: feedbacks with emphasis on the location of the ITCZ and mid- and high latitudes heat budget, Climate of the Past 3 (2), p. 279-296, (2007).*

These papers describe the second phase of the Paleoclimate Modeling Intercomparison Project (PMIP2), an intercomparison study of coupled ocean-atmosphere simulations of the Last Glacial Maximum and Mid-Holocene. PMIP2 simulations are in better agreement with data than previous PMIP1 simulations, for which sea surface temperature was prescribed or computed using simple slab ocean formulations.

· *Weber S. L.; Drijfhout S. S.; Abe-Ouchi A.; et al., The modern and glacial overturning circulation in the Atlantic Ocean in PMIP coupled model simulations, Climate of the Past 3(1), p. 51-64, (2007).*
This model intercomparison study illustrates the challenges of modeling correctly the LGM. The Atlantic Meridional Overturning circulation (AMOC) slows down by 20-40% during the LGM as compared to the modern climate in four models, there is a slight reduction in one model and four models show an increase in AMOC strength by 10-40%. A major controlling factor for the AMOC response is the density contrast between Antarctic Bottom Water (AABW) and North Atlantic Deep Water (NADW) at their source regions. Changes in the density contrast are determined by the opposing effects of changes in temperature and salinity, with more saline AABW as compared to NADW consistently found in all models and less cooling of AABW in all models but one.

· *Rojas Maisa; Moreno Patricio I.; Kageyama Masa; et al., The Southern Westerlies during the last glacial maximum in PMIP2 simulations , Climate Dynamics 32(4), p. 525-548, doi: 10.1007/s00382-008-0421-7, (2009).*
This study compares four coupled ocean-atmosphere simulations of the LGM carried out by the Palaeoclimate Modelling Intercomparison Project Phase 2 (PMIP2). Three out four models indicate decreased southern westerlies at the near surface and in the upper troposphere at the LGM and as a consequence decreased upwelling in a latitudinal band over the Southern Ocean. Although the LGM atmosphere is colder and the equator to pole surface temperature gradient generally increases, the tropospheric temperature gradients actually decrease, explaining the weaker circulation.

· *d'Orgeville, M., W. P. Sijp, M. H. England, and K. J. Meissner, On the control of glacial-interglacial atmospheric CO_2 variations by the Southern Hemisphere westerlies, Geophys. Res. Lett. 37, L21703, doi: 10.1029/2010GL045261, (2010).*
This paper confirms the importance of the general mechanism proposed by Toggweiler et al. 2006 in the context of global GCM studies. A northward shift of the SHW and a decrease of their amplitude both decrease bottom meridional overturning circulation (and hence the loss of deep ocean carbon to the atmosphere) and increase deep ocean carbon storage. A southward shift or a strengthening of the SHW has the opposite effect. Doubling the SHW amplitude increases atmospheric CO_2 by 36 ppm, halving reduces it by 20 ppm, while the latitudinal shifts (north-or southward) have very small impact on atmospheric CO_2.

V. Good Review papers on glacial-interglacial mechanisms:

The bibliography compiled above is necessarily incomplete. For further details and reviews on the topic -that I have found very useful and inspiring - please see the following.

· *Broecker W. S. and Peng T.-H. (1982) Tracers in the Sea. Eldigio Press.*
See in particular Chapter 9.

· *Broecker W. S. and Peng T.-H. (1998) Greenhouse Puzzles. Eldigio Press.*
See in particular “Martin’s World”.

· *Sigman DM; Boyle EA, Glacial/interglacial variations in atmospheric carbon dioxide, Nature 407, 6806, p: 859-869, doi: 10.1038/35038000 (2000)*

Here the authors review the biological-physical hypotheses for glacial-interglacial change and propose a synthesis scenario that combines several of the proposed scenarios above into a single framework. A combined physical and biologically induced closure of the Southern Ocean window is suggested to have reduced atmospheric CO_2. In this hypothesis, a cooler climate caused a northward shift in the belt of eastward winds that drives upwelling and northward surface flow in the modern Antarctic. This shift caused a decrease in the upwelling of deep water into the Antarctic surface, replacing it with upwelling of intermediate-depth water into the subantarctic surface. The hypothetical glacial Antarctic, because of reduced wind-driven upwelling, was able to develop a stable, fresh, frequently ice-covered surface layer, further reducing deep-ocean ventilation in the open Antarctic. These changes in circulation resulted in a lower rate of nutrient supply to the Antarctic surface and reduced CO_2 outgassing.

· *Ridgwell, A., and R. E. Zeebe, The role of the global carbonate cycle in the regulation and evolution of the Earth system, Earth Planet. Sci. Lett., 234, 299–315 (2005).*

· *KE Kohfeld and A. Ridgwell, Glacial-interglacial variability in atmospheric* CO_2*, In: C. Le Quéré and E. S. Saltzman, (eds),* Surface Ocean - *Lower Atmosphere Processes, Geophysical Monograph 187, Washington, DC: American Geophysical Union, pp 251-286, (2009).*

· *Sigman Daniel M.; Hain Mathis P.; Haug Gerald H., The polar ocean and glacial cycles in atmospheric* CO_2 *concentration , Nature 466 (7302), p 47-55, doi: 10.1038/nature09149, (2010).*