



Two contributors to the glacial CO₂ decline



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ABSTRACT

It is generally accepted that the glacial drawdown of atmospheric CO₂ content is the sole result of uptake by the ocean. Here we make a case that the reduction of planetary CO₂ outgassing made a significant contribution. We propose that the ocean contribution to CO₂ reduction closely followed Northern Hemisphere summer insolation and was superimposed on a ramp-like decline resulting from a reduction in the input of planetary CO₂. We base this scenario on new records of $\delta^{13}\text{C}$ and B to Ca ratio in cores from the upper and lower portions of the deep Atlantic. They demonstrate that the waxing and waning of the stratification of Atlantic deep water follows summer insolation. Our thoughts were driven by the observation that over the last 30 kyr the extent of mountain glaciation in both hemispheres appears to have tracked the atmosphere's CO₂ content, suggesting that the connection between orbital cycles and land ice cover is via the ocean. Instead of a direct connection between ice extent and summer insolation, the tie is a modulation of the heat and fresh water budgets of the northern Atlantic. Changes in the boundary conditions lead to reorganizations of ocean circulation and, as a consequence, changes in CO₂ storage in the ocean.

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1. Introduction

The air trapped in Antarctic ice tells us that the CO₂ content of the atmosphere during peak glacial time was about 30 percent lower than that during the late Holocene (Lüthi et al., 2008; Marcott et al., 2014; Monnin et al., 2001). For the last thirty years the focus as to what caused this drop has been on CO₂ uptake by the ocean. An alternate scenario (Huybers and Langmuir, 2009) is that the weight of excess glacial ice on the world's volcanoes may have squelched eruptions and thereby reduced the input of CO₂ to the ocean–atmosphere reservoir. This reduction would have led to a drawdown of the CO₂ content of the atmosphere. As the turnover time of ΣCO_2 in the ocean is comparable to the length of a glacial cycle (i.e. $\sim 10^5$ yr), this drawdown may have contributed to the reduction in the atmosphere's CO₂ content. Here, we consider a CO₂ scenario that involves both ocean uptake and volcano shutdown.

2. CO₂ drives ice

The presence of an orbital pulsebeat superimposed upon the Late Quaternary 100 000-yr glacial cycles was recognized nearly 50

years ago (Broecker, 1966). Hays et al. (1976) referred to an orbital 'pacemaker' of the ice ages. However, as first recognized by Mercer (1984) and more recently shown by ¹⁰Be and ¹⁴C chronologies of glacial landforms (e.g., Clark et al., 2009; Denton et al., 1999a; Lowell et al., 1995; Putnam et al., 2013), the maximum extent of mountain glaciers and ice sheets worldwide was achieved between ~ 25 and ~ 18 kyr ago (Fig. 1; Clark et al., 2009). For example, during that time period, mountain glaciers in North America (Porter and Swanson, 1998), Europe (Monegato et al., 2007), Hawaii (Anslow et al., 2010), Africa (Kelly et al., 2014), the tropical Andes (Bromley et al., 2011, 2009), Papua New Guinea (Barrows et al., 2011), southern South America (Denton et al., 1999a, 1999b; Kaplan et al., 2008), and New Zealand (Doughty et al., 2015; Putnam et al., 2013) had all stood at their maximum extents. Further, the LGM snowline lowering is similar across the globe. At this same time Northern Hemisphere Laurentide Ice Sheet had attained its maximum extent (Lowell et al., 1999). These observations are at odds with the scenario that glaciation is driven directly by local summer insolation in each hemisphere (see Fig. 1). If this were the case, then Southern Hemisphere mountain glaciers should have a different time history from Northern Hemisphere mountain glaciers. The reason is that the ~ 20 -kyr precession in summer insolation is antiphased between the hemispheres.

The global cooling effects of lower atmospheric CO₂ concentrations offer an explanation for the global synchrony of peak glaciation (Broecker, 2013; Shakun et al., 2012). If it is CO₂ that drives

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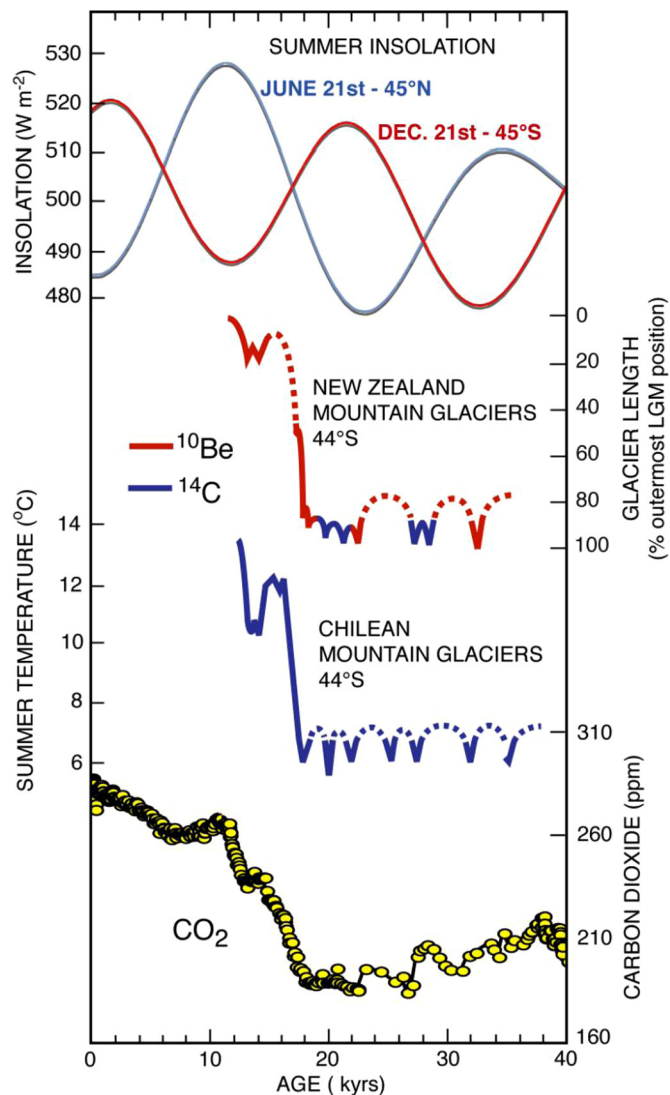


Fig. 1. Evidence in support of the assertion that the snowline lowering for mountain glaciers in both New Zealand and Chile are driven by CO_2 rather than by summer insolation. As can be seen, these glaciers stood at their maximum extent at a time when Southern Hemisphere summer insolation was at a maximum. Further, they went into rapid retreat at the onset of the deglacial CO_2 rise.

glacial cycles, then it follows that orbital cycles must somehow drive CO_2 . As outlined by Broecker (2013), a case can be made that the uptake and release of CO_2 by the ocean is driven by reorganizations in the mode of thermohaline circulation. If so, these reorganizations would have to be triggered by changes in the density contrast between winter waters at the surface of the northern Atlantic and those at the surface of the Southern Ocean. This being the case, uptake of CO_2 by the ocean serves to cool the atmosphere and thereby causes glacier cover to expand.

As proposed by Huybers and Langmuir (2009), the weight of this extra ice would decrease the CO_2 release from volcanoes. If so, the volcanic contribution to the CO_2 change would create a downward ramp. The oceanic contribution would modulate this drawdown, sometimes making it larger and at other times reducing it.

3. Time history of ocean contribution

If both ocean uptake and volcano shutdown contribute to the lowering of the atmosphere's CO_2 content, then we need to understand the magnitude and time history of each. Unfortunately we

are a long way from being able to do this. We do, however, have a suggestion as to how the shape of the ocean contribution might be assessed. The one thing we know for sure about the glacial ocean is that the water mass structure in the Atlantic Ocean was very different from today's. The Pacific remained much as it is today. No significant changes occurred in the distributions of ^{14}C , ^{13}C or CO_3^{2-} (Broecker et al., 2004, 2008; Broecker and Clark, 2001; Matsumoto et al., 2002; Yu et al., 2013, 2010a). Our evidence comes from changes in the distribution of two constituents of the ocean's salt, PO_4 and CO_3^{2-} . Both are influenced by biological cycling. PO_4 is carried to the deep sea in organic detritus where it is released after ingestion by bacteria and other benthic dwellers. Along with the release of PO_4 is the release of CO_2 depleted in ^{13}C . This allows the ^{13}C to be used as a proxy for the addition of PO_4 . The stoichiometry is a $\sim 1\%$ drop in $\delta^{13}\text{C}$ for each micromole of PO_4 released (Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995). Although the situation for CO_3^{2-} is more complicated, it is also related to respiration CO_2 which reacts with CO_3^{2-} ion to produce two HCO_3^- ions (Yu et al., 2008). As shown by one of us (J.Y.), the ratio of boron to calcium in the shells of benthic foraminifera serves as a proxy for carbonate ion (Yu and Elderfield, 2007).

In today's deep sea, the concentrations of both PO_4 and the carbonate ion are higher in the Atlantic than in the Pacific. Further, in both deep oceans the concentrations are quite uniform with water depth.

Currently the deep Atlantic has a uniform PO_4 and CO_3^{2-} content from a depth of about 1.5 km down to the top transition zone separating it from the thin wedge of Antarctic Bottom Water. By contrast, during peak glacial time the water above 2.7 km was deficient in PO_4 and enriched with CO_3^{2-} relative to today's and that below 2.7 km showed opposite changes (Boyle, 1992; Curry and Oppo, 2005; Marchitto and Broecker, 2006; Yu et al., 2008). Our knowledge of this stratification comes from two proxies: $\delta^{13}\text{C}$ and the B/Ca in the shells of the benthic foraminifer *Cibicoides*. In today's ocean, there is a strong correlation between the $\delta^{13}\text{C}$ of these shells and the phosphate content of bottom water in which they live. As shown by Yu and Elderfield (2007), there is also a strong correlation between the B to Ca ratio in *Cibicoides wuellerstorfi* and the extent of calcite supersaturation. At a given sediment core site, calcite saturation state is proportional to carbonate ion concentration; the B/Ca ratio serves as a CO_3^{2-} proxy.

We present here the $\delta^{13}\text{C}$ and B/Ca record for the past 150 kyr from two sediment cores. The record in Caribbean core V28-122 (12°N , 79°W , 3.5 km) (Yu et al., 2010b) is representative of water at about 1.8 km depth in the open Atlantic (Ribbat et al., 1976). This water spills over a sill that isolates the Caribbean from the deep Atlantic. Hence it provides a record of the water above 2.7 km depth in the open Atlantic. As shown in Fig. 2, the record from Ceara Rise core RC16-59 (4°N , 43°W , 3.5 km) reported here (this study) is representative of the water below 2.7 km depth in the open Atlantic. During the Holocene the $\delta^{13}\text{C}$ and B/Ca for the two cores were similar. But during Marine Isotope Stage (MIS) 2, MIS 4 and MIS 6, they diverged widely. During MIS 3, the magnitude of the divergence was reduced.

In Fig. 2, we also compare the $\delta^{13}\text{C}$ and B/Ca records for the Atlantic Ocean on the one hand and those for CO_2 and sea level on the other. Also shown is the summer insolation record at 60°N . As can be seen, there is a prominent difference in shape. The ocean records lack the strong asymmetrical triangular shape evident in the CO_2 and sea level records. The prevailing explanation is that the Northern Hemisphere ice sheets continued to grow until they became unstable (Abe-Ouchi et al., 2013). But, if CO_2 is the primary driver of ice sheets, then it is the asymmetrical triangular shape of the CO_2 record which must be explained.

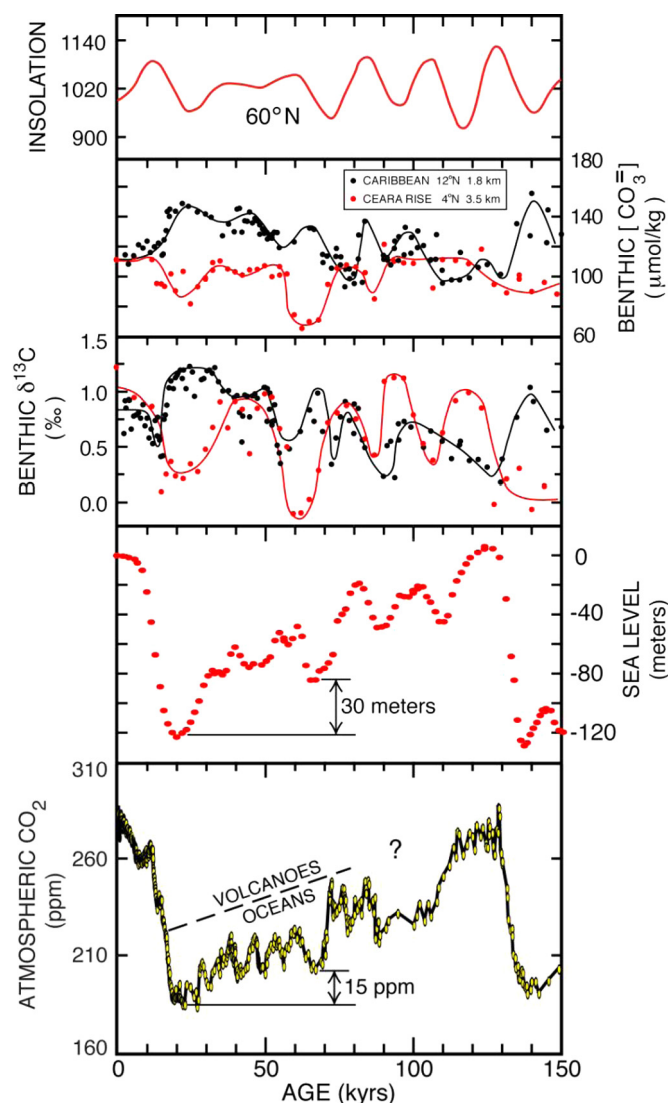


Fig. 2. Comparison between the ^{13}C and CO_3^{2-} for Caribbean core VM 28-122 (Yu et al., 2013, 2010a) and Ceara Rise core RC16-59 (this study) for the last 150 kyr. The chronologies for these cores are based on the ^{18}O record for benthic *Cibicides*. As can be seen, as is the case for the summer insolation record, they fail to show the asymmetrical triangular shape so prominent in the CO_2 and sea level records. We attribute this difference to a downward ramp in CO_2 content caused by the shutdown of volcanoes. It is superimposed on an ocean contribution assembling the Ceara Rise ^{13}C and CO_3^{2-} records.

4. Tie to Northern Hemisphere summer insolation

Why might the shape of the deep Atlantic record resemble that for the ocean's contribution to the drawdown of CO_2 ? Although the answer remains elusive, there is circumstantial evidence for such a tie. The record in the abyssal Atlantic resembles that for the Northern Hemisphere summer insolation. This is consistent with our hypothesis that the link between climate and orbital cycles is through the ocean. Changes in seasonality perturb the high latitude temperature and salinity boundary conditions leading to reorganizations of the ocean's thermohaline circulation which, in turn, lead to the uptake and release of CO_2 . It is tempting to postulate that the ocean's contribution to the CO_2 drawdown is related to the stratification of the deep ocean and that the deep Atlantic $\delta^{13}\text{C}$ and B/Ca records provide a measure as to how the strength of this stratification changed during the course of the last glacial cycle.

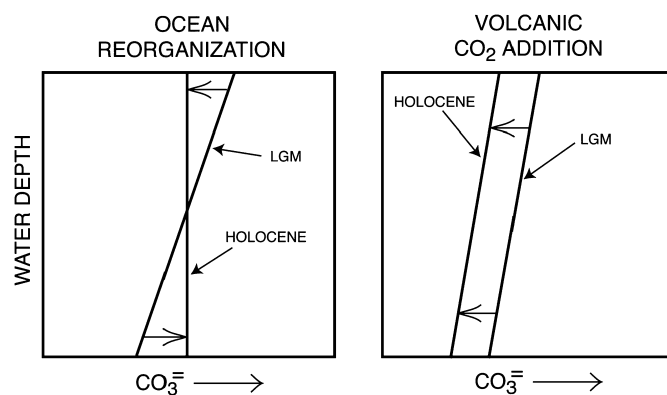


Fig. 3. Effects of ocean reorganization (left panel) and volcanic CO_2 addition (right panel) on the deep ocean CO_3^{2-} were the deglacial rise in the atmosphere's CO_2 content mainly result of release of CO_2 stored in the deep ocean, it would have produced a deep sea deglacial preservation event. By contrast, were it mainly the result of an increase in the CO_2 release from volcanoes, then it would have produced a deep sea dissolution event. In either case, the event would have lasted only 5 or so thousand years. As there is no clear indication that either is present in the deep-sea carbonate ion records, perhaps one may have largely compensated for the other.

5. Solid Earth contribution

In order to explain this difference in shape, we invoke the Huybers–Langmuir volcanic hypothesis (2009). Although there is currently no way to assess the shape or magnitude of the CO_2 drawdown created in this way, it stands to reason that it would steadily increase throughout the cycle, perhaps changing in slope as the ice load varied. Hence, it would have a quasi-ramp-like shape. If a volcanic contribution to the CO_2 record were removed (see Fig. 3), then the shape of the residual (presumably the ocean contribution) would look more like Earth's orbital signature and more like the $\delta^{13}\text{C}$ and CO_3^{2-} records for the deep Atlantic.

6. Deglacial dissolution event

Ocean-only scenarios for the CO_2 cycle call for a deep sea CaCO_3 preservation event during the period of deglaciation. The reason is that a release of CO_2 stored in the glacial deep ocean would have increased its carbonate ion concentration (Fig. 3). Such an increase would be recorded, for example, by a reduction in shell breakage in the zone of partial dissolution that separates the CaCO_3 supersaturated upper deep sea from the CaCO_3 undersaturated deep sea. However, were the buildup of CO_2 the result of adding volcanic CO_2 to the ocean atmosphere reservoir, it would have caused the carbonate ion concentration to decrease and created a CaCO_3 dissolution event. Neither a prominent preservation event nor a prominent dissolution event is seen during deglaciation. If these two contributors to the deglacial rise in atmospheric CO_2 content were comparable, it is possible that the tendency toward increased dissolution largely counterbalanced the tendency toward preservation (see Fig. 3).

7. Cause for glacial Atlantic stratification

A question arises regarding the origin of these two glacial-age water masses. It is likely that the upper water mass formed in the northern Atlantic in a manner similar to that for today's North Atlantic Deep Water (i.e., in the open ocean outside the winter sea ice margin). It is tempting to look upon the deep water mass as an expanded version of today's Antarctic Bottom Water (AABW). But, as documented by Broecker (2013), this cannot be the case. Today's AABW has the same PO_4 content as the water entering the abyssal Pacific. Based on ^{13}C reconstructions, the PO_4 content of

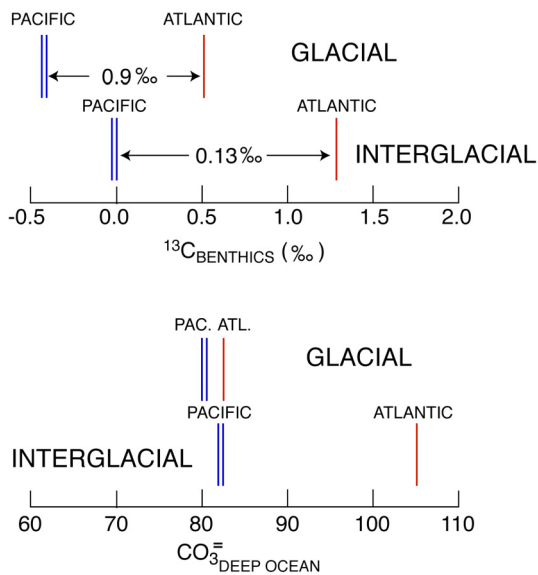


Fig. 4. Comparison of the LGM and Holocene differences in carbon isotope composition (top panel) and in carbonate ion content (bottom panel) between the abyssal Atlantic–abyssal Pacific based on measurements on the benthic foraminifera *Cibicides wuellerstorfi*. Although during peak glacial time today's large CO_3^{2-} difference was largely eliminated, that for $\delta^{13}\text{C}$ was not. Although today the abyssal water entering the Atlantic from the Southern Ocean has the same $\delta^{13}\text{C}$ as that entering the deep Pacific, during the LGM they remained quite different. Because of the sizable range in the ^{13}C measurements on benthic foraminifer shells, the uncertainty in the 0.9‰ Atlantic–Pacific difference is about 0.15‰ (see Broecker, 2013).

the abyssal Atlantic was about $0.9 \mu\text{mol/kg}$ (0.9‰ change in $\delta^{13}\text{C}$ roughly equivalent to $0.9 \mu\text{mol/kg}$ change in PO_4) lower than that in the abyssal Pacific during the last glacial period (see Fig. 4).

As it is not possible that a phosphate gradient anywhere near this large could exist in the rapidly circulating circumpolar current, perhaps this water mass was created in the northern Atlantic. If so, the difference in composition of the upper and lower deep water could be that one formed in an ice-free region and the other formed beneath sea ice. The larger the density difference between the two, the stronger the stratification. The ^{13}C and CO_3^{2-} records give the impression that the density difference between them varied through the course of the glacial cycle.

Consistent with a northern origin, both the ^{13}C and CO_3^{2-} records from 53°N (Yu et al., 2008) are identical to those for the Ceara Rise core. Furthermore, based on shell weights and size fraction analyses, Broecker and Clark (2001) demonstrated that the strong MIS 4 dissolution peak is present in equatorial Atlantic cores ranging in depth from 2.8 to 4.6 km.

In order to explain the opposite trends of $\delta^{13}\text{C}$ and CO_3^{2-} between the upper and lower glacial Atlantic water masses, it would be necessary to reduce the contribution of respiration CO_2 to the upper mass and increase it in the lower mass. This would require that the rain of organic matter somehow bypass the upper layer. Also, it should produce stoichiometric changes in $\delta^{13}\text{C}$ and CO_3^{2-} . As the 0.4 per mil decrease in the deep Atlantic–deep Pacific $\delta^{13}\text{C}$ difference corresponds to about a $27 \mu\text{mol}$ per liter drop in CO_3^{2-} concentration, the observed lowering during MIS stage 2 (~ 20 kyr) is about $20 \mu\text{mol}$ per liter and that during stage 4 (~ 65 kyr) is about $35 \mu\text{mol}$ per liter.

The drawdown of atmospheric CO_2 by the ocean very likely involved an increase in the utilization of the growth-limiting nutrient phosphate (Sigman and Haug, 2003). Today only about one third of the upwelled PO_4 is utilized. One way to increase the utilization efficiency would be to fertilize the Southern Ocean with extra iron (Martin, 1990). Open ocean experiments have demonstrated that given more iron, the extent of utilization of PO_4 in-

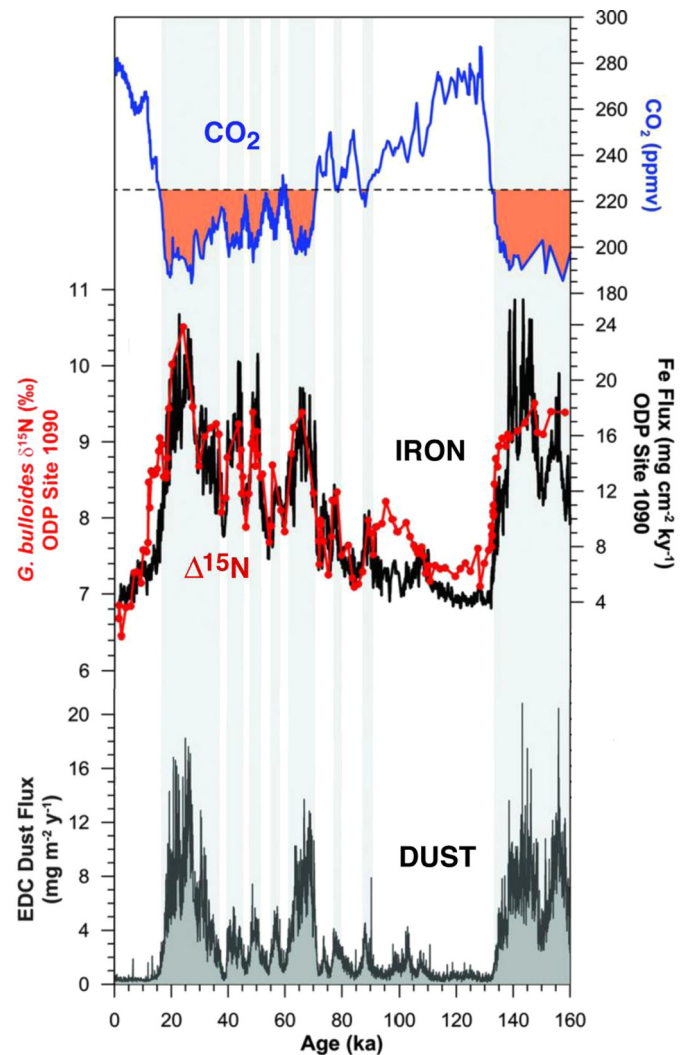


Fig. 5. Southern Ocean dust and nutrient utilization during the last glacial. As shown by Martínez-García et al. (2014) at least for the last 70 kyr, a close tie exists between the flux of dust and the iron it carries and to the Southern Ocean and the atmosphere's CO_2 content. Nitrogen isotope measurements are interpreted as showing that the extent of nutrient utilization in the Southern Ocean increased during times of glacial maxima. Although this correlation applies to the second half of the decline, the correlation is less convincing during the first half. Hence, if extra iron was the driver, then the sensitivity to its input would have to have been much greater during the first half of the decline than during the second half.

creases (Smetacek et al., 2012). Most of the ocean's iron is supplied by dust blown off the continents. Records of dust rain from Antarctic ice and from Southern Ocean sediments show that rain of dust was much higher during MIS 2 and MIS 4 than today (Lambert et al., 2008; see Fig. 5). Furthermore, the nitrogen isotope record kept in foraminifera shells demonstrates that during times of enhanced dust fall, nutrient utilization increased (Martínez-García et al., 2014). So a case can be made that enhanced dust fall increases the strength of the biologic pump which, in turn, pulls CO_2 out of the atmosphere (Jaccard et al., 2013).

But, if iron is responsible for the nutrient drawdown, the hypothesis presented here is in trouble. The reason is that a strong case can be made that dustiness is controlled by gustiness (McGee et al., 2010). Gustiness is related to the frequency and strength of the cyclonic storms which, in turn, depends on the magnitude of the equator to pole temperature difference. Seemingly then, if iron fertilization is responsible for the uptake of CO_2 by the ocean, the glacial cooling of the polar regions must have preceded the CO_2 decline (see Fig. 6).

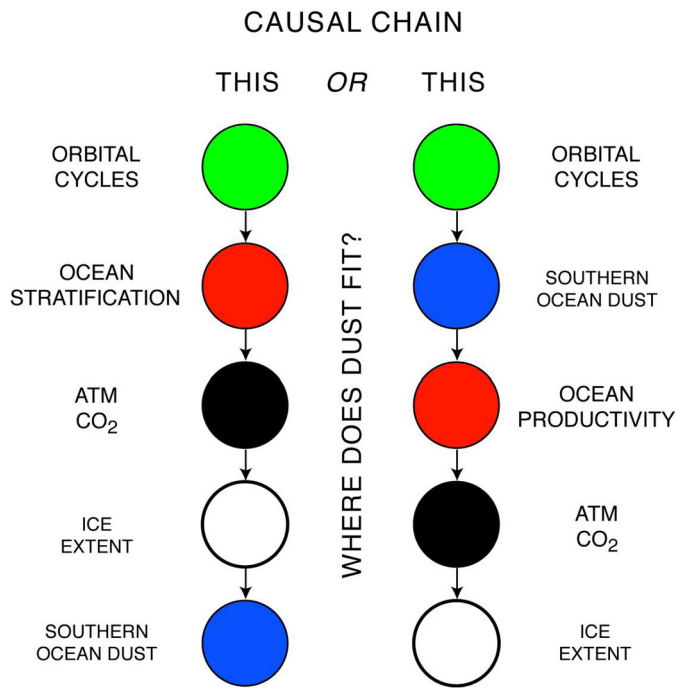


Fig. 6. Comparison of our preferred causal chain (on the left) with that required if the delivery of iron to the surface of the Southern Ocean was the primary driver of CO₂ drawdown (on the right). If, as shown on the right, iron carried by dust drives the atmospheric CO₂ drawdown, then something other than pole to equator temperature must drive dust delivery.

Although atmospheric CO₂ has emerged as a strong contender among potential mechanisms responsible for governing Earth's climate over glacial-to-interglacial cycles (Broecker, 2013; Shakun et al., 2012), there has yet to emerge a complete explanation for what processes gave rise to the CO₂ changes of late Quaternary time. Here we suggest a role for both the oceans and the solid earth for explaining observed CO₂ changes over the course of the past glacial cycle. However important questions still remain regarding the mechanism by which deep ocean stratification modulates CO₂, and also the role of dust deposition as a contributor to atmospheric CO₂ drawdown. Also, much is yet to be learned regarding the Huybers–Langmuir hypothesis that the weight of glacial ice pulsed the CO₂ emissions by volcanoes. In particular, it must be determined how the release of CO₂ at mid-ocean's ridges responded to the changes in the sea level. If our speculation that the role of the ocean was to modulate a continuing CO₂ drawdown caused by a reduction in the output from the solid Earth proves to be correct, then we are right back at where we were in the early 1980s when the glacial lowering of CO₂ was first discovered.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2015.07.019>.

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