



## Two contributors to the glacial CO<sub>2</sub> decline



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### ABSTRACT

It is generally accepted that the glacial drawdown of atmospheric CO<sub>2</sub> content is the sole result of uptake by the ocean. Here we make a case that the reduction of planetary CO<sub>2</sub> outgassing made a significant contribution. We propose that the ocean contribution to CO<sub>2</sub> reduction closely followed Northern Hemisphere summer insolation and was superimposed on a ramp-like decline resulting from a reduction in the input of planetary CO<sub>2</sub>. 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 CO<sub>2</sub> 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 CO<sub>2</sub> storage in the ocean.

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### 1. Introduction

The air trapped in Antarctic ice tells us that the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> to the ocean–atmosphere reservoir. This reduction would have led to a drawdown of the CO<sub>2</sub> content of the atmosphere. As the turnover time of  $\Sigma\text{CO}_2$  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 CO<sub>2</sub> content. Here, we consider a CO<sub>2</sub> scenario that involves both ocean uptake and volcano shutdown.

### 2. CO<sub>2</sub> drives ice

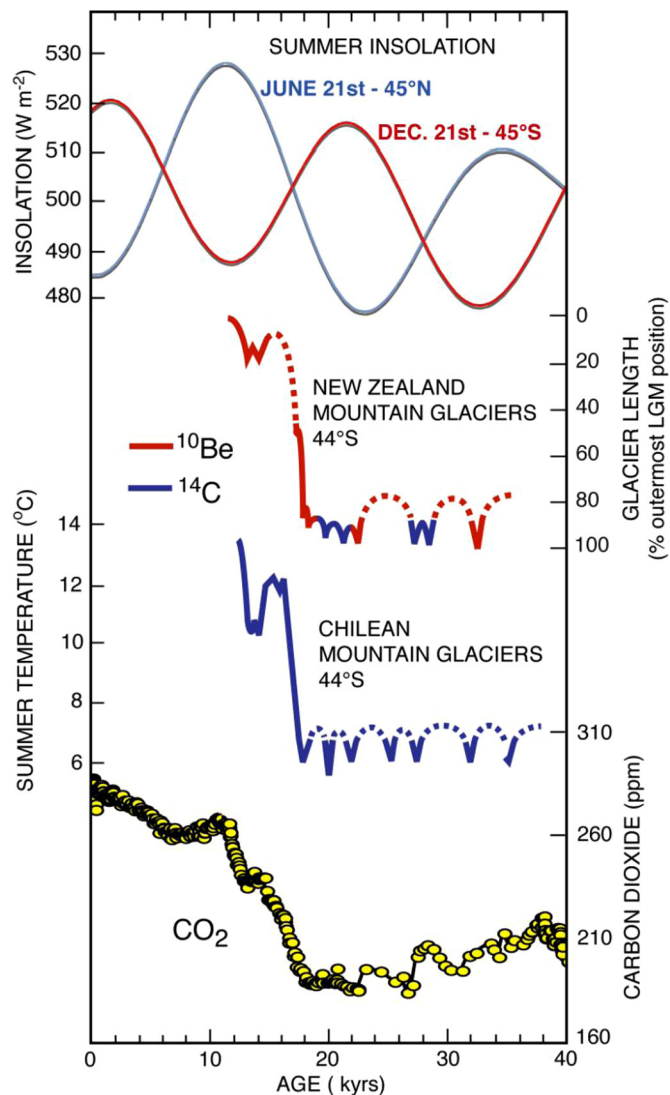
The presence of an orbital pulsebeat superimposed upon the Late Quaternary 100 000-yr glacial cycles was recognized nearly 50

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 <sup>10</sup>Be and <sup>14</sup>C 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  $\sim 25$  and  $\sim 18$  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  $\sim 20$ -kyr precession in summer insolation is antiphased between the hemispheres.

The global cooling effects of lower atmospheric CO<sub>2</sub> concentrations offer an explanation for the global synchrony of peak glaciation (Broecker, 2013; Shakun et al., 2012). If it is CO<sub>2</sub> 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  $\text{CO}_2$  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  $\text{CO}_2$  rise.

glacial cycles, then it follows that orbital cycles must somehow drive  $\text{CO}_2$ . As outlined by Broecker (2013), a case can be made that the uptake and release of  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  release from volcanoes. If so, the volcanic contribution to the  $\text{CO}_2$  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  $\text{CO}_2$  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  $^{14}\text{C}$ ,  $^{13}\text{C}$  or  $\text{CO}_3^{2-}$  (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,  $\text{PO}_4$  and  $\text{CO}_3^{2-}$ . Both are influenced by biological cycling.  $\text{PO}_4$  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  $\text{PO}_4$  is the release of  $\text{CO}_2$  depleted in  $^{13}\text{C}$ . This allows the  $^{13}\text{C}$  to be used as a proxy for the addition of  $\text{PO}_4$ . The stoichiometry is a  $\sim 1\%$  drop in  $\delta^{13}\text{C}$  for each micromole of  $\text{PO}_4$  released (Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995). Although the situation for  $\text{CO}_3^{2-}$  is more complicated, it is also related to respiration  $\text{CO}_2$  which reacts with  $\text{CO}_3^{2-}$  ion to produce two  $\text{HCO}_3^-$  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  $\text{PO}_4$  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  $\text{PO}_4$  and  $\text{CO}_3^{2-}$  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  $\text{PO}_4$  and enriched with  $\text{CO}_3^{2-}$  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 *Cibicides*. 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 *Cibicides 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  $\text{CO}_3^{2-}$  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 ( $12^\circ\text{N}$ ,  $79^\circ\text{W}$ , 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 ( $4^\circ\text{N}$ ,  $43^\circ\text{W}$ , 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  $\text{CO}_2$  and sea level on the other. Also shown is the summer insolation record at  $60^\circ\text{N}$ . As can be seen, there is a prominent difference in shape. The ocean records lack the strong asymmetrical triangular shape evident in the  $\text{CO}_2$  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  $\text{CO}_2$  is the primary driver of ice sheets, then it is the asymmetrical triangular shape of the  $\text{CO}_2$  record which must be explained.

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