Broecker Brief #7

Elements of the last glacial cycle CO₂ decline and recovery June 2017

Introduction:

In an attempt to distinguish between the two major means by which the atmosphere's CO_2 content was drawn down during times of glaciation (i.e., ocean storage and input starvation), I have taken a close look at how the features of the last of these drawdowns relates to those of sea level, $\delta^{18}O$ of benthic foraminifera, Antarctic dust, Atlantic stratification and deep sea carbonate ion concentration.

Comparison with sea level and benthic ¹⁸O:

As shown in Figure 1, although similar, the shape for the atmospheric CO_2 content record for the last glacial cycle differs from that for sea level and that for benthic ¹⁸O in three respects.

- 1) The post 5e decline in CO_2 lags that for Antarctic air temperature by about 7 kyrs.
- 2) Instead of the three interglacial peaks seen in the sea level and the δ^{18} O records, there are only two CO₂ peaks, one at ~124 kyrs and the other at ~82 kyrs. There is no peak at 103 kyrs in the CO₂ record.
- The pronounced sea-saw character so prominently displayed in the CO₂ record for MIS 3 isn't present in the benthic ¹⁸O record.

On the other hand all three of these records have minima at 65 kyrs and 23 kyrs. Further, in all three records these bumps are superimposed on a 100-kyr-duration downward ramp.

In the paragraphs which follow, I comment on each of these differences and similarities. In particular, I ponder on whether they are the result of CO_2 storage in the glacial ocean or a pulsing of the CO_2 input from the Earth's interior. I conclude that both ocean storage and input modulation likely contributed. However, separating their respective contributions will be a tough task and likely will take a long time to carry out. Their contributions to the 'ramp' will be particularly difficult to sort out.

Delayed onset of the CO₂ decline:

As shown in Figure 1, both the initial drop in sea level and the initial increase in the δ^{18} O of benthic foraminifera occurred roughly 7 kyrs before the onset of the CO₂ decline. While not inconsistent with Huybers and Langmuir (i.e., ice load shuts down volcanism), the CO₂ decline appears to be far too steep to be caused by input starvation. One way to explain this offset lag would be to hypothesize that the decrease in Northern Hemisphere summer insolation triggered a reorganization of the ocean's thermohaline circulation and, this somehow increased in cloud albedo (Severinghaus scenario). The cooling by clouds allowed Northern Hemisphere ice sheets to grow. Note that ocean cooling as well as ice sheet growth is required to explain the expanded size of the 5e benthic δ^{18} O peak relative to that for sea level (see Figure 1).

Minima at 23 and 65 kyrs:

Based on the comparison of Jimin Yu's δ^{13} C record for a core from the upper NADW with that for a core from lower NADW (see Figure 2), one could conclude that these CO₂ minima were the result of ocean CO₂ storage driven by Atlantic stratification. However, these minima could also be explained by iron fertilization of the Southern Ocean (see Figure 3). Important in this regard is that when stratification broke down (or when the dust rain waned), this stored CO₂ must have been released to the atmosphere. Hence this mode of storage is restricted to the Northern Hemisphere 20-kyr-duration summer insolation minima. Note that the Atlantic stratification record lacks a ramp. But if dust were the villain, then as shown in Figure 3, there is a suggestion of a ramp. However, as the peaks of Southern Ocean dust loading for MIS 2 and MIS 4 are so large that iron fertilization is an unlikely explanation for the ramp.

Maxima at 80 and 120 kyrs:

I am intrigued by the observation that the broad CO_2 maxima centered at 124 kyrs and 82 kyrs are matched by peaks in David Lund's record for iron and manganese release from the East Pacific Rise (see Figure 4). If CO_2 release from ridge crests also peaked during times of deglaciation, then perhaps the upward bumps in CO_2 are related to enhanced release of CO_2 from the Earth's interior rather than from the ocean. Note that the duration of these CO_2 peaks is much

longer than those for iron and manganese. As shown in Figure 5, a similar situation exists for the last 20 kyrs. Although the iron and manganese peaks are confined to the period of deglaciation, the CO_2 high continues through the entire Holocene.

The second peak in Mn and Fe release from the East Pacific Rise is unexpected. But perhaps it is tied to the CO_2 release during the sea level rise leading up to the maximum at 82 kyrs.

Heinrich event related CO₂ peaks:

As can be seen in Figure 1, between 60 kyrs and 40 kyrs, there are three maxima prominent in the atmospheric CO₂ record. These peaks are either absent or highly muted in the benthic ¹⁸O record. They appear to be related to Heinrich events. Each Heinrich event occurs at the termination of a CO₂ decline and is followed by a CO₂ rise. Of interest is that these three peaks show up prominently in the Antarctic dust record and also in the Southern Ocean $\Delta^{15}N$ record (see Figure 3). When dust is high, CO₂ is falling; when it is low, CO₂ is rising. Smells like iron fertilization!!

The ramp:

As for the ramp, part of it must be storage in the ocean. The reason is that the progressive cooling of the ocean surface reduced the vapor pressure of CO_2 in surface ocean water and hence also that in the atmosphere. The CO_2 removed from the atmosphere in this way was stored in the ocean. Although this could explain as much as a 40 µatm of the 95 µatm drop in atmospheric CO_2 pressure, account must also be taken of the increase in CO_2 resulting from the increase in ocean salinity. For a 120 meter lowering of sea level this amounts to about 10 µatm. Further, if as is generally thought, the 0.35% drop in the ocean's $\delta^{13}C$ is the result of a reduction in terrestrial biomass, then after adjustment related to $CaCO_3$ compensation this would create an increase of about 15 µatm in the atmosphere's CO_2 partial pressure. Hence taken together, cooling, salinification and terrestrial carbon reduction account for only ~15 of the 90 µatm LGM reduction of the atmosphere's CO_2 content. The remainder (~80 µatm) must be explained either by storage in the ocean or a reduction in the planetary CO_2 outgassing.

Until Huybers and Langmuir suggested that a reduction of the input of CO_2 from the Earth's interior played a role in the CO_2 drawdown, the effort to explain the ramp focused on storage in the deep sea. Putting aside the temporary storage centered at 65 kyrs and 23 kyrs, this requires an ocean reservoir which over a 100-kyr time interval accumulated evermore CO_2 . Despite much effort by many researchers, no convincing evidence has been put forward regarding the identity of such a storehouse. Because of this, I have developed an interest in input starvation.

The Huybers and Langmuir group have accumulated enough evidence to make a case that at least some of the volcanoes in the vicinity of ice masses were shut down during much of the last glacial cycle. Further, a burst of eruptions began about 14 kyrs ago and continued until about 7 kyrs ago. To me, this indicates that continental volcanism contributed to the second half of the CO_2 rise (i.e., that which took place after the Antarctic Cold Reversal). But, as both the magnitude of the continental CO_2 contribution and the extent to which it was reduced by ice loading remain uncertain, the contribution of the deglacial burst of activity to the deglacial CO_2 rise cannot be estimated.

The case for input starvation rests strongly on what went on in the ocean. As pressure on the ridge crests was reduced by the storage of water in continental ice sheets, one might conclude that CO_2 release increased (rather than decreased) during times of glaciation. If so, it would have tended to cancel the continental contribution. Modeling by Richard Katz of the ridge-crest lava wedge makes clear that the situation is sufficiently complex to allow a range of possible scenarios regarding the phasing between the contributions of sea floor CO_2 and continental CO_2 . Critical in this regard is the order of magnitude uncertainty in the rate of ascent of lava through the wedges crystal mesh. Because of this uncertainty, I turn to direct evidence.

Anderson's opal peaks

At this point I must make clear that Bob Anderson makes a strong case that the post glacial rise in CO_2 involved upwelling in the Southern Ocean. He documents two episodes of excess opal accumulation separated by the Antarctic Cold Reversal. Their timing appears to

correspond to that of the two portions of the CO_2 rise. As this is a convincing piece of evidence, it may well trump any other scenario. I can only say that there is no proof that excess CO_2 accompanied the upwelled silica. Also, there is perhaps a way to reconcile Anderson's first opal peak with a starvation scenario. The extra CO_2 stored in the ocean during MIS 2 would be released as stratification broke down (or as the dust rain subsided).

Sea floor emissions

Ocean observations appear to be telling us that there was a pronounced increase of CO_2 emissions from the sea floor during periods of deglaciation. The evidence comes from measurements of ¹⁴C in benthic forams in cores from continental margins. At several places in the depth range 700 to 1200 meters, the ¹⁴C ages are several thousand years older than expected. Two explanations can be given to these occurrences. One is that they are the result of the breakdown of CO_2 clathrates formed during times of glaciation. During the period of deglaciation, waters in this depth range warmed by about 2°C causing the clathrate stability depth to move up about 500 meters. The other explanation is the release of planetary CO_2 from ridge crests that was enhanced during time of rapid sea level rise (see above). Unpublished measurements on deglacial-age sediment by Patrick Rafter document low $\Delta^{14}C$ benthic (and planktic) foraminifera shells at the mouth of the Gulf of California. As segments of the East Pacific Rise are present in the Gulf, it is not clear whether the source of this ¹⁴C depleted CO_2 was from clathrates or from the mantle.

Radiocarbon:

The most difficult thing to explain is the 20 percent drop in radiocarbon to carbon ratio for atmosphere which occurred between 18 and14 kyrs ago (see Figure 6). One way to accomplish this would be to invoke a twofold reduction in the production rate of radiocarbon during this time interval. Another way would be to isolate 20 percent of the deep sea for several ¹⁴C half-lives and then mix it back into the whole. A third way would be to propose that the average isolation time for ocean carbon during the LGM was 1800 years greater than today's.

Then starting 18 kyrs ago it returned to its Holocene situation. Finally, the air-sea $\Delta \delta^{14}$ C increased from its ~50 per mil to ~250 per mil.

Taken alone none of these seem to be anywhere near large enough to do the job. But together perhaps they could. I like to point to benthic and planktic age differences Steve Barker and I obtained for various depths in the equatorial Pacific Ocean. As listed in Table 1, at depths ranging from 1.9 to 4.4 km, we get planktic-benthic age differences close to today's difference of 1600 years. This tells me that there was neither an isolated reservoir nor an 1800-year age offset! Further, in the core from 6°N, we used a wood-planktic pair to show that the surface reservoir age during the LGM was similar to today's. These benthic-planktic age differences make it unlikely that the ocean was the dominant contributor to the 20 percent drop in ocean ¹⁴C to C ratio.

This leaves only two explanations. Either the drop is the result of the addition of 14 C-free CO₂ from the sea floor or it is the result of a decrease in 14 C production rate.

There are two approaches to reconstructing the production rate of radiocarbon. One is to use the record for ¹⁰Be accumulation rate record in ice cores. As the ratio of ¹⁰Be to ¹⁴C produced by cosmic rays does not change with production rate, ¹⁰Be serves as a proxy for ¹⁴C. Finkle and Nishiizumi generated such a record for the GISP2 Greenland ice cores shown in Figure 7. It shows no significant drop in production during the period 18 kyrs to 14 kyrs. However, as there are outstanding issues regarding the interpretation of ¹⁰Be measurements, future work may alter this conclusion.

Reconstructions of the Earth's magnetic field are based on measurement of the magnetic field strength in deep sea sediment. It has been shown that broadly speaking the time history of the magnitude of the offset between ¹⁴C ages and calendar ages mirrored changes in the Earth's magnetic field strength. There was a steep rise in the ¹⁴C to C ratio in atmospheric carbon at the onset the Lachamp event. Since then, the ¹⁴C to C ratio has declined as the magnetic field strengthened. But there is no evidence that this increase in strength steepened during the 18 kyr to 14 kyr period.

My impression based on both the ice core ¹⁰Be record and the deep-sea sediment magnetic record is that changes in ¹⁴C production were not large enough to produce the 20 percent ¹⁴C decline that occurred between 18 kyrs and 14 kyrs ago.

With regard to ¹⁴C-free CO₂, we know that it was being added to the ocean during the period of deglaciation but we as yet have no way to estimate how much. Were it to explain the entire 20 percent drop, then about 7000 gigatons of carbon would be required. Were this amount added as CO₂ then it would have created a huge ocean-wide dissolution event. Although compensation by dissolution of CaCO₃ in sediments would gradually neutralize this CO₂, this would take many thousands of years. During this period, the CO₃⁼ concentration would be greatly reduced and the foraminifera in the sediments would either be dissolved away or badly fragmented. As shown in Figure 8, no such drop is seen in Yu's B to Ca-based carbonate ion reconstruction.

So while CO_2 release from the sea floor could be called on to raise the CO_2 content of the atmosphere, it cannot be called on to explain the drop in ¹⁴C. Hence, we are left with a mystery. Neither ocean isolation, production reduction, nor ¹⁴C-free CO_2 addition appears to be capable of explaining a major portion of the 20 percent reduction in ¹⁴C to C ratio which occurred between 18 kyrs and 14 kyrs ago.

Carbonate ion response:

Were ocean storage dominant, then the release to the atmosphere of CO_2 during periods of deglaciation would have increased the carbonate ion concentration in the ocean creating a calcite preservation event. Were input starvation dominant, then the addition of CO_2 during periods of deglaciation would have decreased the carbonate ion concentration in the ocean creating a calcite preservation event. Using Yu's B to Ca ratio carbonate ion proxy, it should be possible to detect carbonate ion excursions during times of deglaciation. In most open ocean sediments these signals are muted by bioturbation. So efforts must be focused on high deposition rate sediments. Further, the effort should be focused on low latitude Pacific Ocean sediments. The reason is that, unlike the Atlantic, the glacial to Holocene change of carbonate ion

concentration was quite small. Hence dissolution and preservation events would be more easily seen. Ideal cores for this purpose are MD98-2181 from the Morotai Basin (6°N, 126°E, 2.1 km) with a sedimentation rate of 65 cm per kyr, and core MD2386 from the Ontong Java Plateau (1°N, 130°E, 2.8 km) with a sedimentation rate of 40 cm/kyr. Jimin Yu has carried out preliminary B to Ca measurements of benthics from MD2386. As can be seen in Figure 8, there is no indication of either a significant deglacial preservation or a significant dissolution event. It should be mentioned in this regard that the ocean's carbonate ion concentration recovers exponentially from dissolution or preservation spikes with a half time on the order of 5 kyrs. Hence the impact of events which took place during the deglacial time interval would extend into the Holocene. One way to explain the absence of either a CaCO₃ dissolution or preservation event would be to conclude that both ocean storage and input starvation were at play.

A complication in this strategy is that the regrowth of forests must have produced a preservation event which overlapped whatever happened during deglaciation.

Conclusions:

So we see that it is a mixed bag (see Figure 9). Some of the evidence points to ocean storage. Other evidence points to input starvation.

Table 1. Summary of benthic-planktic radiocarbon-age differences for samples of LGM age from
the deep equatorial Pacific Ocean. For each sample, ¹⁴ C was measured on several planktic and
mixed benthic species. Only cores free of the Barker effect are included. The mean of 1525 years
is within the uncertainty of today's deep to surface ¹⁴ C age difference.

Latitude	Longitude	Depth km	Calendar Age kyrs	∆B-P yrs	
1°S	Equatorial Pacific				
15	Broecker et al., 20	04	21.5 21.9	$1950 \pm 220 \\ 1640 \pm 250$	
6°N	126°E Broecker et al. 20	2.1	10 1	1325 ± 200	
	Dibecker et al., 20	04	19.1 18.7 19.6	1325 ± 200 1170 ± 220 1325 ± 200	
1°N	130°E Broecker et al., 20	2.8 08	17.9 18.6	1790 ± 170 1510 ± 120	
2°S	140°W	4.4	19.2	1700 ± 130	
	Broecker and Clark,	2010	17.2 22.0 24.2	1550 ± 300 1500 ± 300 1700 ± 300	
	Averag	ge of the 11 L	GM results	1575 ± 150	



Figure 1. Comparison of the CO_2 record for the last glacial cycle with those for sea level and the $\delta^{18}O$ of benthic foraminifera. Although similar in some ways, there are important differences (see text). The CO_2 record was generated by Ed Brook.



Figure 2. Comparison of the δ^{13} C record for benthic foraminifera for a core bathed in upper NADW with that for a core bathed in lower NADW. The core from the Caribbean records the water spilling over the 1.8 km depth sill which separates the deep Caribbean from the deep Atlantic. The core from 3.6 km depth on the Ceara Rise records for lower NADW. The large separation between these two records during MIS 2 and MIS 4 records times of strong stratification in the deep Atlantic. The time scales are based on the δ^{18} O in benthic foraminifera. These measurements were made by Jimin Yu.



Figure 3. Record of dust rain over the Antarctic ice cap compared with those for the flux of iron and the $\Delta^{15}N$ in Southern Ocean sediment. The $\Delta^{15}N$ record demonstrates that increases in NO₃ utilization match those for the delivery of iron confirming that nutrient utilization in Southern Ocean surface waters peaked during MIS 2 and MIS 4. Note that the three peaks between 60 kyrs and 40 kyrs also show up in the CO₂ record. As discussed in the text, they are related to Heinrich events. The nitrogen isotope measurements were made by Daniel Sigman.



Figure 4. Comparison of the records for the fluxes of iron and manganese from two Pacific Rise sediment cores for the period 50 kyrs to 150 kyrs with that for atmospheric CO₂. The time scales for both records are based on companion δ^{18} O records for benthic foraminifera. The iron and manganese measurements were made by David Lund and the CO₂ measurements by Ed Brook.



Figure 5. Comparison of the atmospheric CO_2 record for the last 50 kyrs with those for the fluxes of iron and manganese from the East Pacific Rise at 6°S. The CO_2 record is by Ed Brooks and the Fe and Mn records by David Lund.



Figure 6. Following the last glacial maximum, the ¹⁴C to C ratio in the atmosphere began to decease. This created a decrease in the offset between the ²³⁰Th and ¹⁴C age scales. By 14 kyrs it had fallen from 3.5 to 2.3 kyrs. This required a 20 percent drop in the ¹⁴C to C ratio in the oceanatmosphere carbon reservoir. The ²³⁰Th measurements were made by Hai Cheng and the ¹⁴C measurements by John Southon.



Figure 7. Finkle and Nishiizumi's (1997) 10 Be record for Greenland's GISP2 ice core. Note that the accumulation rate of this cosmogenic isotope appears to be about the same during the 18 to 15 kyr time interval as it was during the LGM. Taken at face value, this record rules against a two-fold drop in 14 C production during the first half of the last deglaciation.



Figure 8. Carbonate ion concentrations based on B to Ca ratio measurements on the shells of benthic foram *Cibicides* from western equatorial Pacific core MD2386 (1.1°N, 130°E). These analyses were performed by Jimin Yu. They are as yet unpublished.

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FEATURES	OCEAN STORAGE	INPUT STARV.	
23 AND 65 KYR MINIMA	\checkmark		
80 AND 120 KYR MAXIMA		\checkmark	
HEINRICH RELATED OSC.	\checkmark		
INITIAL CO ₂ DROP	\checkmark		
100 KYR RAMP	2	2	
TWO STEP RISE	<u></u>	f	
20 PERCENT ¹⁴ C DROP	?	?	?
			MAG. FIELD STR.

Figure 9. Best guesses regarding the origin of the primary features of the CO_2 records for the last climate cycle. Note that the ramp and two-step rise are linked.