Ocean carbon storage during the Last Glacial Maximum

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Ocean Carbon and Biogeochemistry
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Ice core records reveal tight coupling between CO$_2$ and climate.
Carbon must have been transferred to the deep ocean during the ice ages

The deep ocean is:

1) The only C reservoir large enough to accommodate 200 GtC from the atmosphere during each peak ice age...

2) ...and a much larger inventory of carbon released from the terrestrial biosphere.

3) The only large C reservoir capable of exchanging carbon with the atmosphere as rapidly as indicated by the ice cores.
Modern ocean reference: Maximum nutrients ($\text{CO}_2$ storage) at intermediate depths.
Possible LGM “Nutrient-deepening” scenario: Deep ocean filled with CO$_2$-rich O$_2$-poor water

Modern Pacific intermediate water

Dark Blue:
Low O$_2$
High CO$_2$

LGM global deep ocean nutrient deepening
Sigman et al., 2010
Boyle, 1988
Deep-ocean CO$_2$ storage represents a balance between biology and physics.

Atmospheric CO$_2$ reflects a global balance between biological drawdown and physical ventilation.  

*Figure of K Speer redrawn by T Trull*
Changes in the biological pump that would lower atmospheric CO$_2$

Increased “Capacity” = Ocean nutrient inventory

Increased “Efficiency” = Fraction of upwelled nutrients consumed biologically and exported to depth as organic matter

*Knox and McElroy, JGR 1984
Volk and Hoffert, AGU monograph, 1985.*
“Efficiency” = Fraction of upwelled nutrients consumed biologically and exported to depth as organic matter

Nutrient utilization controls amount of POC “pumped” to deep sea

Preformed nutrients are a lost opportunity to “pump” carbon into the deep sea.

Sigman and Boyle, Nature, 2000
LGM “Nutrient-deepening” scenario: Involves $\Delta$ circulation & $\Delta$ Bio Pump Efficiency

Modern Pacific intermediate water

Dark Blue:
Low $O_2$
High $CO_2$

LGM global deep ocean nutrient deepening
Sigman et al., 2010
Boyle, 1988
Where and How was CO$_2$ stored in the deep ocean?

Guiding principle:

“All biological pump mechanism for lowering ice-age pCO$_2^{atm}$ decreases the dissolved O$_2$ content of the ocean interior”

Sigman et al., 2010, summarizing one of the main points from Broecker, 1982.
How do we assess changes in \([O_2]\)?

There is no direct geochemical “proxy”. Therefore:

\(\Delta O_2\) constrained indirectly:

1) Sediment redox (oxic vs. anoxic) state; depends on:
   a) Bottom water \([O_2]\) (oxygen supply),
   b) Organic carbon supply to sediments,
      Fuels respiration - oxygen removal.

2) Measure:
   Supply of organic carbon to the sea floor (e.g., xsBa, opal)
   Sediment redox state (e.g., authigenic U, Re)
   Infer: Bottom water \([O_2]\)
Reduced LGM deep-ocean $O_2$ based on:
1) More reducing sediments
2) Lower C-org rain to the sea bed

Subarctic N Pacific:
Use two C-org flux proxies with unrelated sensitivity to variable preservation to ensure reliable C-org flux reconstruction.

*Jaccard et al., 2009*
Compelling qualitative evidence for the Pacific Ocean


Subarctic Pacific evidence for a glacial deepening of the oceanic respired carbon pool
S.L. Jaccard a,d,* , E.D. Galbraith b , D.M. Sigman c , G.H. Haug a,g , R. Francois d , T.F. Pedersen e , P. Dulski f , H.R. Thierstein a


A deeper respired carbon pool in the glacial equatorial Pacific Ocean
L.I. Bradtmiller a,* , R.F. Anderson b,c , J.P. Sachs d , M.Q. Fleisher b

Nature Geoscience 5 (2012) 151–155

Large climate-driven changes of oceanic oxygen concentrations during the last deglaciation
Samuel L. Jaccard 1,* and Eric D. Galbraith 2,*
Compelling qualitative evidence for the Atlantic Ocean

Glacial-interglacial changes in bottom-water oxygen content on the Portuguese margin

Babette A. A. Hoogakker1, Henry Elderfield2, Gerhard Schmiedl3, I. Nick McCave2 and Rosalind E. M. Rickaby1

Biological and physical controls in the Southern Ocean on past millennial-scale atmospheric CO2 changes

Julia Gottschalk1, Luke C. Skinner1, Jörg Lippold2, Hendrik Vogel2, Norbert Frank3, Samuel L. Jaccard2 & Claire Waelbroeck4

Covariation of deep Southern Ocean oxygenation and atmospheric CO2 through the last ice age

Samuel L. Jaccard1,2, Eric D. Galbraith3,4,5, Alfredo Martínez–García6,7 & Robert F. Anderson8
Most of the interior ocean had lower O$_2$ during the LGM

Atlantic

Indian

Pacific

Holocene minus LGM Global database of $\Delta$O$_2$

Reduced LGM deep-ocean O$_2$ based on:
1) More reducing sediments
2) Lower C-org rain to the sea bed.

Jaccard et al., 2014
Deep N Pacific (>5000m): Magnetic minerals lost from glacial sediments due to low BWO

Korff et al., 2016, Paleoceanography
1) Qualitative evidence for lower ice-age deep-ocean O$_2$ has been produced by several investigators. Conclusion seems robust.

2) Increase in biological pump efficiency contributed to lower ice-age atmospheric CO$_2$.

3) Unknown - How low was deep-sea O$_2$?

4) Unknown - How much extra CO$_2$ was stored?

5) Unknown - What physical and biogeochemical factors contributed?
Deep Pacific O$_2$ levels constrained using preservation of organic compounds
Equatorial Pacific: Productivity maxima on ice-age terminations

TT013-PC72: 0.1°N, 140°W

xsBa and opal fluxes are consistent over the past 500,000 years.

Conclude: History of C-org rain to sea bed can be estimated reliably from opal and xsBa.

Winckler, Anderson, Jaccard & Marcantonio, PNAS, 2016
EqPac: Opal & xsBa increase from LGM to Holocene.

Glacial organic biomarker fluxes during LGM >> Holocene.

Inconsistent with inorganic PP proxies.

Infer enhanced LGM organic preservation due to low $\text{O}_2$.

Darker color is PC72, lighter color is PC18.
Calibrating organic preservation sensitivity to $O_2$:
Use the Arabian Sea as a natural laboratory

Organic carbon preservation increases rapidly for
BWO $< 35 \mu$mol/kg
(Keil and Cowie, 1999)

Assume 35 $\mu$mol/kg as a conservative limit.

Modern bottom water $[O_2]$ at core sites: 168 $\mu$mol/kg

Equatorial Pacific:
LGM bottom water $[O_2]$ was $\sim 133$ $\mu$mol/kg $< $ modern
Deep Pacific O$_2$ levels constrained using preservation of organic compounds
Divergence of alkenone concentrations indicates deglacial shoaling of low-O$_2$ water.

Productivity: Infer similar trend with time due to proximity.

Oxygen: Divergence of concentrations implies divergence of preservation, which is sensitive to bottom water oxygen.

Alkenone data from Koutavas and Sachs, 2008
Possible LGM O$_2$ profile
Crossover roughly at 1000 m

Pattern of alkenone concentration in V19-27 follows that of deeper cores. Only V21-30 had greater O$_2$ during LGM.

Alkenone data from Koutavas and Sachs, 2008
Calculate glacial increase in respiratory CO$_2$

<table>
<thead>
<tr>
<th></th>
<th>Salinity</th>
<th>Temp</th>
<th>PotTemp</th>
<th>O2</th>
<th>O2 Solubility</th>
<th>AOU</th>
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<tbody>
<tr>
<td>Modern</td>
<td>34.694</td>
<td>1.41</td>
<td>1.0616</td>
<td>168</td>
<td>351</td>
<td>183</td>
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<tr>
<td>LGM</td>
<td>35.73482</td>
<td>-0.59</td>
<td>-0.9384</td>
<td>35</td>
<td>371</td>
<td>336</td>
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</tbody>
</table>

Assume deep water formed at O$_2$ saturation with atm.
AOU was greater by 153 µmol/kg in LGM
For RQ=1.415 (ΔO$_2$/ΔCO$_2$, Anderson, 1995)
Respiratory CO$_2$ was 108 µmol/kg higher in LGM
No difference in Indo-Pacific deep water $[\text{CO}_3^{2-}]$ between LGM and Holocene

Includes TT013-PC61 @1°S Between PC18 and PC72

Allen et al., 2015 QSR
Calculating backwards from modern to LGM deepwater carbonate chemistry

<table>
<thead>
<tr>
<th>Graph Points</th>
<th>TCO2</th>
<th>TALK</th>
<th>CO3</th>
<th></th>
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<tbody>
<tr>
<td>1</td>
<td>Modern 4.2 km 0°, 140</td>
<td>2320</td>
<td>2425</td>
<td>79</td>
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<tr>
<td>2</td>
<td>Modern + ice volume</td>
<td>2385.72327</td>
<td>2497.75</td>
<td>82.8</td>
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<tr>
<td>3</td>
<td>Mod+ice+DeltaRespCO₂</td>
<td>2494.09551</td>
<td>2497.75</td>
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<tr>
<td>4</td>
<td>Plus resp HNO₃</td>
<td>2494.09551</td>
<td>2481.39193</td>
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<td>100 +CaCO₃ dissolution</td>
<td>2594.09551</td>
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<td>2699.39193</td>
<td>79.3</td>
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</tr>
</tbody>
</table>

**Initial conditions**

**Final Conditions**

INCLUDES loss of alk from respiratory generation of nitrate (C:N = 106:16)

Accumulating respiratory CO₂ lowers [CO₃²⁻]

CaCO₃ dissolution required to restore initial [CO₃²⁻]

DIC increased 217 µmol/kg: Significant contributions from respiratory CO₂ (108 µmol/kg), ice volume and CaCO₃ dissolution.
Details of calculation

Calculations using CO2SYS v2.1
Component of TCO2 and ALK change

**GLODAP DIC & ALK and CO2SYS v2.1**
K1, K2 from Mehrbach et al., 1973 refit by Dickson and Millero, 1987
Seawater pH scale (mol/kg-SW)
KHSO4 from Dickson
Total B from Uppstrom 1974
Modern to LGM evolution of deep Pacific carbonate chemistry
Global mass budget

If, during the LGM, half the global ocean volume (~6.5X10^{20} liters) contained:

108 µmol/kg more respiratory CO\textsubscript{2} than today

This amounts to 846 Gt Carbon stored in the deep sea

Close to the value needed to balance:

CO\textsubscript{2} uptake from the atmosphere (~200 GtC)
Carbon from the terrestrial biosphere (~600 GtC)

Values need to be refined with more detailed models, including reduced DIC in the upper ocean.
Consistent estimate from reconstructed $^{14}$C ventilation ages & models

If, during the LGM, half the global ocean volume (~6.5X10$^{20}$ liters) contained:

108 µmol/kg more respiratory CO$_2$ than today

This amounts to 846 Gt Carbon stored in the deep sea

Extrapolating modern $^{14}$C-DIC correlations to the LGM:
85 – 115 µmol/kg increase in total DIC
730 – 980 GtC increase in global total DIC
*Sarnthein et al., 2013*

590 – 790 GtC increase in global respiratory DIC
From model fit to global $\delta^{13}$C and $\delta^{15}$N in LGM
*Schmittner and Somes, 2016*
Current status

1) Qualitative evidence for lower ice-age deep-ocean $\text{O}_2$ has been produced by several investigators. Conclusion seems robust.

2) Increase in biological pump efficiency contributed to lower ice-age atmospheric $\text{CO}_2$.

3) Unknown - How low was deep-sea $\text{O}_2$?

4) Unknown - How much extra $\text{CO}_2$ was stored?

5) Unknown - What physical and biogeochemical factors contributed?
Atlantic radiocarbon age depth profiles indicate slower LGM deep water ventilation

Freeman et al., NatComm, 2016  DOI: 10.1038/ncomms11998
Rate of C-org regeneration unchanged: LGM to Holocene

Assuming $\delta^{13}C$ of DIC reflects mainly addition of respiratory CO$_2$: Ice-age storage of CO$_2$ was due to slower ventilation, not enhanced biological pump.  

Freeman et al., 2016, NatComm
NADW formed during the LGM, but more sluggishly than today. Based on the distribution of Nd isotopes throughout the deep Atlantic during the LGM. Sluggish circulation allowed greater CO$_2$ accumulation than today.  

Howe et al., 2016, NatComm
Why did the ice-age deep ocean hold more CO$_2$?

Combination of factors:

1) Cooler Ocean Temperatures
   Greater solubility of CO$_2$
   Reduced metabolic rates deepened C-org respiration

2) Greater ocean stratification/reduced ventilation ($^{14}$C ages)

3) Greater nutrient utilization in the Southern Ocean
   Reduced upwelling
   Dust fertilization of the Subantarctic Zone

   (2) and (3) contributed to lower deep-ocean oxygen.

4) CaCO$_3$ compensation

All operated synergistically
Extra slides
Conceptual view of the S Pacific based on work near New Zealand

Deep, poorly ventilated water mass; High CO$_2$ & Low O$_2$

Ronge et al., 2015, 2016
So Ocean: Opal, TOC and xsBa flux increase from LGM to Holocene.

Consistency among 3 geochemical tracers lends confidence to inferred pattern of export flux.

Jaccard et al., 2016
Figure S2
Greater organic preservation in EqPac sediments during LGM explains longstanding enigmas

EEP paleo-productivity studies in 1980’s based on C-org accumulation suggested greater LGM productivity (Sarnthein; Lyle; Pedersen) whereas non-organic proxies disagreed.

Sediment combustion oxygen demand (Perks & Keeling) explained.
Climate-related variability of sediment combustion oxygen demand explained

Precessionally forced productivity variations across the equatorial Pacific

Helen M. Perks, Christopher D. Charles, and Ralph F. Keeling
Paleoceanography, 2002

◆ COD variability in WEP in phase with EEP; expect the opposite if ENSO-like forcing of the tilt of the thermocline; covariance reflects low ice-age $O_2$.

◆ Greater COD at RNDB 74P, despite lower productivity than above ODP849, consistent with lower $O_2$ in overlying water (greater C-org preservation).