Ocean carbon storage during the Last Glacial Maximum

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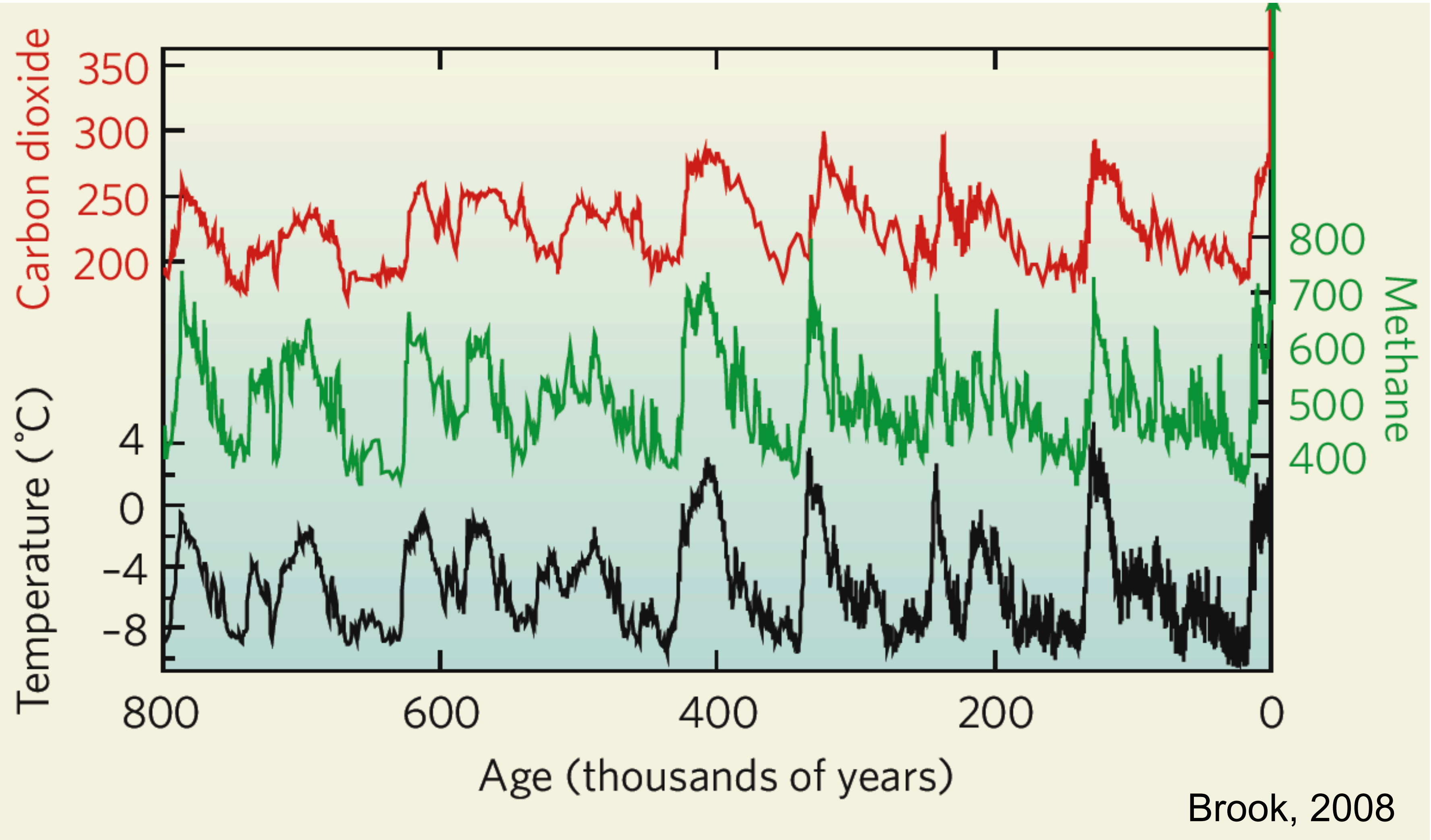
Ocean Carbon and Biogeochemistry
26 July 2016

Ice core records reveal tight coupling between CO_2 and climate



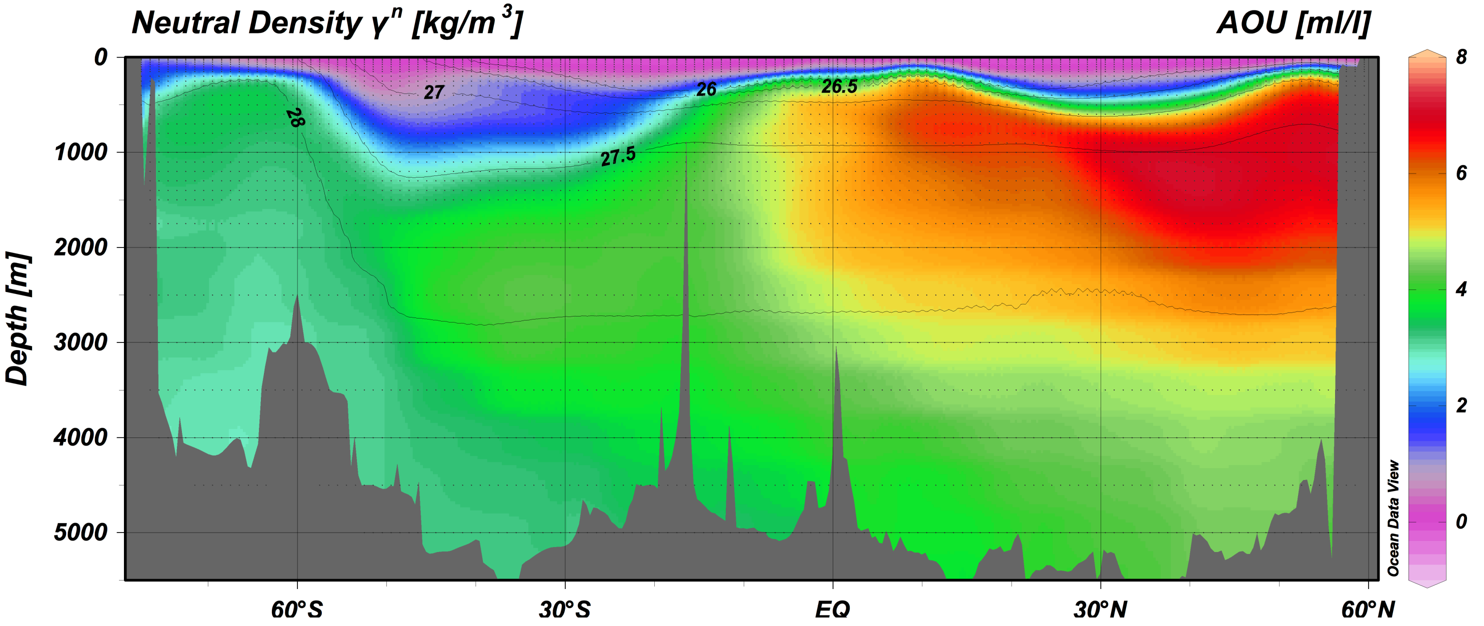
Brook, 2008

Carbon must have been transferred to the deep ocean during the ice ages

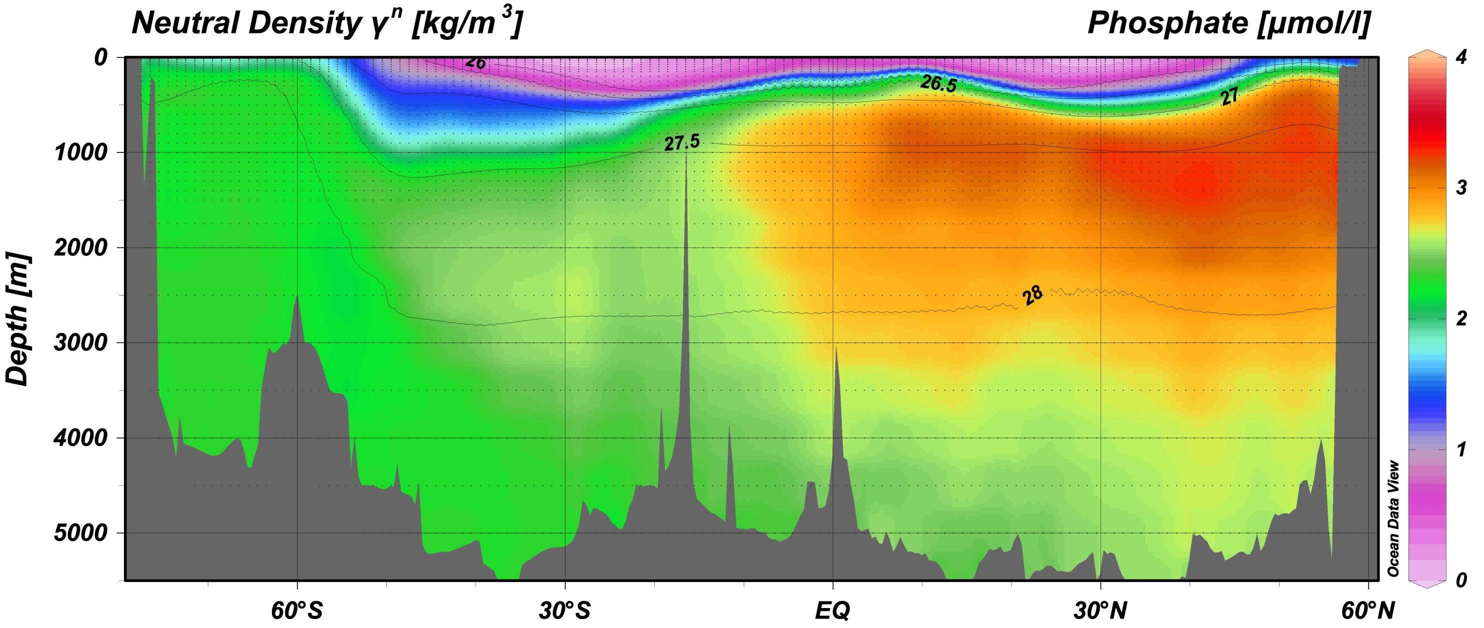
The deep ocean is:

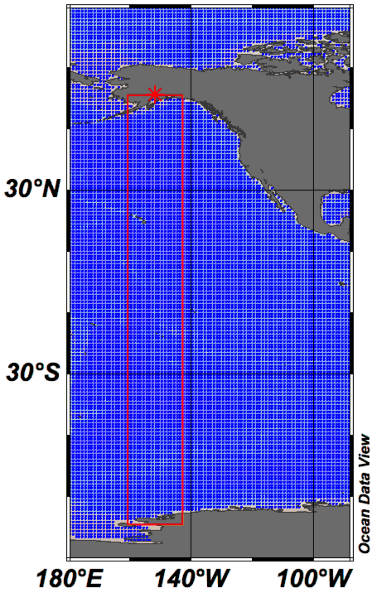
1) The only C reservoir large enough to accommodate 200 GtC from the atmosphere during each peak ice age...
2) ...and a much larger inventory of carbon released from the terrestrial biosphere.
3) The only large C reservoir capable of exchanging carbon with the atmosphere as rapidly as indicated by the ice cores.

Pacific Ocean - 150°W

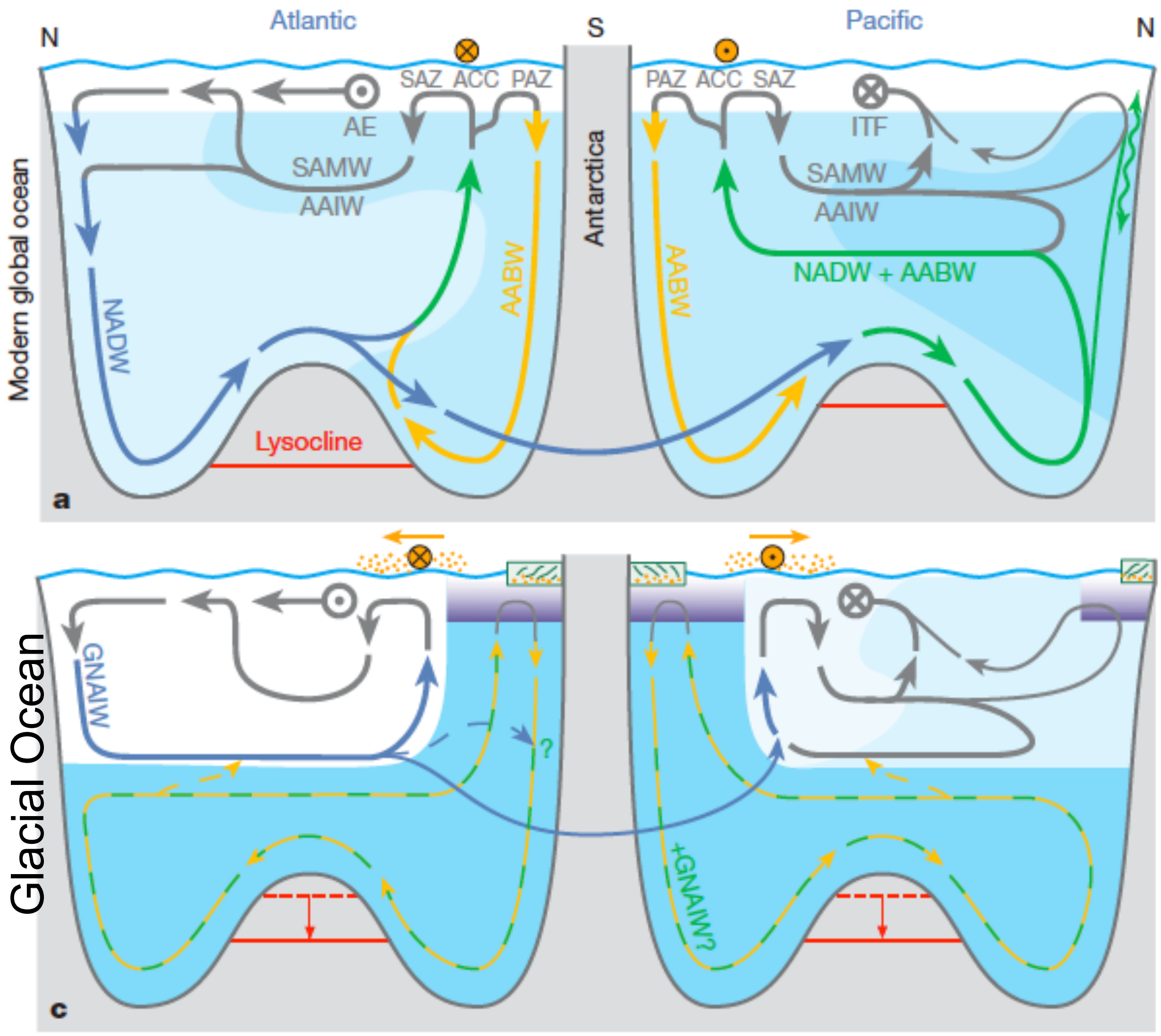


Modern ocean reference: Maximum nutrients (CO_2 storage) at intermediate depths.





Possible LGM "Nutrient-deepening" scenario: Deep ocean filled with CO_2-rich O_2-poor water



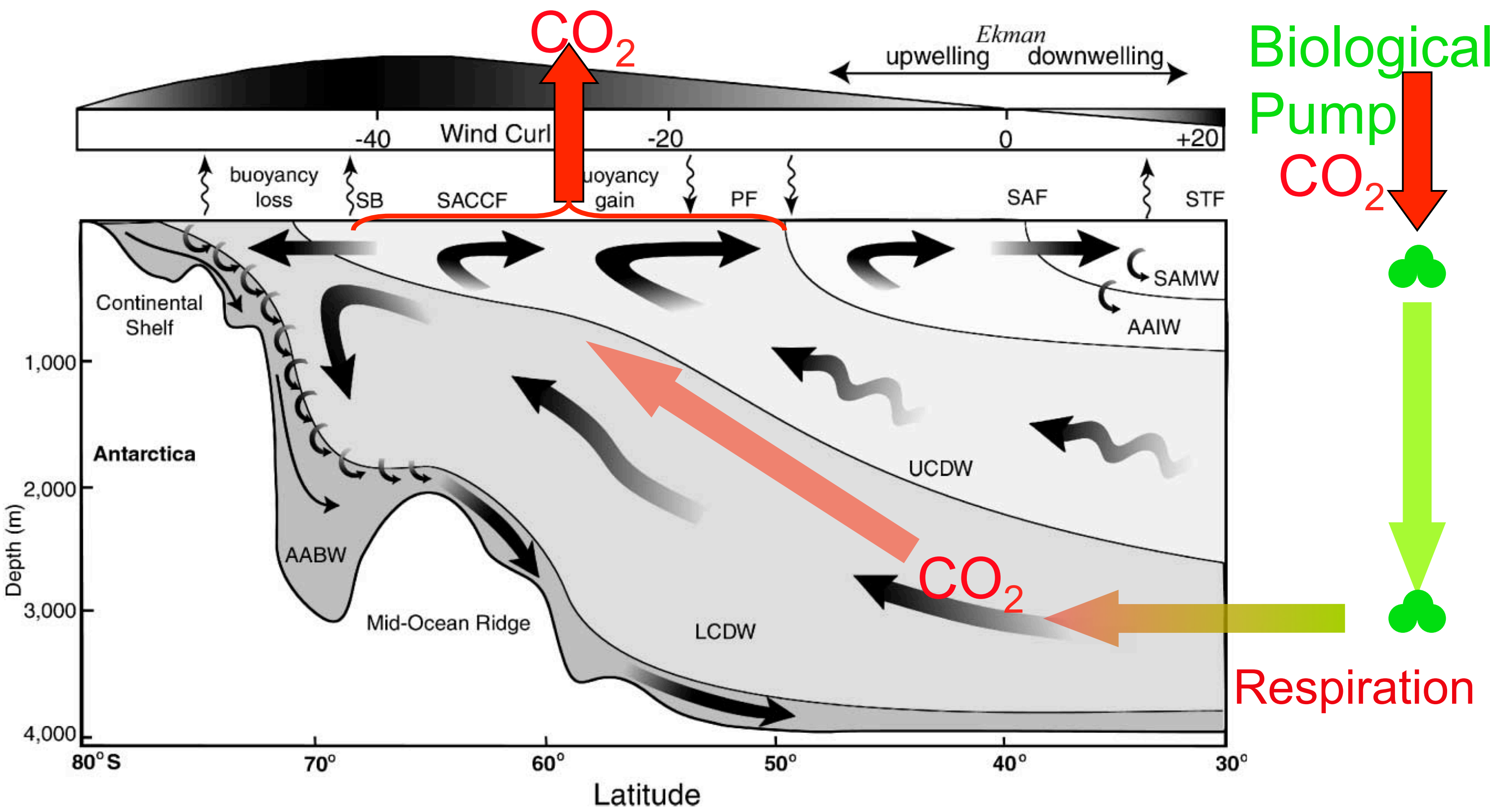
Modern Pacific intermediate water

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

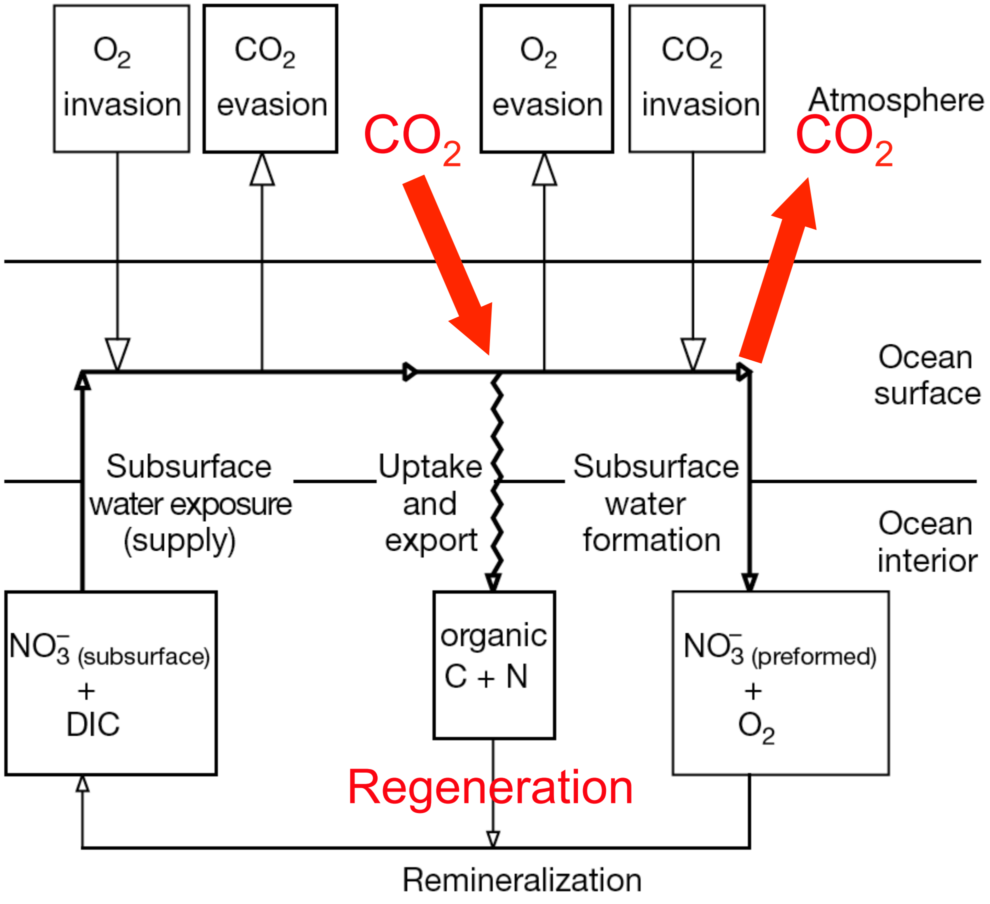
Increased "Capacity" = Ocean nutrient inventory

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.

“<u>Efficiency</u>” = Fraction of upwelled nutrients consumed biologically and exported to depth as organic matter



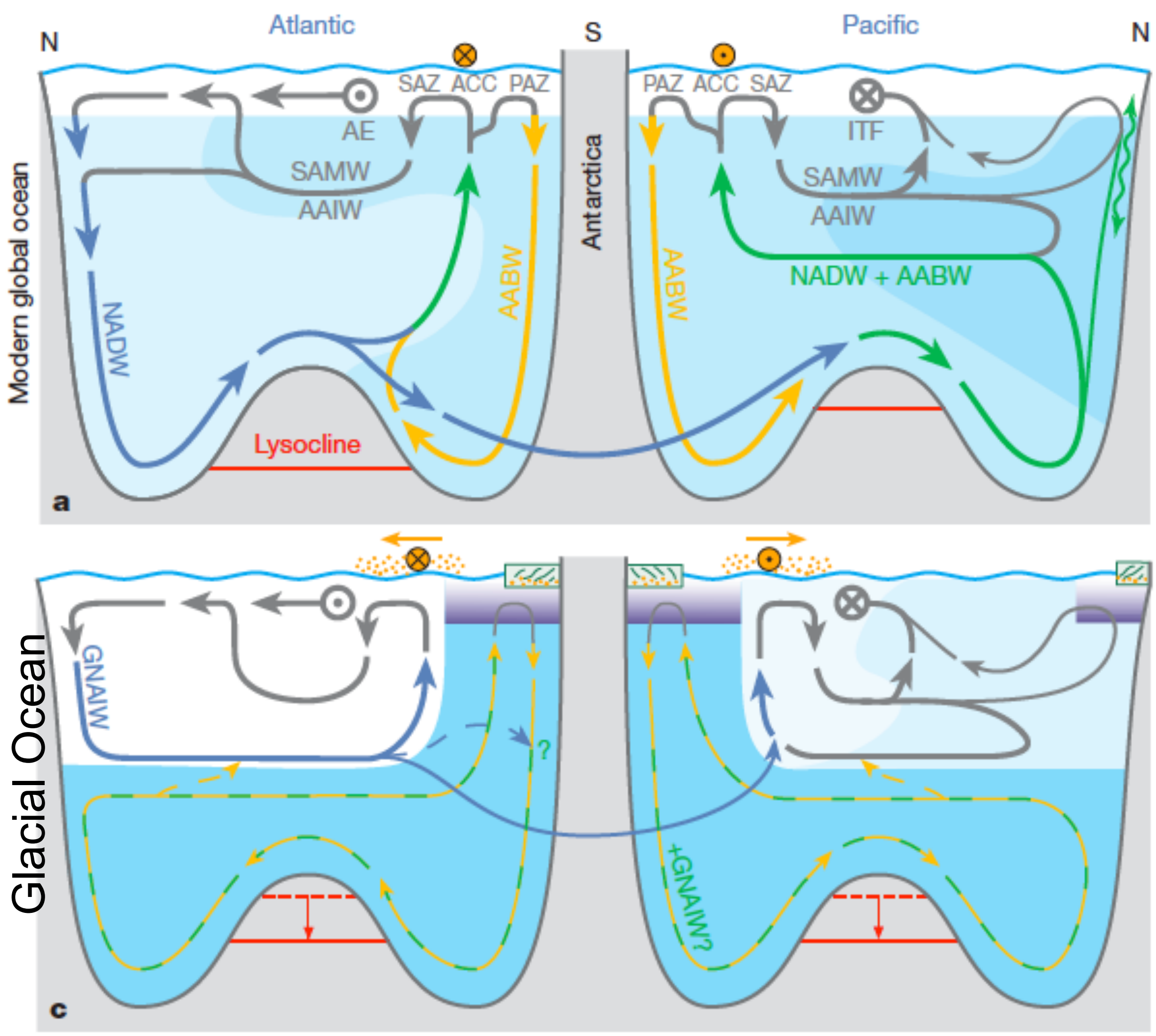
$$\text{Nutrient utilization} \equiv \frac{\text{Uptake}}{\text{Supply}} = 1 - \frac{[NO_3^-]_{\text{preformed}}}{[NO_3^-]_{\text{subsurface}}} \propto \frac{CO_2\ \text{invasion}}{CO_2\ \text{evasion}}$$

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

Preformed nutrients are a **<u>lost opportunity</u>** to “pump” carbon into the deep sea.

Sigman and Boyle, Nature, 2000

LGM "Nutrient-deepening" scenario: Involves Δ circulation & Δ 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:

"Any 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.

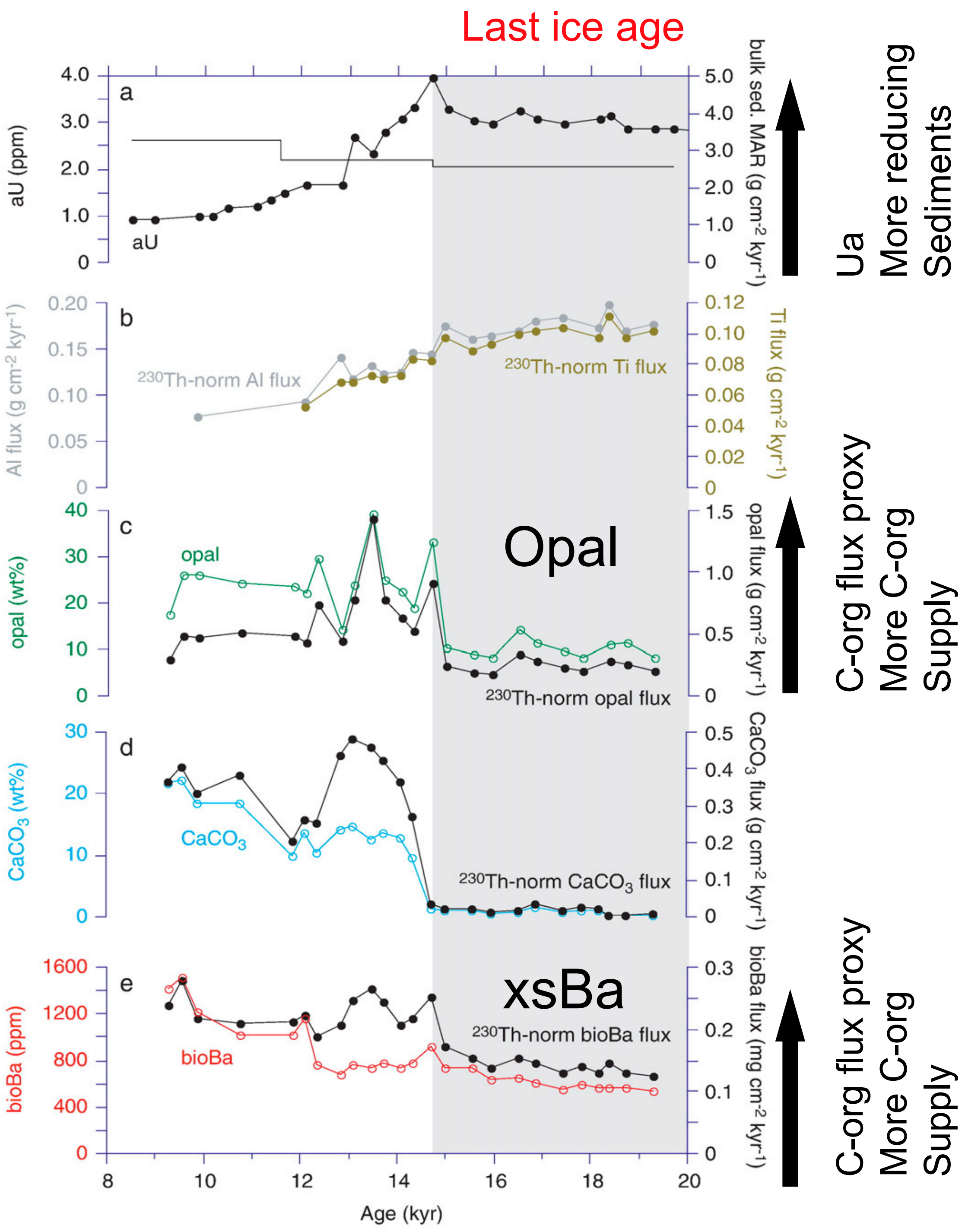
How do we assess changes in $[O_2]$?

There is no direct geochemical “proxy”. Therefore:

ΔO_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

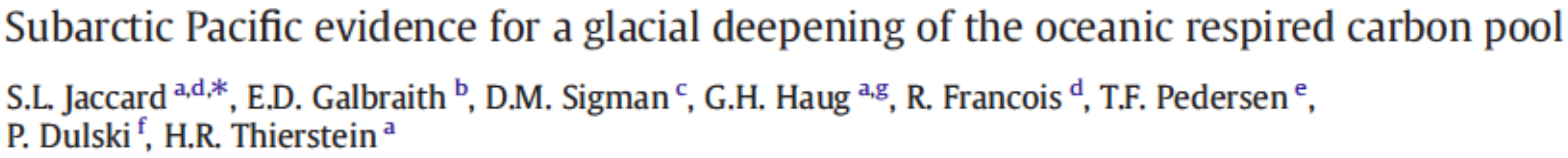
Subarctic N Pacific:

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

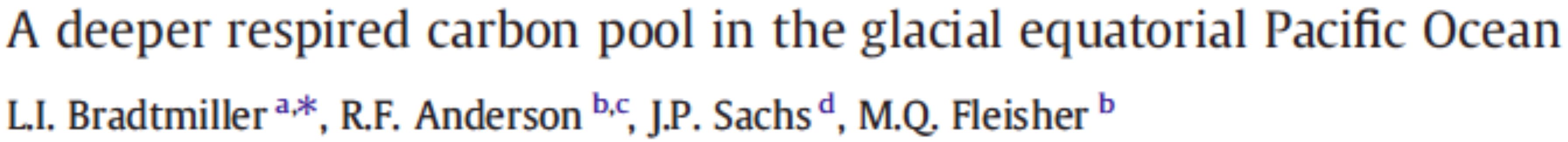
Earth and Planetary Science Letters 277 (2009) 156–165



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]

Earth and Planetary Science Letters 299 (2010) 417–425



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

Nature Geoscience 8 (2015) 40-43 North Atlantic

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

Babette A. A. Hoogakker[1*], Henry Elderfield[2], Gerhard Schmiedl[3], I. Nick McCave[2] and Rosalind E. M. Rickaby[1]

Nature Communications 7 (2016) doi 10.1038/ncomms11539 South Atlantic

Biological and physical controls in the Southern Ocean on past millennial-scale atmospheric CO_2 changes

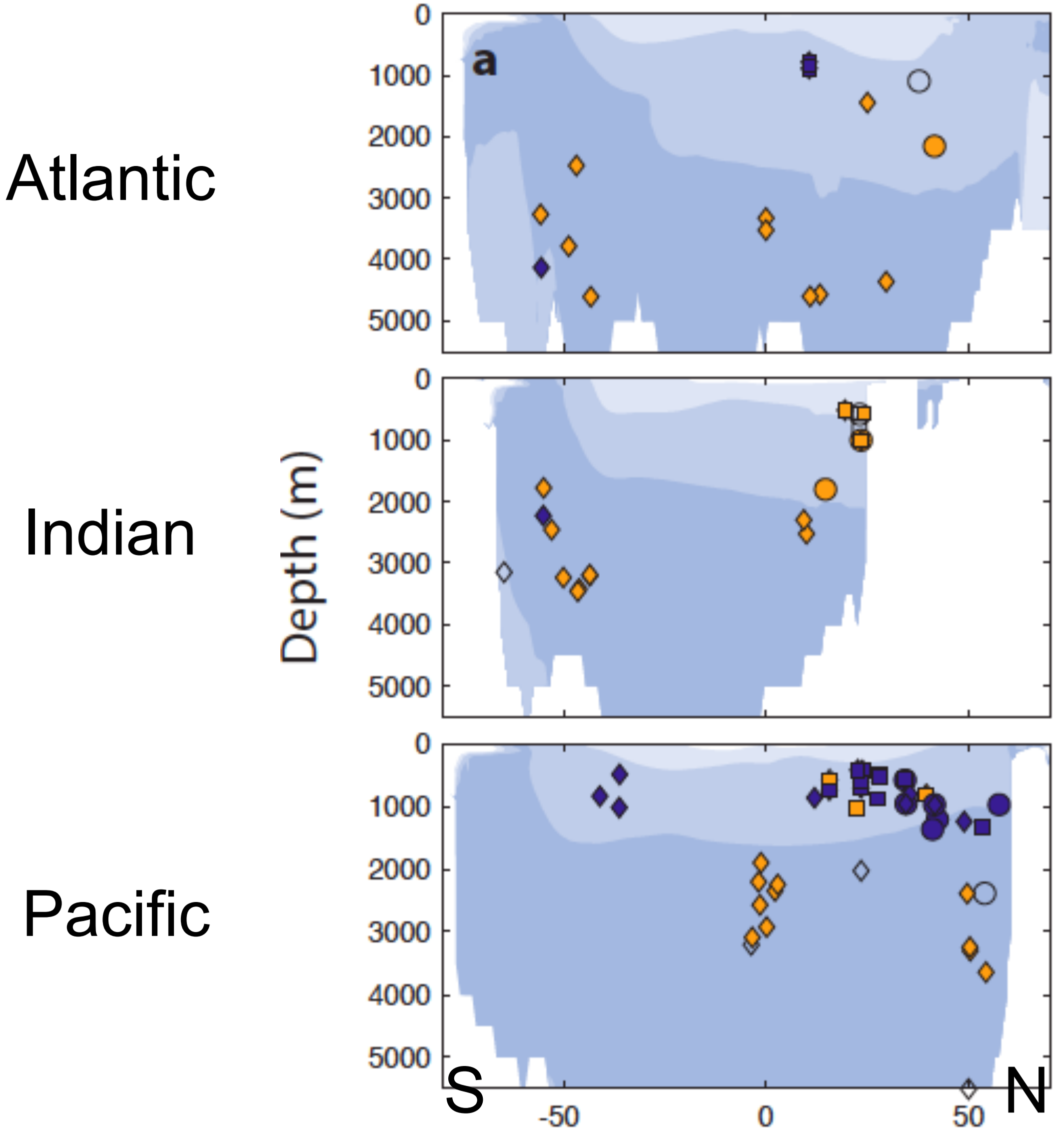
Julia Gottschalk[1], Luke C. Skinner[1], Jörg Lippold[2], Hendrik Vogel[2], Norbert Frank[3], Samuel L. Jaccard[2] & Claire Waelbroeck[4]

Nature 530 (2016) 151–155 Southern Ocean

Covariation of deep Southern Ocean oxygenation and atmospheric CO_2 through the last ice age

Samuel L. Jaccard[1,2], Eric D. Galbraith[3,4,5], Alfredo Martínez-García[6,7] & Robert F. Anderson[8]

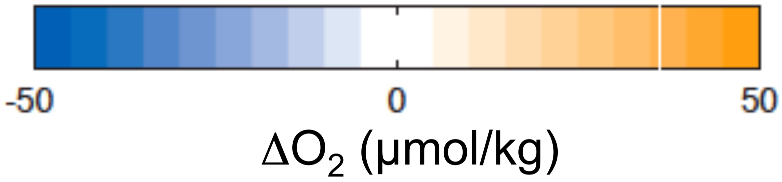
Most of the interior ocean had lower O_2 during the LGM



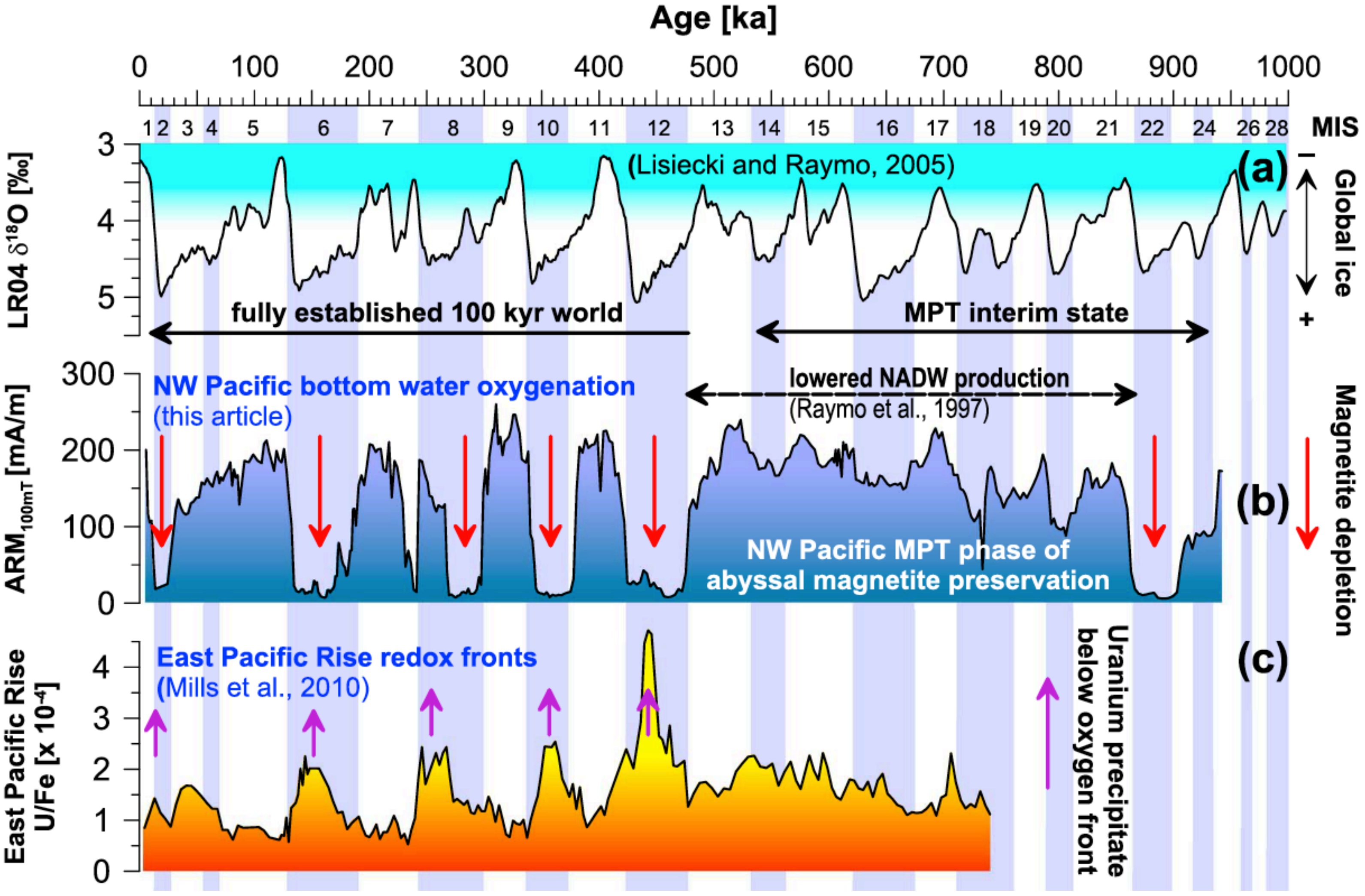
Holocene minus LGM
Global database of ΔO_2

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

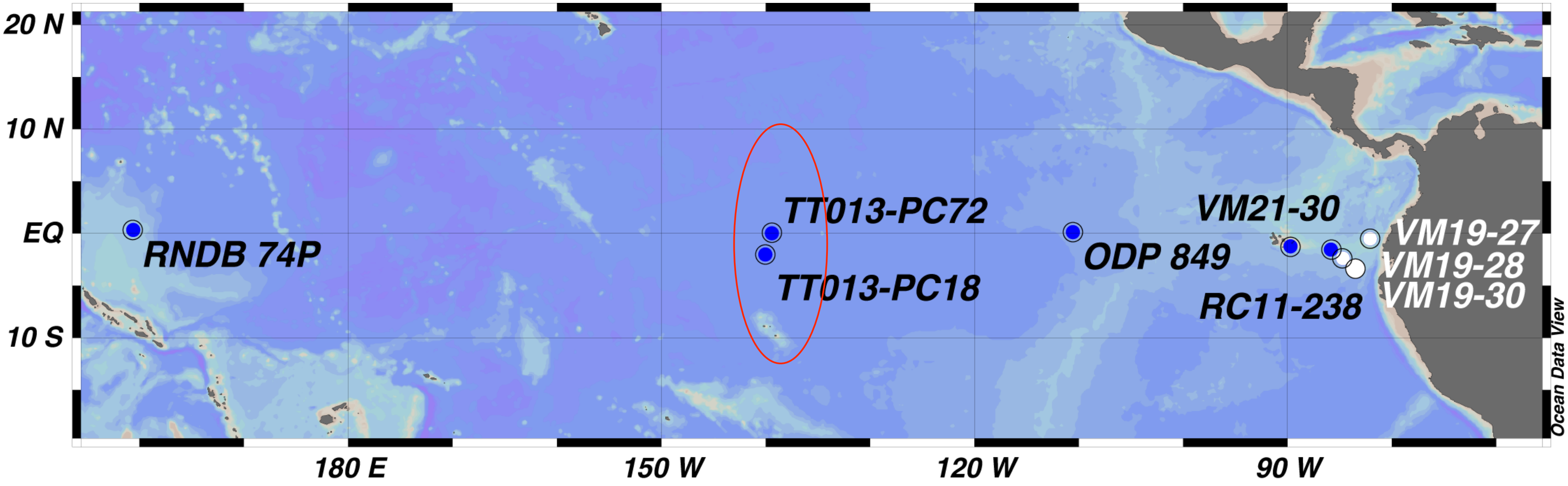


Korff et al., 2016, Paleoceanography

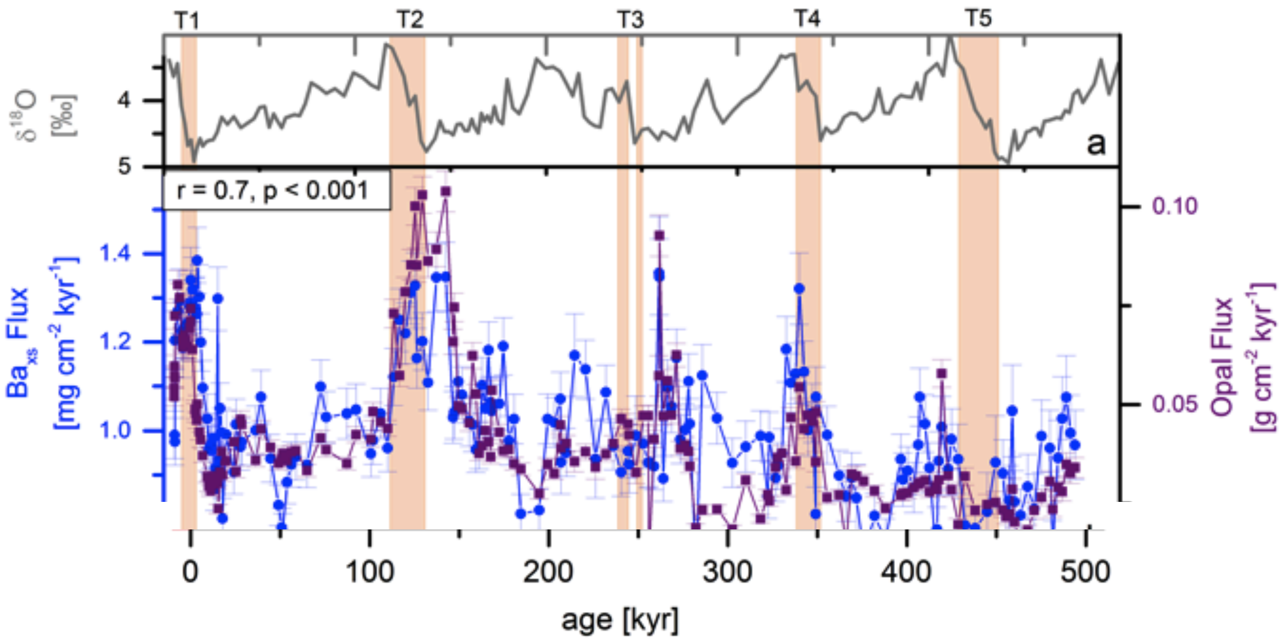
Current status

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



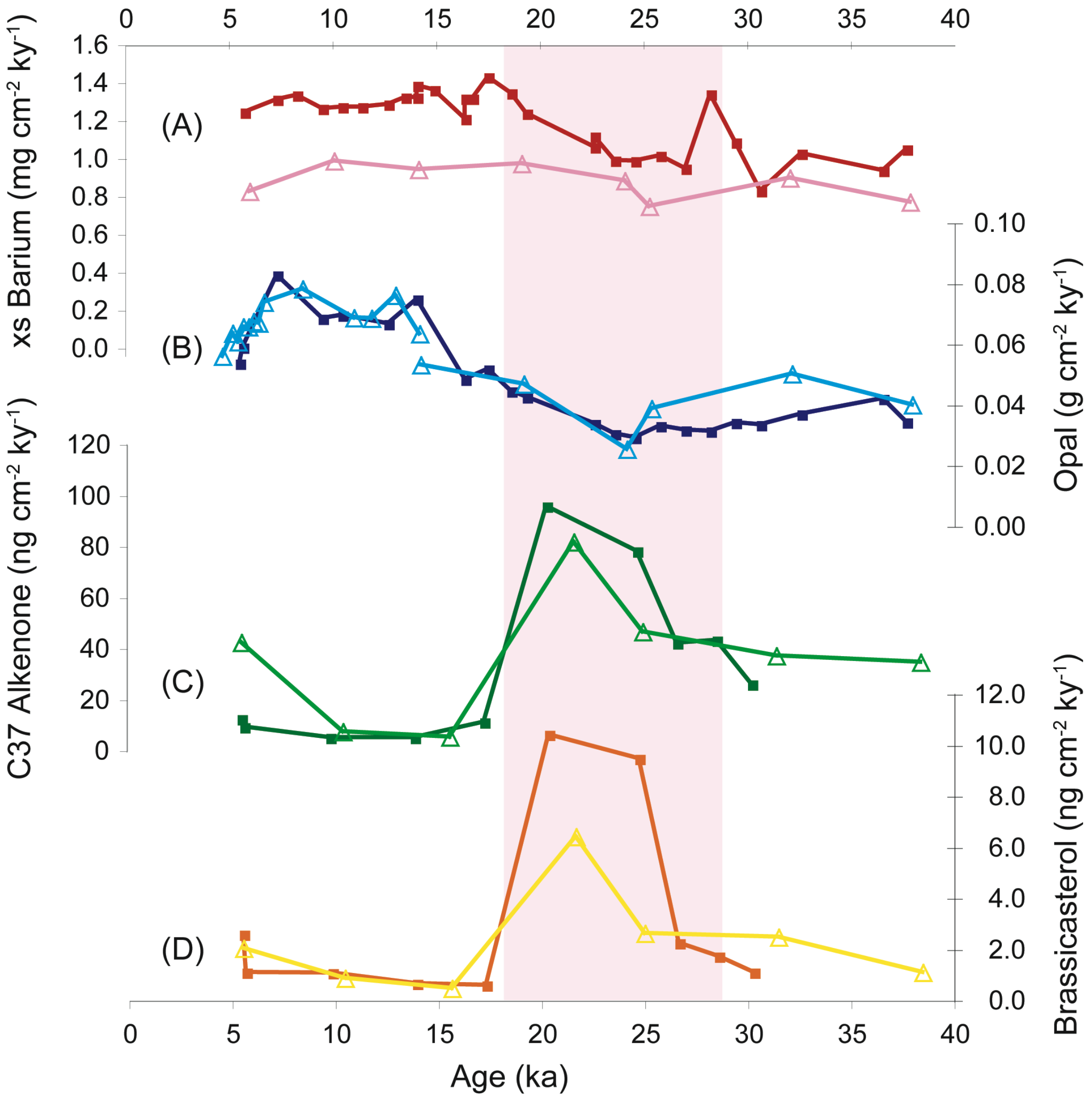
TT013-PC72:
0.1°N, 140°W

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



Darker color is PC72, lighter color is PC18

Glacial organic biomarker fluxes during LGM >> Holocene.

Inconsistent with inorganic PP proxies.

Infer enhanced LGM organic preservation due to low O_2.

Calibrating organic preservation sensitivity to O_2: Use the Arabian Sea as a natural laboratory

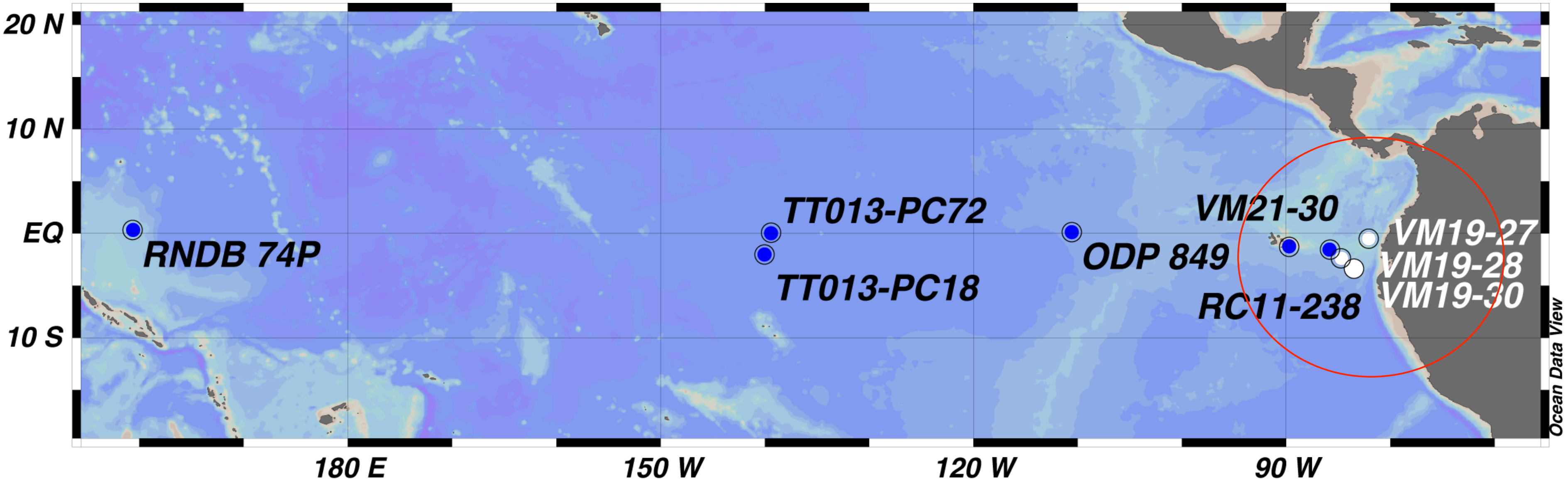
Organic carbon preservation increases rapidly for
BWO < 35μmol/kg
(Keil and Cowie, 1999)

Assume 35 μmol/kg as a conservative limit.

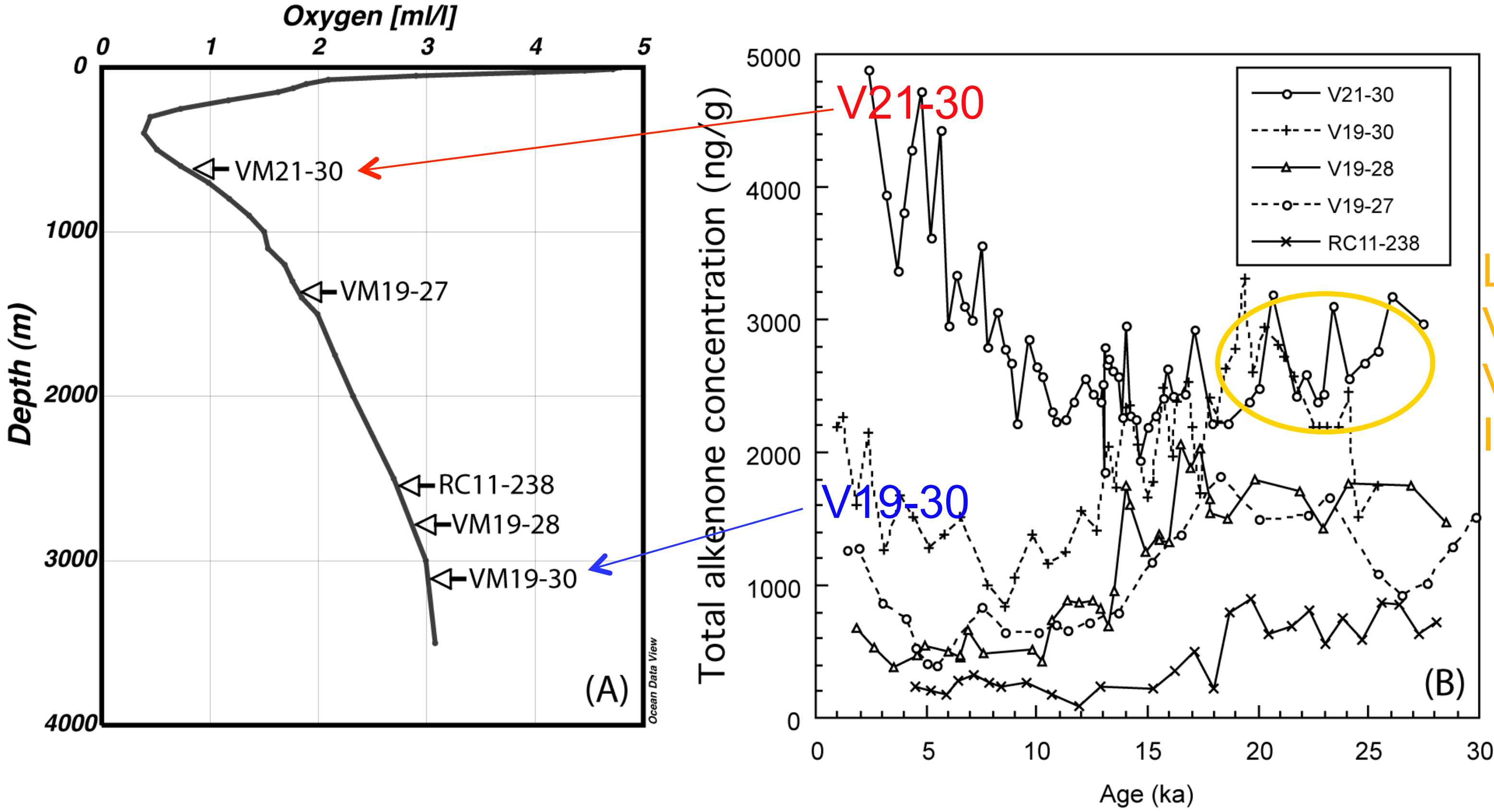
Modern bottom water [O_2] at core sites: 168 μmol/kg

Equatorial Pacific:
LGM bottom water [O_2] was ~133 μmol/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

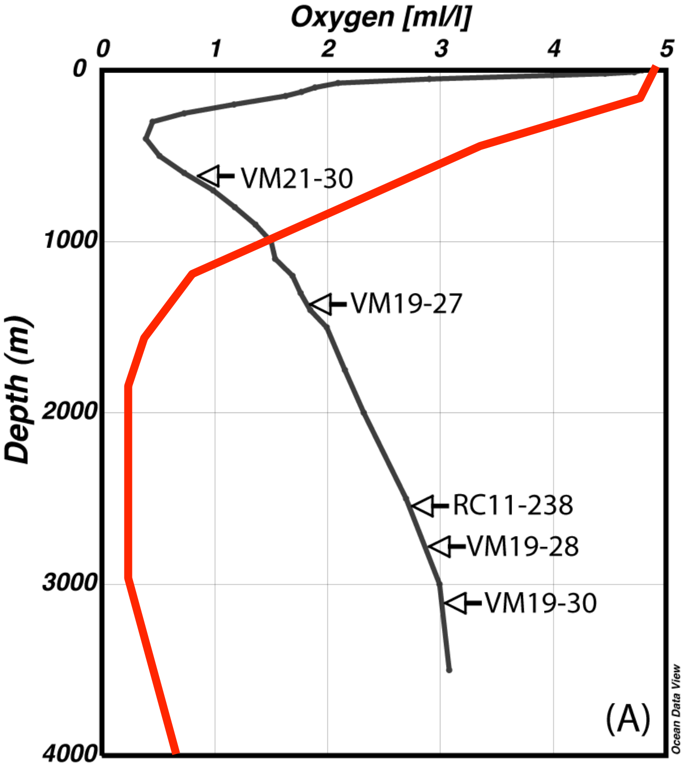


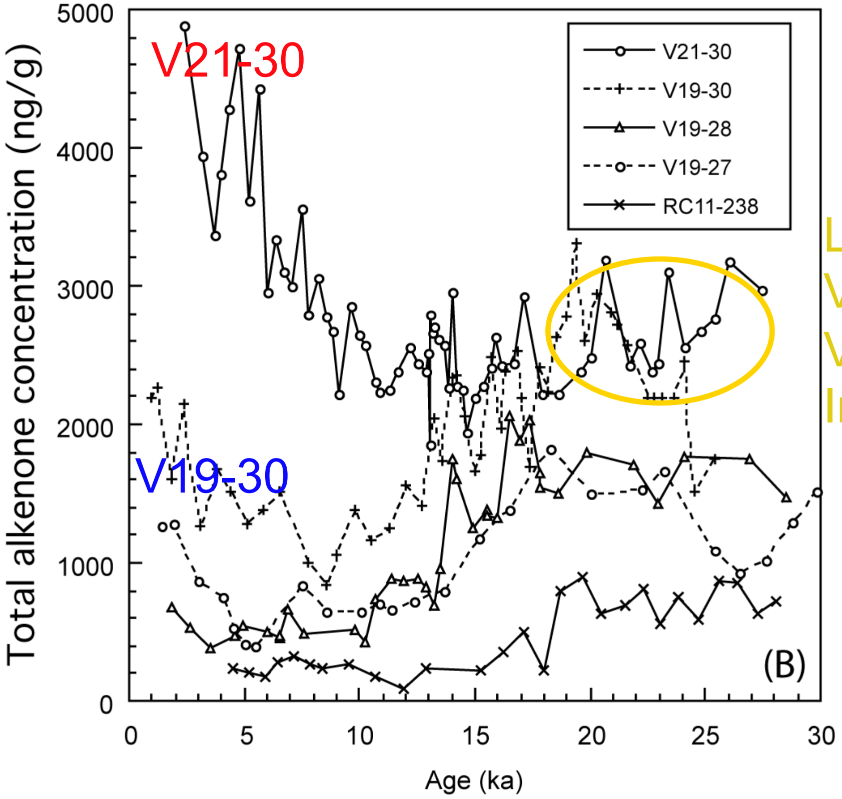
LGM
V19-30 +
V21-30 O
Indistinguishable

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





LGM
V19-30 +
V21-30 O
Indistinguishable

Pattern of alkenone concentation 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

	3%	2°C				
	Salinity	Temp (°C)	PotTemp (°C)	O2 (μmol/kg)	O2 Solubility (μmol/kg)	AOU (μmol/kg)
Modern	34.694	1.41	1.0616	168	351	183
LGM	35.73482	-0.59	-0.9384	35	371	336

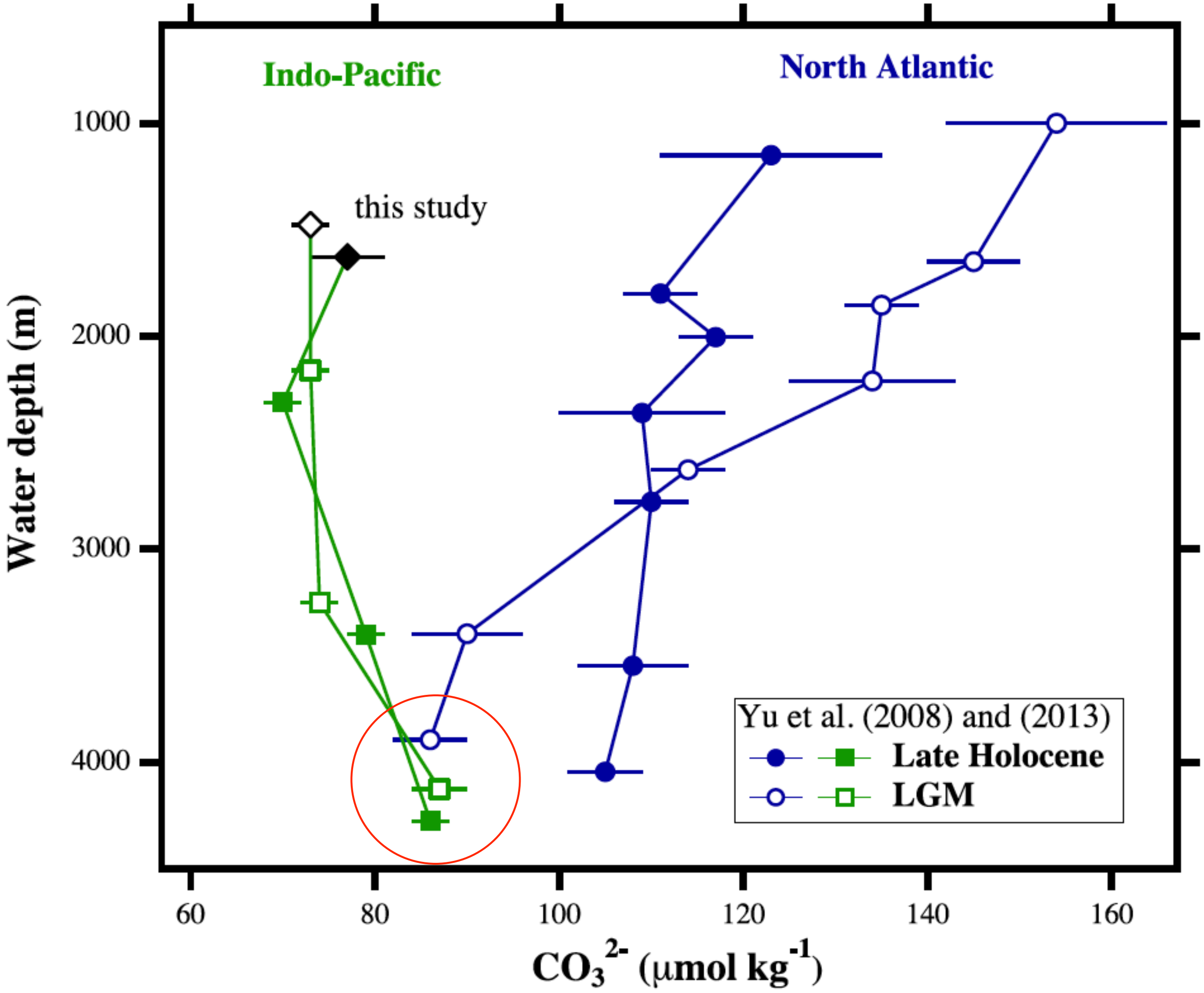
Assume deep water formed at O_2 saturation with atm.

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 $[CO_3^{2-}]$ 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

Graph Points			TCO2	TALK	CO3	
1		Modern 4.2 km 0°, 140	2320	2425	79	**Initial conditions**
2		Modern + ice volume	2385.72327	2497.75	82.8	
		Mod+ice+DeltaRespCO	2494.09551	2497.75	39.3	
3		Plus resp HNO3	2494.09551	2481.39193	34.4	
	100	.+CaCO3 dissolution	2594.09551	2681.39193	74.7	Iterate to initial [CO3]
	110		2604.09551	2701.39193	79.8	Ignore cells shaded grey
4	109		2603.09551	2699.39193	79.3	**Final Conditions**

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

Accumulating respiratory CO_2 lowers $[CO_3^{2-}]$

$CaCO_3$ dissolution required to restore initial $[CO_3^{2-}]$

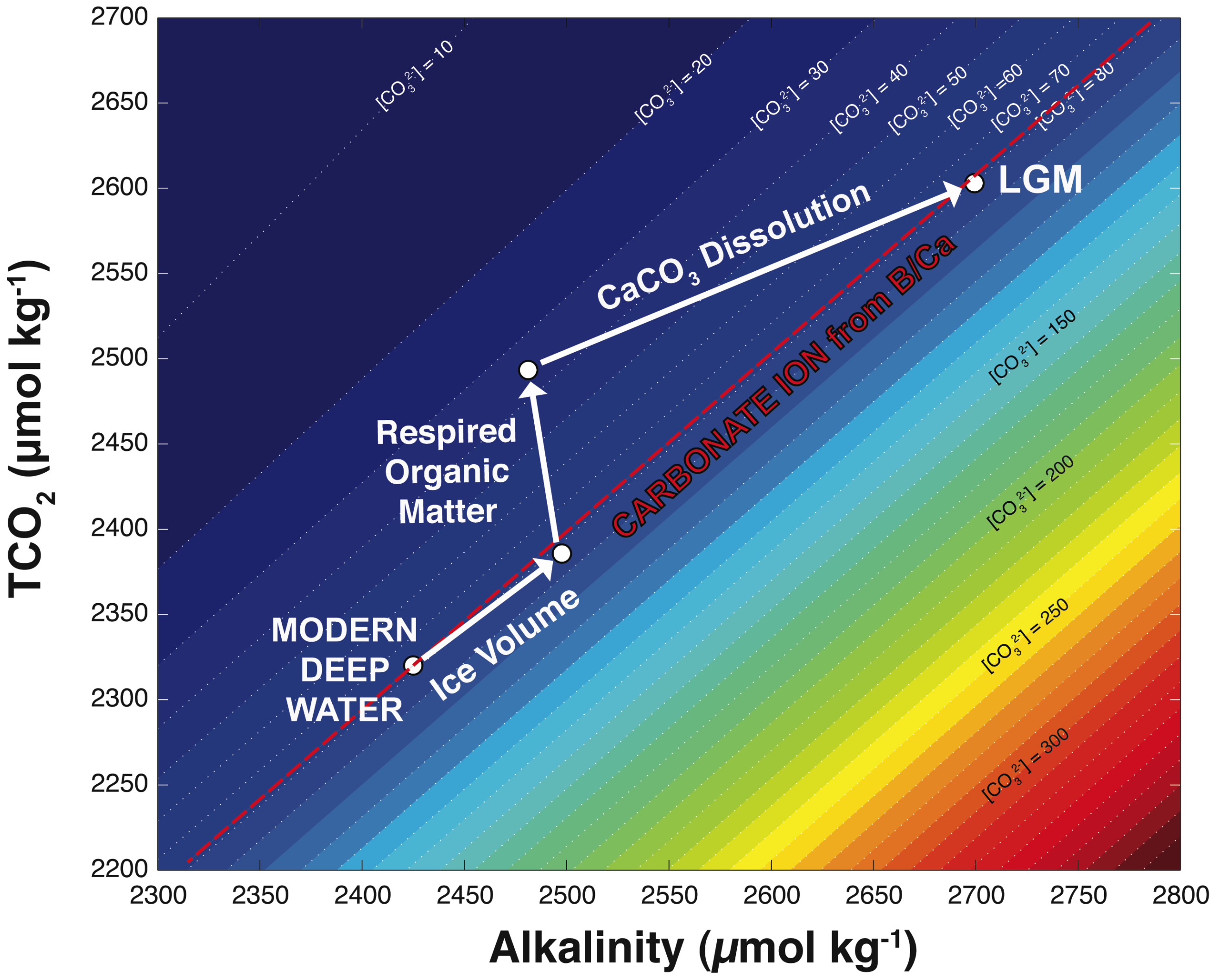
DIC increased 217 μmol/kg: Significant contributions from respiratory CO_2 (108 μmol/kg), ice volume and $CaCO_3$ dissolution.

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_2 than today

This amounts to **846 Gt Carbon stored in the deep sea**

Close to the value needed to balance:

CO_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 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.
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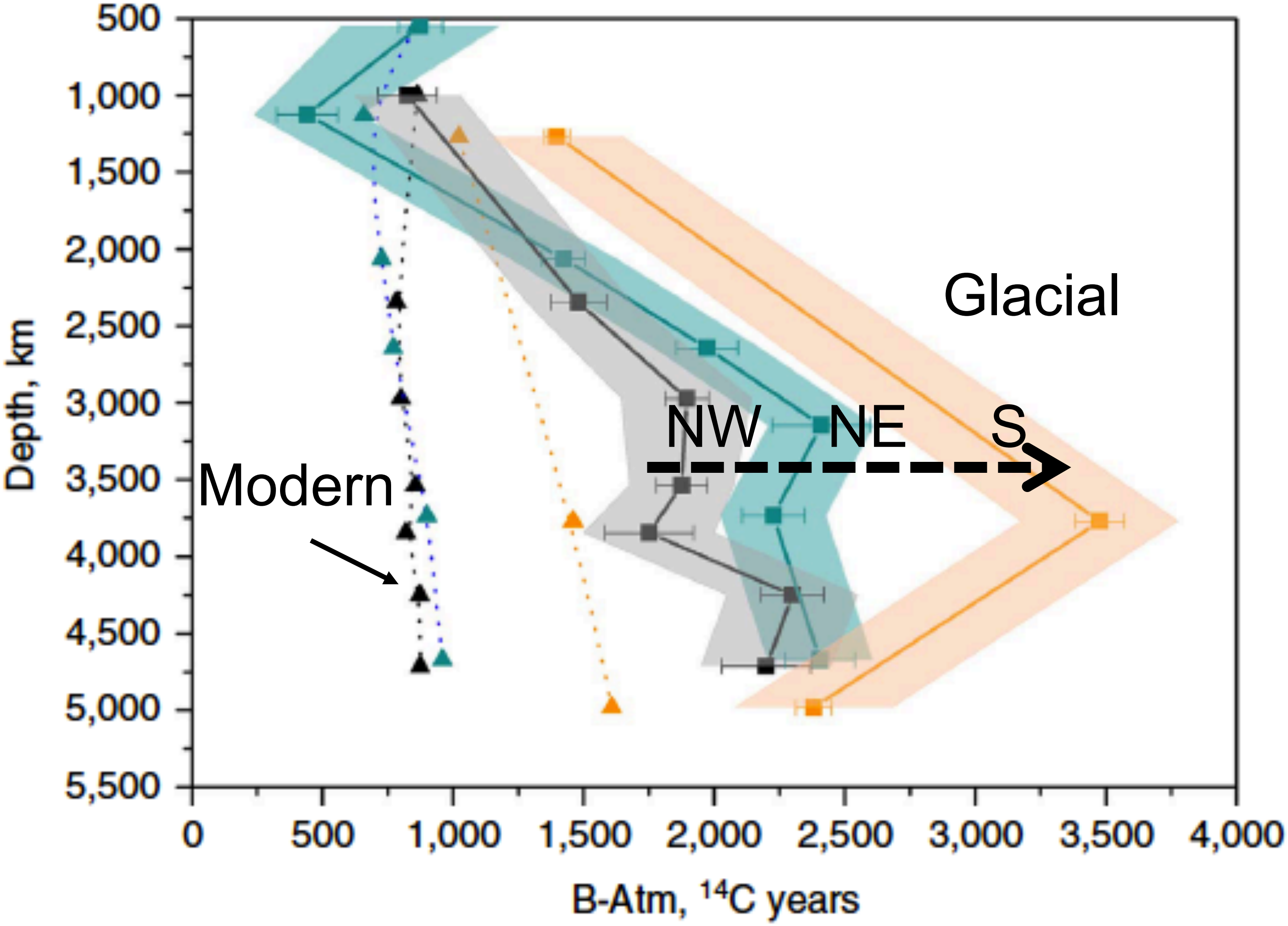
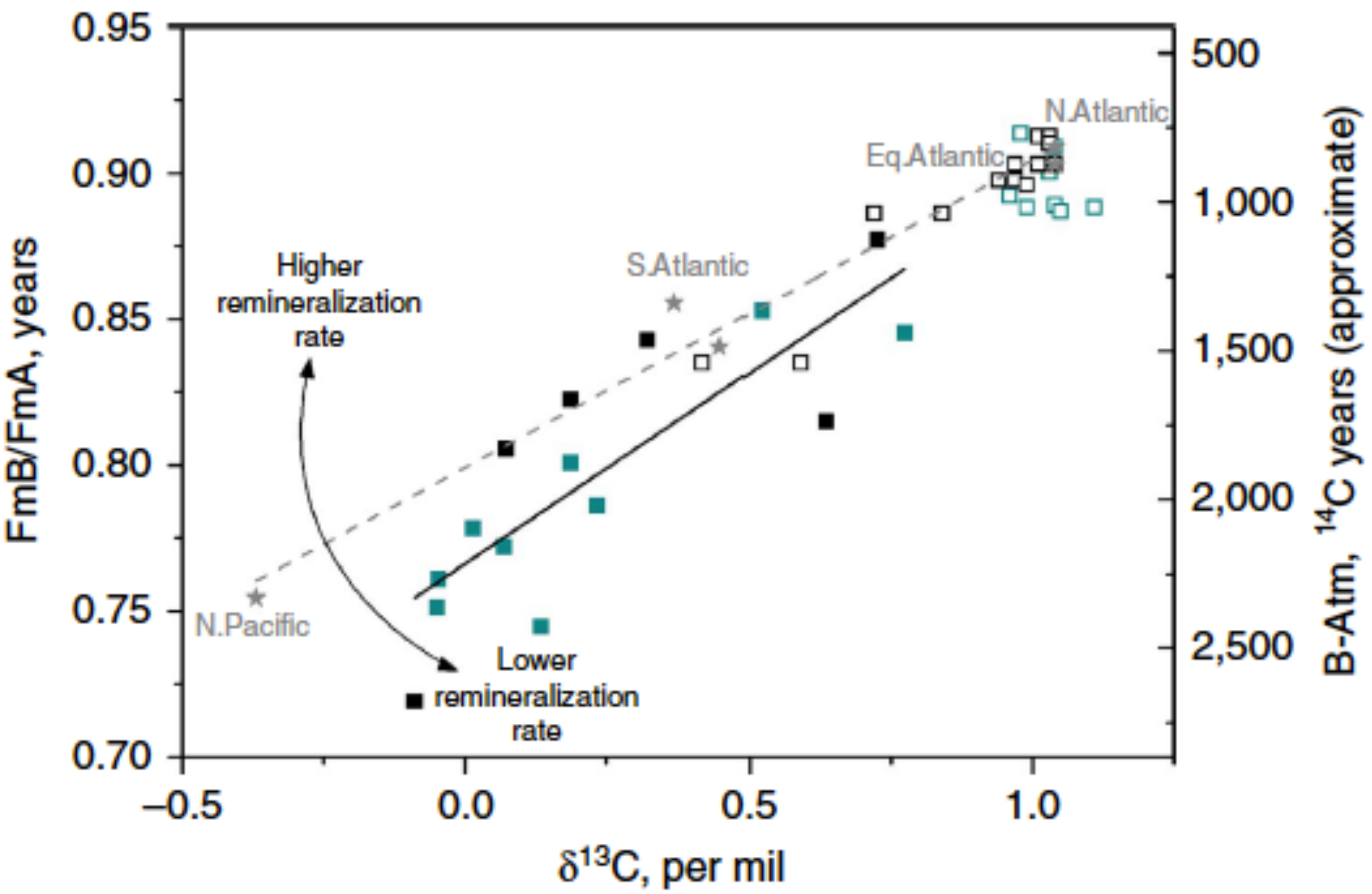
4) Unknown - How much extra CO_2 was stored?
5) Unknown - What physical and biogeochemical factors contributed?

Atlantic radiocarbon age depth profiles indicate slower LGM deep water ventilation



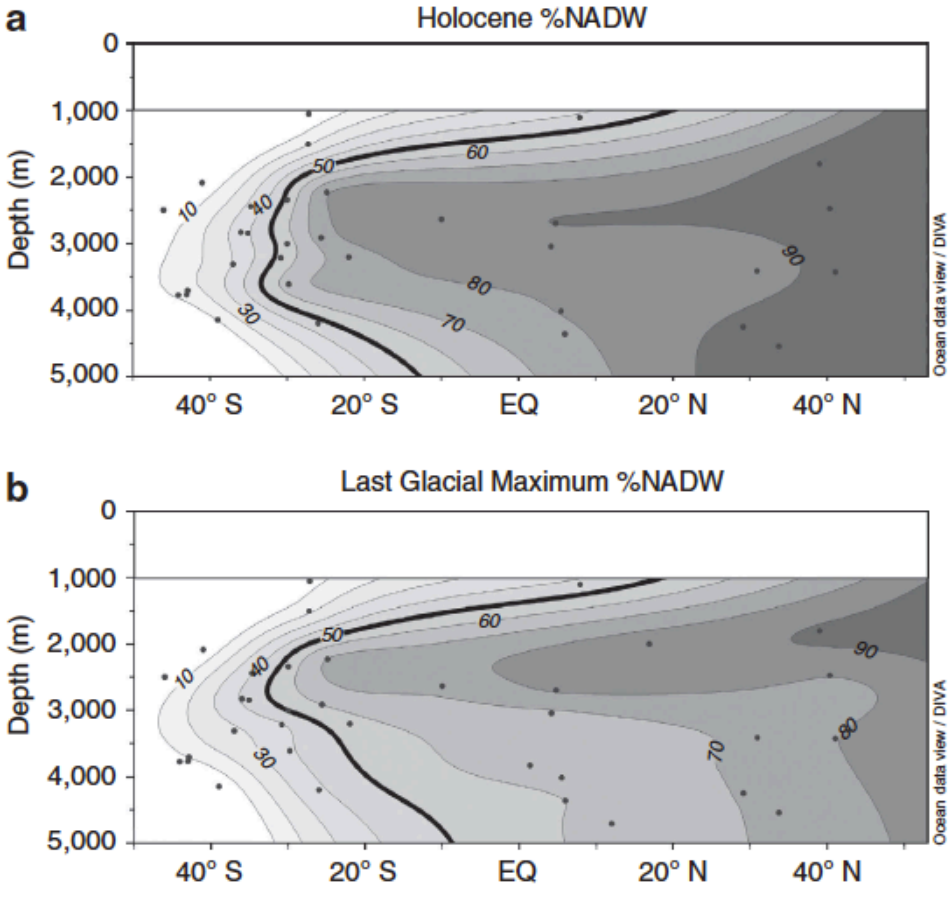
Freeman et al., NatComm, 2016 DOI: 10.1038/ncomms11998

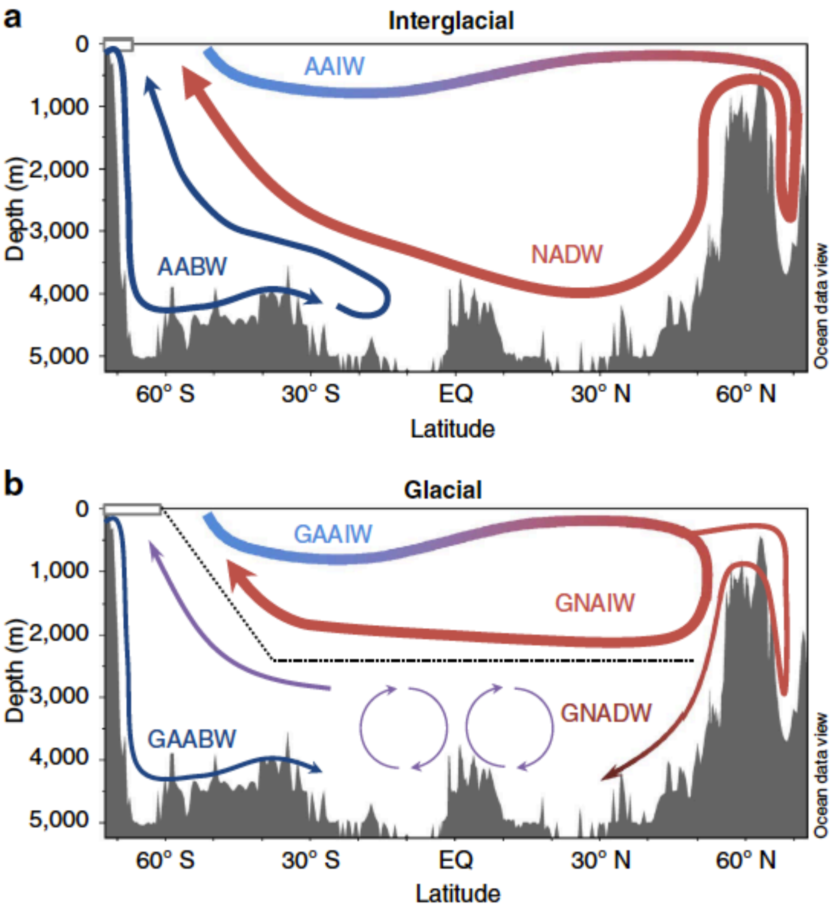
Rate of C-org regeneration unchanged: LGM to Holocene



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

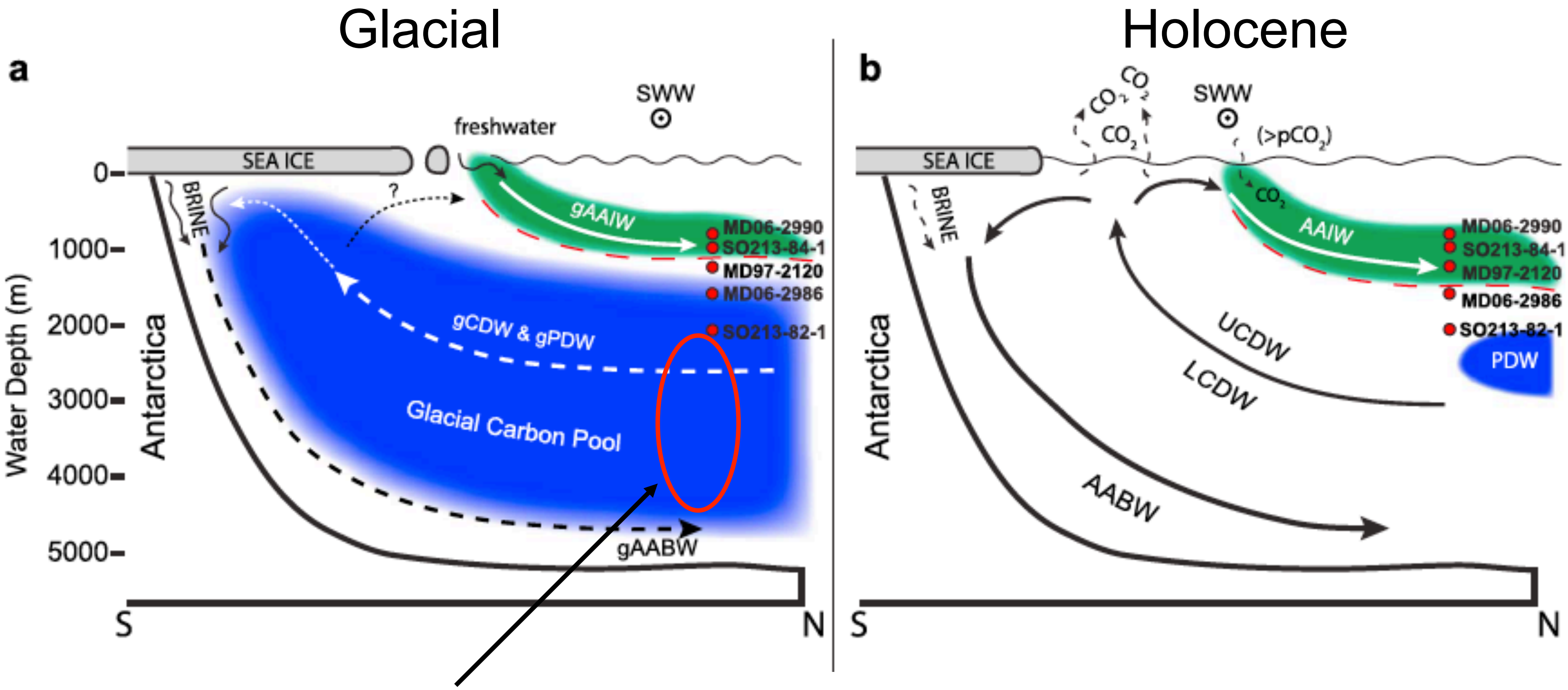
   (2) and (3) contributed to lower deep-ocean oxygen.

4) $CaCO_3$ compensation

All operated synergistically

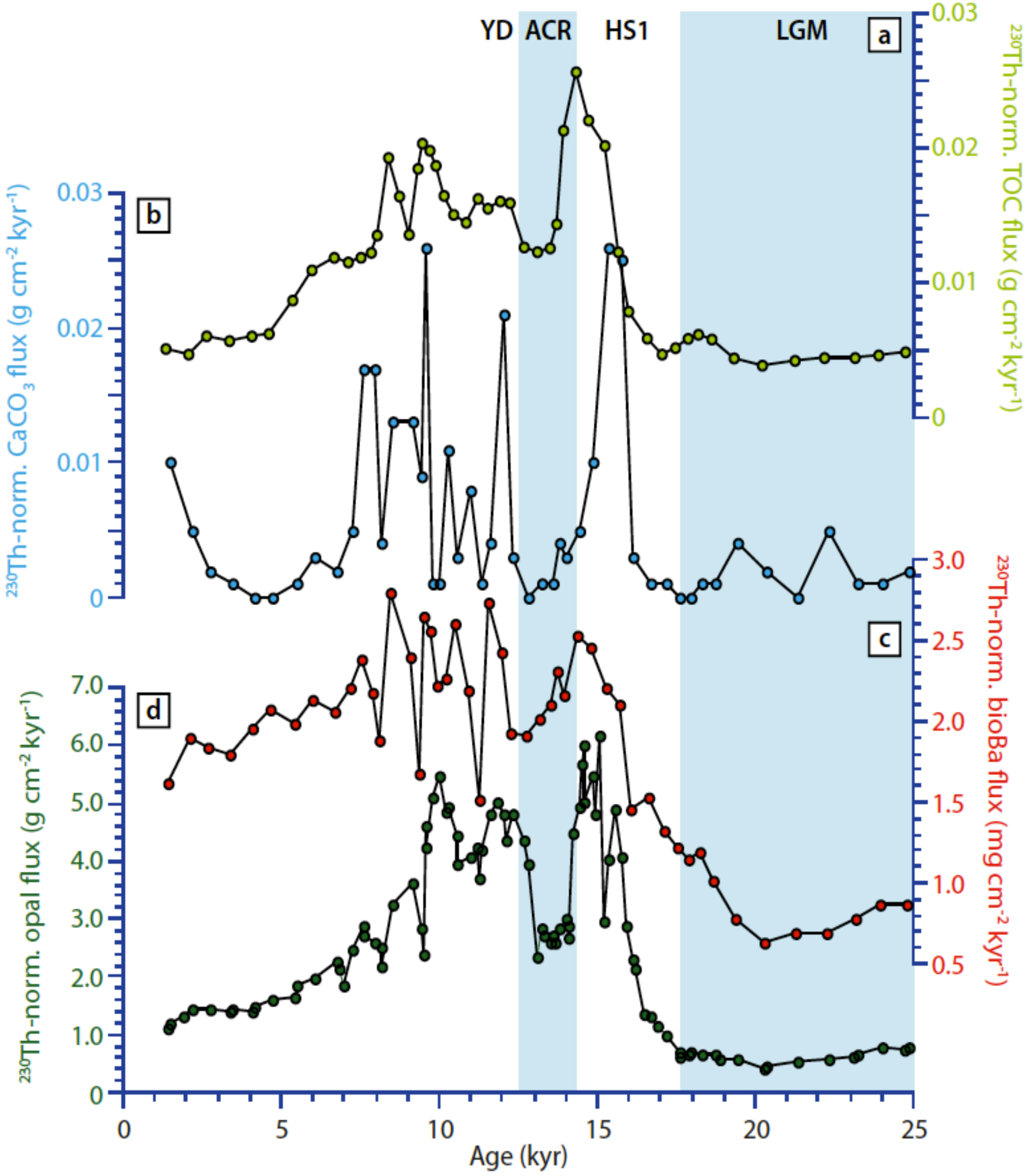
Extra slides

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

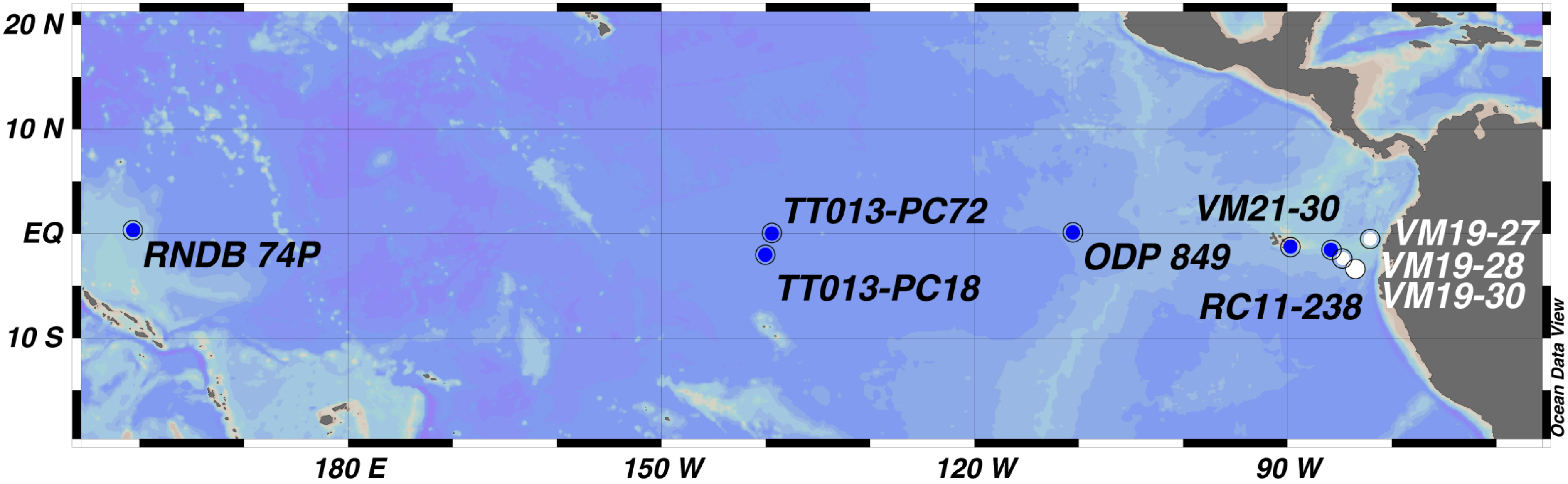


So Ocean: Opal, TOC and xsBa flux increase from LGM to Holocene

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.

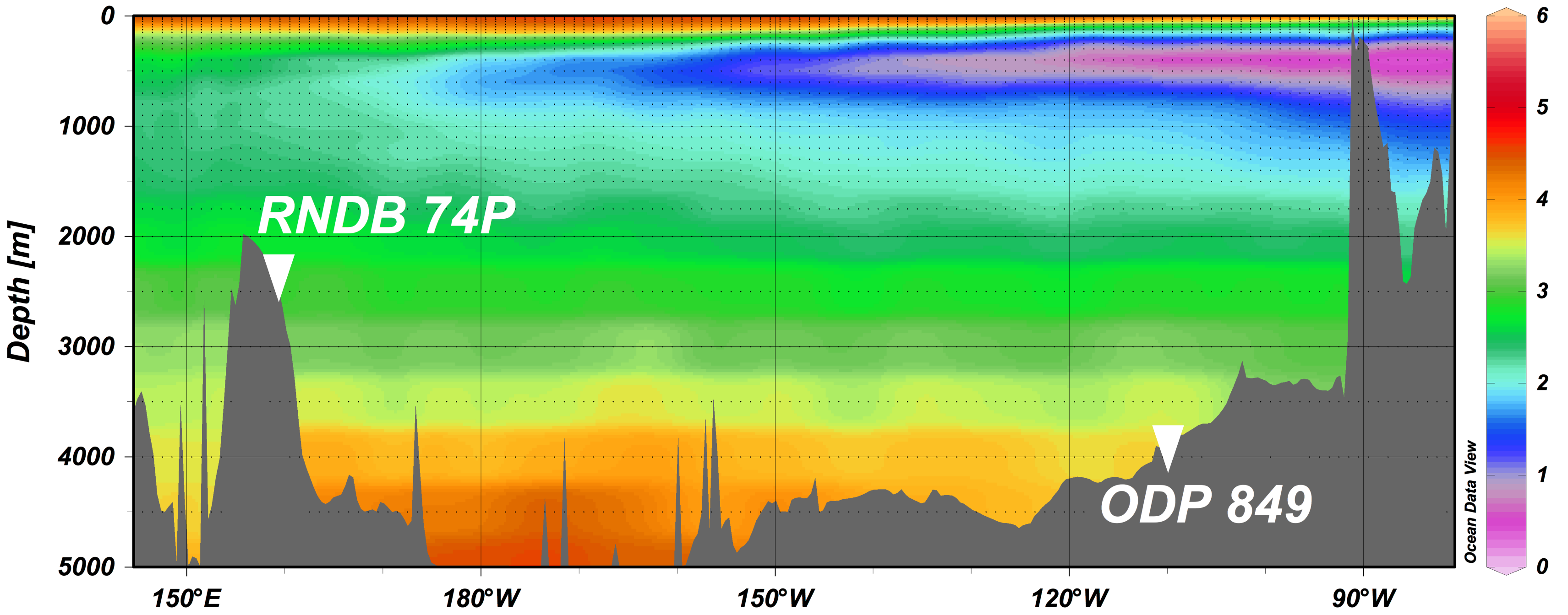
Sediment combustion oxygen demand (Perks & Keeling) explained.

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

Paleoceanograhy, 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).