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SUPPLEMENTARY INFORMATION

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Supplementary Online Material for:

Southern Ocean source of ^{14}C-depleted carbon in the North Pacific during the last deglaciation

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Nd isotopes systematics:

Neodymium has a residence time in the ocean (~600-1200 yrs) [S1, S2] that is shorter than the mixing time of the global conveyer (~1500 yrs) [S3] and it is sourced primarily from the continents [S4, S5, S1, S6, S7]. As a result different ocean basins have different ε_{Nd} values. For example, North Atlantic Deep Water (NADW) has a value close to -13.5 [S8, S9] which reflects weathering of Precambrian shield material, while Pacific Deep Water has a value between -4 to -6 [S10], reflecting deep sea mixing and weathering of young volcanic ash. Major water masses carry their initial Nd isotopic signal as they circulate through the ocean; however, that signal can be altered along the route by weathering inputs and boundary exchange [S9], particularly in marginal marine settings. As a result, Nd isotopes are often referred to as "quasi-conservative" tracers of water masses. Owing to the large differences in ε_{Nd} values between the major water masses in the world oceans, minor modifications of end-member values generally do not erase the differences that distinguish water masses.

Modification and pathways of Antarctic Intermediate Water (AAIW)

Under modern hydrographic conditions AAIW is a low salinity, high oxygen intermediate water mass. This intermediate water occupies depths of 500 to 1000 meters below sea level (mbsl) and over 50% of global AAIW is located in the Pacific Ocean [S11]. In general, northern flow of AAIW in the southern Pacific occurs along the eastern margin of the basin [S12] with return flow southward along the western boundary. Near the

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Coral Sea some of the water from this gyre is deflected equatorward and passes through the Papua New Guinea (PNG) region before turning east near the equator and ultimately feeding into the Equatorial Intermediate water (EqIW; see fig. 1 in S11).

At its source region in the Southern Ocean modern AAIW ε_{Nd} values range between -6 to -8, representing a mixture of Atlantic and Pacific waters. Currently the intermediate water found along the equatorial Pacific is similar to AAIW with respect to its hydrological properties, while the Nd signature is strongly modified. The modified AAIW in the equatorial region has an average ε_{Nd} value of ~- 2.8 [S13]. This dramatic increase in the ε_{Nd} value of AAIW occurs through inputs from easily weathered volcanic rocks in the tropical Pacific [S13]. The young volcanic rocks of PNG have an ε_{Nd} value of ~+7, which is highly distinct from seawater values and thus small inputs alter AAIW ε_{Nd} values to ~ -2.8 [S13]. Our core site is located at 23°N within a shadow zone at the confluence of EqIW and NPIW. EqIW is a mixture of AAIW modified in the PNG region and upwelled PDW. There are no previously published water column or core top ε_{Nd} data for EqIW; however, limited data for PDW from the deep tropical waters indicate very little variation in ε_{Nd} since the LGM [S14]. Thus, variations in ε_{Nd} at the Baja site are expected to primarily reflect the interaction between NPIW and modified AAIW.

The Hydrography and ε_{Nd} of North Pacific Intermediate Water (NPIW)

NPIW is a mixture of waters from the Kuroshio Current, intermediate water ventilated in the Okhotsk Sea (OSIW) and intermediate water ventilated in the western North Pacific (WNP)[S15, S16, S17]. End-member ε_{Nd} values for these waters measured prior to ventilation and mixing are ~-5.6 for the Kuroshio Current, -3.6 for the Okhotsk Sea, and -0.1 for the WNP [S17, S10]. These three waters mix at depth to form NPIW. Varying percentages of these source waters along the flow path of NPIW account for the high spatial variability in ε_{Nd} values reported within the upper 1 km of the NW Pacific water column (-4 to 0) [S10, S17, S18, S19].

Previous studies suggest that during the LGM, NPIW (Glacial NPIW) was well ventilated [S20, S21] with probable contributions from the Bering Sea, Okhotsk Sea and/or Gulf of Alaska [S22] introducing additional radiogenic Nd. This is consistent with our observation that NPIW at Baja has a radiogenic value of ~-1 during the LGM. Even more pronounced intermediate and deep water production rates have been observed in the WNP during HS1 according to a drop in ventilation age of ~600 years between LGM and HS1 based on the ^{14}C age difference between benthic and planktonic foraminifera[S23]. Increased contributions of radiogenic WNP intermediate water (ε_{Nd} ~-0.1) to NPIW would result in an NPIW ε_{Nd} value that was similar to, or more radiogenic than, LGM values. Therefore, anticipated changes in the end-member composition of NPIW during HS1 are expected to produce increasing ε_{Nd} values at the Baja site, in direct contradiction to the observed decreasing values at the onset of HS1 (Fig. 2). Moreover, modeling studies by Okazaki et al.(S23) predict this young LGM/HS1 NPIW flowed out of the Pacific Ocean as a western boundary current, leaving southern sourced waters as the primary component in the eastern Pacific.

Benthic foraminiferal $\delta^{13}C$

Ideally we would like to have a robust record of benthic $\delta^{13}C$ for the Baja site, allowing us to begin addressing the question of coupling/decoupling of ^{14}C and ^{13}C. Unfortunately, the core's benthic assemblage is dominated by infaunal, low-O_2 taxa like *Bolivina* and *Uvigerina* which are known to be unreliable recorders of bottom water $\delta^{13}C$;

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the more reliable genus *Cibicidoides* is rare and might well suffer from the so-called "Mackensen" photodetritus effect in this high-productivity environment. The supplemental material in Marchitto et al. (S24) does list several $\delta^{13}C$ measurements on mixed benthic species from the deglacial, and they are about 0.7-0.8‰ lighter than Holocene or MIS2-3 values. However we have little confidence in these values since they are on mixed infaunal taxa, and since unpublished *Uvigerina* measurements (J. Carriquiry, personal communication) indicate a heavy productivity overprint on this core. They do, however, rule out sedimentary methane as a potential source of the old carbon.

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Table S1: Nd isotopes from fossil fish teeth/derbis of core MV99-MC19/GC31/PC08

Sample	Composite depth (m)	Calendar age (kyr BP)	ε_{Nd}	error (+/-)
MC19, 10-11cm	0.100	0.32	-1.4	0.4
MC19, 25-26cm	0.250	0.81	-0.7	0.2
MC19, 40-41cm	0.400	1.29	-0.9	0.2
GC31-3, 22-23cm	0.475	1.54	-0.9	0.2
GC-31-3, 50-51cm	0.755	2.44	-0.3	0.2
GC31-3, 70-71 cm	0.950	3.08	-0.4	0.3
GC31-3, 100-101 cm	1.255	4.07	-1.6	0.2
GC-31-3, 123-124 cm	1.480	4.79	-0.8	0.2
GC31-2, 0-1cm	1.755	5.69	-1.1	0.2
GC31-2, 50-51cm	2.255	7.31	-1.0	0.1
GC31-2, 100-101cm	2.755	9.01	-1.3	0.2
GC31-1, 8-9 cm	3.255	10.79	-0.8	0.2
PC08-9, 60cm	3.410	11.32	-0.3	0.5
PC08-9, 85cm	3.660	12.12	-1.7	0.2
PC08-9, 110cm	3.910	12.88	-1.4	0.2
PC08-9, 130cm	4.110	13.57	-1.3	0.2
PC08-9, 140-142cm	4.220	13.94	-1.5	0.3
PC08-9, 140-142cm	4.220	13.94	-1.7	0.3
PC08-9, 150 cm	4.310	14.2	-2.0	0.3
PC08-8, 16-17cm	4.475	14.65	-1.8	0.2
PC08-8, 25-26 cm	4.565	14.96	-1.7	0.2
PC08-8, 35 cm	4.660	15.3	-1.7	0.1
PC08-8, 45-46cm	4.765	15.67	-2.0	0.2
PC08-8, 65-66 cm	4.965	16.37	-3.0	0.3
PC08-8,105-106	5.365	17.78	-1.9	0.1
PC08-8,115-117cm	5.470	18.12	-1.3	0.1
PC08-8,125cm	5.560	18.41	-0.9	0.2
PC08-7,60-61cm	6.415	21.14	-1.0	0.1
PC08-7,80-81cm	6.615	21.77	-1.9	0.2
PC08-7,132-133cm	7.135	23.43	-1.5	0.2
PC08-6,20-21	7.585	25.15	-1.8	0.2
PC08-5,25cm	9.010	30.7	-2.2	0.2
PC08-5,130cm	10.060	34.55	-2.3	0.2
PC08-4,15cm	10.410	35.89	-1.8	0.2
PC08-4,65cm	10.910	37.92	-0.9	0.2

$\varepsilon_{Nd}=((^{143}Nd/^{144}Nd)_{measured}/(^{143}Nd/^{144}Nd)_{CHUR})-1) * 10^4$. All reported $^{143}Nd/^{144}Nd$ ratios were corrected for mass fractionation using $^{146}Nd/^{144}Nd$ =0.7219. International standard JNdi-1 was analyzed between every 5-6 unknown samples and the average of these standard runs were compared to a long term TIMS JNdi-1 value of 0.512103 +/- 0.000014 to determine a correction factor for each of the samples analyzed on that day. Long term external reproducibility of JNdi-1 analyses on the Nu is 0.000014 (0.3 ε_{Nd} units). Error bars for all figures in the text represent external reproducibility unless the internal error is larger.

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Supplementary Online References:

S1. Jeandel, C. Concentration and isotopic composition of Nd in the South Atlantic Ocean. *Earth and Planetary Science Letters* **117**, 581-591 (1993).

S2. Tachikawa, K., Handel, C. & Dupre, B. Distribution of rare earth elements and neodymium isotopes in settling particulate material of the tropical Atlantic Ocean (EUMELI site). *Deep Sea Research Part I: Oceanographic Research Papers* **44**, 1769-1792 (1997).

S3. Broecker, W. S., Peng, T.H. *Tracers in the sea* (Lamont-Doherty Geol. Obs., Palisades, N.Y., 1982).

S4. Goldstein, S. L. & Jacobsen, S. B. The Nd and Sr isotopic systematics of river-water dissolved material: Implications for the sources of Nd and Sr in the seawater. *Chemical Geology* **66**, 245-272 (1987).

S5. Elderfield H. The oceanic chemistry of the rare-earth elements. *Phil. Trans. Roy. Soc. London Ser. A: Math. Phys. Eng. Sci.* **3256**, 105–12 (1988).

S6. Tachikawa K., Jeandel C. & Roy-Barman M. A new approach to the Nd residence time in the ocean: the role of atmospheric inputs. *Earth Planet. Sci. Lett.* **170**, 433–446 (1999).

S7. Tachikawa, K., Athias, V. & Jeandel, C. Neodymium budget in the modern ocean and paleo-oceanographic implications. *J. Geophys. Res.,* **108**, 3254 (2003).

S8. Piepgras, D. J. & Wasserburg, G. J. Rare earth element transport in the western North Atlantic inferred from Nd isotopic observations. *Geochimica et Cosmochimica Acta* **51**, 1257-1271 (1987).

S9. Lacan, F. & Jeandel, C. Acquisition of the neodymium isotopic composition of the North Atlantic Deep Water. *Geochem. Geophys. Geosyst.* **6**, doi:10.1029/2005GC000956 (2005).

S10. Piepgras, D. J. & Jacobsen, S. B. The isotopic composition of neodymium in the North Pacific. *Geochimica et Cosmochimica Acta* **52**, 1373-1381 (1988).

S11. Bostock, H. C., Opdyke, B. N. & Williams, M. J. M. Characterising the intermediate depth waters of the Pacific Ocean using $\delta^{13}C$ and other geochemical tracers. *Deep Sea Research Part I: Oceanographic Research Papers* **57**, 847-859 (2010).

S12. Tomczak, M. & Godfrey, J. S. *Regional oceanography: an introduction* (Pergamon Press, 1994).

S13. Lacan, F. & Jeandel, C. Tracing Papua New Guinea imprint on the central Equatorial Pacific Ocean using neodymium isotopic compositions and Rare Earth Element patterns. *Earth and Planetary Science Letters* **186**, 497-512 (2001).

S14. Marchitto, T. M., Lynch-Stieglitz, J. & Hemming, S. R. Deep Pacific $CaCO_3$ compensation and glacial-interglacial atmospheric CO2. *Earth and Planetary Science Letters* **231**, 317-336 (2005).

S15. You, Y. The pathway and circulation of North Pacific intermediate water. *Geophys. Res.Lett.* **30** (2003).

S16. Talley L.D. in *Mechanisms of Global Climate Change at Millennial Time Scales* (eds. Clark, P. U., Webb, R. S. & Keigwin, L. D.) 1–22 (Geophys.Mono, 1999).

S17. Amakawa H. et al. Neodymium isotopic variations in Northwest Pacific water. *Geochim. Cosmochim. Acta* . **68**, 715–727 (2004a).

S18. Amakawa H., S., A. D. & Y., N. Nd abundance and isotopic composition distributions of surface seawaters of the Northwest Pacific Ocean and its adjacent seas. *Geochem. J.* **38**, 493–504 (2004b).

S19. Amakawa, H., Sasaki, K. & Ebihara, M. Nd isotopic composition in the central North Pacific. *Geochimica et Cosmochimica Acta* **73**, 4705-4719 (2009).

S20. Keigwin, L. D. Glacial-age hydrography of the far northwest Pacific Ocean. *Paleoceanography* **13**, 323-339 (1998).

S21. Matsumoto, K., Oba, T., Lynch-Stieglitz, J. & Yamamoto, H. Interior hydrography and circulation of the glacial Pacifi c Ocean. *Quaternary Science Reviews* **21**, 1693–1704 (2002).

S22. Horikawa, K., Asahara, Y., Yamamoto, K. & Okazaki, Y. Intermediate water formation in the Bering Sea during glacial periods: Evidence from neodymium isotope ratios 10.1130/G30225.1 *Geology* **38** 435-438 (2010).

S23. Okazaki, Y. et al. Deepwater Formation in the North Pacific During the Last Glacial Termination 10.1126/science.1190612. *Science* **329**, 200-204 (2010).

S24. Marchitto, T. M., Lehman, S. J., Ortiz, J. D., Fluckiger, J. & van Geen, A. Marine Radiocarbon Evidence for the Mechanism of Deglacial Atmospheric CO_2 Rise. *Science* **316**, 1456-1459 (2007).