

## A conservative tracer for glacial ocean circulation from carbon isotope and palaeo-nutrient measurements in benthic foraminifera

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**THE ratio of cadmium to calcium (Cd/Ca) and the carbon isotope ratio ( $\delta^{13}\text{C}$ ) in the calcite tests of benthic foraminifera both record nutrient distributions in the ocean<sup>1,2</sup>. Strict interpretation of both  $\delta^{13}\text{C}$  and Cd as nutrient tracers has led to conflicting views of glacial ocean circulation<sup>3-5</sup>. Here we show that, when one takes into account the fact that  $\delta^{13}\text{C}$  reflects air-sea exchange as well as nutrient distributions, these two proxies can provide complementary information about the movement of deep water in the glacial ocean. We use the Cd concentration (assumed to be controlled primarily by biological cycling) to infer the age history of glacial deep water, and deduce the sources of deep water from the carbon isotope air-sea exchange signature, a conservative tracer that we construct using both Cd and  $\delta^{13}\text{C}$  measurements. Our analysis suggests that there were at least two sources of glacial deep water: a less dense component originating in the North Atlantic Ocean, and a more dense component which may have originated in the Pacific Ocean. As well as demonstrating the potential of this approach, our findings provide further support for a Pacific glacial deep water source, evidence for which has until now been both scarce and conflicting<sup>3,5-12</sup>.**

The distribution of cadmium in the ocean resembles that of the major nutrient, phosphorus. Although the mechanism by which Cd becomes incorporated into organisms is not understood, the relationship between Cd and P in the deep ocean is very strong, although not quite linear<sup>1</sup>. Foraminifera incorporate varying amounts of Cd into their calcite tests, depending primarily on seawater Cd concentrations and the depth of calcification<sup>1,5</sup>. Core-top calibrations show that foraminiferal Cd/Ca ratios can be used to estimate seawater Cd to an accuracy of  $\sim\pm 0.1$  nmol kg<sup>-1</sup> (ref. 5).

The isotope composition of carbon in sea water also follows the nutrient distribution within the ocean, with low  $\delta^{13}\text{C}$  values corresponding to nutrient-rich waters and high  $\delta^{13}\text{C}$  to nutrient-depleted waters<sup>2</sup>. Photosynthesis discriminates against the heavier carbon isotope, and as this isotopically light organic matter oxidizes in the deep sea, the deep water gains nutrients and the  $\delta^{13}\text{C}$  of dissolved inorganic carbon decreases. However, seawater  $\delta^{13}\text{C}$  can also be altered by exchange with atmospheric CO<sub>2</sub> without associated changes in nutrient concentration. Isotope equilibrium of surface ocean waters with atmospheric CO<sub>2</sub> will cause higher  $\delta^{13}\text{C}$  in cold surface waters, and lower  $\delta^{13}\text{C}$  in warm surface waters<sup>13,14</sup>. Deep-water  $\delta^{13}\text{C}$  is recorded by benthic foraminifera as oceanic carbon is incorporated into their calcite tests. *Planulina wuellerstorfi* has been shown to record seawater  $\delta^{13}\text{C}$  to an accuracy of  $\sim\pm 0.2\text{‰}$  (ref. 15).

The air-sea exchange signature,  $\delta^{13}\text{C}_{\text{as}}$ , can be isolated by subtracting the  $\delta^{13}\text{C}$  predicted for an ocean with no air-sea carbon isotope exchange from the actual  $\delta^{13}\text{C}$  (ref. 13). The oxidation of organic material within a parcel of water will change both the concentration of phosphate (PO<sub>4</sub><sup>3-</sup>) and  $\delta^{13}\text{C}$ , but leave  $\delta^{13}\text{C}_{\text{as}}$  unchanged. This means that  $\delta^{13}\text{C}_{\text{as}}$  is a conservative tracer in the deep sea, its distribution only reflecting the relative mixtures of water from different sources. ( $\delta^{13}\text{C}_{\text{as}}$  is the same as  $\Delta\delta^{13}\text{C}$  defined by Broecker and Maier-Reimer<sup>13</sup>, but is renamed here to avoid confusion with the common usage of  $\Delta\delta^{13}\text{C}$  to

denote the difference between  $\delta^{13}\text{C}$  in surface and deep waters.  $\delta^{13}\text{C}_{\text{as}}$ , as defined by Broecker and Maier-Reimer<sup>13</sup>, is actually not quite conserved, with small non-conservative behaviour introduced by the assumption of constant dissolved inorganic carbon throughout the ocean, and the assumption of constant  $\delta^{13}\text{C}$  of organic material.) Because of the close relationship between the concentrations of Cd and PO<sub>4</sub><sup>3-</sup> in the ocean, we can calculate  $\delta^{13}\text{C}_{\text{as}}$  using  $\delta^{13}\text{C}$  and Cd estimates from benthic foraminifera. Here we use the global compilation of  $\delta^{13}\text{C}$  and Cd estimates of Boyle<sup>5</sup> to calculate the distribution of  $\delta^{13}\text{C}_{\text{as}}$  in the modern and glacial ocean (Table 1, Fig. 1).

The distribution of  $\delta^{13}\text{C}_{\text{as}}$  calculated for the modern ocean (Fig. 1c) is consistent with previous estimates<sup>13,16</sup>. We can see that there are at least two sources of water to the deep ocean, each with its own distinct  $\delta^{13}\text{C}_{\text{as}}$  signature. The North Atlantic source has a low  $\delta^{13}\text{C}_{\text{as}}$  signature ( $-0.4\text{‰}$ ), reflecting a lesser influence of equilibration at low temperatures than average deep water. The Southern Ocean source has a higher  $\delta^{13}\text{C}_{\text{as}}$  signature ( $+0.2\text{‰}$ ), reflecting the greater influence of equilibration of this water with the atmosphere at low temperatures<sup>13,14</sup>. The Cd estimates reflect the regeneration of organic material in the deep ocean waters from their ultimate origin in the Atlantic, through the Southern Ocean and into the deep Indian and Pacific Oceans. Although they also reflect the different  $\delta^{13}\text{C}_{\text{as}}$  values for the deep-water sources, the  $\delta^{13}\text{C}$  estimates also (to first order) reflect this nutrient regeneration pattern.

Estimates of glacial  $\delta^{13}\text{C}_{\text{as}}$  require at least two sources of deep water, one with a high  $\delta^{13}\text{C}_{\text{as}}$  signature ( $\sim+0.8\text{‰}$ ) and one with a low  $\delta^{13}\text{C}_{\text{as}}$  signature ( $\sim-0.6\text{‰}$ ) (Fig. 1f). Intermediate values of  $\delta^{13}\text{C}_{\text{as}}$  (eastern tropical Pacific, Indian Ocean, Deep Atlantic probably represent a mixture of waters from these two sources). By definition, the mean glacial deep ocean  $\delta^{13}\text{C}_{\text{as}}$  was 0‰, implying roughly equal contributions from the high and low  $\delta^{13}\text{C}_{\text{as}}$  sources. Because of the wide range in  $\delta^{13}\text{C}_{\text{as}}$  values for the glacial deep-water sources (1.4‰ in the glacial ocean relative to the modern spread of 0.6‰),  $\delta^{13}\text{C}$  no longer reflects the nutrient regeneration implied by the deep-water Cd estimates. However, this wide range in glacial  $\delta^{13}\text{C}_{\text{as}}$  values makes this property an excellent conservative water-mass tracer. Understandably, the increased range in  $\delta^{13}\text{C}_{\text{as}}$  has confounded attempts to reconstruct deep-water circulation changes using  $\delta^{13}\text{C}$  exclusively.

Deep waters displaying  $\delta^{13}\text{C}_{\text{as}}$  values near the high ( $+0.8\text{‰}$ ) end member resided in the shallower portions (1–2 km) of the Atlantic and Pacific Oceans. In the Atlantic, this water mass had low Cd values (0.2 nmol kg<sup>-1</sup>), indicating a likely source region in the North Atlantic. This water mass was probably the glacial North Atlantic intermediate water (GNAIW)<sup>3</sup>. Although a shallow high- $\delta^{13}\text{C}_{\text{as}}$  water mass also occupied the Pacific Ocean, in the Pacific this water mass had very high Cd values (0.8 nmol kg<sup>-1</sup>) indicating either a greater distance from the source for this water mass in the Pacific, or higher nutrient values at the time of formation. So it is possible that the GNAIW was not only a dominant water mass in the Atlantic, but made its way into the upper deep waters of the Pacific as well. This communication of low-density deep water between the Atlantic to the Pacific could have been accomplished by way of the lower density (northward) portions of the Antarctic circumpolar current. It is possible that a separate high- $\delta^{13}\text{C}_{\text{as}}$ , high-preformed-nutrient water mass occupied the upper glacial Pacific, possibly reflecting the contributions of high  $\delta^{13}\text{C}_{\text{as}}$  Southern Ocean surface waters.

Low  $\delta^{13}\text{C}_{\text{as}}$  values were concentrated not only in the deep Antarctic, but also in the deep Pacific. Glacial Cd values for these water masses in the Antarctic and North Pacific are quite similar, and therefore cannot be used to distinguish the source. Although the 'anomalously low' glacial  $\delta^{13}\text{C}$  is thought of as peculiar to the Southern Ocean, it seems unlikely that this was the source area for the low- $\delta^{13}\text{C}_{\text{as}}$  water. In both the modern and glacial oceans, Antarctic surface water  $\delta^{13}\text{C}_{\text{as}}$  is much higher (by  $\sim 1\text{‰}$ ) than that of the deep water which upwells into the

TABLE 1 Oceanic Cd concentrations and carbon isotope ratios

	Depth (km)	Modern Cd (nmol kg <sup>-1</sup> )	Modern $\delta^{13}\text{C}$ (‰)	Modern $\delta^{13}\text{C}_{\text{as}}$ (‰)	Glacial Cd (nmol kg <sup>-1</sup> )	Glacial $\delta^{13}\text{C}$ (‰)	Glacial $\delta^{13}\text{C}_{\text{as}}$ (‰)
North Atlantic	1–2	0.20	1.10	-0.35	0.20	1.60	0.69
	2–3	0.25	1.00	-0.31	0.23	1.00	0.17
	3–4	0.26	1.00	-0.28	0.37	0.60	0.15
	4–5	0.28	0.90	-0.33			
Tropical Atlantic	1–2	0.25	0.85	-0.46	0.20	1.60	0.69
	2–3	0.30	0.85	-0.32	0.30	0.70	0.06
	3–4	0.32	0.83	-0.29	0.55	0.20	0.24
	4–5	0.35	0.78	-0.26	0.50	0.00	-0.10
Antarctic	surface	0.5	1.6	1.0	0.5	0.8	0.71
	1–2	0.30	0.70	-0.47			
	2–3	0.30	0.70	-0.47	0.40		
	3–4	0.50	0.60	-0.03	0.55	-0.40	-0.36
	4–5	0.62	0.40	0.10	0.47	-0.40	-0.58
North Indian	1–2	0.80	-0.10	0.10	0.55	0.20	0.24
	2–3	0.75	0.00	0.06	0.60	-0.50	-0.32
	3–4	0.70	0.10	0.03	0.50		
	4–5	0.70	0.10	0.03			
Northwest Pacific	1–2	0.84	-0.15	0.16	0.80	0.25	0.97
	2–3	0.82	-0.10	0.16	0.55	-0.10	-0.06
	3–4	0.75	0.05	0.11	0.45	-0.30	-0.53
	4–5	0.75	0.05	0.11			
East tropical Pacific	1–2	0.83	-0.10	0.18	0.87	-0.15	0.77
	2–3	0.75	0.05	0.11	0.65	-0.30	0.01
	3–4	0.70	0.15	0.08	0.65	-0.30	0.01
	4–5	0.70	0.15	0.08			

Subsurface  $\delta^{13}\text{C}$  and Cd inventory estimates from Boyle<sup>5</sup> who used a depth-dependent distribution coefficient to estimate seawater Cd from the foraminiferal Cd/Ca ratio. Values that were extrapolated from adjacent depth intervals were not used. Modern surface Antarctic  $\delta^{13}\text{C}$  values are from Kroopnick *et al.*<sup>20</sup>. Modern surface Cd values were estimated from the global  $\text{PO}_4^{3-}$ -Cd relationship<sup>1</sup>. Glacial surface  $\delta^{13}\text{C}$  is calculated by subtracting 0.8‰, the glacial/interglacial  $\delta^{13}\text{C}$  difference recorded in planktonic foraminifera<sup>14</sup>, from the modern value. Glacial surface Cd is taken to be the same as the modern value, reflecting the lack of glacial/interglacial change in the Cd/Ca ratio recorded in Southern Ocean planktonic foraminifera<sup>23,24</sup>. Modern  $\delta^{13}\text{C}_{\text{as}}$  values are calculated using the equation of Broecker and Maier-Reimer<sup>13</sup> for  $\delta^{13}\text{C}_{\text{as}}$  (their  $\Delta\delta^{13}\text{C}$ ) along with the Cd- $\text{PO}_4^{3-}$  relationship for waters containing  $>1.3 \mu\text{mol PO}_4^{3-}$  per kg (ref. 1) ( $\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + (2.75 \times \text{Cd}) - 2.0$ ). For glacial values, the  $\delta^{13}\text{C}_{\text{as}}$  equation is modified to account for an oceanic Cd concentration which is 13% lower<sup>5</sup>, organic-matter  $\delta^{13}\text{C}$  which 2‰ higher<sup>25</sup>, a mean ocean  $\delta^{13}\text{C}$  which was 0.3‰ lower<sup>4,5</sup>, and a corresponding increase in total inorganic carbon of 4% ( $\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + (2.73 \times \text{Cd}) - 1.5$ ). The oceanic phosphate inventory is assumed to be the same as today.

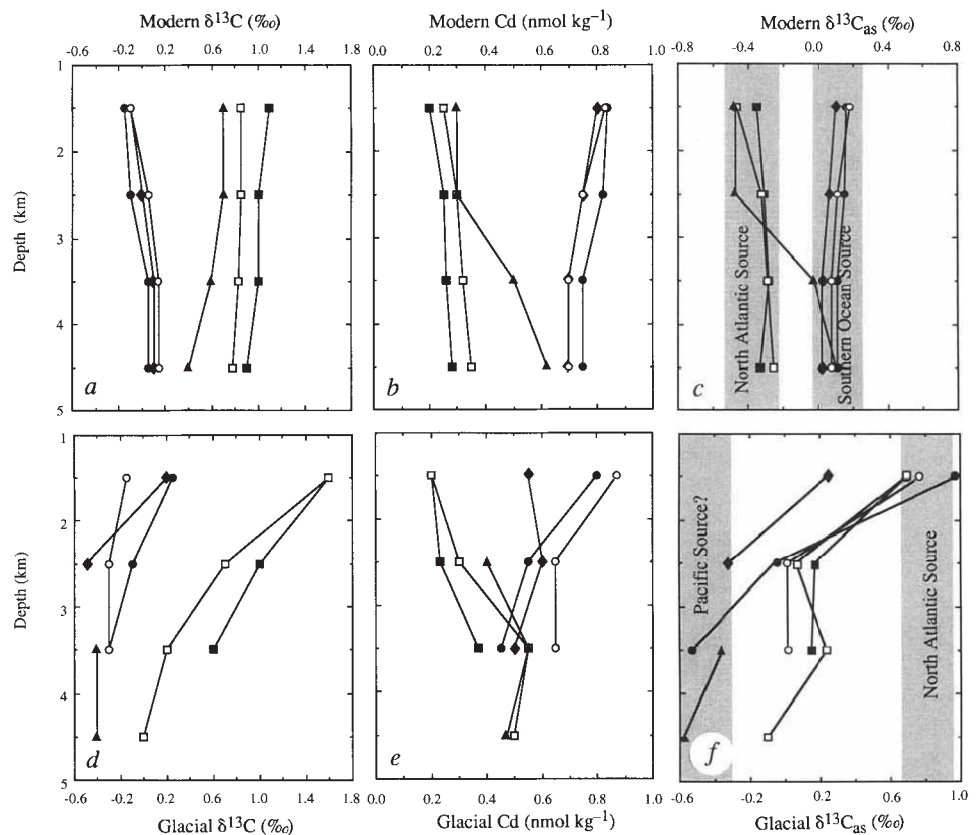


FIG. 1 Values of  $\delta^{13}\text{C}$ , Cd concentration and estimated  $\delta^{13}\text{C}_{\text{as}}$  values for the modern (a-c) and glacial (d-f) oceans (Table 1). Symbols used: Filled squares, North Atlantic; empty squares, tropical Atlantic; filled triangles, Antarctic; filled diamonds, North Indian; filled circles, northwest Pacific; empty circles, eastern tropical Pacific. Differences between Cd concentrations  $<0.1 \text{ nmol kg}^{-1}$ , and between  $\delta^{13}\text{C}_{\text{as}}$  and  $\delta^{13}\text{C}$  values  $<0.2\text{‰}$ , are beyond the limits of the errors of the methods.

surface ocean (Table 1). So surface processes would, if anything, imprint a high  $\delta^{13}\text{C}_{\text{as}}$  signature on deep water formed in the region. In the extreme case where deep waters formed exclusively from these relatively well equilibrated surface waters, the new deep waters would have the same  $\delta^{13}\text{C}_{\text{as}}$  signature as the surface water (1‰ today, 0.7‰ during the last glaciation). In the extreme case where new deep waters formed in the Southern Ocean without any isotopic exchange with the atmosphere, and with no contributions from the well equilibrated surface waters, the new deep waters would have a  $\delta^{13}\text{C}_{\text{as}}$  signature identical to the upwelled deep waters formed elsewhere (that is, the North Atlantic). Because of the extensive entrainment of subsurface waters during deep water formation, today Southern Ocean source waters ( $\delta^{13}\text{C}_{\text{as}} = 0.2\text{‰}$ ) are only slightly enriched from the upwelled North Atlantic deep water value ( $\delta^{13}\text{C}_{\text{as}} = -0.4\text{‰}$ ) as compared with the surface water ( $\delta^{13}\text{C}_{\text{as}} = 1\text{‰}$ ). In the glacial ocean, deep water renewal in the Southern Ocean could have either modified the  $\delta^{13}\text{C}_{\text{as}}$  of the upwelled water towards more positive values, or, in the other extreme case, not modified the  $\delta^{13}\text{C}_{\text{as}}$  of incoming water at all. Thus, the low  $\delta^{13}\text{C}_{\text{as}}$  signature we find in the dense portions of the glacial oceans cannot have been generated in the Southern Ocean, but must have been imported from elsewhere.

Where did the waters in the Southern Ocean and the deep Pacific get their low  $\delta^{13}\text{C}_{\text{as}}$  signature if not in the Antarctic? Contributions from, and exchange with, both Southern Ocean surface waters and GNAIW would have drawn the deep Pacific/Antarctic  $\delta^{13}\text{C}_{\text{as}}$  to positive values. We are left with the need for a source of glacial Pacific deep water (GPDW), the Pacific being the only other part of the glacial ocean showing the low  $\delta^{13}\text{C}_{\text{as}}$  end-member values. Glacial Cd values in the deep eastern equatorial Pacific were considerably higher than in the northwest Pacific. This enhanced ventilation on the western side of the ocean basin is analogous to today's Atlantic, where the waters in the western basin are replenished more quickly by the newly formed North Atlantic deep waters from the north, and Antarctic bottom waters from the south, supporting the existence of GPDW.

The presence of GPDW has been suggested previously, but has not been widely accepted primarily because of the low  $\delta^{13}\text{C}$  values in the deep glacial Pacific. A high nutrient content was inferred from these data without regard to the potentially large effects of air-sea exchange on  $\delta^{13}\text{C}$  (refs 6, 7). But an intermediate water source (1–2 km) for the glacial Pacific has been postulated, based on the relatively high  $\delta^{13}\text{C}$  values and inferred low nutrient concentration<sup>3,8</sup>. In contrast, the study reported here suggests that, when allowance is made for the effects of both biological cycling and air-sea exchange, the  $\delta^{13}\text{C}$  values in the deep glacial Pacific are not inconsistent with a GPDW source, and when combined with the planktonic data from the Southern Ocean in fact suggest a GPDW source.

Other studies have also supported the presence of GPDW, based on sedimentological evidence for bottom-water flow<sup>9</sup>, changes in the redox conditions of North Pacific sediments<sup>10</sup>, increased calcite preservation<sup>11,12</sup> and low Cd concentrations in the glacial deep Pacific<sup>5</sup>. An ocean model shows that the atmospheric circulation patterns generated by atmospheric models using last glacial maximum boundary conditions increase surface salinity in the northwest Pacific enough to induce deep convection<sup>17</sup>.

What information about the glacial ocean can we glean from the end-member  $\delta^{13}\text{C}_{\text{as}}$  values themselves? By definition,  $\delta^{13}\text{C}_{\text{as}}$  of average deep ocean water was 0‰. If all deep water sources had similar temperatures and initial nutrient concentrations, positive  $\delta^{13}\text{C}_{\text{as}}$  means only that this source was exposed to air-sea exchange processes which led to more complete isotopic equilibration of the oceanic carbon with the atmosphere at cold temperatures than the other deep water sources; a negative  $\delta^{13}\text{C}_{\text{as}}$  means only that this water mass was less well equilibrated than other deep sources when it left the surface. Only by consid-

ering the  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  along with the mean ocean changes in  $\delta^{13}\text{C}$  can we determine in an absolute sense whether there was increased equilibration of the glacial deep water masses with the atmosphere. There is evidence that the  $\delta^{13}\text{C}$  of the glacial atmosphere was no different<sup>18</sup> or only slightly (1‰) lighter<sup>19</sup> than today, indicating that deep water, on average, was equilibrated with the glacial atmosphere to about the same degree as it is today. It is important to note that today, high-latitude surface water  $\delta^{13}\text{C}$  is out of equilibrium with atmospheric carbon by up to 2‰ (refs 2, 20). A change in the residence times, temperature history or the biological history of the waters that eventually contribute to the sinking deep waters could easily cause the range of  $\delta^{13}\text{C}_{\text{as}}$  values observed in the glacial ocean. The GNAIW with their high  $\delta^{13}\text{C}_{\text{as}}$  may have reflected the closed-loop circulation in the North Atlantic, with the constant re-exposure of its waters to the atmosphere at low temperatures<sup>21</sup>. By analogy to today's low- $\delta^{13}\text{C}_{\text{as}}$  Atlantic source, the low- $\delta^{13}\text{C}_{\text{as}}$  GPDW may also have reflected a warm surface water history of the contributing waters with insufficient time for these waters to re-equilibrate isotopically with the atmosphere at low temperatures.

Many uncertainties remain about the reliability of benthic foraminifera as recorders of nutrient and  $\delta^{13}\text{C}$  distributions in the ocean. For example, Mackensen *et al.*<sup>22</sup> find that modern foraminiferal  $\delta^{13}\text{C}$  can be significantly lower than ambient bottom water in the Southern Ocean,<sup>22</sup> and Boyle<sup>5</sup> finds inexplicably low Cd concentrations in North Pacific core tops. As our understanding of how oceanic  $\delta^{13}\text{C}$  and Cd are recorded in benthic foraminifera improves, the specific conclusions about glacial ocean circulation reached here may well change; but the extraction of the air-sea exchange signature, a conservative tracer, from  $\delta^{13}\text{C}$  measurements provides a powerful palaeoceanographic tool. When glacial  $\delta^{13}\text{C}$  and Cd estimates<sup>5</sup> are interpreted literally as the glacial deep-ocean values, a coherent picture of the glacial ocean circulation can be seen. These tracers indicate at least two distinct sources of deep water to the glacial ocean, one less-dense source originating in the North Atlantic with a high  $\delta^{13}\text{C}_{\text{as}}$  signal, and one more-dense source with a low  $\delta^{13}\text{C}_{\text{as}}$  signal which may have formed somewhere in the North Pacific. There is no reason to believe that deep water did not upwell in the Antarctic, densify and sink as deep waters of Antarctic origin but this process left no distinct  $\delta^{13}\text{C}_{\text{as}}$  signature. □

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