Earth and Planetary Science Letters 411 (2015) 45–52

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

# Reduced ventilation and enhanced magnitude of the deep Pacific carbon pool during the last glacial period

L. Skinner [a,*], I.N. McCave [a], L. Carter [b], S. Fallon [c], A.E. Scrivner [a], F. Primeau [d]

[a] Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge, CB2 3EQ, UK
[b] National Institute of Water and Atmosphere, Private Bag 14 701, Wellington, New Zealand
[c] Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia
[d] Department of Earth System Science, University of California, Irvine, CA, USA

ARTICLE INFO

*Article history:*
Received 13 January 2014
Received in revised form 21 October 2014
Accepted 6 November 2014
Available online 15 December 2014
Editor: J. Lynch-Stieglitz

*Keywords:*
radiocarbon
ocean ventilation
carbon cycling
palaeoceanography

ABSTRACT

It has been proposed that the ventilation of the deep Pacific carbon pool was not significantly reduced during the last glacial period, posing a problem for canonical theories of glacial–interglacial $CO_2$ change. However, using radiocarbon dates of marine tephra deposited off New Zealand, we show that deep- (>2000 m) and shallow sub-surface ocean–atmosphere $^{14}C$ age offsets (i.e. 'reservoir-' or 'ventilation' ages) in the southwest Pacific increased by ~1089 and 337 yrs respectively, reaching ~2689 and ~1037 yrs during the late glacial. A comparison with other radiocarbon data from the southern high-latitudes suggests that broadly similar changes were experienced right across the Southern Ocean. If, like today, the Southern Ocean was the main source of water to the glacial ocean interior, these observations would imply a significant change in the global radiocarbon inventory during the last glacial period, possibly equivalent to an increase in the average radiocarbon age >2 km of ~700 yrs. Simple mass balance arguments and numerical model sensitivity tests suggest that such a change in the ocean's mean radiocarbon age would have had a major impact on the marine carbon inventory and atmospheric $CO_2$, possibly accounting for nearly half of the glacial–interglacial $CO_2$ change. If confirmed, these findings would underline the special role of high latitude shallow sub-surface mixing and air–sea gas exchange in regulating atmospheric $CO_2$ during the late Pleistocene.



## 1. Introduction

Radiocarbon can provide unique insights into the ocean's large-scale overturning circulation, in particular its impact on the average timescale of carbon exchange between the atmospheric and marine carbon pools. The latter, set against the rate of biogenic-carbon and carbonate export to the deep ocean, determines the ocean's capacity to sequester $CO_2$ from the atmosphere. Indeed, it has been proposed that the ~90 ppmv increase in atmospheric $CO_2$ that accompanied the last deglaciation (Monnin et al., 2001) was associated with a significant increase in the rate at which $CO_2$ was exchanged between the deep ocean and the atmosphere, in particular via the Southern Ocean (Anderson et al., 2009; Burke and Robinson, 2012; Skinner et al., 2010, 2013). While atmospheric radiocarbon (Hughen et al., 2006; Muscheler et al., 2004) and stable carbon isotope ($\delta^{13}CO_2$) (Lourantou et al., 2010) records spanning the last deglaciation are consistent with this proposition (Lourantou et al., 2010; Skinner et al., 2010), it continues to be challenged as inadequately verified, refuted or even physically impossible (Broecker et al., 2008; Cleroux et al., 2011; De Pol-Holz et al., 2010; Hain et al., 2011). Marine radiocarbon evidence is crucial in this regard: if the average time-scale of ocean–atmosphere $CO_2$ exchange was greatly increased during the last glacial period, then a significant reduction of the marine radiocarbon inventory should be observed relative to the contemporary atmosphere. Despite existing and apparently conflicting marine radiocarbon evidence (e.g. Broecker et al., 2008; Burke and Robinson, 2012; De Pol-Holz et al., 2010; Galbraith et al., 2007; Marchitto et al., 2007; Robinson et al., 2005; Sarnthein et al., 2007, 2013; Sikes et al., 2000; Skinner et al., 2010; Skinner and Shackleton, 2004; Thornalley et al., 2011), the true magnitude of the glacial marine radiocarbon inventory, let alone its temporal evolution across the last deglaciation, has yet to be established. Pinning down the radiocarbon inventory of the glacial Pacific is particularly important in this regard, as this basin accounts for ~50% of the global ocean volume (Menard and Smith, 1966).

It has previously been proposed that the deep Pacific Ocean was not significantly more radiocarbon-depleted during the last

* Corresponding author. Tel.: +44 1223 764 912; fax: +44 1223 333 450.
*E-mail address:* luke00@esc.cam.ac.uk (L. Skinner).

http://dx.doi.org/10.1016/j.epsl.2014.11.024

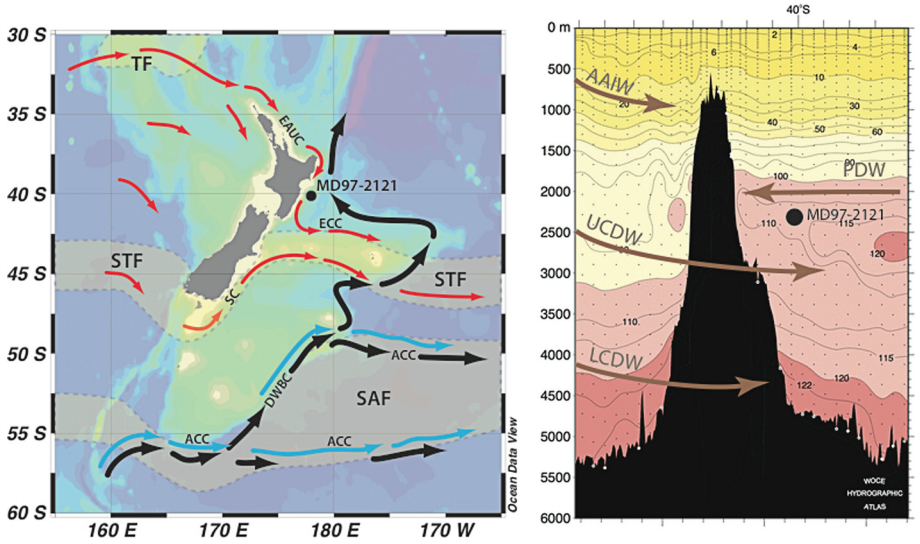


**Fig. 1.** Location of core MD97-2121, after Carter et al. (2008), relative to the modern regional hydrography, including the sub-tropical front (STF), sub-Antarctic front (SAF), Deep Western Boundary Current (DWBC), Antarctic Circumpolar Current (ACC), Tasman Front (TF), East Auckland Current (EAUC), East Cape Current (ECC), Southland Current (SC). The right hand panel shows modern contoured silicate concentrations (μmol/kg) from WOCE section P15, illustrating the influence of Antarctic Intermediate Water (AAIW), Upper Circumpolar Deep Water (UCDW), Pacific Deep Water (PDW), and Lower Circumpolar Deep Water (LCDW).

glacial period, *versus* today (Broecker et al., 2004a, 2004b, 2007, 2008). Despite the identification of transient ventilation anomalies of varying magnitude and sign across the last deglaciation, primarily in the intermediate/shallow Pacific (<2000 m) (Ahagon et al., 2003; De Pol-Holz et al., 2010; Marchitto et al., 2007; Siani et al., 2013; Stott et al., 2009), the majority of these studies appear to confirm the absence of a large change in the radiocarbon ventilation age during the last glacial period, prior to the onset of deglaciation. Studies of the deep Pacific (>2000 m) are more equivocal, with conflicting evidence from the deep northwest Pacific (Galbraith et al., 2007; Lund et al., 2011), conflicting evidence in the eastern- and western equatorial Pacific (Broecker et al., 2008; Shackleton et al., 1988), and widespread and at times conflicting evidence (based on a novel ventilation age reconstruction method) for greatly increased ventilation ages in the western- and northern Pacific (Sarnthein et al., 2013). The null hypothesis that the glacial deep Pacific ventilation age was similar to modern also conflicts with reconstructions from the deep- and intermediate Southern Ocean (Burke and Robinson, 2012; Sikes et al., 2000; Skinner et al., 2010). The latter is particularly surprising, as the Southern Ocean is currently the source of ~56% of the ocean interior water mass budget (i.e. below the surface mixed layer) (DeVries and Primeau, 2011). If the Southern Ocean was also the main origin of deep water during the last glacial, or indeed an even greater contributor (Curry and Oppo, 2005; Skinner, 2009), then we should expect some similarity between radiocarbon ventilation changes in the deep Pacific and the deep Southern Ocean.

A principal challenge in advancing data that might resolve this apparent conflict lies in the assessment of the true 'calendar' age of marine radiocarbon dates. This, along with an accurate record of changing atmospheric radiocarbon concentrations, is required to determine the extent of radiocarbon-depletion in a given water mass relative to its contemporary atmosphere (i.e. its 'apparent ventilation age', or 'B-Atm' age offset). Here, in order to overcome this challenge, we make use of volcanic tephra, synchronously deposited on land and at sea, as marker horizons that link marine radiocarbon dates with correlative atmospheric radiocarbon ages obtained in terrestrial sequences (e.g. Siani et al., 2001; Sikes et al., 2000). We apply this approach to a marine sediment core off the east coast of New Zealand to demonstrate that both surface- and deep-water (>2000 m) radiocarbon reservoir ages in the southwest Pacific increased significantly during the last glacial period. This contradicts the null hypothesis of an invariant radiocarbon inventory in the deep Pacific across the last deglaciation, with implications for the ocean's role in glacial–interglacial $CO_2$ change.

## 2. Methods

Core MD97-2121 was recovered off the coast of New Zealand by the *R.V. Marion Dufresne* at 40°22.935′S; 177°59.68′E in a water depth of 2314 m (Fig. 1). The core site is currently just north of the Subtropical Front that separates subtropical surface water (STSW) in the north from southern sub-Antarctic surface water (SASW), with Antarctic Intermediate Water (AAIW) dominating the subsurface from ~600 to 1400 m depth, and a mixture of Upper Circumpolar Deep Water (UCDW) and Pacific Deep Water (PDW) dominating the remainder of the water column (Carter et al., 2008; McCave et al., 2008; Talley et al., 2011). The modern circulation is complex, with the upper ~800 m of the ocean dominated by a southward current overprinted with southward migrating mesoscale eddies (Chiswell, 2005; Roemmich and Sutton, 1998), and the deeper flow predominantly northward in concert with the Pacific deep western boundary current that underlies a deep reaching southwest Pacific sub-tropical gyre (Talley et al., 2011). MD97-2121 is characterised by high sedimentation rates (~30 cm/kyr; though these may be affected by 'stretching', Skinner and McCave, 2003) and frequent deposition of volcanic tephra time-markers, as described previously by Carter et al. (2008). For this study, mixed benthic foraminifera (excluding agglutinated and broken shells) and monospecific samples of the planktonic foraminifer *Globigerina inflata* were picked from within or immediately below tephra-bearing horizons. Samples were cleaned by hand on a glass plate and rinsed in deionised water and methanol prior to drying and sealing in evacuated double-wadded 3.5 ml septum vials for hydrolysis in 0.5 ml of dry phosphoric acid at 60 °C. Carbon dioxide evolved from the samples was graphitised at the University of Cambridge using a standard hydrogen/iron-catalyst protocol (Vogel et al., 1984). Samples were graphitised in parallel with size-matched Iceland Spar calcite backgrounds, as well as primary and secondary standards for normalisation and quality control (Santos et al., 2007). Pressed graphite

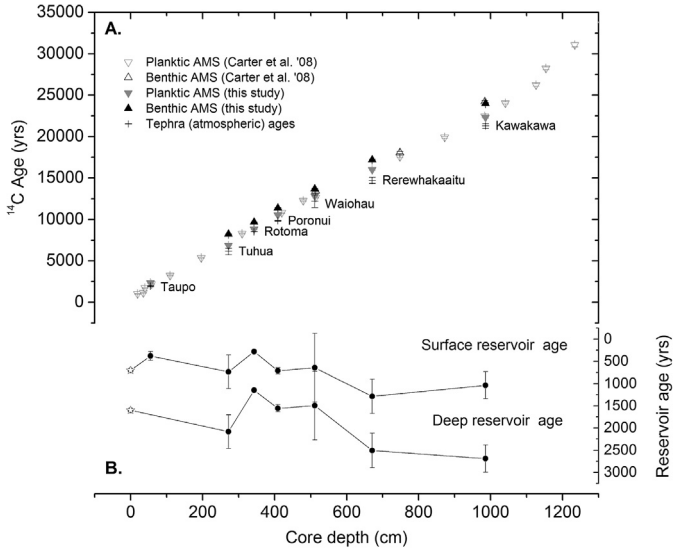


**Fig. 2.** A. Foraminiferal radiocarbon dates in core MD97-2121 (open downward- and upward pointing triangles are planktonic and benthic dates respectively from Carter et al., 2008; closed downward- and upward pointing triangles are planktonic and benthic dates respectively from this study), compared with atmospheric radiocarbon ages for corresponding named tephra (crosses, see text). B. Offsets between planktonic/benthic radiocarbon dates and their corresponding tephra atmospheric radiocarbon ages: open stars at left indicate modern ventilation age estimates from seawater data (Key et al., 2004).

targets were analysed by single stage accelerator mass spectrometry (SSAMS) at the Australian National University (Fallon et al., 2010). Radiocarbon ages are reported according to the standard protocol of Stuiver and Polach (1977).

## 3. Results and discussion

Our new planktonic radiocarbon results are in near perfect agreement with pre-existing radiocarbon dates from core MD97-2121 (see Fig. 2A), and as expected are consistently older than the atmospheric radiocarbon ages attributed to each respective tephra. Here we adopt calendar ages and averaged atmospheric radiocarbon ages for the Taupo, Tuhua, Rotoma, Poronui, Waiohau, Rerewhakaaitu and Kawakawa tephras, as reported by Carter et al. (2008), Hajdas et al. (2006), Hogg et al. (2012), Lowe et al. (2013) (Table 1). For the Kawakawa tephra we adopt the revised atmospheric calendar age of 25 358 ± 162 yr BP and the corresponding average atmospheric radiocarbon age of 21 285 ± 292 yrs (Vandergoes et al., 2013). On the basis of these dates we are able to reconstruct the evolution of surface- and deep water reservoir ages at the site of MD97-2121 (Fig. 2B), which show a clear glacial–interglacial trend, from late glacial reservoir/ventilation ages of 2689 ± 308 yrs (2507 ± 388 yrs at the onset of HS1) and 1037 ± 304 yrs (1286 ± 387 yrs at the onset of HS1) to modern ventilation ages of ~1500 yrs and 700 yrs, for deep- and surface waters respectively (Key et al., 2004).

Fig. 3 shows surface- and deep water reservoir ages (i.e. 'ventilation ages') from MD97-2121 compared to other existing records specifically from the southern high latitudes, including similar data from the southwest Pacific off New Zealand (Sikes et al., 2000), as well as data from the Chilean Margin (Carel et al., 2011; Haberle and Lumley, 1998; Siani et al., 2013) (we show only the reported tephra-based reservoir age estimates from this location), the sub-Antarctic Atlantic (Skinner et al., 2010) and the Drake Passage (Burke and Robinson, 2012). These radiocarbon datasets are distinct from others in possessing a high signal-to-noise ratio and independent calendar age constraints that permit the calculation of surface- and deep water *versus* atmosphere $^{14}$C-age offsets. Ben-

**Table 1**
Calendar and radiocarbon ages for tephra identified in MD97-2121 (see text), and associated (raw/uncorrected) benthic and planktonic foraminifer radiocarbon dates, as well as the 'surface-' and 'deep reservoir ages' that are given by the offsets between the foraminifer and corresponding tephra $^{14}$C ages. The modern reservoir ages are based on pre-bomb sea-water radiocarbon estimates (Key et al., 2004).

| Depth (cm) | Tephra | Cal. age (tephra) (yrs) | $^{14}C_{atm}$ age tephra (yrs) | ±2σ | Benthic $^{14}$C age (yrs) | ±2σ | Planktonic $^{14}$C age (yrs) | ±2σ | Surface *R*-age (yrs) | ±2σ | Deep *R*-age (yrs) | ±2σ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Modern | – | – | – | – | – | – | – | – | 700 | – | 1600 | – |
| 55 | Taupo | 1718 | 1952 | 90 | – | – | 2331 | 40 | 379 | 98 | | |
| 272 | Tuhua | 7027 | 6149 | 376 | *8231* | 42 | 6884 | 30 | 735 | 377 | 2082 | 378 |
| 343 | Rotoma | 9906 | 8530 | 10 | *9677* | 41 | 8812 | 36 | 282 | 37 | 1147 | 42 |
| 409 | Poronui | 11 195 | 9840 | 60 | *11 395* | 51 | 10 552 | 38 | 712 | 71 | 1555 | 79 |
| 511 | Waiohau | 14 324 | 12 198 | 769 | *13 695* | 47 | 12 839 | 45 | 641 | 770 | 1497 | 770 |
| 671 | Rerewhakaaitu | 17 845 | 14 700 | 383 | *17 207* | 61 | 15 986 | 56 | 1286 | 387 | 2507 | 388 |
| 986 | Kawakawa | 25 358 | 21 285 | 292 | *23 974* | 97 | 22 322 | 85 | 1037 | 304 | 2689 | 308 |

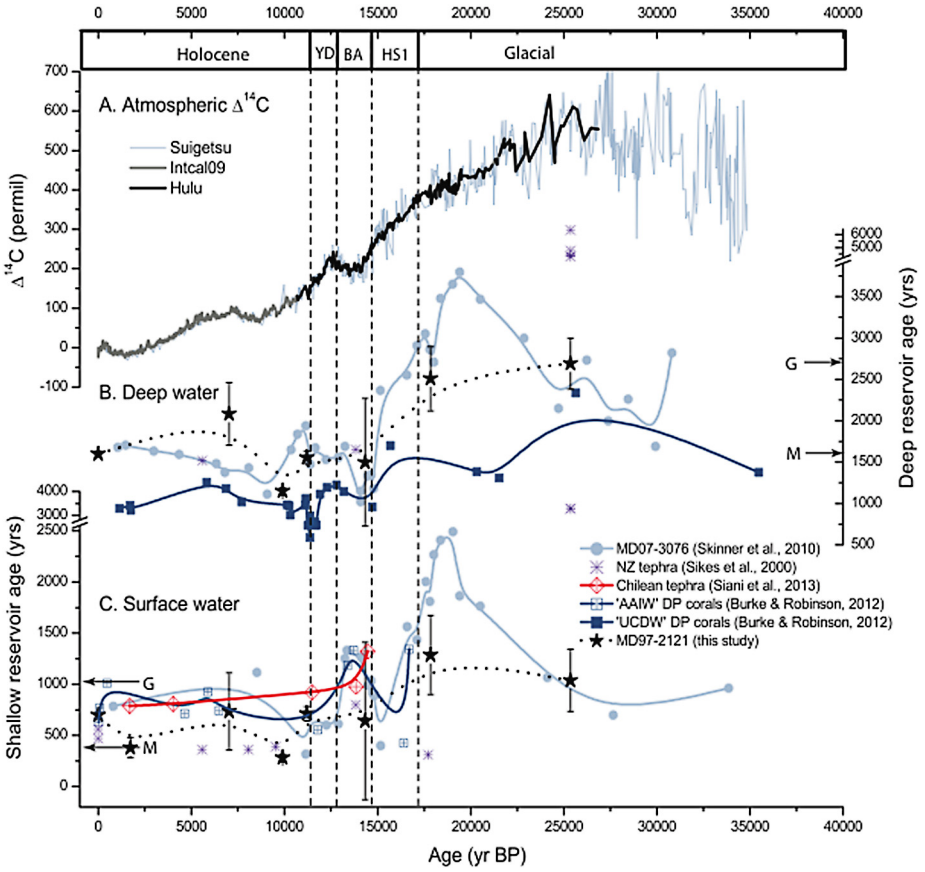


**Fig. 3.** Atmospheric $\Delta^{14}C$ (plot A; grey line from IntCal09, Reimer et al., 2009; black line from the Hulu H82 speleothem, Southon et al., 2012; light blue line from Lake Suigetsu, Bronk Ramsey et al., 2012), compared with deep-water reservoir ages (plot B), and shallow sub-surface water reservoir ages (plot C) derived from paired tephra and foraminifera in MD97-2121 (this study; dotted black line and filled stars), paired tephra and foraminifera from the Bay of Plenty and Chatham Rise (Sikes et al., 2000; purple crosses), paired tephra and foraminifera from the Chilean Margin (Carel et al., 2011; Haberle and Lumley, 1998; Siani et al., 2013, solid red line and crossed diamonds), Drake Passage corals (Burke and Robinson, 2012; Robinson and van de Flierdt, 2009; solid blue line and filled/open crossed circles), sub-Antarctic Atlantic planktonic/benthic foraminifera (Skinner et al., 2010; solid light blue line and filled circles). Error bars are shown for data from this study, indicating 2-sigma ranges arising from radiocarbon dating uncertainties. Horizontal arrows indicate modern (M) and glacial (G) reservoir ages at the location of MD97-2121. Vertical dashed lines indicate North Atlantic climatostratigraphic chronozones: the Younger Dryas (YD); Bølling–Allerød (BA); and Heinrich Stadial 1 (HS1), which marks approximately the onset of deglaciation. Note the *y*-axis breaks in plots B and C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

thic stable carbon isotope profiles from the Last Glacial Maximum (LGM) suggest that the site of MD97-2121 was bathed primarily in southern sourced UCDW during the last glacial (McCave et al., 2008). The records in Fig. 3 thus yield a broadly consistent picture of ventilation age changes in both the southern high-latitude shallow sub-surface (i.e. planktonic foraminifer habitat) and southern sourced deep-water (e.g. UCDW). We speculate that the lower ventilation ages reported in the shallow- *versus* the deep sub-Antarctic Atlantic could reflect the influence of different water mass mixtures at ~695–1750 m *versus* 3770 m in this region (with the former possibly influenced to a greater degree by AAIW than previously interpreted, and the latter more influenced by LCDW). Differences between our results and the extremely high reservoir ages obtained by Sikes et al. (2000) for the Kawakawa tephra are not easily explained, though both datasets clearly confirm the existence of radiocarbon depleted deep water during the last glacial period, prior to the onset of deglaciation.

The consistency of the shallow sub-surface reservoir age estimates in Fig. 3 is particularly important. Given that ~60% of the ocean interior is currently sourced from the surface ocean south of 40°S (Gebbie and Huybers, 2011; Primeau, 2005), a change in the shallow sub-surface reservoir age of this region should yield a significant change in the global ocean radiocarbon inventory, unless the ocean circulation changed so drastically that the Southern Ocean ceased to be a major region for deep-water export. The latter is unlikely, not least since existing evidence points overwhelmingly to a near constant (Gebbie, 2014) or else increased (Curry and Oppo, 2005; Piotrowski et al., 2004) volumetric contribution of southern sourced deep water during the last glacial maximum.

To first order, the implications of a doubling of shallow sub-surface reservoir ages in the Southern Ocean for the global marine radiocarbon inventory can be explored by 'conveying/mixing' this change into the ocean interior via the modern advection/diffusion pathways. For this we use the transport operator (a sparse matrix that fully describes advection–diffusion tracer transport at steady state) from a data-constrained numerical model simulation of the modern ocean circulation. The model formulation and data-assimilation procedure is identical to the one described in DeVries (2014) except that we explicitly model the air–sea exchange of radiocarbon instead of prescribing its surface concentration. With this transport operator, restoring surface radiocarbon in the top layer of the model (36 m thickness) to the atmospheric value on a time-scale of 7.2 yrs reproduces the observed modern 'natural' marine radiocarbon distribution (Key et al., 2004) with a root mean square error (RMSE) of only 7.2‰. However, if instead we restore surface reservoir ages south of 40°S to 80.4% of the atmospheric value (so as to obtain shallow sub-surface reservoir ages of ~1000–1200 yrs at site MD97-2121 near the southern sub-tropical front off New Zealand), and allow steady state radiocarbon concentrations 'downstream' of the Southern Ocean surface to adjust accordingly, the global average marine radiocarbon age is found to increase by 722 yrs, while the average age below 2000 m increases

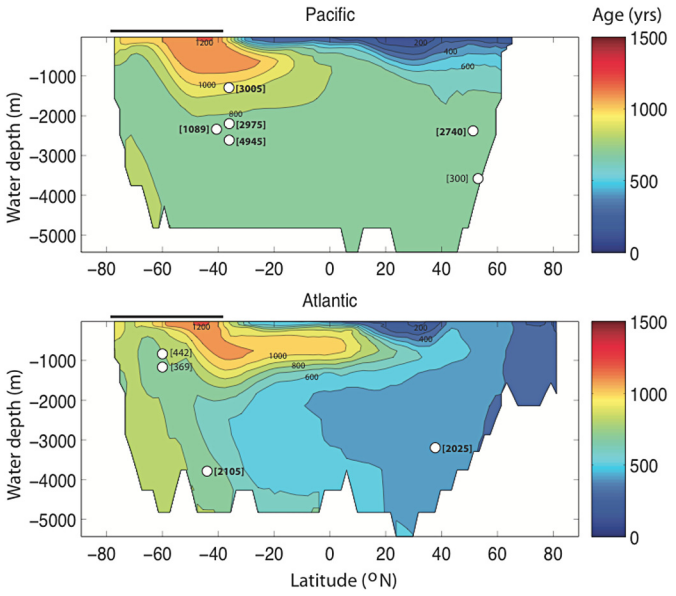


**Fig. 4.** Atlantic and Pacific basin averaged meridional sections from a numerical model simulation of the global marine radiocarbon field, showing the difference between the modern (control) radiocarbon field and the radiocarbon field that would result simply from an increase in surface reservoir ages south of 40°S (restoring region indicated by solid black line), due to the redistribution of this reservoir age anomaly to the rest of the global ocean via the modern circulation. Numbers in brackets indicate a selection of observed offsets between glacial (LGM) and modern ventilation ages where independent calendar age constraints have been used (Burke and Robinson, 2012; Sarnthein et al., 2013; Sikes et al., 2000; Skinner et al., 2010, 2014); bold numbers indicate significantly larger observed ventilation age increases than predicted by the numerical model experiment. The change in the global radiocarbon field illustrated here corresponds to a 722-year increase in the global average marine radiocarbon age (699 yrs >2000 m).

by 699 yrs (Fig. 4). This thought experiment does not aim to provide an explicit reconstruction of the glacial marine radiocarbon budget, or indeed the glacial circulation (the modern circulation is assumed); rather, it serves as a 'dynamically assisted' means of extrapolating the putative impacts on the global marine radiocarbon budget of our inferred changes in surface boundary conditions in the southern high latitudes, assuming a global circulation broadly similar to the modern. The simulated 'aging' of the deep ocean by ~699 yrs thus reflects a first estimate of what the inferred 'aging' of the shallow sub-surface Southern Ocean (alone) would imply for the global radiocarbon inventory, prior to other possible changes in the ocean's main transport pathways or transit times.

This estimate is broadly consistent with the 600 yr higher average LGM ocean radiocarbon age >2000 m obtained from compiled and directly averaged radiocarbon data (Sarnthein et al., 2013). However, it is also notable that the imposition of increased sub-Antarctic surface reservoir ages on the modern circulation pathways and transit times is of course not sufficient to reproduce all of the ventilation ages that have been observed in the ocean interior. For illustrative purposes we underline here observations (where independent calendar age constraints have been used) from the deep southwest Pacific (Sikes et al., 2000), the deep North Pacific (Sarnthein et al., 2013), the deep- and shallow South Atlantic (Burke and Robinson, 2012; Skinner et al., 2010), and the deep North Atlantic (Robinson et al., 2005; Skinner et al., 2014; Skinner and Shackleton, 2004). This would suggest that some of the premises of our numerical model assisted thought experiment must be wrong, and that a significant change in the transport-pathways and/or rates also occurred during the last glacial period, and/or that other sources of significantly radiocarbon depleted deep-water existed during the last glacial, for example in the North Atlantic (Thornalley et al., 2011), the Arctic or perhaps the North Pacific. To the extent that they would have enhanced further the radiocarbon deficit in the glacial ocean, such changes may have compounded any carbon cycle impacts of restricted ocean–atmosphere $CO_2$ exchange in the Southern Ocean (Kwon et al., 2011).

The putative impact of the inferred drop in the marine radiocarbon inventory on the atmospheric radiocarbon concentration ($\Delta^{14}C_{atm}$) is not easily determined. This is because the global radiocarbon inventory does not have to remain constant (due to changes in the relative magnitudes of old- and young carbon pools, and therefore the total amount of radiocarbon decay *versus* production), precluding a simple mass balance calculation. Changes in radiocarbon production since the last glacial period, and their uncertainty, present a further difficulty (Guyodo and Valet, 1999; Laj et al., 2004; Muscheler et al., 2005). However, numerical model experiments exploring the link between deep ocean ventilation, driven by changes in Southern Ocean wind stress, and $\Delta^{14}C_{atm}$ suggest a ~0.1‰ increase in $\Delta^{14}C_{atm}$ per year increase in the average age of the ocean below 2000 m (Tschumi et al., 2011). For a hypothetical increase in the average ventilation age >2000 m of 699 yrs, this would imply an increase in $\Delta^{14}C_{atm}$ of 69.9‰. Thus, even without a (compounding) reduction in the average overturning rate of the ocean circulation (which seems likely – see above), the surface reservoir age change in the Southern Ocean suggested by our results could alone explain nearly half of the 'mystery' drop in atmospheric $\Delta^{14}C$ since the Last Glacial Maximum (Broecker and Barker, 2007), in principle.

An 'aging' of the global marine carbon pool (i.e. reduced ocean–atmosphere $CO_2$ exchange), set against continuing organic carbon export to the deep ocean, would also bear on the partitioning of $CO_2$ between the atmosphere and ocean. Thus, if the global average rate of biological carbon export to the deep ocean did not change significantly (despite regional anomalies), such that the modern rate of dissolved inorganic carbon (DIC) accumulation in the ocean remained broadly similar to today at ~1.22 μmol/kg increase in DIC per 1‰ decrease in radiocarbon concentration below 2000 m (Sarnthein et al., 2013), then for a 699 yr (~67‰) change in the ventilation age ($\Delta^{14}C$) below 2000 m, we might expect the average DIC below 2000 m to have increased in parallel by ~82 μmol/kg to ~2325 μmol/kg during the last glacial. Notably, a similar magnitude of DIC change (i.e. a 3% or >75 μmol/kg increase) has been inferred on the basis of oxygenation and nutrient concentration reconstructions in the deep sub-Arctic Pacific (Jaccard et al., 2009). If we assume that changes in marine carbon pool >2000 m exerted a dominant control on atmospheric $CO_2$ (e.g. via high latitude outcrops) (Broecker, 1999) (or equivalently that changes in DIC >2000 m are representative of changes in total mean ocean DIC), it can be estimated that an 82 μmol/kg change in the deep ocean DIC would directly account for a ~49 ppmv change in atmospheric $CO_2$ (see Appendix A), or about half of the observed glacial–interglacial range (Monnin et al., 2001). This estimate of the impact on atmospheric $CO_2$ is based on the theoretical framework of Kwon et al. (2011) and assumes invariant biological export productivity (which is likely to have decreased in a more poorly ventilated ocean) and a fixed link between $C_{org}$ and $C_{carb}$ export to the deep ocean. It also ignores the effects of carbonate compensation in the glacial ocean (which in this case would likely enhance the inferred impact on atmospheric $CO_2$ via changes in global alkalinity). Therefore, at best, our simple analysis may be taken to suggest a non-negligible (though potentially significant) impact of a ~700 yr aging of the deep ocean on atmospheric $CO_2$. Nevertheless, a similar magnitude of change in atmospheric $CO_2$ (i.e. 46 ppmv) was obtained with the Bern3D+C model when average ocean ages below 2000 m were increased by 519 yrs, driven by an 80% reduction in Southern Ocean winds (Tschumi et al., 2011). Taken together, these results would suggest that, to first order, the

magnitude of ventilation age changes that we infer for the deep- and in particular the shallow southern high latitudes could be sufficient to rule in a major impact on atmospheric $CO_2$ via changes in the global ocean overturning circulation and in particular via high latitude air–sea carbon exchange. The question of what climatic feedbacks caused the ventilation age of the southern high latitudes to change so dramatically remains to be resolved. However, we speculate that the strong cooling and the approximate doubling of winter sea ice extent around Antarctica during the last glacial period (much of which appears to have melted during the summer season) (Gersonde et al., 2003) would have had a significant impact on buoyancy forcing in the Southern Ocean (Watson and Naveira Garabato, 2006), convective stability of the water column (de Boer et al., 2010), and the efficiency of air–sea $CO_2$ exchange over the annual cycle (Mackensen, 2012), in particular due to sea–ice cover in the winter and a strong halocline in the spring and summer.

## 4. Conclusions

The results presented here demonstrate that an assessment of the ocean's role in glacial–interglacial $CO_2$ change should not be based on the assumption of constant ventilation ages in the deep Pacific, in particular given emerging evidence for significant changes in the radiocarbon ventilation age (reservoir age) of the shallow sub-surface Southern Ocean. Our results from the late glacial southwest Pacific are broadly consistent with other radiocarbon data from the southern high latitudes (Burke and Robinson, 2012; Siani et al., 2013; Sikes et al., 2000; Skinner et al., 2010), and demonstrate ~1089 and ~337 yr increases in subtropical southern Pacific reservoir ages in the deep- (2314 m) and shallow sub-surface ocean respectively. These results would suggest that deep water upwelling in the Southern Ocean during the last glacial and deglaciation did not re-equilibrate completely with the atmosphere before reaching the sub-Antarctic southern Pacific (Rose et al., 2010), and disagree with the proposition that a more poorly ventilated deep Pacific (relative to today) did not or could not exist (Broecker et al., 2008; Hain et al., 2011). Instead, they add to a growing body of evidence (e.g. Galbraith et al., 2007; Sarnthein et al., 2013; Shackleton et al., 1988; Sikes et al., 2000) demonstrating that a significant portion of the Pacific interior was indeed less well ventilated during the last glacial period. We argue that, all else being equal (i.e. biological export productivity and ocean circulation pathways/times being invariant), this magnitude of ventilation age change, at this location near the region of Southern Ocean deep/intermediate water export, would have been associated with significant changes in the global marine radiocarbon and carbon inventories, potentially driving a decrease in atmospheric $CO_2$ by tens of ppmv, or a significant portion of the full glacial–interglacial range. Other records of reservoir/ventilation age change, in particular from high latitude regions of deep-water export (crucially with accurate and independent calendar age control), are needed to confirm the proposed changes in the global marine radiocarbon/carbon inventories. Numerical model experiments are also needed to refine our understanding of the link between local radiocarbon concentrations and the global radiocarbon field (i.e. the glacial ocean circulation), as well as the link between the marine radiocarbon inventory and atmospheric $CO_2$ (due to the prevailing organic carbon and carbonate remineralisation rates of the glacial ocean). However, our results clearly demonstrate that the extent of ocean–atmosphere $CO_2$ equilibration in a region that currently influences nearly 60% of the global ocean interior, was significantly reduced during the last glacial period.

## Acknowledgements

We are grateful for the critical comments of two anonymous reviewers and of Michael Sarnthein. This work was supported by the Royal Society, through a University Research Fellowship granted to LCS, and by NERC grant NE/L006421/1.

## Appendix A

Our estimate of the impact of a change in the global radiocarbon inventory is based on the empirical approach of Sarnthein et al. (2013), who use modern seawater data to show that on average DIC increases by ~1.22 μmol/kg per ‰ decrease in radiocarbon concentration in the ocean interior (>2000 m water depth). Extending this rate of carbon accumulation to the glacial ocean requires the assumption that the rate of organic carbon remineralisation did not change on average. Given a constant ocean volume >2000 m of approximately $5.5 \times 10^{17}$ $m^3$ (e.g. Menard and Smith, 1966), a change in the average ocean DIC >2000 m by 1 μmol/kg would require the addition of approximately 8.4 GtC. Thus, a 699 yr increase (67‰ decrease) in the global ocean radiocarbon age (concentration), would correspond to an 82 μmol/kg increase in average ocean DIC, and a consequent increase in the deep ocean carbon inventory of perhaps ~687 GtC. In order to infer the impact of a change in deep ocean DIC on atmospheric $CO_2$, we apply the theoretical framework of Kwon et al. (2011):

$$\frac{\Delta pCO_2^{atm}}{pCO_2^{atm}} = \Delta\overline{C_{org}}\left(-\frac{R_c}{\overline{C_{sat}}} + r_{N:C}\frac{R_A}{\overline{Alk_{pref}}}\right) + \Delta\overline{C_{carb}}\left(-\frac{R_c}{\overline{C_{sat}}} + 2\frac{R_A}{\overline{Alk_{pref}}}\right)$$

where $R_c$ is the 'Revelle factor' (~10), $R_A$ is the alkalinity factor relating alkalinity to $pCO_2$ for constant DIC (~−9.4), $r_{N:C}$ is the 'Redfield' ratio of nitrogen to carbon in organic carbon (~0.14), $C_{sat}$ is the equilibrium DIC value due to exchange with the atmosphere (assumed to be 2100 μmol/kg, from modern observations), $Alk_{pref}$ is the average surface ocean alkalinity (assumed to be 2300 μmol/kg, from modern observations), $\Delta C_{org}$ is the change in average ocean DIC due to organic carbon export and $\Delta C_{carb}$ is the change in average ocean DIC due to carbonate export. If the average remineralisation ratio of $C_{org}/C_{carb}$ is 3 (Kwon et al., 2011), then the above relationship becomes:

$$\frac{\Delta pCO_2^{atm}}{pCO_2^{atm}} = 0.75\Delta\overline{C_{tot}}\left(-\frac{R_c}{\overline{C_{sat}}} + r_{N:C}\frac{R_A}{\overline{Alk_{pref}}}\right) + 0.25\Delta\overline{C_{tot}}\left(-\frac{R_c}{\overline{C_{sat}}} + 2\frac{R_A}{\overline{Alk_{pref}}}\right)$$

or

$$\frac{\Delta pCO_2^{atm}}{pCO_2^{atm}} = -0.003125\Delta\overline{C_{tot}}$$

If we further assume that the deep ocean >2000 m was the marine carbon pool that exerted a dominant control on atmospheric $CO_2$, e.g. via high latitude outcrops (Broecker, 1999) (or equivalently that changes in DIC >2000 m were broadly representative of average ocean changes in DIC), then an 82 μmol/kg decrease in its DIC since the LGM would correspond to a 49 ppmv increase in atmospheric $pCO_2$ (an 82 μmol/kg drop in DIC from pre-industrial conditions would correspond to a 72 ppmv drop in $CO_2$ due to the reduced buffering capacity of a high DIC ocean). This estimate is very approximate and is intended only to indicate a non-negligible (and potentially quite significant) impact on atmospheric $CO_2$. Although it rests of a set of tentative assumptions

(the most important being that export productivity was on average invariant and that changes in DIC >2000 m exerted a dominant control on atmospheric $CO_2$), it might be seen to represent a relatively conservative estimate in two respects: 1) $C_{sat}$ at the LGM would probably have been lower than modern, resulting in a larger multiplier on $\Delta C_{tot}$ in the above equations; and 2) changes in ocean alkalinity have been ignored (e.g. due to carbonate compensation in response to reduced carbonate ion concentration and higher dissolved $CO_2$ to the deep ocean), which would have the effect of counteracting the 'alkalinity trapping' mechanism that is incorporated into the framework of Kwon et al. (2011), thus increasing $Alk_{pref}$ in the above equations.

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