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How old is too old? Implications of averaging ^{14}C-Based estimates of ventilation age to assess the Pacific Ocean's role in sequestering CO_2 in the past

Lowell D. Stott

Department of Earth Sciences, University of Southern California, 3651, Trousdale Pkwy, Los Angeles, CA, 90089, USA

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A B S T R A C T

Compilations of benthic foraminiferal ^{14}C-based ventilation age estimates from the deep North Pacific have been used to argue the average age of bottom waters during the last glacial maximum was 3000 years, or about 1000 years older than modern. If true, glacial bottom waters would have accumulated additional respired carbon and contributed to the drop in atmospheric CO_2. By the same reasoning, ventilation ages that were 1000 years older, would have lost dissolved oxygen and become anaerobic and thereby unable to support epibenthic fauna. The current study re-analyzed the Pacific ^{14}C data and finds the glacial ventilation age average is biased by inclusion of data from low sediment accumulation rate cores that have been affected by bioturbation and contaminated with older specimens. Removal of data from cores with sedimentation rates less than 10 cm/ky reduces the old-bias and results in an average ventilation age that is close to the modern ocean.

1. Introduction

The concept of a statistical average applied to oceanographic observations is used to characterize the mean state of the system at a point in time and space. This has direct application in oceanography for defining water mass properties. For example, temperature and salinity describe the mean state of a water mass because these are conservative properties that exhibit small variance over wide swaths of the ocean. Parcels of seawater water are distinct from one another because they have unique temperature and salinity. Consequently, temperature and salinity are used to ‘trace’ the distribution of a water mass in the ocean. For example, Pacific Deep Water, one of the primary water masses found in the Pacific basin, exists between 1000 and 3000 m in the North Pacific where it has a narrow range of potential temperatures between 1 and 3 °C. The distribution of these temperatures throughout the North Pacific has been validated with hundreds of measurements to an accuracy of 0.1 °C (Talley, 1995). Given the small variance and accuracy of the measurements, the modern observations can be taken as a robust estimate of the mean temperature of this system, Pacific Deep Water. Similarly, the salinity of Pacific Deep Water is 34.6–34.8‰. This very narrow range is also well constrained by hundreds of measurements with an accuracy of <0.1 practical salinity units (Saunders, 1986). Other water mass properties in the modern ocean are non-conservative and are influenced by biogeochemical processes operating in both space and time. Dissolved oxygen, radiocarbon activity (Δ^{14}C) and ventilation age (the amount of time a water mass remains isolated from the atmosphere) are properties that vary in space and time. These properties have also been measured sufficiently to provide a robust representation of how they vary throughout the modern ocean.

In the modern Pacific Ocean, the ^{14}C ventilation age of abyssal water formed in the Southern Ocean increases as it flows toward the North Pacific. This aging is captured in the radiocarbon activity (Δ^{14}C) of dissolved inorganic carbon (Fig. 1). If one were to take the average Δ^{14}C of abyssal waters in the Pacific below 3000 m north of 10°S the radiocarbon values would exhibit a small amount of variance (Fig. 1). This variance stems from analytical uncertainty in the measurements itself, which is typically measured in units of 10s of years and the natural aging (loss of radiocarbon) of waters during the transit through the basin. In the modern ocean the abyssal waters in the North Pacific are between 1700 and 2200 ^{14}C years older the preindustrial atmosphere. There is a discernible latitudinal gradient in ^{14}C age that reflects the progressive northward aging as these waters transit from the Southern Ocean to the North

E-mail address: stott@usc.edu.

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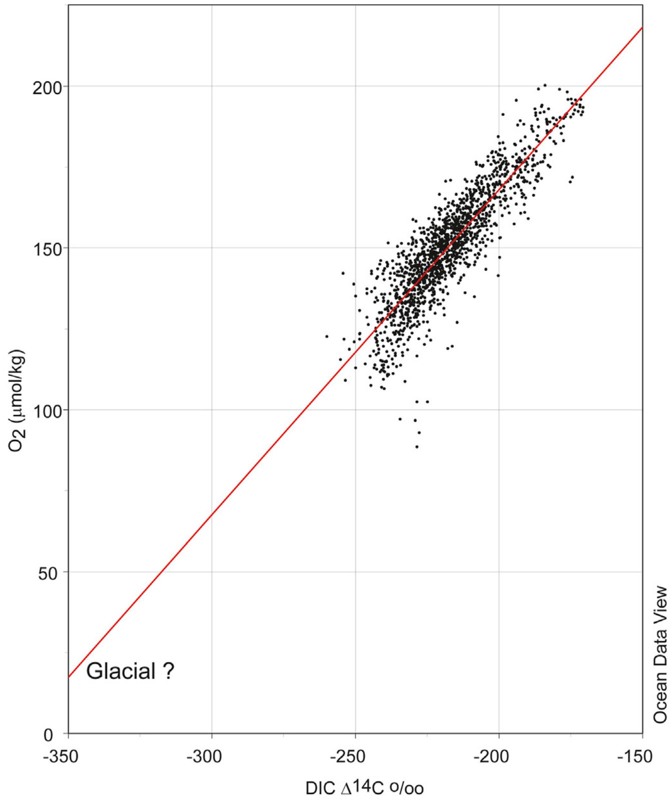

Fig. 1. $\Delta^{14}C$ of DIC from abyssal depths in the North Pacific vs. dissolved oxygen from the same suite of samples. The red line is a least squared fit. Extrapolating the regression to a change in $\Delta^{14}C$ values like that suggested for the glacial deep Pacific (Rafter et al., 2022), which effectively doubles the offset between the deep Pacific and atmosphere. Such a large change in ventilation age would imply an additional loss of O_2 of ~100 µmol/kg that would make the abyssal Pacific nearly anaerobic. The ocean data is from the GLODAP database (Key et al., 2015).

Pacific. Abyssal waters at around 40°N are about 2200 ^{14}C years older the preindustrial atmosphere whereas the abyssal waters around 10°S are closer to 1700 years older than the preindustrial atmosphere. There is also a longitudinal gradient with oldest waters in the northeast Pacific (Matsumoto, 2007). These spatial differences in ^{14}C age are a clear reflection of the transit pathway and temporal evolution of water flowing throughout the abyssal North Pacific. But importantly, despite the long transit times, the overall variance is small. The overall variance in ^{14}C ventilation ages is no more than ~500 years. It is important to keep this small range in mind when evaluating reconstructed estimates from paleoarchives such as benthic foraminifera extracted from sediment cores. An equally important observation is that as abyssal waters in the North Pacific age, they also lose oxygen via metabolic respiration. In fact, there is a direct relationship between the aging of these waters, as measured in radiocarbon, and the loss of oxygen via respiration (Fig. 1). For every 100‰ decrease in $\Delta^{14}C$, oxygen decreases by about 100 µmol/kg in the modern ocean. This relationship between abyssal water mass aging and dissolved oxygen depletion places an important limit on how "old" abyssal waters can become before they would be devoid of dissolved oxygen and lose the capacity to support aerobic organisms such as benthic foraminiera that inhabit the sea floor. Extrapolating from the relationship shown in Fig. 1, if the residence time of abyssal waters were to increase by 1000 years, the deep Pacific would be effectively anaerobic. In the modern ocean this does not occur because the rate of overturning has been sufficient to replenish the bottom waters with oxygenated waters from the Southern Ocean. But if in the past the rate of ocean overturn was slower it is possible that more oxygen was consumed via respiration and in doing so additional respired CO_2 accumulated, which would have acted to reduce the flux of carbon from the ocean to the atmosphere and thereby lower atmospheric CO_2 concentrations.

Emperical observations from proxies indicate there was less dissolved oxygen in the deep Pacific during the last glacial (Anderson et al., 2019; Jacobel et al., 2019). At the same time, there is debate about what caused the lower dissolved oxygen values. Anderson et al. (2019) argued that lower dissolved oxygen in the Pacific below 1500 m implies there was increased oxygen utilization relative to ventilation rate during the last glacial. But this would require that other variables such as the surface to subsurface $\delta^{13}C$ gradient increased, which is not reflected in proxy records from the Pacific (Stott et al., 2021). The alternative explanation for lower oxygen concentrations during the glacial would be lower preformed oxygen in the source regions where deep waters form (Cliff et al., 2021; Köhler and Munhoven, 2020; Stott et al., 2021). This too is important in the context of radiocarbon changes because the preformed ^{14}C content of waters subducted in the Southern Ocean is also affected by air-sea gas exchange. For the same reasons that oxygen was likely not fully equilibrated with the glacial atmosphere in the Southern Ocean, the preformed carbon isotopes in dissolved inorganic carbon (DIC) would have been affected as well (Khatiwala et al., 2019; Schmittner, 2003; Schmittner et al., 2013) thereby lowering the ^{14}C content of deep waters that flowed toward the North Pacific (Galbraith and Skinner, 2020). But these effects depend very much on the extent of reduced air-sea gas exchange, and ventilation rates which are not well constrained for the glacial ocean. This is one reason why obtaining unbiased estimates of deep sea ^{14}C ages and ventilation rates is so important, but also difficult.

Over the past 20 years many radiocarbon age measurements have been obtained from the carbonate tests of benthic foraminifera and deep sea corals recovered from deep sea sediments in efforts to assess whether ventilation ages have varied in the past. In a recent effort to evaluate if the ventilation rate of deep waters in the oceans decreased during the last glacial maximum (LGM) Rafter et al. (2022) compiled published radiocarbon ages together with some new radiocarbon data from the calcite tests of benthic foraminifera extracted from deep sea cores. This includes cores from a wide swath of the deep Pacific Ocean north of 20°S. Their study followed previous efforts by Zhao et al. (2018) and Skinner et al. (2017) who similarly compiled published radiocarbon ages.

Rafter et al. argued that during the LGM deep waters (1500–2500 m) in the North Pacific were younger than the abyssal waters (>2700 m), implying a reversal in the distribution of ventilation ages compared to the modern ocean. Such a finding would be a major departure from modern ocean dynamics where waters sink to abyssal depths in the Southern Ocean and then slowly flow northward. In the modern ocean abyssal waters mix upward via diapycnal mixing adding progressively older and more oxygen depleted waters to intermediate waters that flow southward to the Southern Ocean where excess carbon is released back to the atmosphere in regions of high ΔpCO_2 (Chen et al., 2022; Prend et al., 2022). As a result of this overturning circulation, the oldest and most oxygen depleted and carbon rich waters in the Pacific today occur between 1500 and 2500 m in the North Pacific. These waters constitute Pacific Deep Water. If the conclusions presented by Rafter et al. are correct, it would be fundamental breakthrough, not only in ocean dynamics but in the long-standing effort to understand what regulated glacial/interglacial CO_2 variability. If the ventilation age of abyssal waters in the Pacific was 1000 years older it would imply that a larger quantity of respired metabolic CO_2 accumulated in the deep sea during the glacial. When viewed from this perspective (Fig. 2), an increase in the

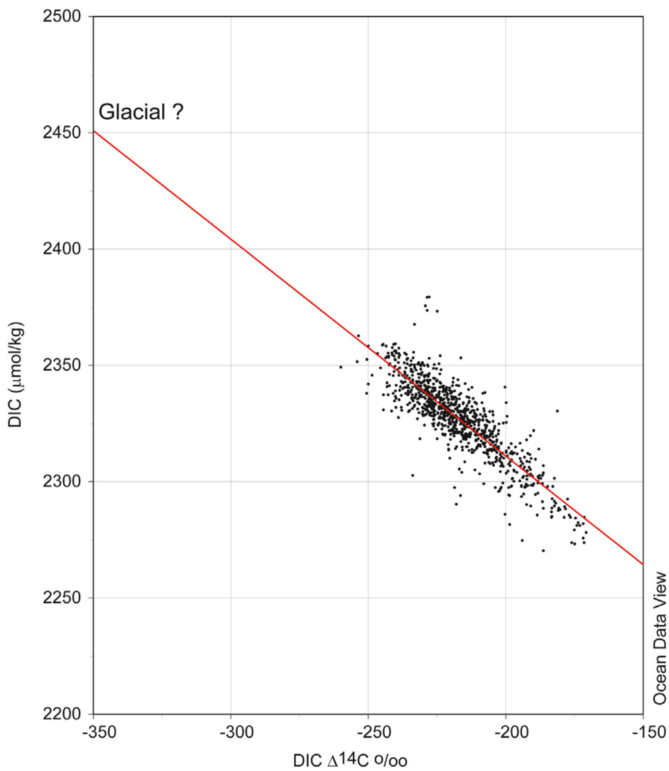

Fig. 2. $\Delta^{14}C$ of DIC from abyssal depths in the North vs. total dissolved inorganic carbon (DIC) from the same suite of samples. The red line is a least squared fit. Extrapolating the regression to $\Delta^{14}C$ values like those suggested for the glacial ocean (Rafter et al., 2022) would imply a gain of ~100 µmol/kg of DIC in the abyssal glacial ocean.

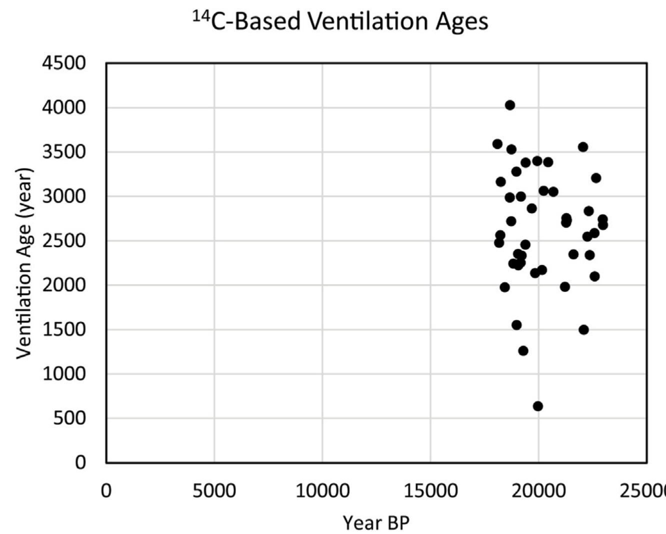

Fig. 3. The distribution of reconstructed ventilation ages from the deep (>2700 m) North Pacific obtained from the ^{14}C of benthic foraminifera (Rafter et al., 2022). Note the >3000-year dispersion of age estimates for the LGM (18-23kyBP).

ventilation age of abyssal waters in the Pacific from 2000 years (modern age) to 3000 years could have increased dissolved inorganic carbon by as much as 100 µmol/kg (assuming a constant oxygen to carbon molar ratio and no change in preformed oxygen values). That would be a nearly 10% increase in dissolved carbon above modern values in the North Pacific. But, as pointed out above, if such an increase in inorganic carbon accumulation occurred, it would have been accompanied by a reduction in dissolved oxygen. In fact, extrapolating the ^{14}C age vs dissolved oxygen shown in Fig. 1 implies that if the abyssal waters aged by an additional 1000 years in the North Pacific during the LGM, the dissolved oxygen content would have been close to 0 µmol/kg. This puts an upper limit on what can be considered ‘reliable’ ventilation age estimates from benthic foraminiferal carbonate because radiocarbon ventilation ages of 3000 years or older would mean the deep sea was virtually anoxic and could not have accommodated the benthic foraminifera used to obtain the ^{14}C ages.

In an earlier study of Pacific ^{14}C ventilaton ages Skinner et al. (2017) did not find such a reversal in the ventilation age of abyssal versus intermediate waters in the Pacific but did present evidence for an average increase in Pacific ^{14}C ventilation age of about 800 years at depths between 2000 and 3000 m, also a significant increase. However, in their compilation of ventilation ages from abyssal depths (below 3000 m), the ventilation ages were only a few hundred years older than in present day ocean. The Rafter et al. and Skinner et al. studies differed in their approach to fitting vertical profiles to the ^{14}C observations. Skinner et al. imployed an ‘abyssal recipes’ approach to fit the compiled ^{14}C ages. In this case two physical parameters were adjusted to find a best fit to the vertical ^{14}C profiles, a downwad diffusion of buoyancy and slow upward advection of mass (Munk, 1966). Rafter et al. used an averaging strategy that combined ^{14}C ages from multiple cores and attempted to remove regional biases due to volume weighted portions of the ocean where there tends to be a larger number of measured values. Both the Skinner study and the Rafter study suffer from a small number of data points from depths below 3000 m in the Pacific, which constitutes much of the abyssal North Pacific. And most importantly, the compilations that were used in both studies contain large variance in ventilaton age estimates at any given depth. Unlike in the modern ocean where the range of ^{14}C age is small at any depth in the North Pacific, in the proxy archives the range of ventilation age for the LGM at varying depths is in thousands of years (Fig. 3). This means that erroneously old ventilation age estimates act to ‘pull’ the vertical profile towards older ages, leading to a conclusion that the ventilation rates of the deep Pacific was slower than the modern ocean and therefore could have accumulated additional respired carbon.

Given the important implications of glacial ventilations ages much older than the modern ocean, the present study was motivated to evaluate why there are such wide ranging ventilation age estimates among the proxy records at all water depths, particularly at deeper water depths in the North Pacific.

2. Materials and methods

For the present study two sources of data were used. The GLODAP compilation of modern ocean observations (Key et al., 2015; Olsen et al., 2016) and the compilation of published benthic radiocarbon measurements and assigned calendar ages used to estimate ventilation ages (Rafter et al., 2022). Of the Rafter et al. compilation the focus here is solely on the bias corrected estimates of benthic ventilation age, $\Delta^{14}C$ and their associated calendar ages for the deepest North Pacific. In their study Rafter et al. refer to sites below a neutral density of 28kg/m3 as representative of the abyssal Pacific. The actual density of abyssal waters depends on the absolute temperature pressure and salinity of waters in the glacial ocean. And for this reason, if is difficult to precisely state where this horizon would have existed in the LGM Ocean. In the modern Ocean, the 27.8 kg/m^3 horizon deepens progressively from the Southern Ocean as Antarctic Bottom Water (AABW) subducts to the abyss and moves northward. In their original calculations of the neutral density surfaces in the deep Pacific Jackett and McDougall (1997) found that the 27.8 kg/m^3 horizon is below 4000 m throughout much of the North Pacific. As there is only one core below 4000 m in the database used by Rafter et al. it is not possible to put confident constraints on the ventilation age in the deepest porton of the Pacific Ocean. The closest one can come to measuring ^{14}C-based ventilation ages of the deep North Pacific using sediment archives is from 2700 to about 3700 m. Even so, there are very few cores with radiocarbon records from depths below 3000 m. In fact, there are only two cores in the data base from water depths below 3600 m. The majority of the cores are from water depths between 2700 and 3200 m, which overlaps with the depth of Pacific Deep Water in the modern Ocean. The age models for each core in the Pacific database were developed using a consistent chronologic dating method where planktic ^{14}C ages were converted to calendar years after accounting for estimated regional differences in surface reservoir age. This allowed Rafter et al. to give sediment accumulation rates for each core.

3. Results and considerations

3.1. Does combining inaccurate ventilation ages make an average better?

When examining the database of ventilation ages from the Rafter et al. compilation, three features stand out. The first observation is that the dispersion of ventilation ages from the Pacific plotted as a function of age for the LGM is approximately 3000 years (Fig. 3). The glacial values between 19 and 18kyBP range from 1260 to 4000 years whereas in the modern ocean the range is no more than 400–500 years. A similarly large range characterizes the period 19 to 23kyBP. The abyssal Pacific could not have accommodated such a large range of ventilation ages during the LGM. This is underscored by the fact that cores near one another have very different ventilation age estimates. And closely adjacent samples from the same core differ by as much as 700–900 years, which means some of these ventilation ages are not correct and act to bias the averaging scheme. Given the wide dispersion of ventilation ages from the LGM how does one determine which values are wrong and what values should be included in an estimate? Ventilation ages of 3000 years and older are suspect because if those estimates were a true, the abyssal Pacific would have been virtually anoxic and therefore unable to support the benthic foraminifers used to obtain the ^{14}C ages unless there was an increase in preformed oxygen. As pointed out above oxygen concentrations throughout the intermediate and deep Pacific were lower during the LGM (Anderson et al., 2019; Jacobel et al., 2020), which is best attributed to lower preformed oxygen concentrations, not greater respiration (Cliff et al., 2021; Köhler and Munhoven, 2020; Stott et al., 2021). The fact that preformed oxygen was lower during the LGM puts a limit on any decrease in ventilation rate, because abyssal waters would have become anaerobic sooner. Of the 42 estimates from the LGM (below 2700 m water depth), 14 (33%) are 3000 years or older. If those estimates were true, the deep Pacific would have been anoxic and for this reason the values should be considered highly suspect. And because these older ventilation age estimates represent more than a third of the data they impose a significant influence on any average.

The second observation is that the range of ventilation ages in the compilation increases significantly in cores with the lowest sediment accumulation rate, particularly below 10 cm/ky (Fig. 4). Rafter et al. attempted to evaluate whether their estimated ventilation age averages were sensitive to sedimentation rate but only considered cores with sediment accumulation rates below 2 cm/ky.

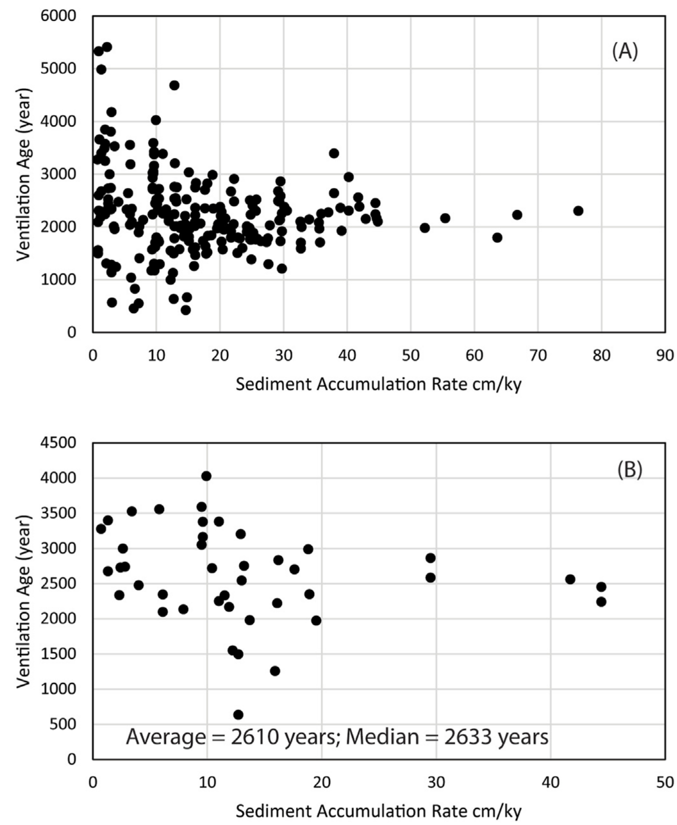

Fig. 4. Panel A is all the data from Pacific cores below 2700 m water depth used in the Rafter et al. analysis. The Holocene, deglacial and LGM values are plotted as a function of sediment accumulation rate. Note how the dispersion of ages increases as sedimentation rates decrease. Panel B depicts the LGM samples spanning 23-18kyBP from cores below 2700 m water depth.

They concluded that their mean estimates were robust. Here an alternative perspective is found by plotting the ventilation ages after filtering for differing sediment accumulation rates. The average LGM ventilation age from cores with sediment accumulation rates of 1–5 cm/ky is 3162 years (median = 2871 years, std = 376 years). Similarly, cores with sediment accumulation rates of 5–10 cm/ky have an average age of 3164 years (median = 3108 years, std = 655 years). But for cores with sedimentation rates of 10–20 cm/ky the average ventilation age decreases to 2705 years (median = 2627 years, std = 779 years). And for cores with sediment accumulation rates above 20 cm/ky the average ventilation age is 2449 years (median = 2510 years, std = 280 years), significantly lower than estimates from lower sedimentation rate cores. Because of the very large variance in each subpopulation, a student t-test was used to evaluate whether there are statistically distinct populations among the glacial estimates. Estimates from cores with sedimentation rates below 10 cm/ky were separated from cores with higher sedimentation rates. The t-score for these two populations is 4.39 with 42 degrees of freedom. This value is well above the null hypothesis at the 95% confidence level of 2.00. Hence, the two populations are statistically distinct. The estimates from lower sedimentation rates cores are clearly old-biased.

The large variance observed in the lower sedimentation rate cores is likely due to bioturbation that mixed older benthic specimens into the LGM samples. If the mean ventilation age estimate from cores with the higher sedimentation rates is a better reflection of the true ventilation age of the deep glacial Pacific it would imply that Pacific bottom waters were only ~200–300 years older than the modern, not 1000 years older as Rafter et al. argue. Even so, the variance in the higher sediment accumulation rate cores is also large, particularly in the LGM population of samples where the total number of samples within the LGM population is small. Therefore, the true LGM mean ventilation age must lay somewhere within the wide range of estimated values. The large variance in the current compilation of glacial ventilation age estimates limits our ability to pin down the true ventilation age offset to better than several hundred years.

The third observation made from an evaluation of the available estimates is how ventilation ages vary as a function of water depth. Of the available records from the LGM only one core is from depths below 4000 m. The ventilation rate from that core is 2339 years (Fig. 5). If that value is correct, there would be virtually no difference between the ventilation age of the abyssal Pacific in the LGM and modern ocean. And of the six cores with sedimentation rates of >20 cm/ky, none occur below 3000 m in the Pacific. These higher deposition rate cores are from 2700 to 2800 m (Fig. 5). Consequently, the representation of ventilation rates for the LGM abyssal Pacific is heavily weighted to cores with sediment accumulation rates below 15 cm/ky and from water depths shallower than 3000 m.

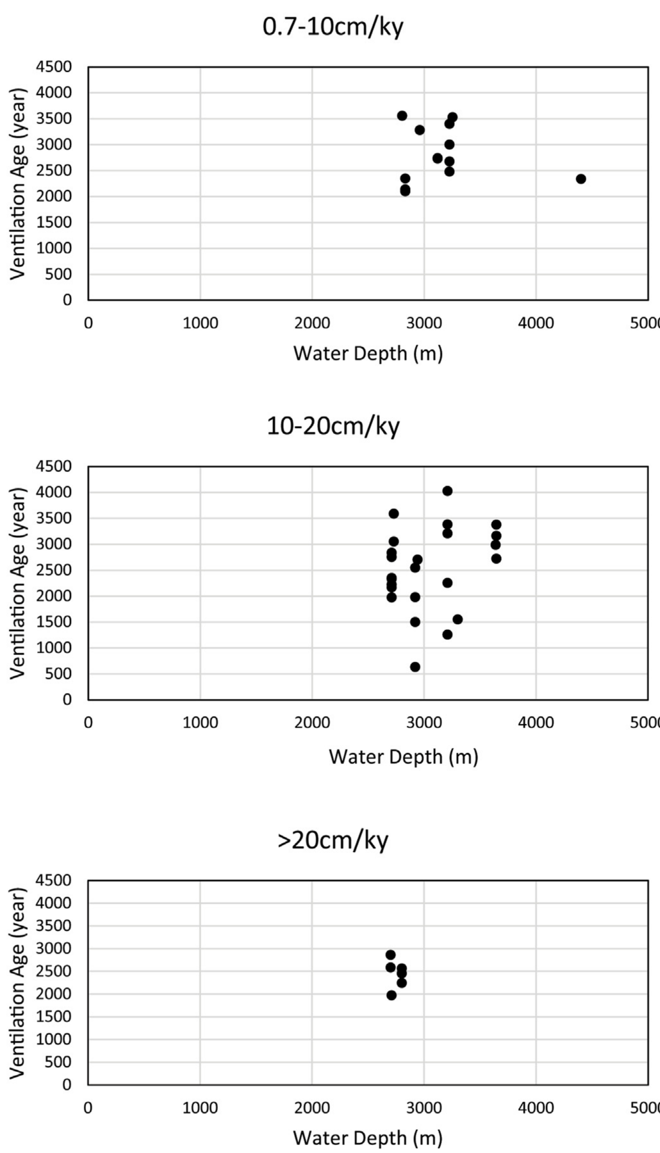

Fig. 5. Plots of ventilation age from the Rafter et al. (2022) compilation filtered by sediment accumulation rate and plotted as a function of water depth.

3.2. Bioturbation biasing

The effects of bioturbation that influence the variance seen in the ventilation age estimates are significant and particularly apparent in cores with sediment accumulation rates of less than 10–15 cm/ky and for cores that may have experienced varying levels of dissolution (Barker et al., 2007; Broecker et al., 1984; Lougheed et al., 2018). This is exacerbated when working with rare or low abundant epibenthic foraminifera from deep sea sediments. Searching for and finding enough benthic foraminifera to combine in a sample large enough (typically around 3–5 mg) for a conventional (multispecimen) radiocarbon age measurement introduces age bias (both old and young). Even in cores where sediment accumulation rates are higher there can be anomalous intervals where bioturbation has disrupted the stratigraphic continuity of radiocarbon ages (Stott, 2020). Hence, when trying to resolve oceanographic variables such as ventilaton age using ^{14}C ages from benthic foraminifera it is crucial to focus on cores with high accumulation rates and this means working with cores near continental margins. Unfortunately, this also means that much of the open ocean cannot be relied upon to provide unbiased estimates unless it can be shown that bioturbation has not mixed older and younger specimens together.

The potential implications of a much older abyssal ventilation ages in the Pacific should prompt a concerted effort to increase the number of ^{14}C ventilation age estimates from high deposition rate environments around the North Pacific. And the new gas ion source method for ^{14}C dating provides an opportunity to evaluate the effects of bioturbation by analyzing individual shells within a sample (Fagault et al., 2019). In this way cores can be screened for their suitability.

4. Conclusions

There exists large variance among LGM ventilation age estimates for the deep North Pacific. Of 42 current estimates for the LGM from water depths greater than 2700 m 11 are from cores that have very low sediment accumulation rates and exhibit ventilation ages that are 600–700 years older than those with sediment accumulation rates greater than 20 cm/ky. It is clear that among the wide range of ventilation ages for the LGM, many are simply wrong and those that estimate ventilation ages 3000 years and greater are highly suspect because if those ages were real, the deep Pacific would have been effectively anoxic, which is not the case. Combining wrong ventilation ages in an averaging scheme makes the average less accurate, not more accurate. Given the state of current estimates, there is no basis to conclude that the abyssal Pacific was more than a 200–300 hundred years older during the last glacial. And because preformed reservoir ages in the Southern Ocean were likely older during the LGM, the data currently available cannot be used to argue that ocean dynamics were fundamentally different or that there was greater accumulation of respired CO_2 in the deep Pacific during the LGM. Nonetheless, the potential importance of validating much older ventilation ages in the glacial Pacific, a concerted effort is needed to obtain data from high sediment accumulation rates sites around the North Pacific.

Author contribution

Lowell Stott: Designed the study, conducted the study and wrote the manuscript describing the results and findings.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data have been published and available

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