

1 **Geometry of the Meridional Overturning Circulation at the Last Glacial**

2 **Maximum**

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ABSTRACT

Understanding the contribution of ocean circulation to glacial-interglacial climate change is a major focus of paleoceanography. Specifically, many have tried to determine whether the volumes and depths of Antarctic- and North Atlantic-sourced waters in the deep ocean changed at the Last Glacial Maximum (LGM, ~22-18 kyr BP) when atmospheric pCO₂ concentrations were 100 ppm lower than the preindustrial. Measurements of sedimentary geochemical proxies are the primary way that these deep ocean structural changes have been reconstructed. However, the main proxies used to reconstruct LGM Atlantic water mass geometry provide conflicting results as to whether North Atlantic-sourced waters shoaled during the LGM. Despite this, a number of idealized modeling studies have been advanced to describe the physical processes resulting in shoaled North Atlantic waters. This review aims to critically assess the approaches used to determine LGM Atlantic circulation geometry and lay out best practices for future work. We first compile existing proxy data and paleoclimate model output to deduce the processes responsible for setting the ocean distributions of geochemical proxies in the LGM Atlantic Ocean. We highlight how small-scale mixing processes in the ocean interior can decouple tracer distributions from the large-scale circulation, complicating the straightforward interpretation of geochemical tracers as proxies for water mass structure. Finally, we outline promising paths toward ascertaining the LGM circulation structure more clearly and deeply.

³⁰ **1. Introduction**

³¹ The global ocean's overturning circulation joins the surface to the deep, transports large amounts
³² of heat around the globe, and regulates ocean carbon uptake and release. The overturning circulation
³³ contributes approximately 1/2 to 1/3 of the global equator to pole heat transport (Talley 2003),
³⁴ and the deep ocean contains roughly 60 times more carbon than the atmosphere (Sigman and
³⁵ Boyle 2000). As a result, the overturning circulation plays a primary role in global climate,
³⁶ both today and over glacial-interglacial cycles of the past (Adkins 2013; Sigman et al. 2010,
³⁷ 2020). While we can observe the modern ocean to understand how circulation impacts global
³⁸ climate, our understanding of past ocean circulation changes relies on geochemical proxy data.
³⁹ It is therefore crucial to understand how tracer distributions record information about the ocean
⁴⁰ circulation structure, and to determine how the effects of small-scale processes might complicate
⁴¹ our interpretations of these tracer distributions.

⁴² The modern ocean is proposed to have “figure-eight” circulation structure (Talley 2013). While
⁴³ the figure-eight is admittedly a simplification of the complex pathways subsurface water masses
⁴⁴ take in the Atlantic (Bower et al. 2019), we find it to be a useful starting point when considering
⁴⁵ possible circulation changes in the geologic past. North Atlantic Deep Water (NADW) is formed
⁴⁶ via deep convection in the Nordic, Irminger, and Labrador Seas (Johnson et al. 2019; Bower et al.
⁴⁷ 2019) and flows southward through the Atlantic basin. When it reaches the Southern Ocean, this
⁴⁸ water, now mixed with other water masses and called Lower Circumpolar Deep Water (LCDW),
⁴⁹ upwells as it flows around the Southern Ocean within the Antarctic Circumpolar Current (ACC)
⁵⁰ (Tamsitt et al. 2017, 2018), moves southward, and eventually reaches the continental shelves of the
⁵¹ Weddell and Ross Seas (Figure 1A). Here LCDW is densified by cooling and brine rejection, and
⁵² sinks to form Antarctic Bottom Water (AABW), which flows into the Atlantic, Pacific, and Indian

53 ocean basins. There, the downward diffusion of heat, which is aided by enhanced mixing over
54 rough topography (Polzin et al. 1997; Waterhouse et al. 2014), causes AABW to upwell across
55 isopycnals. The AABW that flows into the Atlantic upwells back into NADW, but the AABW that
56 flows into the Pacific and Indian oceans can upwell further to form Indian and Pacific Deep Water
57 (IDW/PDW). This water is sufficiently light, that when it returns to the Southern Ocean, now called
58 Upper Circumpolar Deep Water (UCDW), it upwells in a region of the Southern Ocean where
59 it becomes less dense due to warming and sea ice melt freshening, thus allowing the meridional
60 overturning circulation to close via northward transport of surface and intermediate waters in the
61 Atlantic (Figure 1A&C).

62 In the surface ocean, the process of primary production converts inorganic carbon into organic
63 matter. When this organic matter sinks and is regenerated back to dissolved inorganic carbon via
64 respiration, it is sequestered in the deep ocean, a process known as the biological pump. The global
65 overturning circulation operates on timescales of $O(1000)$ years (Stuiver et al. 1983), providing
66 a mechanism for deeply-regenerated CO₂ to be isolated from the atmosphere for long timescales.
67 Therefore through changes in overturning circulation, the deep ocean is thought to exert a strong
68 influence on the pCO₂ of the atmosphere and thus global temperatures. As described above,
69 the North Atlantic and the Southern Ocean are the only two places in the global ocean where
70 deep waters are formed. It is generally thought that changes in both the physical overturning
71 circulation and the biological pump are necessary to achieve full glacial-interglacial atmospheric
72 pCO₂ changes (Sarmiento and Toggweiler 1984; Siegenthaler and Wenk 1984; Knox and McElroy
73 1984; Toggweiler 1999; Watson and Naveira Garabato 2006; Sigman et al. 2010; Skinner et al.
74 2010), although a recent study challenges whether circulation changes are needed (Khatiwala et al.
75 2019).

76 In addition to changes in the overturning circulation rate (see e.g. Kwon et al. 2012), changes in
77 ocean overturning circulation geometry may also contribute to deep ocean carbon sequestration.
78 Our understanding of water mass structure during the Last Glacial Maximum (LGM) is largely
79 based on meridional sections of chemical tracers with distinct values in Northern- and Southern-
80 sourced deep water endmembers (Figure 1B). Based on these reconstructions, some have suggested
81 that the Last Glacial Maximum (LGM, ~22–18 kyr BP) ocean had a two-cell circulation structure,
82 with greater separation between the upper and lower cells compared with the modern ocean
83 circulation (Curry and Oppo 2005; Lund et al. 2011; Ferrari et al. 2014). This structure could have
84 allowed for longer deep ocean residence times and more carbon sequestration in the glacial ocean
85 (Burke et al. 2015; Skinner et al. 2017), and it could have contributed a substantial portion of the
86 documented atmospheric pCO₂ draw-down at the LGM. However, recent analyses using different
87 paleocean circulation tracers suggest much more modest changes in water mass distributions (Howe
88 et al. 2016; Poppelman et al. 2020), challenging the means by which the glacial deep ocean
89 contributed to atmospheric pCO₂ draw-down. In order to fully understand the role of the ocean in
90 glacial-interglacial climate change, it is important to understand these apparent discrepancies in the
91 interpretation of paleoproxy measurements and to determine the overturning circulation structure
92 at the LGM.

93 Ocean mixing plays a first-order role in determining ocean circulation structure, and it also
94 directly impacts ocean tracer distributions. Recent work suggests that the strength of diapycnal
95 mixing, which moves tracers across constant density surfaces, and the strength of isopycnal mixing,
96 which moves tracers along constant density surfaces, may have been different at the LGM (Wilmes
97 et al. 2019; Jones and Abernathey 2019). Ocean stratification also likely changed at the LGM,
98 influencing the strength of vertical transport by diapycnal mixing. Temporal changes in mixing

⁹⁹ strength and spatial heterogeneity in ocean mixing significantly complicate the relationship between
¹⁰⁰ ocean circulation geometry and ocean tracer distributions, as explored in sections 2b and 4b.

¹⁰¹ Given the central role that deep ocean circulation changes play in many explanations for glacial-
¹⁰² interglacial climate change, it is not surprising that this subject has interested physical oceanogra-
¹⁰³ phers as well as paleoceanographers. Several modelling studies have sought to provide a physical
¹⁰⁴ basis for paleo observations that suggest the presence of a shoaled upper cell at the LGM (Curry
¹⁰⁵ and Oppo 2005; Galbraith and de Lavergne 2018), possibly driven by changes in Southern Ocean
¹⁰⁶ sea ice (Ferrari et al. 2014; Watson et al. 2015; Jansen and Nadeau 2016; Marzocchi and Jansen
¹⁰⁷ 2017; Sun et al. 2018; Nadeau et al. 2019; Baker et al. 2020; Sun et al. 2020), terrestrial ice inputs
¹⁰⁸ (Miller et al. 2012), and/or increased density stratification between the upper and lower cells (Lund
¹⁰⁹ et al. 2011; Jansen 2017). While these studies provide crucial assessments of the physical realism
¹¹⁰ of proposed glacial circulation structures, they are often difficult to compare with observations,
¹¹¹ because they focus on differences in the large scale circulation between the modern ocean and
¹¹² the LGM. We believe that faster progress will be made if physical oceanographers work together
¹¹³ with paleoceanographers to assess what circulation geometries are possible given constraints from
¹¹⁴ paleoproxy data: here we take new steps on that journey. We hope this paper can provide a stronger
¹¹⁵ physical intuition for paleoceanographers to apply as they use geochemical techniques to ascer-
¹¹⁶ tain the ocean circulation structure in the past, and increase understanding of paleoceanographic
¹¹⁷ concepts within the physical oceanographic community.

¹¹⁸ In this paper, we suggest that deep ocean mixing processes may exert critical controls on recon-
¹¹⁹ structed tracer distributions during the LGM, and outline alternative methods of utilizing tracer
¹²⁰ data to understand LGM circulation changes. In Section 2, we discuss the physical mechanisms
¹²¹ by which the overturning circulation could have shoaled and mixing could have changed at the
¹²² LGM, and in Section 3, we review the systematics of paleo proxies that are commonly used for

¹²³ reconstructing ocean circulation geometry. In Section 4, we discuss different LGM circulation
¹²⁴ scenarios that are physically-based and can explain the available proxy data. In section 5, we offer
¹²⁵ suggestions of fruitful new avenues of exploration, which we hope will clarify the geometry of the
¹²⁶ ocean circulation at the LGM.

¹²⁷ 2. Ocean circulation

¹²⁸ a. Possible shoaling of the MOC's upper cell

¹²⁹ Meridional transport in the Southern Ocean is created by the slight imbalance between two
¹³⁰ competing processes: wind-driven Ekman flow in the frictional surface and bottom boundary
¹³¹ layers, which acts to steepen isopycnal surfaces; and baroclinic eddies, which form in response
¹³² to steepened isopycnal surfaces and act to reduce isopycnal slopes (Marshall and Radko 2003;
¹³³ Marshall and Speer 2012). The resulting advective meridional transport by the residual flow
¹³⁴ is primarily oriented along isopycnals. Buoyancy fluxes at the surface of the Southern Ocean
¹³⁵ cause transport across isopycnals in the surface mixed layer. Water that upwells in a region of
¹³⁶ positive buoyancy flux moves northward at the surface, and water that upwells in a region of
¹³⁷ negative buoyancy flux moves southward at the surface, as shown in Figure 1A. Thus the pattern
¹³⁸ of Southern Ocean buoyancy fluxes impacts whether water moves northward or southward in the
¹³⁹ Southern Ocean, influencing the pathway of the MOC.

¹⁴⁰ The surface buoyancy flux comprises heat and freshwater components, which are exchanged
¹⁴¹ between the ocean and atmosphere and/or between the ocean and overlying sea ice or terrestrial
¹⁴² ice. Abernathey et al. (2016) and Pelichero et al. (2018) have demonstrated that water mass
¹⁴³ transformations south of the Polar Front are dominated by sea-ice-driven surface buoyancy fluxes.
¹⁴⁴ Water mass transformation into denser classes occurs in coastal polynyas around Antarctica, where

¹⁴⁵ sea-ice formation leads to buoyancy loss via brine rejection. As sea ice is redistributed by winds
¹⁴⁶ and currents, it eventually melts at a more northern latitude than it formed, leading to buoyancy
¹⁴⁷ gain and water mass transformation into lighter buoyancy classes (Saenko et al. (2003), and see
¹⁴⁸ red arrows in Figure 1A).

¹⁴⁹ Sea surface temperatures in the LGM Southern Ocean were lower (Ho et al. 2012) and sea-ice
¹⁵⁰ extended further north (Gersonde et al. 2005). Hence, the latitudinal position of the boundary
¹⁵¹ between positive and negative buoyancy fluxes probably moved northward at the LGM. Ferrari
¹⁵² et al. (2014) presented a theory that suggests that moving this boundary further north will shoal
¹⁵³ the isopycnals associated with this boundary. They argue that Southern Ocean isopycnal slopes s
¹⁵⁴ are approximately equal to:

$$s \simeq \frac{\tau_0}{\rho_0 f K}, \quad (1)$$

¹⁵⁵ where τ_0 is the time-mean zonal wind stress, ρ_0 is the surface reference density, K is the eddy
¹⁵⁶ transfer coefficient and f is the Coriolis parameter. Isopycnal surfaces are generally flat in the ocean
¹⁵⁷ basins to the north of the Southern Ocean. Hence, if the growth of Antarctic sea-ice pushes surface
¹⁵⁸ density contours northward, the isopycnals in the ocean interior associated with these contours will
¹⁵⁹ shoal if isopycnal slopes remain constant through time (see Ferrari et al. (2014) Figure 4).

¹⁶⁰ Ferrari et al. (2014) argued that this happened during the LGM, and that isopycnals associated
¹⁶¹ with buoyancy gain were shoaled above 2000 m depth. Vertical ocean mixing is weaker above
¹⁶² 2000 m and stronger below 2000m due to the presence of rough topography at depth (Ledwell et al.
¹⁶³ 2000). Ferrari et al. (2014) suggest that diapycnal transport across the isopycnal that separates
¹⁶⁴ positive and negative buoyancy flux regions at the surface of the Southern Ocean would have been
¹⁶⁵ reduced, causing the upper cell of the MOC to separate from the lower cell of the MOC. Because of
¹⁶⁶ its clarity, the Ferrari et al. (2014) paper has been widely read and cited in the paleo-oceanographic
¹⁶⁷ community.

Recent work by Sun et al. (2018); Nadeau and Jansen (2020) and Baker et al. (2021) has shown that the Ferrari et al. (2014) hypothesis is an incomplete view of the ocean dynamics at the LGM, because it focuses on the sign of surface buoyancy forcing as the primary control on ocean stratification, and does not consider the effects of subsurface Southern Ocean mixing, the effects of changes in global diapycnal mixing or how changes in the magnitude of Southern Ocean buoyancy loss might further impact the stratification. The AMOC is comprised of two components: an adiabatic component, which upwells in the Southern Ocean and is directly driven by the strong zonal winds there (loop a in Figure 1C); and a diabatic component, in which water upwells across isopycnals, primarily driven by small-scale vertical mixing in the Indian and Pacific oceans (loop b in Figure 1C; Jones and Cessi (2016); Ferrari et al. (2017)). Sun et al. (2018) shows that diabatic upwelling in the Southern Ocean is also important. The depth of the adiabatic component of the AMOC is directly linked to the outcrop latitude of the isopycnal that separates positive and negative buoyancy flux regions at the surface of the Southern Ocean. The diabatic component of the AMOC usually extends deeper into the water column than the adiabatic component, and its strength and depth are set by multiple factors, including the strength of cross-isopycnal upwelling due to small-scale mixing and the density of AABW formed in the Southern Ocean (Nadeau and Jansen 2020).

Nadeau and Jansen (2020) and Baker et al. (2021) show that increasing the strength of diapycnal mixing deepens the upper cell of the overturning circulation. An increase in the strength of diapycnal mixing at the LGM seems likely and is discussed further in section 2b. Jansen and Nadeau (2016); Nadeau et al. (2019); Nadeau and Jansen (2020) and Baker et al. (2021) found that increasing the buoyancy loss around Antarctica (due to an increase in sea-ice formation at the LGM) increases the stratification, which inhibits this cross-isopycnal transport. This reduces the AMOC transport due to the diabatic component of the circulation, leading to shoaling of the

¹⁹² AMOC. Taken together, this recent work demonstrates that multiple factors are involved in setting
¹⁹³ the depth of the AMOC, and calls into question the earlier consensus view that sea-ice extent is the
¹⁹⁴ main control on AMOC depth.

¹⁹⁵ *b. Possible changes to ocean mixing*

¹⁹⁶ While much attention has been paid to large differences in circulation geometry between the
¹⁹⁷ modern and LGM oceans, significant differences in small-scale ocean processes like mixing are
¹⁹⁸ also probable in some key locations. Most notably, a 120 to 130 m drop in sea level at the LGM
¹⁹⁹ may have caused an increase in tidal dissipation in the deep ocean, particularly in the North Atlantic
²⁰⁰ (Arbic et al. 2004; Egbert et al. 2004; Griffiths and Peltier 2009; Green 2010; Schmittner et al.
²⁰¹ 2015; Wilmes et al. 2019). Vertical diffusivity is controlled by both tidal energy dissipation and
²⁰² by stratification as follows:

$$\kappa_z = \Gamma \frac{\epsilon}{N^2} \quad \text{where} \quad N = \sqrt{\frac{-g}{\rho_0} \frac{\partial \rho}{\partial z}}, \quad (2)$$

²⁰³ where κ_z is the vertical diffusivity, Γ is the mixing efficiency, ϵ is the rate of tidal energy dissipation
²⁰⁴ and N^2 is the buoyancy frequency, which is a measure of ocean stratification. In idealized models,
²⁰⁵ higher vertical diffusivities lead to deepening of the upper cell of the AMOC, particularly in the
²⁰⁶ North Atlantic (Baker et al. 2021). For a constant abyssal ocean stratification, increased tidal
²⁰⁷ dissipation at the LGM would lead to larger vertical diffusivities in the abyssal ocean. Increased
²⁰⁸ ocean stratification in the deep ocean may have partially compensated for the increase in tidal
²⁰⁹ energy dissipation, leading to a more modest increase in the vertical diffusivity of the deep ocean.
²¹⁰ On the other hand, increased tidal mixing may itself decrease the ocean stratification. Wilmes
²¹¹ et al. (2019) tested a range of ocean stratifications from Muglia et al. (2018), including some
²¹² scenarios with saltier AABW. They found the buoyancy frequency was relatively insensitive to

213 AABW salinity, concluding that the vertical diffusivity of the abyssal Atlantic was probably larger
214 at the LGM.

215 Larger vertical mixing probably causes more exchange between the upper and abyssal cells of
216 the overturning circulation: this is explored further in section 4b. Many Paleoclimate Modelling
217 Intercomparison Project phase 3 and 4 (PMIP3&4) models parameterize tidal mixing using a
218 sensible parameterization like St. Laurent et al. (2002). These models often use high resolution
219 tidal models to generate a mixing distribution, which is then applied to the ocean in the fully
220 coupled production run of the climate model.

221 Recent work by Ferrari et al. (2016) and Callies and Ferrari (2018) highlights that when vertical
222 mixing increases towards the bottom of the ocean, this can cause downward velocities in the interior,
223 with upward velocities along the sloping boundaries of the ocean. This sort of vertical mixing
224 profile may lead to larger diapycnal tracer transport into the deep ocean (Jones and Abernathay
225 2021). This new paradigm highlights the role of lateral fluxes in bringing water close to rough
226 topography, where diapycnal mixing is strongest (Mashayek et al. 2017). The complex relationship
227 between the large scale flow and patterns of small-scale mixing may complicate the interpretation of
228 paleotracer estimates, because these are only available for water masses that are close to topography.

229 An additional (though smaller) change in ocean mixing might have been caused by changes to
230 the surface wind stress over the Southern Ocean. Evidence for such a change is mixed (Stuut
231 et al. 2002; Kim et al. 2003; Kohfeld et al. 2013; Gottschalk et al. 2019). Stronger surface winds
232 drive higher eddy kinetic energy in the upper ocean, which is associated with larger isopycnal
233 mixing (Abernathy and Ferreira 2015). Higher isopycnal mixing rates in the Southern Ocean
234 are associated with more southern-sourced water reaching the deep ocean, particularly in the deep
235 Pacific (Jones and Abernathy 2019). Isopycnal mixing may be important for explaining deep ocean
236 tracer distributions at the LGM (Burke et al. 2015). This effect is unlikely to be well-represented

237 in PMIP3 and PMIP4 models: detailed study of isopycnal mixing is in its early stages, so many
 238 paleoclimate model simulations still specify an isopycnal mixing field that is constant in time (see
 239 e.g. Rackow et al. 2019; Lin et al. 2020; Chassignet et al. 2020), despite findings from physical
 240 oceanographers that isopycnal mixing rates are likely not constant (e.g. Gent 2016)

241 **3. Background on proxy systematics**

242 In lieu of direct observations of mixing rates and overturning streamfunctions, chemical and
 243 paleoceanographers turn towards observations of tracers. Chemical species in the ocean are
 244 sensitive to the physical transport phenomena described in the preceding sections, as well as
 245 biogeochemical transformations that can add and remove these tracers from a given water parcel
 246 as it flows in the ocean.

247 A simple physical and biogeochemical equation describes the time rate of change of a chemical
 248 species at a given location: the conservation equation,

$$\frac{\partial C}{\partial t} = -\mathbf{U} \cdot \nabla C + \nabla \cdot (\mathbf{D} \cdot \nabla C) + J(C) \quad (3)$$

249 The first term in this equation describes the change in concentration due to advective flux divergence
 250 (\mathbf{U}) acting on the tracer concentration C , the second term represents the flux divergence due to
 251 diffusive processes (\mathbf{D}), while the third term $J(C)$ represents non-conservative biogeochemical
 252 sources and sinks. In this paper, where we are primarily interested in the meridional and vertical
 253 changes in tracer concentrations, we consider the two-dimensional form of this equation between
 254 two isopycnal surfaces ζ_1 and ζ_2 where $\zeta_2 - \zeta_1 = h$ is the distance in metres between the two
 255 isopycnals:

$$\underbrace{\frac{\partial(hC)}{\partial \tilde{t}}}_{\text{Tendency}} = \underbrace{-\frac{\partial(VC)}{\partial \tilde{y}}}_{\text{(along-)isopycnal advection}} - \underbrace{[\Omega C]_{\zeta_1}^{\zeta_2}}_{\text{Diapycnal advection}} + \underbrace{\frac{\partial}{\partial \tilde{y}} \left(K_h h \frac{\partial C}{\partial \tilde{y}} \right)}_{\text{along-isopycnal diffusive transport}} + \underbrace{\left[K_z \frac{\partial C}{\partial z} \right]_{\zeta_1}^{\zeta_2}}_{\text{diapycnal diffusive transport}} + \underbrace{\int_{\zeta_1}^{\zeta_2} J(C) dz}_{\text{source or sink}}, \quad (4)$$

where $(\tilde{x}, \tilde{y}, \tilde{b}, \tilde{t})$ are buoyancy coordinates, as described in (Young 2012). This equation describes the effects of isopycnal advection by the meridional velocity, integrated between ζ_1 and ζ_2 (V , units m^2/s); diapycnal advection by the diapycnal velocity (Ω , units m/s); isopycnal diffusion by the isopycnal diffusivity (K_h , units m^2/s); vertical diffusion by the vertical diffusivity (K_z , units m^2/s); and sources and sinks due to nonconservative fluxes ($J(C)$, units $[C]/s$) on a tracer C . These are averaged in the zonal direction over the whole ocean basin. The meridional volume transport (V), the isopycnal diffusivity (K_h), and the tracer concentrations (C) are assumed to be vertically uniform between the two isopycnals. A simple explanation of this coordinate system, as well as a proof of the equation above, is given in the supplementary material. Even at steady state (i.e. when the tendency term is zero), five different processes act to set the tracer concentration at any point, so isopycnal advection may not always be the most important factor for determining deep ocean tracer concentrations. This two-dimensional simplification also neglects zonal advective and diffusive fluxes, which may be important in the real ocean.

Tracers that have either no subsurface biogeochemical sources or sinks (e.g. salinity), or are corrected for their biogeochemical transformations via stoichiometric relations to other tracers (e.g. PO_4^* , Broecker et al. 1998) are considered to be conservative (i.e., the fifth term in equation 5 equals zero). When two water masses with different initial concentrations of a conservative tracer undergo binary mixing, the tracer concentration of the mixture reflects the proportional contribution from each water mass. Thus, provided that the initial, or “endmember”, tracer concentration for water masses are known, measurements of that tracer can be used to quantify the relative proportions of the two source water masses, for example NADW and AABW. This approach of course relies on the assumption that the deep Atlantic is mostly made up of these two water masses, and that there aren’t additional water masses setting the tracer budget of the deep Atlantic.

279 A wide variety of proxies have been used to study the the overturning circulation in the geologic
280 past, but conservative tracers are relatively rare in paleoceanography. Here we focus on three
281 tracers, with varying degrees and modes of conservative-ness, that have been used to reconstruct
282 water mass geometry of the deep Atlantic Ocean since the LGM: stable carbon isotopes of dissolved
283 inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$), the air-sea exchange component of carbon isotopes ($\delta^{13}\text{C}_{\text{AS}}$), and the
284 seawater neodymium isotopic composition (ε_{Nd}) (schematically introduced in Figure 1B). We
285 recognize that other tracers such as radiocarbon (^{14}C) (e.g., Stuiver et al. 1983; Key et al. 2004)
286 and $^{231}\text{Pa}/^{230}\text{Th}$ (e.g., McManus et al. 2004; Gherardi et al. 2009; Lippold et al. 2012) have also
287 been extensively used to examine ocean circulation in the past, but as these tracers are typically
288 interpreted to contain more information about circulation strength rather than geometry, we have
289 omitted them from this review. An interesting recent study suggests that radiocarbon distributions
290 may be more sensitive to AMOC depth than previously thought (Muglia and Schmittner 2021).
291 This is a significant departure from the traditional interpretation and warrants further investigation.

292 *a. Stable Carbon Isotopes*

293 Because ^{13}C is marginally heavier than ^{12}C , chemical and physical processes act on the two
294 isotopes at slightly different rates. The ratio of ^{13}C to ^{12}C of dissolved inorganic carbon (DIC) in
295 seawater, which is expressed in delta notation ($\delta^{13}\text{C}_{\text{DIC}}$) as the parts per thousand variation with
296 respect to a standard, is altered by photosynthesis, respiration of organic matter, and air-sea gas
297 exchange. Below we describe how each of these processes affect this ratio.

298 1) $\delta^{13}\text{C}$ AND ORGANIC MATTER

299 Phytoplankton preferentially take up ^{12}C . Thus, as phytoplankton photosynthesize and grow, they
300 cause nutrients to become more completely utilized at the sea surface, and cause the remaining

301 $\delta^{13}\text{C}_{\text{DIC}}$ of surface seawater to become heavier. Surface waters subducting into the interior with
302 more complete nutrient utilization will have heavier $\delta^{13}\text{C}_{\text{DIC}}$ at the time of subduction, while waters
303 subducting with high initial nutrient concentrations will have lighter $\delta^{13}\text{C}_{\text{DIC}}$. As subsurface waters
304 age, they gain DIC via the remineralization of particulate and dissolved organic carbon, both of
305 which are isotopically light. Thus, the $\delta^{13}\text{C}_{\text{DIC}}$ of a water parcel decreases with ventilation age, as
306 remineralization occurs during aging.

307 In the modern Atlantic, there is a roughly 1‰ difference between AABW and NADW. AABW
308 has an initial $\delta^{13}\text{C}_{\text{DIC}}$ value of ~0.4‰ and NADW has $\delta^{13}\text{C}_{\text{DIC}}$ of 1.3‰ (Figure 2A). Because
309 of the relatively fast circulation timescales of the deep Atlantic and low carbon remineralization
310 fluxes in deep waters, a binary mixing formulation can be used to determine the fraction of NADW
311 (f_{NADW}) present using $\delta^{13}\text{C}_{\text{DIC}}$ measurements:

$$f_{\text{NADW}} = \frac{\delta^{13}\text{C}_{\text{DIC}}^{\text{meas}} - \delta^{13}\text{C}_{\text{DIC}}^{\text{south}}}{\delta^{13}\text{C}_{\text{DIC}}^{\text{north}} - \delta^{13}\text{C}_{\text{DIC}}^{\text{south}}}, \quad (5)$$

312 where the superscript “meas” indicates the measured $\delta^{13}\text{C}_{\text{DIC}}$ of a particular water sample, and
313 the superscripts “north” and “south” refer to the endmember $\delta^{13}\text{C}_{\text{DIC}}$ values. This equation is a
314 slight simplification, as it neglects DIC concentration differences between water masses. However,
315 since DIC concentration differences are much smaller than $\delta^{13}\text{C}_{\text{DIC}}$ differences, this simplification
316 is reasonable when considering mixing of NADW and AABW.

317 2) $\delta^{13}\text{C}$ AND AIR-SEA EXCHANGE

318 Carbon isotopes in seawater are also affected by air-sea gas exchange. There are three air-sea
319 exchange processes of importance: 1) temperature-dependent equilibrium fractionation (heavier
320 $\delta^{13}\text{C}_{\text{DIC}}$ at colder temperatures), 2) fractionation due to the degree of air-sea equilibration (heavier
321 $\delta^{13}\text{C}_{\text{DIC}}$ for more complete equilibration), and 3) net gain/loss of DIC due to gas exchange (heavier

³²² $\delta^{13}\text{C}_{\text{DIC}}$ for net DIC loss) (Lynch-Stieglitz et al. 1995). These combined effects alter the $\delta^{13}\text{C}_{\text{DIC}}$
³²³ composition during air-sea interaction.

³²⁴ Phosphate (PO_4) is a key nutrient required for biological activity, and it can thus be used to
³²⁵ isolate the biological effects on $\delta^{13}\text{C}_{\text{DIC}}$ from the physical effects. The slope of the modern ocean
³²⁶ biological $\delta^{13}\text{C}_{\text{DIC}}\text{-PO}_4$ relationship has a value of -1.1 , which is dictated by the photosynthetic
³²⁷ fractionation of carbon isotopes, the ratio of carbon to phosphorus in organic matter, and the
³²⁸ mean ocean concentration of DIC (see Supplementary Text). The intercept is chosen such that the
³²⁹ physical air-sea component of $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{AS}}$) in the deep Indo-Pacific has a value of 0 .

$$\delta^{13}\text{C}_{\text{AS,modern}} = \delta^{13}\text{C}_{\text{DIC}} + 1.1[\text{PO}_4] - 2.75 \quad (6)$$

³³⁰ This equation corrects the measured $\delta^{13}\text{C}$ value for biological effects, therefore leaving an isotope
³³¹ signature that represents only physical processes (temperature, air-sea equilibration, and net DIC
³³² exchange).

³³³ The deep Atlantic Ocean is characterized by two distinct $\delta^{13}\text{C}_{\text{AS}}$ endmembers (Figures 2B and
³³⁴ Supplemental Figure 1A). NADW has $\delta^{13}\text{C}_{\text{AS}} = -0.5\text{\textperthousand}$, and AABW has $\delta^{13}\text{C}_{\text{AS}} = 0.4\text{--}0.5\text{\textperthousand}$ (Eide
³³⁵ et al. 2017; Lynch-Stieglitz et al. 1995; Mackensen 2012). These endmember $\delta^{13}\text{C}_{\text{AS}}$ values are
³³⁶ driven by differences in air-sea equilibration temperature (warmer for NADW, colder for AABW)
³³⁷ and CO_2 uptake (invasion of atmospheric CO_2 in the North Atlantic, evasion of CO_2 from the
³³⁸ Southern Ocean). To reconstruct $\delta^{13}\text{C}_{\text{AS}}$, paleoceanographers must use proxy measurements for
³³⁹ past ocean PO_4 . The micronutrient Cd bears striking similarity to PO_4 (Elderfield and Rickaby
³⁴⁰ 2000; Boyle 1988; Middag et al. 2018), and the modern relationship between these two species
³⁴¹ can be used to reconstruct PO_4 in the past, where past ocean Cd is calculated using measurements
³⁴² of the Cd/Ca ratio in foraminifera (see Supplementary Text for additional detail). Calculations of

³⁴³ past ocean $\delta^{13}\text{C}_{\text{AS}}$ also must take into account changes in the mean ocean [DIC] and $\delta^{13}\text{C}$, and
³⁴⁴ photosynthetic fractionation.

³⁴⁵ Assuming known changes in mean ocean terms, $\delta^{13}\text{C}_{\text{AS}}$ values should be a conservative tracer in
³⁴⁶ the ocean interior (Charles et al. 1993; Lynch-Stieglitz and Fairbanks 1994). Similarly to $\delta^{13}\text{C}_{\text{DIC}}$,
³⁴⁷ the distinct values of $\delta^{13}\text{C}_{\text{AS}}$ between NADW and AABW allow for a binary mixing formulation
³⁴⁸ to determine the fraction of NADW present in a water parcel:

$$f_{\text{NADW}} = \frac{\delta^{13}\text{C}_{\text{AS}}^{\text{meas}} - \delta^{13}\text{C}_{\text{AS}}^{\text{south}}}{\delta^{13}\text{C}_{\text{AS}}^{\text{north}} - \delta^{13}\text{C}_{\text{AS}}^{\text{south}}}, \quad (7)$$

³⁴⁹ where the superscript “meas” indicates the calculated $\delta^{13}\text{C}_{\text{AS}}$ value from the measured $\delta^{13}\text{C}_{\text{DIC}}$ and
³⁵⁰ $[\text{PO}_4]$ of a particular water sample (using Equation 6 or its glacial equivalent), and the superscripts
³⁵¹ “north” and “south” refer to the endmember $\delta^{13}\text{C}_{\text{AS}}$ values.

³⁵² b. Authigenic Neodymium Isotopes (εNd)

³⁵³ Another commonly applied tracer for reconstructing water mass changes in the geologic past
³⁵⁴ is the neodymium isotope ratio εNd , the ratio of ^{143}Nd to ^{144}Nd as the parts per ten thousand
³⁵⁵ variation with respect to the composition of the chondritic reservoir (Jacobsen and Wasserburg
³⁵⁶ 1980). Seawater acquires neodymium from the input of lithogenic material, either at the surface,
³⁵⁷ through dust deposition and fluvial input (Goldstein and Hemming 2003; Siddall et al. 2008), or at
³⁵⁸ the seafloor by benthic fluxes of Nd out of sedimentary porewaters (e.g. Haley et al. 2017; Jeandel
³⁵⁹ 2016). Away from regions of external Nd input or exchange, the seawater isotopic composition is
³⁶⁰ largely conserved. Thus, the εNd value of seawater reflects the εNd of the local source rocks which
³⁶¹ deliver this Nd to the ocean and mixing between water masses with different εNd compositions.
³⁶² Neodymium isotope ratios are set by decay of ^{147}Sm to ^{143}Nd with a half-life of 106 Ga, and
³⁶³ therefore reflect the initial Sm/Nd ratio of a rock and the amount of time it has spent in the

³⁶⁴ continental crust. Because ε_{Nd} varies significantly between old, continental rocks found around
³⁶⁵ the North Atlantic and young, volcanic rocks found around the North Pacific, individual basins and
³⁶⁶ water masses have unique ε_{Nd} signatures reflecting their inputs, and relative proportions of waters
³⁶⁷ from Pacific and Atlantic ε_{Nd} endmembers (e.g. Goldstein and Hemming 2003, and references
³⁶⁸ therein).

³⁶⁹ In the modern Atlantic Ocean, NADW has an ε_{Nd} of about -13.5 (Lambelet et al. 2016), while
³⁷⁰ AABW has an ε_{Nd} of -8 (van de Flierdt et al. 2016) (Figure 2C). Unlike carbon isotopes and
³⁷¹ cadmium which are directly taken up into benthic foraminiferal calcite, deepwater ε_{Nd} is primarily
³⁷² recorded in authigenic sedimentary phases, such as ferromanganese coatings. This necessitates
³⁷³ that authigenic signals are fully separated from detrital signals (i.e. local continental input) when
³⁷⁴ sedimentary records are analyzed to reconstruct past ocean ε_{Nd} . In the past, the North Atlantic ε_{Nd}
³⁷⁵ endmember composition may have been affected by changes in the supply of continental material
³⁷⁶ to the ocean (Zhao et al. 2019), the strength or pathway of boundary currents, and/or changes in
³⁷⁷ the zonal location of deep-water formation. Deep water that passes through the Labrador Sea tends
³⁷⁸ to have more negative ε_{Nd} values than NADW that is formed in the GIN (Greenland, Iceland,
³⁷⁹ Norwegian) seas. Hence, a reduction in deep-water formation in the Labrador Sea, or a reduction
³⁸⁰ in NADW transit through the Labrador Sea, could lead to an increase in the northern endmember
³⁸¹ ε_{Nd} value. In the interior Atlantic, the ε_{Nd} values of NADW and AABW are modified partially
³⁸² by benthic Nd fluxes, but due to the advection-dominated circulation regime, these water masses
³⁸³ primarily mix conservatively (Haley et al. 2017; Du et al. 2020). Assuming conservative mixing,
³⁸⁴ the fraction of NADW can be calculated from Nd isotope measurements using the following binary
³⁸⁵ mixing equation (e.g. Howe et al. 2016):

$$f_{\text{NADW}} = \frac{R_S[\text{Nd}]_S - R_{\text{Meas}}[\text{Nd}]_S}{R_{\text{Meas}}([\text{Nd}]_N - [\text{Nd}]_S) - R_N[\text{Nd}]_N + R_S[\text{Nd}]_S}, \quad (8)$$

386 where R denotes the ε Nd value of an endmember or measurement and [Nd] is the Nd concentration
387 of an endmember, where subscripts “S” and “N” are “Southern-source” and “Northern-source”,
388 and “meas” is the measured value for a given sample consisting of a mixture of NADW and AABW.
389 There is no proxy for past ocean [Nd], so this is generally assumed to be constant at the modern
390 ocean values.

391 *c. Proxy preservation and fidelity*

392 In addition to the systematics of proxy behavior in seawater, it is also necessary to account
393 for alteration of proxy signals in microenvironments as they are recorded and/or after they are
394 incorporated into sediments and buried. Such processes are well-known to bias records and cause
395 them to deviate from bulk seawater. For $\delta^{13}\text{C}$, there are two common ways that this occurs:
396 either via the Mackensen Effect (Mackensen et al. 1993) wherein organic matter respiration at
397 the sediment-water interface decreases the $\delta^{13}\text{C}$ values recorded by benthic foraminifera within
398 that microenvironment relative to the surrounding seawater, or by vertical migration of benthic
399 foraminifera within the sediment column (Gottschalk et al. 2016), which also tends to bias recorded
400 values toward lower values relative to surrounding seawater (Schmittner et al. 2017). For $\delta^{13}\text{C}_{\text{AS}}$,
401 the same biases exist as for $\delta^{13}\text{C}$, but there may be additional complications arising from using
402 Cd/Ca ratios to reconstruct PO₄, which is sensitive to seawater saturation state with respect to calcite
403 and dissolution (Marchitto and Broecker 2006, and references therein). Finally, authigenic ε Nd
404 records can also be biased in either direction by overprinting within pore water microenvironments
405 (Blaser et al. 2019). This occurs when detrital material dissolves and then reprecipitates in an
406 authigenic phase.

⁴⁰⁷ In an attempt to overcome these issues and their possible spatial heterogeneity, in this paper we
⁴⁰⁸ compile all available data for the LGM Atlantic for each of these three proxies, without attempting
⁴⁰⁹ to filter the data for preservation issues.

⁴¹⁰ **4. Discussion**

⁴¹¹ If nonconservative fluxes are small or can be ignored, then physical transport by advection
⁴¹² and eddy diffusion govern the distribution of a tracer in the ocean interior. Tracers with this
⁴¹³ characteristic thus have their concentrations or isotope ratios controlled by admixture of water
⁴¹⁴ masses with different initial compositions, or endmembers. The ε_{Nd} and $\delta^{13}\text{C}_{\text{AS}}$ proxies are
⁴¹⁵ considered to be largely conservative in the deep Atlantic (Du et al. 2020; Haley et al. 2017; Lynch-
⁴¹⁶ Stieglitz et al. 1995; Oppo et al. 2018). Since these tracers have distinct values in subducting NADW
⁴¹⁷ and AABW (see next section), measuring their values downcore allows for the reconstruction of
⁴¹⁸ the fraction of those two water masses present at a given location, assuming binary mixing between
⁴¹⁹ NADW and AABW.

⁴²⁰ Application of these principles qualitatively (Duplessy et al. 1988; Curry and Oppo 2005) and
⁴²¹ quantitatively (Piotrowski et al. 2004; Howe et al. 2016; Pena and Goldstein 2014; Poppelmeier
⁴²² et al. 2020) is one of the primary ways that changes in water mass structure in the paleo Atlantic
⁴²³ Ocean has been reconstructed. The two most critical assumptions underlying the application of
⁴²⁴ these proxies are: 1) limited effects of non-conservative behavior of the tracer, and 2) accurate
⁴²⁵ knowledge of the NADW and AABW endmembers in the binary mixing equations.

⁴²⁶ We identify an additional complication in interpreting sections of paleoceanographic data in terms
⁴²⁷ of changing water mass structure: the effects of ocean mixing. Specifically, changes in vertical
⁴²⁸ mixing rates (the diapycnal diffusive transport term in Equation 5) may cause large changes in the
⁴²⁹ spatial distributions of tracers and only modest changes in overturning circulation outside the North

430 Atlantic. Below, we detail the conventional use of tracer sections to delineate Atlantic circulation
431 geometry, show how conservative tracers purely depend on circulation streamfunctions in PMIP
432 models, and outline paths forward to reconstruct paleo Atlantic water mass geometry that take into
433 account changes in ocean vertical mixing.

434 *a. Observational evidence*

435 Perhaps the most well-established evidence in support of shoaled NADW at the LGM has come
436 from comparing meridional sections of modern seawater $\delta^{13}\text{C}_{\text{DIC}}$ and LGM benthic foraminiferal
437 $\delta^{13}\text{C}$ (Duplessy et al. 1988; Curry and Oppo 2005; Oppo et al. 2018). These data show striking
438 differences in $\delta^{13}\text{C}$ distributions in the LGM compared to modern seawater (Figure 2D). Recon-
439 structed LGM data from the western Atlantic show deep waters with more depleted $\delta^{13}\text{C}$ values
440 that penetrate into the northern part of the basin and a 500–1000 m shoaling of $\delta^{13}\text{C}$ -enriched
441 water, generally interpreted to be the glacial version of NADW (often called glacial North Atlantic
442 Intermediate Water ‘GNAIW’) (Figure 2D).

443 More recently, some studies have challenged the interpretation that $\delta^{13}\text{C}$ changes at the LGM
444 are indicative of major water mass reorganizations, due to the non-conservative behavior of $\delta^{13}\text{C}$.
445 Gebbie (2014) used a steady-state model of the ocean circulation that takes into account both
446 modern seawater observations and paleoproxy data. His steady-state solution showed that while
447 the core of NADW shoaled during the LGM, the depth at which NADW and AABW were a 50-50
448 mixture remained unchanged. The apparent shoaling of the NADW could be explained by an
449 increase in the respired nutrient content of glacial NADW rather than a change in circulation.
450 Using the same modeling framework with additional data, Oppo et al. (2018) concluded that the
451 core of NADW shoaled by ~500 m at the LGM, with a strong reduction in the NADW fraction

⁴⁵² in the deepest North Atlantic. This is roughly half of what was suggested in earlier studies (e.g.
⁴⁵³ Curry and Oppo 2005; Lund et al. 2011).

⁴⁵⁴ Given the potential for changes in nutrient contents to confound the use of $\delta^{13}\text{C}$ as a conservative
⁴⁵⁵ tracer, other studies have turned to $\delta^{13}\text{C}_{\text{AS}}$, which corrects for the non-conservative remineralization
⁴⁵⁶ effects on $\delta^{13}\text{C}$ using Cd as a proxy for phosphate. Marchitto and Broecker (2006) compiled benthic
⁴⁵⁷ foraminiferal $\delta^{13}\text{C}$ and Cd/Ca measurements from the LGM Atlantic, finding very low $\delta^{13}\text{C}_{\text{AS}}$
⁴⁵⁸ values associated with glacial AABW penetrating into the deep North Atlantic. The authors also
⁴⁵⁹ argued for a shoaling of LGM NADW, based on observations of high $\delta^{13}\text{C}_{\text{AS}}$ from 1000–2000 m
⁴⁶⁰ throughout the Atlantic, but acknowledged that incomplete understanding of endmember $\delta^{13}\text{C}_{\text{AS}}$
⁴⁶¹ values for NADW, AABW, and AAIW hindered unique interpretation of this signal.

⁴⁶² Indeed, Gebbie (2014) and Oppo et al. (2018) included $\delta^{13}\text{C}_{\text{AS}}$ in their data-constrained steady-
⁴⁶³ state modeling efforts. They noted that since $\delta^{13}\text{C}_{\text{AS}}$ has fairly large errors (0.3‰), and the AAIW
⁴⁶⁴ and NADW endmembers seem to converge during the LGM towards 0, discriminating between
⁴⁶⁵ AAIW and NADW in the upper LGM Atlantic is difficult. Only the inclusion of new depth
⁴⁶⁶ transect $\delta^{13}\text{C}_{\text{AS}}$ data by Oppo et al. (2018) allowed for the delineation of vertical gradients in
⁴⁶⁷ $\delta^{13}\text{C}_{\text{AS}}$ in the LGM western Atlantic (Figure 2E). The steady-state solution of Oppo et al. (2018),
⁴⁶⁸ which finds 500 m of NADW shoaling, requires a unique $\delta^{13}\text{C}_{\text{AS}}$ signature in Nordic Sea-derived
⁴⁶⁹ NADW formed by open ocean convection, but $\delta^{13}\text{C}_{\text{AS}}$ has not yet been measured from this source
⁴⁷⁰ region. Additionally, little data is yet available on LGM $\delta^{13}\text{C}_{\text{AS}}$ from sediment cores south of
⁴⁷¹ 40 °S (potentially related to preservation issues, see Section c). A general paucity of data and
⁴⁷² difficulty inferring glacial endmembers are the main factors inhibiting broad conclusions about
⁴⁷³ LGM Atlantic water mass structure from $\delta^{13}\text{C}_{\text{AS}}$.

⁴⁷⁴ The third tracer often used to assess whether NADW shoaled at the LGM is εNd . Unlike $\delta^{13}\text{C}$
⁴⁷⁵ and $\delta^{13}\text{C}_{\text{AS}}$, most studies measuring εNd have argued for no major changes in LGM Atlantic water

mass geometry, and compiled LGM ε Nd shows a similar meridional depth structure as today, with very negative (ε Nd < -10) filling the deep North Atlantic (Figure 2F). Howe et al. (2016) attempted to quantify the change in NADW present in the deep Atlantic, using an approach similar to Eq. 9. They conduct a sensitivity analysis using one site at 4500 m in the North Atlantic (Roberts et al. 2010), and find between 50 and 100% NADW at that depth, depending on the isotopic composition of the northern endmember and the relative neodymium concentrations of the northern and southern endmembers (a component of the endmember calculation for which there is no paleo proxy). The results of Howe et al. (2016) were further supported by a study in the Southwest Atlantic by Poppelmeier et al. (2020). These authors highlighted the conflicting water mass geometries that arise from using $\delta^{13}\text{C}$ versus ε Nd as a water mass proxy. Du et al. (2020) used a box model of the global ocean to examine changes in the mixing ratio of northern and southern source water, allowing for changes in the ε Nd endmember composition at the LGM. They found that the LGM authigenic ε Nd data were best supported by an increase in the northern source water endmember composition, without a substantial change in the relative northern source water-southern source water mixing fraction (Du et al. 2020). These studies collectively suggest nearly no change in AMOC geometry during the LGM, in direct conflict with the shoaling of NADW implied by $\delta^{13}\text{C}$ reconstructions.

Aside from the two most commonly-cited circulation scenarios: shoaled upper cell or no structural change from the modern, there have been several other glacial circulation schemes that have been proposed in the literature, mostly in paleo-observational papers. These circulation configurations are attempts to satisfy a variety of (potentially conflicting) paleo proxy data, but have not necessarily been tested for their feasibility, i.e. by attempting to simulate these scenarios using physical models. One such scheme has a bifurcated glacial NADW (Howe et al. 2016; Poppelmeier et al. 2020; Du et al. 2020)—an attempt to reconcile conflicting $\delta^{13}\text{C}$ and ε Nd data. In this hy-

500 pothesis, both flavors of glacial NADW have negative ε_{Nd} values, but the shallower version of
501 GNADW is forms via open-ocean deep convection, imparting a heavy $\delta^{13}\text{C}$ composition, while
502 the deeper version forms under sea ice with restricted air-sea gas exchange, and thus light $\delta^{13}\text{C}$.
503 Coupled-climate models of the LGM sometimes have large mixed-layer depths in both the Nordic
504 Sea and in the region south of Iceland (Sherriff-Tadano et al. 2018), but these models do not appear
505 to produce two types of NADW with very different densities. However, to our knowledge, no
506 modeling studies have specifically tried to simulate a bifurcated glacial NADW, so its physical
507 realism is unknown.

508 *b. Physical constraints on LGM circulation*

509 Larger Southern Ocean buoyancy loss is generally thought to cause shoaling of the AMOC, and
510 larger diapycnal mixing is generally thought to cause deepening (as described in Sections 2a and
511 2b). Idealized models have been fundamental to understanding the key processes that set AMOC
512 depth, and they generally point to modest shoaling of the AMOC in the South Atlantic at the LGM
513 (e.g. Nadeau and Jansen 2020; Baker et al. 2021). However, ultimately they cannot tell us whether
514 increased buoyancy loss or increased diapycnal mixing is the most important effect at the LGM,
515 because they do not represent the full complexity of the ocean system. Thus, we turn to more
516 complex simulations to assess how the AMOC circulation may have changed at the LGM.

517 Models forced with glacial boundary conditions as part of PMIP do not produce consistent
518 responses in terms of glacial overturning strength or the depth of the boundary between the upper
519 and lower cells in the Atlantic (Otto Bliesner et al. 2007; Weber et al. 2007; Muglia et al. 2018).
520 As shown in Figure S2, some PMIP simulations produce a deeper AMOC, some a shallower
521 AMOC, and some no change in the depth of the AMOC. Marzocchi and Jansen (2017) attribute
522 a deep AMOC in some of the PMIP simulations to insufficient sea-ice formation, which causes

523 less deep ocean stratification in these models. However, even assimilating proxy observations of
524 LGM surface temperature does not guarantee that the AMOC will shoal (Amrhein et al. 2018).
525 From physical models of the LGM ocean circulation that do not include geochemical tracers,
526 it is difficult to rule out shoaling, no-change or deepening circulation scenarios. These models
527 are a useful starting point for understanding how different ocean circulations impact ocean tracer
528 distributions, as discussed in section 1.

529 There is mounting evidence for increased diapycnal mixing at the LGM. Reduced sea level at the
530 LGM (see section 2b) probably reduced tidal dissipation on continental shelves and caused more
531 tidal energy to be dissipated in the deep ocean (Arbic et al. 2004; Egbert et al. 2004; Griffiths and
532 Peltier 2009; Green 2010; Wilmes et al. 2019). Studies by Schmittner et al. (2015) and Wilmes et al.
533 (2019) found that changes in tidal energy dissipation dominate over changes in ocean stratification,
534 and tidally-induced mixing affects diapycnal diffusivity most strongly in the North Atlantic below
535 2000 m, causing the upper cell to extend to 5000 m. In Wilmes et al. (2019)'s simulations with
536 realistic tidally-induced mixing, the upper cell only deepens by about 500m north of 20 °N and
537 shows little change south of 20°N. A deeper AMOC in the north Atlantic is not completely ruled
538 out by the observational record: more research is needed to explore this possibility.

539 1) SOURCES OF UNCERTAINTY IN OUR PHYSICAL UNDERSTANDING

540 The strength of diapycnal mixing in the global ocean is not well-constrained either today or at the
541 LGM. Vertical variations in the diapycnal diffusivity may lead to significant exchange between the
542 upper and abyssal cells (Mashayek et al. 2017; Jones and Abernathey 2021). This transport may
543 not be visible in the zonally-integrated streamfunction, because downward transport in the interior
544 may be cancelled by upward transport close to the ocean boundaries (Callies and Ferrari 2018),
545 but it is likely to transport tracer between the upper and abyssal ocean. Hence, it is not clear how

546 much a cell separation in the zonal mean streamfunction (as predicted by Ferrari et al. 2014) would
547 influence deep ocean tracer distributions. In this section, we explore how the tracer distributions
548 in Figure 3 may be impacted by mean ocean circulation and by other factors including diapycnal
549 mixing.

550 Most PMIP models do not simulate the distribution of relevant paleo-oceanographic tracers like
551 $\delta^{13}\text{C}$ and εNd , or even passive tracers for water masses like NADW and AABW. In Figure 3, we
552 attempt to estimate the fraction of deep Atlantic water that originated in the North Atlantic in three
553 models based on the temperature distribution in these models. We chose to use temperature rather
554 than salinity because the salinity of AABW and NADW were very similar in some of the LGM
555 simulations. The results shown here are qualitatively very similar if salinity is chosen rather than
556 temperature (as shown in figure S3).

557 The MPI and GISS models have similar Pre-Industrial AMOC streamfunctions, in which the
558 upper cell extends to around 2500 m depth from 25 °N to 25 °S. However, the MPI model has
559 significantly more NADW in the deep ocean. The differences in deep NADW concentration are
560 most likely caused by the differences in ocean mixing between models, or perhaps differences
561 in the zonal structure of the circulation. Changes in ocean mixing between the LGM and today
562 are of similar magnitude as differences in modern mixing between different models (not shown).
563 Thus ocean mixing changes could be *as important* as changes in circulation structure for ocean
564 tracer distributions. CCSM4's pre-industrial AMOC streamfunction extends to 5000m in the North
565 Atlantic at 30 °N, and CCSM4 has much more NADW in the deep Atlantic than the other two
566 simulations.

567 We repeated this analysis to find the concentration of NADW in the last century of the LGM
568 simulations for each of these models. In the MPI model, which was run for 2300 yrs (starting from a
569 previous LGM simulation), the MOC streamfunction does not change much between the LGM and

570 Pre-Industrial times, but there is slightly more NADW in the deep ocean at the LGM, highlighting
571 that changing mixing processes may be important. We chose an extended LGM simulation of
572 CCSM4 (Brady et al. 2013) that was run for 1600 yrs (for more details, see the supplementary
573 information of Marzocchi and Jansen (2017)). In CCSM4, the upper cell shoals at the LGM, and
574 the NADW concentration in the deep ocean reduces as a result of this shoaling.

575 We chose the MPI and CCSM4 models partially because they had long LGM simulations: the
576 MPI model was run for 2300 years (ensemble r1i1p1f1 in the CMIP6 archive; Mauritsen et al.
577 (2019)) and CCSM4 was run for 1600 years (Brady et al. 2013). The GISS model was only run
578 for 300 years (ensemble r1i1p151 in the CMIP 5 archive; Schmidt et al. (2014)), which is not long
579 enough for water that was ventilated at the surface at the beginning of the simulation to reach the
580 deep ocean (greater than 500 years in the deep tropical Atlantic (Khatiwala et al. 2012)). Hence,
581 in the GISS model we cannot find the NADW concentration in the deep ocean with any confidence.
582 The LGM simulations from many models are not very long and it is likely that tracers in the deep
583 ocean are not in equilibrium. If these simulations were run for at least 1500 yrs, it would most likely
584 be possible to analyze how changes in ocean circulation impact deep ocean tracer distributions in
585 these LGM simulations. Alternatively, the transport matrix, a mathematical operator that describes
586 the motion of ocean tracers, could be calculated from short PMIP simulations of the LGM, and
587 the transport matrix could then be used to integrate the tracer distribution forward in time until
588 it reaches equilibrium (see e.g. Bardin et al. (2014); Zanna et al. (2019); John et al. (2020);
589 Chamberlain et al. (2019)). It would also be useful if more model fields, like vertical and lateral
590 diffusivity, were saved and made available. Longer runs and more variables (and funding for these
591 things) are needed for coupled climate models to be used to their full potential in understanding
592 the LGM ocean.

593 It is still unclear how much diapycnal mixing or isopycnal mixing changed at the LGM. Along
594 with the work of Wilmes et al. (2019) and Jones and Abernathey (2019), these experiments suggest
595 that diapycnal mixing may have had a first-order effect on NADW distributions at the LGM.
596 Jones and Abernathey (2019) also highlight the importance of isopycnal mixing, but conclude that
597 changes in isopycnal mixing are likely have only a modest effect on large scales. Further research
598 on how ocean mixing and ocean tracer advection interact to produce large-scale tracer distributions
599 is needed to fully quantify the uncertainties associated with these quantities.

600 A further source of uncertainty is that we do not know the formation sites for NADW at the
601 LGM. Coarse-resolution models often over-emphasize the Labrador sea as a location for deep-
602 water formation (Heuzé 2017), which may cause bias in the location of endmembers in LGM
603 ocean simulations. New observations from the OSNAP (Lozier et al. 2017) array will be helpful
604 for improving the representation of deep-water formation in this area. Without further information,
605 it is difficult to assess whether deep water from two different northern-source locations might be
606 present in NADW at the LGM.

607 *c. Beyond tracer sections*

608 As discussed in section 1, the distribution of tracers like ε_{Nd} and $\delta^{13}\text{C}_{\text{AS}}$ in the deep ocean do
609 not give direct information about the AMOC streamfunction. Alternate methods of looking at the
610 relationship between ocean tracer concentrations, ocean mixing and ocean circulation are sorely
611 needed in order to extract the information stored in paleo-oceanographic observations.

612 One alternate way of examining ocean tracer distributions is to look at tracer-tracer cross plots
613 (e.g. Hines et al. 2019) rather than tracer sections. When binary mixing occurs between two water
614 masses, conservative tracers should plot linearly on a tracer-tracer plot (a common oceanographic
615 example of this is a temperature-salinity diagram). By comparing the relationship between tracers

616 in the modern ocean with their reconstructed relationship for the glacial ocean, we can deduce
617 whether water mass endmembers changed significantly between these two periods.

618 We have compiled and merged datasets of benthic $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{AS}}$, and εNd for the LGM
619 Atlantic below 2000 m (Figure 4), where reconstructions of glacial Atlantic water mass geometry
620 based on these proxies diverge significantly (Figure 2D–F). In particular, $\delta^{13}\text{C}_{\text{AS}}$ is conservative by
621 definition, and εNd is thought to be largely conservative in the interior Atlantic (Du et al. 2020)—
622 any shifts in the relationships between these proxies are likely driven by changing endmembers.

623 There are few locations with co-located LGM $\delta^{13}\text{C}_{\text{AS}}$ and εNd reconstructions (Figure 4A).
624 However, the few observations available show a striking shift in the southern-source $\delta^{13}\text{C}_{\text{AS}}$
625 endmember during the LGM compared to present, with AABW shifted towards significantly
626 lighter values than any observed in the modern Atlantic (Figure 4A). In fact, the *directionality* of
627 the $\delta^{13}\text{C}_{\text{AS}}\text{-}\varepsilon\text{Nd}$ relationship for the LGM is completely reversed during the LGM, with AABW
628 becoming isotopically lighter in $\delta^{13}\text{C}_{\text{AS}}$ than NADW. Since AABW subducts from the surface at
629 the freezing point in the modern ocean, it is unlikely that colder AABW temperatures during the
630 LGM could explain the lower $\delta^{13}\text{C}_{\text{AS}}$. Similarly, since AABW is isotopically lighter than NADW
631 during the LGM, this signal must be primary, and not due to variable entrainment with subsurface
632 NADW. Instead, this signal must be driven by decreased air-sea equilibration during the LGM
633 and/or decreased net sea to air CO₂ flux. This reversal in the $\delta^{13}\text{C}_{\text{AS}}$ gradient at the LGM has
634 been previously documented (Marchitto and Broecker 2006; Oppo et al. 2018; Gebbie 2014) and
635 even simulated in a model (Menviel et al. 2020). It is generally attributed to reduced air-sea gas
636 exchange, possibly by increased sea ice cover, in the Southern Ocean and colder temperatures in
637 the North Atlantic.

638 Another way of using paleoceanographic tracers is to use them as direct physical constraints on
639 circulation. The oxygen isotopic composition of seawater, $\delta^{18}\text{O}$, is a function of its temperature

and salinity, as is density. While $\delta^{18}\text{O}$ isn't a proxy for density per se, this physical relationship is still powerful. Lund et al. (2011) observed shifts in the difference between LGM and Holocene $\delta^{18}\text{O}$ values at approximately 2000 m water depth in two depth profiles from the Brazil Margin (30 °S) and Blake Ridge (30 °N) in the Atlantic. Motivated by this observation, Lund et al. (2011) constructed a two-dimensional tracer budget for the Atlantic across a surface that marks the boundary between a southern sourced water mass (i.e. AABW) and a northern sourced water mass (i.e. NADW). The gradient of a tracer across this surface is proportional to the ratio of the overturning strength of the deep water mass divided by the vertical diffusivity across the surface (Ψ/κ). Accounting for changes in the surface area of that water mass boundary, the authors calculate that Ψ/κ was larger at the LGM compared to today. This could be achieved either by decreasing the vertical diffusivity (κ) or increasing the deep overturning circulation (Ψ). Lund et al. (2011) conclude that the most likely explanation for the change in $\delta^{18}\text{O}$ distribution is that the interface between the abyssal and upper cells of the MOC shoaled, causing a decrease in κ across this interface.

When considering the difficulties in interpreting tracer sections in terms of LGM water mass changes we discussed in Section 4.2., the results of Lund et al. (2011) are perhaps most straightforward approach showing evidence for shoaled NADW during the LGM. Ideally their approach could be applied to the entirety of the LGM Atlantic basin. Unfortunately, as the authors discuss, interlaboratory offsets in $\delta^{18}\text{O}$ of roughly 0.3‰ are on the same order as the vertical LGM $\delta^{18}\text{O}$ kink. Thus, their analysis cannot yet be extended to additional locations or to a compilation of Atlantic LGM benthic $\delta^{18}\text{O}$. Distributed time slice benthic $\delta^{18}\text{O}$ across several depth transects from a single lab would be an extremely valuable step towards confirming (or ruling out) the ubiquity of LGM Atlantic Ψ/κ changes. Recent work by Wilmes et al. (2021), which shows that a large increase in the vertical diffusivity at all depths is not consistent with Lund's result even for

664 a shallow LGM overturning circulation. This highlights the need for more observational evidence
665 to characterize whether Ψ/κ has increased or decreased since the LGM. Such evidence could be
666 useful for understanding both large scale circulation and vertical mixing in the past.

667 Finally, from the modeling side, several studies (e.g. Brovkin et al. 2007; Tagliabue et al. 2009;
668 Bouttes et al. 2011; Men viel et al. 2017; Muglia et al. 2018; Gu et al. 2020; Men viel et al. 2020;
669 Muglia and Schmittner 2021; Wilmes et al. 2021) have included geochemical tracers into LGM
670 simulations in order to directly compare simulated distributions with proxy measurements (given
671 known circulation configurations by definition). Recognizing the computational challenges of
672 incorporating these tracers, it is particularly beneficial to include multiple tracers (e.g. Gu et al.
673 2020; Muglia and Schmittner 2021). This will allow for more unique insights from model output,
674 such as the construction of tracer-tracer plots for diagnosing proxy behavior in the model—the
675 value of which in observational data is discussed earlier in this section.

676 5. Conclusions

677 This paper highlights that neither observations nor models provide clear evidence of whether
678 the AMOC shoaled at the LGM. ε_{Nd} records indicate that NADW reached the deep Atlantic at
679 the LGM, while $\delta^{13}\text{C}$ records suggest that NADW was confined to the top 1500 m or so. Models
680 also disagree about whether the AMOC shoaled at the LGM, and many models only represent
681 the circulation, temperature and salinity, so they provide limited information about past tracer
682 distributions. Models can be tuned to give a range of answers, and while idealized models are
683 very valuable for understanding the processes that set the depth of the AMOC, it is important to
684 understand that existing models only scratch the surface of the possible range of mixing parameters
685 that may have occurred at the LGM.

686 In light of this continued uncertainty about the state of the ocean circulation at the LGM, we
687 conclude this paper with some suggestions for how to clarify the science, while giving proper weight
688 to the huge complexity of inferring ocean circulation from limited ocean tracer observations.

689 We have shown in this paper that co-located records of conservative and quasi-conservative
690 tracers allows for the determination of mixing relationships between water masses, as well as
691 diagnosis of changing proxy endmembers, via tracer-tracer plots. These types of analyses are
692 in their nascent stages, and hold considerable promise for future reconstructions of water mass
693 characteristics. One way to clarify existing discrepancies between ε_{Nd} and $\delta^{13}\text{C}_{\text{AS}}$ would be to
694 greatly expand the number of co-located ε_{Nd} and $\delta^{13}\text{C}_{\text{AS}}$ measurements during the LGM and
695 Holocene, via a time slice approach. Further, these crossplots analyses could be expanded to
696 include non-conservative tracers (e.g. $\Delta\delta^{13}\text{C}_{\text{DIC}}$ for bottom water oxygen concentrations, B/Ca for
697 carbonate ion, etc.).

698 Some paleo-data model comparison has been done to test the validity of PMIP and PMIP-
699 like models (e.g. Brovkin et al. 2007; Tagliabue et al. 2009; Bouttes et al. 2011; Men viel et al.
700 2017; Muglia et al. 2018; Gu et al. 2020; Men viel et al. 2020; Muglia and Schmittner 2021;
701 Wilmes et al. 2021), but the majority of these studies use only $\delta^{13}\text{C}$ or $\delta^{14}\text{C}$ and radiocarbon
702 as a paleoceanographic tracer and all of them focus on a single model. Given that the different
703 PMIP models have naturally resulted in variable glacial circulations, it would be informative to
704 see a model-data comparison across all these models, comparing not only $\delta^{13}\text{C}$ data, but also
705 proxies such as ε_{Nd} and $\delta^{13}\text{C}_{\text{AS}}$, and NADW concentration estimates based temperature and
706 salinity distributions. We acknowledge that implementing such a large number of tracers in all the
707 PMIP models may not be the most efficient use of time, hence one potential solution is to produce
708 transport matrices for these models in order to generate proxy distributions using an offline tool
709 like the Ocean Circulation Inverse Model (OCIM) (DeVries and Primeau 2011).

710 Another challenge in this problem is the huge number of parameters that control ocean tracer
711 distributions, including the 3-D distribution of mixing, the boundary conditions for each of the
712 tracers, and possible changes in circulation. Idealized models are useful for exploring a wide range
713 of parameters at low computational cost. In the future, including tracers for water masses and their
714 ages in idealized modeling studies will allow for their results to be more easily interpreted from an
715 observational standpoint.

716 By working together, observationalists and modelers can better select drilling locations that
717 will provide maximum information content. Selection of these locations should be informed
718 by models (especially those that simulate tracers), but also take into account the expertise of
719 paleoceanographers, who know best whether proxy data can be obtained at a specific location.

720 In conclusion, recent research has shown that paleo-tracers contain a wealth of information about
721 surface and mixing processes, in addition to information about the large-scale ocean circulation.
722 This highlights an opportunity to increase our understanding of past ocean states beyond what was
723 previously assumed. Ultimately, this approach will result in a deeper, more complete understanding
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741 The MPI model data used here can be found at <https://esgf-node.llnl.gov/search/cmip6/>, the GISS data can be found at <https://esgf-node.llnl.gov/search/cmip5/>. The
742 Pre-Industrial run of CCSM4 is available at <https://www.earthsystemgrid.org/search.html?Project=CMIP5>. The LGM CCSM4 data used in this manuscript is from the extended run
743 described in Brady et al. (2013). We regret that this data is not publicly available at this time, but
744 it is present on the glade file system.

747 The data sources in Figures 2 and 4 are as follows. The modern seawater carbon isotope data is
748 from Eide et al. (2017) (<https://doi.pangaea.de/10.1594/PANGAEA.871962>). Modern and
749 LGM ε Nd data is from the supplementary material of Du et al. (2020). LGM $\delta^{13}\text{C}$ and $\delta^{13}\text{C}_{\text{AS}}$ is
750 from the compiled data in the supplementary material of Oppo et al. (2018).

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Fig. 1. Modern ocean circulation. A) Circulation in the Southern Ocean (adapted from Speer et al. 2000). Locations of the Subtropical Front (STF), Subantarctic Front (SAF), and Polar Front (PF) are labeled. Blue arrows mark waters that upwell in a region of negative buoyancy forcing (blue arrows at surface) and red arrows mark waters that upwell in a region of positive buoyancy forcing (red arrows at surface). Circles at top denote the Southern Hemisphere westerly winds. Water masses are also labeled (see text for details). B) Schematic of geochemical and physical processes that affect εNd , $\delta^{13}\text{C}$, and $\delta^{13}\text{C}_{\text{CAS}}$ in the Atlantic Ocean. Green wavy arrows represent biological productivity in the surface ocean that fractionates carbon isotopes. Background colors represent εNd values that are affected by weathering of old rocks in northern Canada and Greenland (negative εNd) and young volcanic rocks around the Pacific (positive εNd), which influence Atlantic εNd distributions via mixing through the Southern Ocean (illustrated by red \odot and \otimes that represent Antarctic Intermediate Water, AAIW, Upper Circumpolar Deep Water, UCDW, and Agulhas Leakage, AL). C) Basin-averaged global ocean circulation (adapted from Nadeau et al. 2019; Nadeau and Jansen 2020). Wavy arrows show diapycnal mixing, and gray shaded region represents enhanced vertical mixing in the deep ocean. The loop labeled “a” is predominantly adiabatic: water flows along isopycnals that join the surface of the North Atlantic with the surface of the Southern Ocean. The loop labeled “b” relies on diapycnal mixing in the deep ocean to return deep water to the surface.

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Fig. 2. Atlantic Ocean section plots for the Modern and Last Glacial Maximum. Panels A) and B) utilize the preindustrial $\delta^{13}\text{C}_{\text{DIC}}$ climatology of (Eide et al. 2017), and show data from the Atlantic Ocean zonally averaged between 45 °W and 10 °W. Calculation of $\delta^{13}\text{C}_{\text{AS}}$ (panel B) was performed by merging the $\delta^{13}\text{C}_{\text{DIC}}$ climatology with the World Ocean Atlas 2018 phosphate grid, and calculating $\delta^{13}\text{C}_{\text{AS}}$ using Equation 6. Panel C) uses the seawater ε_{Nd} database compiled by (Du et al. 2020). Contours in panels A–C show the potential density anomaly in kg/m³ referenced to a pressure of 2000db (σ_2). Panels D–F show analogous sections reconstructed for the LGM. Data in D) and E) come from the compilations of (Oppo et al. 2018), while data in F) comes from the LGM compilation of authigenic ε_{Nd} from (Du et al. 2020). The plots in D–F include all Atlantic basin data from these compilations, regardless of zonal location. Note that the colorbars differ between left and right panels, because endmember values for these proxies differ between the modern and LGM oceans.

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Fig. 3. AMOC streamfunction (top row of panels) in three climate models for Pre-Industrial (yellow contours and background shading) and LGM (black contours) simulations. The thick contour highlights the 0.2 Sv streamline, and can be thought of as the bottom edge of the upper cell. NADW fraction during the Pre-Industrial (PI) simulation, estimated from temperature and using endpoints highlighted by the green rectangles (Middle row of panels). NADW fraction during the LGM simulation minus NADW fraction during the Pre-Industrial simulation, estimated from temperature and using endpoints highlighted by the green rectangles (Bottom row of panels). The second panel in the bottom row of panels is hatched, because the GISS model was not run for long enough at the LGM for the deep ocean to reach equilibrium. The black vertical line indicates the latitude that separates the Atlantic from the Southern Ocean: north of this line, the zonal mean is taken over the Atlantic basin and south of this line the zonal mean is taken over the whole zonal extent of the domain. The Gulf of Mexico and Caribbean Seas are excluded from the zonal mean of CCSM NADW fraction. The MPI model run (Mauritzen et al. 2019; Müller et al. 2018) is part of the PMIP4 dataset (Kageyama et al. 2017), and the Pre-Industrial CCSM (Gent et al. 2011) and GISS model (Schmidt et al. 2014) runs are part of the CMIP5 dataset. The LGM CCSM data is from the same runs used by Brady et al. (2013)

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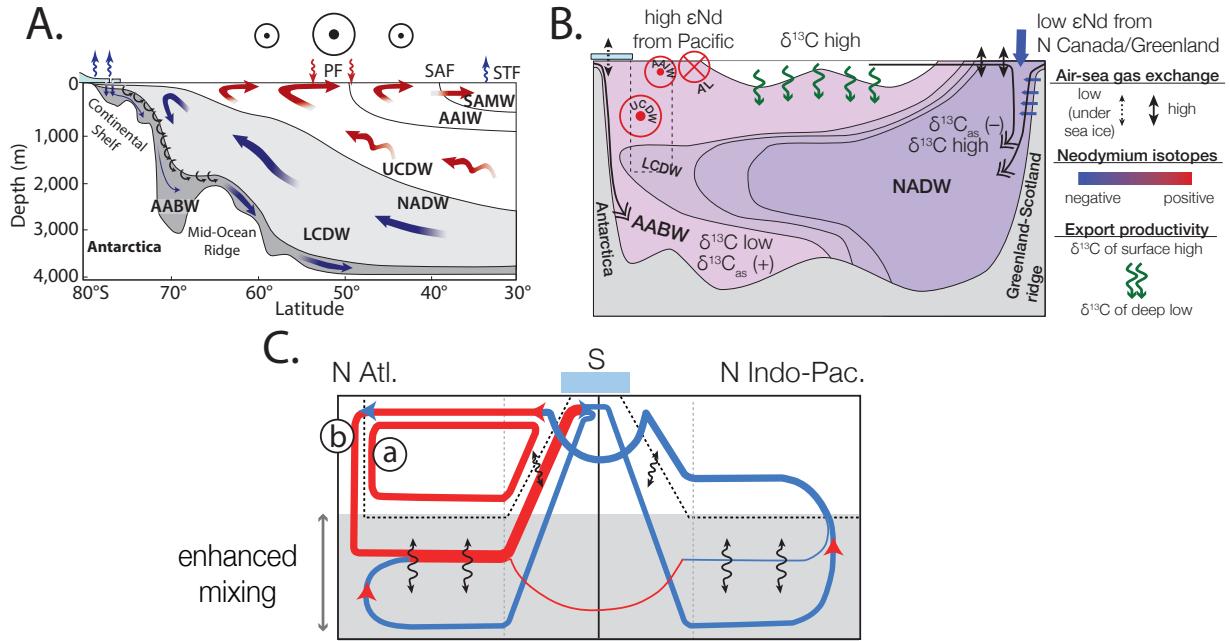
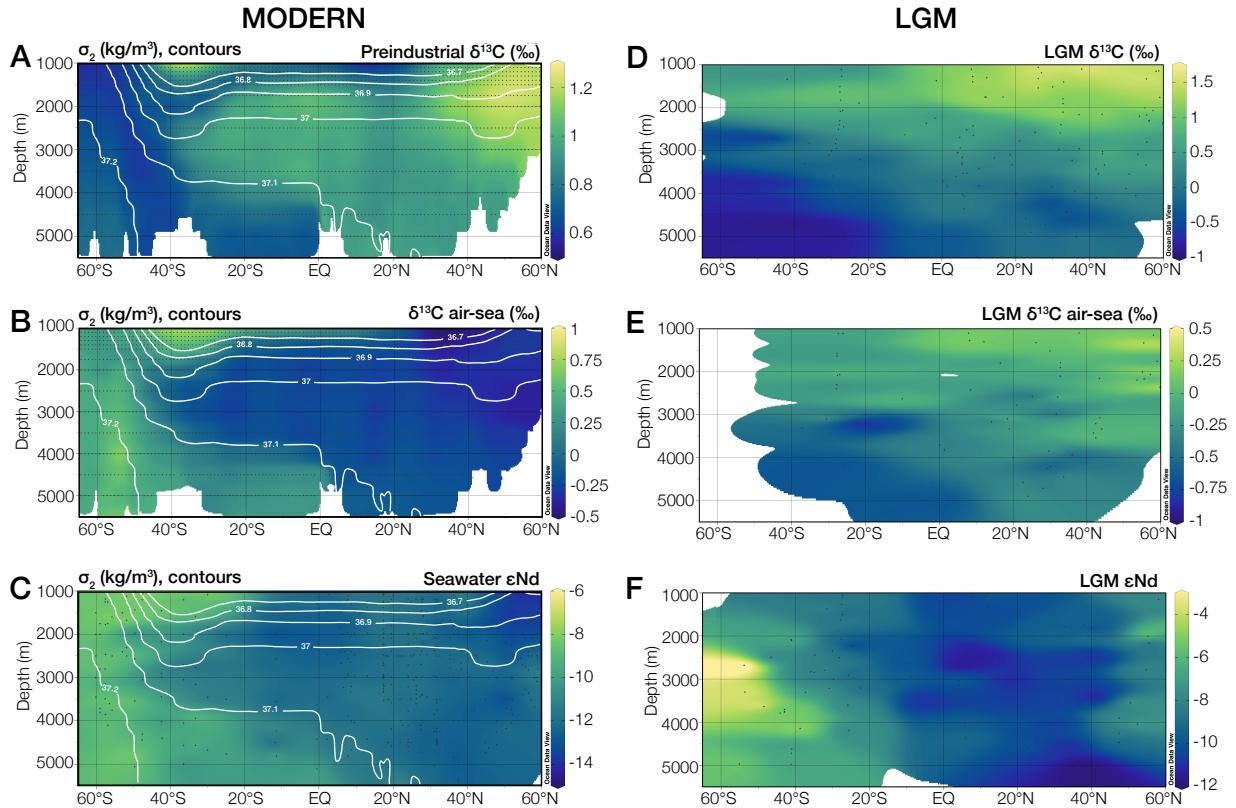
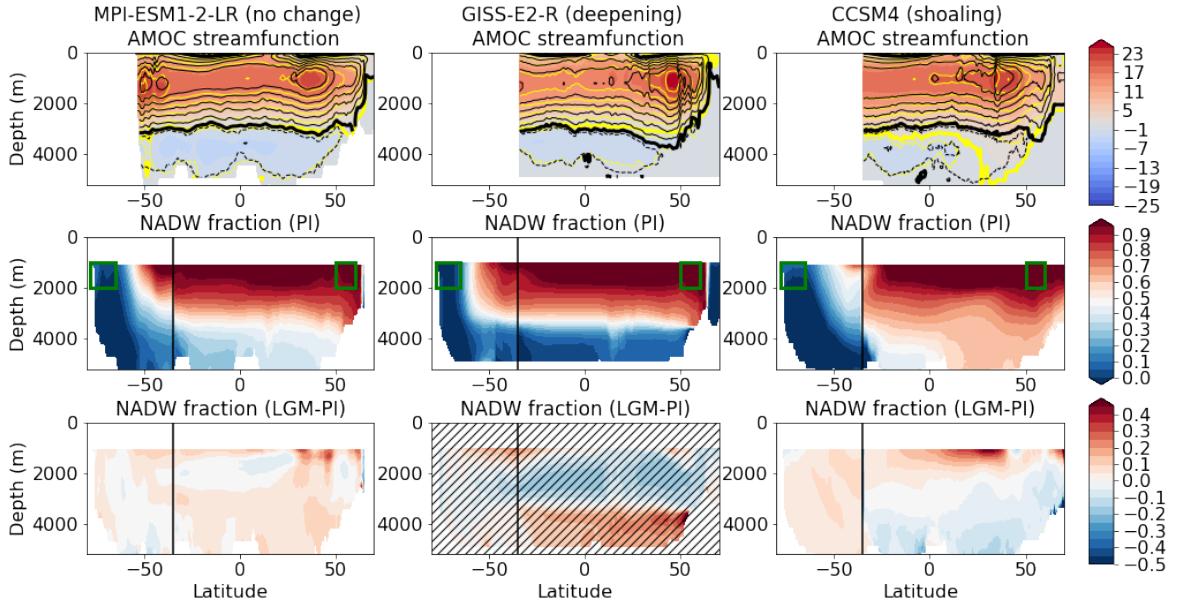


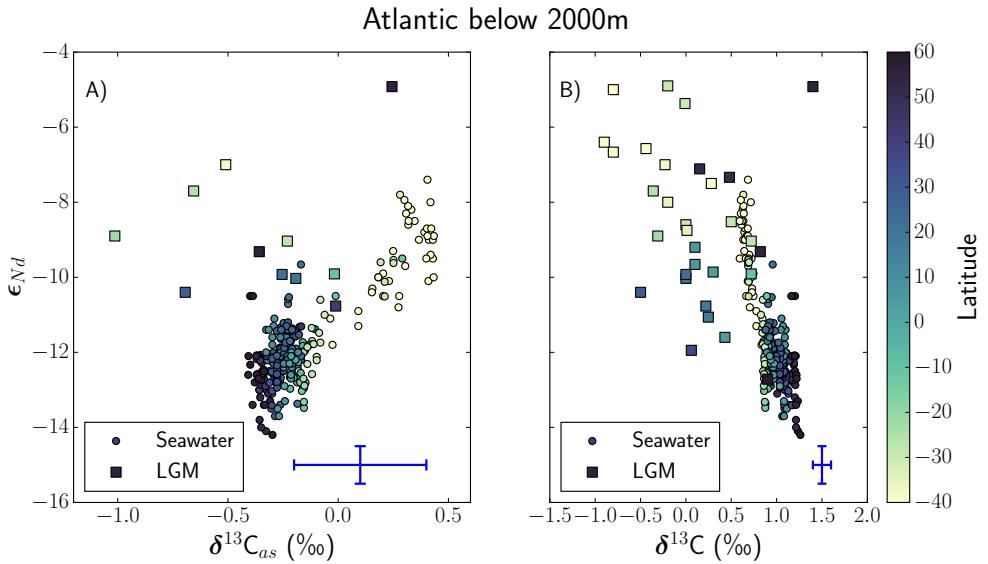
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1193 FIG. 4. Tracer-Tracer plots for modern seawater (dots) and reconstructed values for the LGM (squares). A) ϵ_{Nd}
 1194 and $\delta^{13}\text{C}_{AS}$. B) ϵ_{Nd} and $\delta^{13}\text{C}_{DIC}$. Data source for LGM benthic $\delta^{13}\text{C}_{AS}$ and $\delta^{13}\text{C}$ is (Oppo et al. 2018), and for
 1195 LGM authigenic ϵ_{Nd} the data source is (Du et al. 2020). Seawater data for ϵ_{Nd} also comes from the compilation
 1196 of (Du et al. 2020). For seawater data points, we once again used the (Eide et al. 2017) $\delta^{13}\text{C}$ climatology,
 1197 and combined it with the World Ocean Atlas phosphate climatology to determine $\delta^{13}\text{C}_{AS}$ using Eq. 7. For
 1198 each seawater ϵ_{Nd} measurement in the Atlantic Basin below 2000m, we then extracted $\delta^{13}\text{C}$ and $\delta^{13}\text{C}_{AS}$ values
 1199 from the nearest latitude-longitude-depth grid cell. Blue lines at the bottom of the plots display representative
 1200 uncertainties due to random errors associated with measurements involved in the respective proxies, but do not
 1201 include possible systematic uncertainties associated with diagenetic influences on the proxies, or calibrations for
 1202 the determination of derived parameters (e.g. the conversion of Cd/Ca and $\delta^{13}\text{C}$ to $\delta^{13}\text{C}_{AS}$).