Glacial deep ocean deoxygenation driven by biologically-mediated air-sea disequilibrium

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Abstract

Deep ocean deoxygenation inferred from proxies has been used to support the hypothesis that lower atmospheric carbon dioxide during glacial times was due to an increase in the strength of the ocean's biological pump. This relies on the assumption that surface ocean oxygen (O_2) is equilibrated with the atmosphere such that any O_2 deficiency observed in deep waters is a result of organic matter respiration consuming O_2 and producing dissolved inorganic carbon. However, this assumption has been shown to be imperfect because of disequilibrium. Here we use an Earth System Model tuned to a suite of observations, which reproduces the pattern of glacial-to-Holocene oxygenation change seen in proxy data, to show that disequilibrium plays an important role in glacial deep ocean deoxygenation. Using a novel decomposition method to track O_2, we find a whole-ocean loss of 33 Pmol O_2 from the preindustrial to the Last Glacial Maximum (LGM) despite a 27 Pmol gain from increased solubility due to cooler temperatures. This loss is driven by biologically-mediated O_2 disequilibrium, which increases from contributing 10% of the reduction of the O_2 inventory from solubility equilibrium in the preindustrial, to 27% during the LGM. Sea

ice and iron fertilization are found to be the largest contributors to LGM deoxygenation, which occurs despite overall reduced production and respiration of organic matter in the glacial ocean. Our results challenge the notion that deep ocean glacial deoxygenation was caused by a stronger biological pump or more sluggish circulation, and instead highlights the importance and previously underappreciated role of O_2 disequilibrium.

Main

O_2 is fundamental for life in the ocean, and is intrinsically connected with the cycling of carbon through photosynthesis: CO_2 is fixed and O_2 produced by phytoplankton in the surface ocean, and O_2 is consumed and dissolved inorganic carbon (DIC) released when organic matter is broken down by microbial respiration throughout the ocean. This transfer of carbon to the deep ocean is termed the "soft-tissue pump". O_2 can thus be a powerful tool to understand the cycling and storage of respired carbon in the ocean, the quantification of which is important for answering fundamental questions of carbon cycling under different climate states.

The Last Glacial Maximum (LGM; ~20,000 years before present) is the most recent example of a relatively stable, different climate state. This period saw global mean ocean temperatures 2.5°C colder than preindustrial times, and atmospheric CO_2 ~90 ppm lower [1, 2]. Deep ocean deoxygenation relative to the preindustrial has been observed globally using a variety of O_2 proxies from seafloor sediments [3, 4]. These results have been used to support the hypothesis that deep ocean carbon storage in the LGM was the result of a stronger or more efficient soft-tissue carbon pump [5, 3, 6, 7, 8, 9], which could partially explain the reduction of atmospheric CO_2 during glacial periods [1, 2]. It was recently demonstrated [10] with an observationally-constrained model that glacial carbon storage in the deep ocean was enhanced by air-sea disequilibrium of CO_2 caused by temperature changes and iron fertilization, while changes in circulation and sea ice extent, previously regarded as the primary drivers, played a minor role. Importantly, atmospheric CO_2 was reduced through increased deep ocean carbon storage, even as export production in the modeled glacial ocean decreased. However, deep ocean O_2 still decreased in the model. Here, we show that air-sea disequilibrium of O_2 can be a substantial part of the oxygen budget, potentially decoupling oxygen from biological carbon storage and confounding efforts to use it as a proxy to reconstruct past variations in the efficiency of the biological carbon pump.

Due to the more rapid air-sea gas equilibration timescale of O_2 relative to CO_2 (a few weeks versus ∼a year [11]), O_2 disequilibrium has often been considered a minor component of the O_2 budget [12, 13, 6]. In the modern ocean, observations show summertime O_2 oversaturation caused by photosynthesis, while wintertime undersaturation at high latitudes is driven by heat fluxes, extensive sea ice cover and wind-driven upwelling of oxygen-depleted deep waters [14, 15] (Fig. 1). The deep ocean is supplied with O_2 through subduction at high latitudes in the wintertime, when cold, dense water masses develop, following deep convection and sea ice formation. The effect of disequilibrium may be greater in the Southern Ocean where oxygen-depleted intermediate and deep waters upwelling to the surface have a shorter surface exposure time than those in the North Atlantic [13]. The propagation of undersaturated waters from the Southern Ocean into the interior, a phenomenon supported by observations [16], could have an especially large impact on the ocean's O_2 inventory because a large fraction of the deep ocean is ventilated from the Southern Ocean [17]. The ocean model used in this study shows reasonable agreement with observed surface O_2 saturation (Fig. 1). While modeled wintertime disequilibrium in the northern North Atlantic is larger than observed, likely leading to overestimated disequilibrium in North Atlantic Deep Water, in the high latitude wintertime Southern Ocean, an important region of deep and bottom water formation, the (few) Southern Ocean wintertime measurements available show greater undersaturation than the model.

The Southern Ocean is known to be important in glacial CO_2 storage [2, 7] and the mechanisms affecting LGM carbon disequilibrium have recently been modeled [10]. A number of studies have shown that O_2 disequilibrium can be non-neglible [14, 18] but a mechanistic study of LGM deoxygenation is lacking. While some studies have assumed that O_2 disequilibrium does not vary greatly between the modern and LGM climate states [6, 13], others have suggested that like carbon, O_2 disequilibrium could be larger in the LGM [19, 8]. Here, we apply a comprehensive method of decomposition of O_2 to quantify the magnitude of O_2 disequilibrium and investigate the processes driving glacial deoxygenation. This approach allows the effect of air-sea disequilibrium to be tracked through model simulations, and for physical and biological effects to be separated. The method is applied to biogeochemical fields simulated by two different configurations of the UVic Earth System Model [20] coupled to the Model of Biogeochemistry and Isotopes [21]. The configurations, representing preindustrial control (PIC) and LGM conditions, were tuned to a suite of modern biogeochemical and LGM sedimentary isotope records [22] (see Methods).

Oxygen decomposition analysis

To accurately track the cycling of O_2 in the model (Fig. 2 and Methods) we express the concentration of O_2 as:

$$O_2 = O_{2,\mathrm{eq}} + O_{2,\mathrm{dis,phy}} + O_{2,\mathrm{dis,bio}} + O_{2,\mathrm{soft}} \tag{1}$$

Here, $O_{2,\mathrm{eq}}$ is the theoretical O_2 concentration of the water parcel in solubility equilibrium with the atmosphere; $O_{2,\mathrm{dis,phy}}$ and $O_{2,\mathrm{dis,bio}}$ are the physical and biological components of disequilibrium ($O_{2,\mathrm{dis}}$) that lead to deviation of surface O_2 from $O_{2,\mathrm{eq}}$; and $O_{2,\mathrm{soft}}$ is the O_2 consumed when organic matter is broken down and accumulates as a deficit in the ocean interior, while regenerated dissolved inorganic carbon (DIC), nitrate and phosphate accumulate. Unlike nutrients, O_2 and CO_2 can exchange with the atmosphere at the surface, affecting the preformed O_2 and DIC pools.

Disequilibrium at the surface is driven by both sea surface temperature (SST) gradients and upwelling of waters depleted in O_2 due to biological consumption [14, 19]. To distinguish between these mechanisms, we carry out a parallel set of simulations in which biogeochemical processes are switched off. The difference between the full physical-biogeochemical and physics-only simulations allows us to separate biological ($O_{2,\mathrm{dis,bio}}$) and physical ($O_{2,\mathrm{dis,phy}}$) contributions to $O_{2,\mathrm{dis}}$. Physical disequilibrium occurs when waters moving poleward do not equilibrate fully as they lose heat, while biologically-mediated disequilibrium occurs when waters depleted in O_2 from either $O_{2,\mathrm{soft}}$ or $O_{2,\mathrm{dis,bio}}$ are entrained or upwelled to the surface. Once at the surface the part of this deficit that is not replenished through air-sea gas exchange is relabelled as $O_{2,\mathrm{dis,bio}}$ and becomes part of the preformed O_2 pool that is resubducted into the interior.

We note that $O_{2,\mathrm{soft}}$ is negative, as generally are $O_{2,\mathrm{dis,phy}}$ and $O_{2,\mathrm{dis,bio}}$, i.e., they reduce the O_2

inventory of the ocean from $O_{2,\mathrm{eq}}$. A similar approach was previously applied to carbon using the same model [10], allowing for comparison of O_2 and carbon.

Oxygen distribution in the preindustrial and LGM

The O_2 inventory and its components for the PIC and LGM are shown in Table 1 and in Fig. 3. In the preindustrial configuration total ocean O_2 content is 266 Pmol O_2 (global mean concentration of 196 mmol m^{-3}), similar to estimates of the modern ocean inventory (227 Pmol) [23] and within the range of CMIP5 models (136-231 mmol m^{-3}) [24]. As expected, $O_{2,\mathrm{eq}}$ is the largest component; all other components reduce the inventory so that total O_2 is 40% of the equilibrium value. Two thirds of the reduction is due to consumption during respiration ($O_{2,\mathrm{soft}}$), with the remaining decrease due to disequilibrium, of which 80% is biologically-mediated. The spatial distribution and magnitude of $O_{2,\mathrm{dis}}$ (Fig. S2) are similar to those in a previous study [14].

The glacial ocean has ∼12% less O_2, consistent with proxy-based reconstructions that show widespread deep ocean deoxygenation (Fig. 3; [3, 25, 26, 27, 6, 28, 29, 30, 31, 8, 4, 32]). The majority of proxy data are qualitative, indicating whether O_2 was higher or lower in the LGM (20-22ka BP) relative to the Holocene (5-10ka BP). The model captures the general pattern of upper ocean oxygenation and deep ocean deoxygenation in the LGM relative to PIC, although it may underestimate the full magnitude of deep ocean deoxygenation (see Supplement).

LGM O_2 decreases despite the cooler temperatures that enhance O_2 solubility and thus $O_{2,\mathrm{eq}}$ (by ∼5%) (Figs. 3, S6). O_2 is also enhanced by increases in $O_{2,\mathrm{dis,phy}}$ and $O_{2,\mathrm{soft}}$, both of which are less negative in the LGM (by ∼25% and ∼20%, respectively). Globally, export production in the LGM simulation is reduced causing this $O_{2,\mathrm{soft}}$ increase. While there is no corresponding observational estimate, regional observations do exist [33] and the model captures these variations reasonably well (Fig. S3). The only component of the O_2 budget that drives glacial deoxygenation is $O_{2,\mathrm{dis,bio}}$, which nearly triples in the glacial ocean (to -132 Pmol), overwhelming increases brought about by changes due to physical processes and organic matter export. The decomposition of O_2 into physical and biological components enables a more complete appreciation for the glacial-interglacial difference in O_2 distributions that has not been demonstrated before. That the decline in O_2 during the LGM is driven by biologically-mediated disequilibrium is a novel finding.

Drivers of LGM deoxygenation

To understand the mechanisms behind glacial deoxygenation, a series of perturbation experiments were performed where a single parameter (temperature, circulation, sea ice or iron fertilization) in the preindustrial configuration was changed to its LGM condition and the model run to steady-state. An additional "All" experiment was carried out where these parameters (and salinity) were simultaneously changed. Fig. 4 shows the change in the inventories of the O_2 components due to these perturbation. To probe the dependence of the response on the base state of the model [19], a "reverse" set of experiments was also run where PIC fields were used to perturb the LGM state (Figs. S11- S23).

In the LGM temperature perturbation experiment, a non-uniform temperature change consistent with reconstructions [34, 35] is imposed, increasing the ocean's O_2 inventory by 30 Pmol. The principal effect is an increase in $O_{2,\mathrm{eq}}$ (by 31 Pmol) through enhanced solubility. Changes in $O_{2,\mathrm{eq}}$ closely follow the pattern of temperature change with the largest differences seen in the North Atlantic (Fig. S24). Weakened meridional SST gradients and heat fluxes at high-latitudes reduce heat flux-driven undersaturation, causing $O_{2,\mathrm{dis,phy}}$ to become less negative south of ∼60°S. The resulting small (8 Pmol) increase in oxygen is somewhat countered by biological factors. Cooler temperatures deepen the remineralization depth [36], which reduces O_2 consumption in the upper ocean and increases it in the deep ocean (Fig. S10), leading to a global decrease (by 5 Pmol) in $O_{2,\mathrm{soft}}$. A similar decomposition applied to carbon showed that temperature was a major cause of atmospheric CO_2 drawdown (by 45 ppm) due to enhanced solubility and physical disequilibrium [10], illustrating that carbon and oxygen disequilibrium are controlled by different processes.

The simulated LGM ocean is characterized by a weaker and shallower Atlantic meridional overturning circulation. This reduces upwelling of nutrient-rich deep waters in the Indo-Pacific causing a global reduction in export production [37, 38, 10]. Thus, the primary effect of circulation changes is to increase the ocean's O_2 inventory by reducing O_2 consumption, a phenomenon observed most strongly in the Pacific (Fig. S12). A smaller $O_{2,\mathrm{soft}}$ pool and slower overturning circulation, which allows more time for waters upwelled in the Southern Ocean to equilibrate before subduction, also reduces $O_{2,\mathrm{dis,bio}}$.

The LGM configuration has 50% more sea ice than in PIC, consistent with reconstructions [39]. Sea ice blocks both air-sea gas exchange and penetration of light to the surface ocean. The former enhances disequilibrium by preventing equilibration of O_2-depleted waters, resulting in more negative $O_{2,\mathrm{dis,phy}}$ and $O_{2,\mathrm{dis,bio}}$, whereas the latter reduces phytoplankton growth, and hence export production and biological consumption of O_2. To quantitatively separate these mechanisms we carried out two additional experiments in which sea ice alternatively affected only gas exchange (SI-gasx) or biology through light limitation (SI-bio) (Figs. S16, S18). These show that air-sea gas exchange has a much larger effect, reducing O_2 by 81 Pmol ($\Delta O_{2,\mathrm{dis,phy}} = -25$ Pmol and $\Delta O_{2,\mathrm{dis,bio}} = -56$ Pmol). Light limitation has a smaller and compensating effect, increasing O_2 by 30 Pmol ($\Delta O_{2,\mathrm{soft}} = +15$ Pmol, $\Delta O_{2,\mathrm{dis,bio}} = +15$ Pmol). Their net effect is additive, decreasing the O_2 inventory by 49 Pmol in the sea ice experiment. These changes are largely driven by greater sea ice extent in the Southern Ocean, with decreases of over 50 mmol m^{-3} in AABW in the South Atlantic (Fig. S14). These results are consistent with previous studies that showed the large effect of Southern Ocean sea ice on $O_{2,\mathrm{dis}}$ [14, 19], although those studies did not separate biologically-mediated and physical disequilibrium. While the implementation of sea ice effects in our model is typical of other global models, it does not include polynyas and sea ice leads, which may reduce the strength of these effects as some gas exchange would still be possible and polynyas may allow for pockets of productivity. Polynyas are thought to have been present in the glacial Southern Ocean [40], although their prevalence and mechanisms of formation are not well-understood even in the modern ocean [41]. Similarly, the inclusion of leads would allow for more equilibration in ice-covered waters. These processes may be an important source of uncertainty for glacial-interglacial deep ocean O_2 and carbon and their inclusion should be a priority for future modeling studies.

Consistent with evidence from Antarctic ice cores [42] and ocean sediment records [43], bioavailable iron fluxes to the LGM Southern Ocean increased ten fold [22]. This iron fertilization enhances export production, depleting O_2 due to increased consumption and biological undersaturation ($\Delta O_{2,\mathrm{soft}} = -19$ Pmol; $\Delta O_{2,\mathrm{dis,bio}} = -14$ Pmol; Fig. S20). A recent study with a biogeochemical model also examined the effect of glaciogenic iron fluxes on CO_2 drawdown and deep ocean deoxygenation in the glacial ocean [9]. They showed that high Southern Ocean iron fluxes and an increase in the ocean's nutrient inventory was associated with a third of the change in deep ocean (below 2000 m) Apparent Oxygen Utilization (the deviation of O_2 from theoretical saturation) in their LGM model. While differences in experimental design and model base states makes direct comparisons difficult, our LGM iron perturbation leads to a 32 mmol m^{-3} decline in deep ocean O_2, comparable to the 21 mmol m^{-3} change due to iron fertilization recorded by the other study (their experiment LGM_glac3% which has conditions most similar to ours) [9]. Our decomposition allows us to show that almost half of the deoxygenation brought about by iron fertilization-enhanced export production is a result of biologically-mediated disequilibrium amplifying the strength of the soft-tissue pump [13]. As the other study uses a similar gas exchange parameterization it is likely to have air-sea gas disequilibrium, although the magnitude and role of disequilibrium is not known as $O_{2,\mathrm{pre}}$ was not explicitly considered in that study.

Lastly, we consider the "All" experiment where the above perturbations were imposed simultaneously. The results are largely consistent with the difference between the LGM and PIC equilibrium runs (Table 1 and Figs. 3, S6 and S22). The dominant cause of glacial deoxygenation is a large increase in biologically-mediated disequilibrium ($\Delta O_{2,\mathrm{dis,bio}} = -94$ Pmol). The individual perturbation experiments suggest that this is driven by Southern Ocean sea ice and iron fertilization, in line with the dipolar pattern of export production in the Southern Ocean during the LGM (Fig. S3) [10, 33]. Despite the increase in productivity in the Southern Ocean, global productivity is reduced in the "All" experiment. Deoxygenation is partially compensated by enhanced solubility because of cooling ($\Delta O_{2,\mathrm{eq}} = +24$), and a decrease in export production and consumption ($\Delta O_{2,\mathrm{soft}} = +19$) due to changes in circulation. The results of the individual perturbations do not add to produce the "All" experiment result because of nonlinearities. For instance, in the Southern Ocean the interplay of expanded LGM sea ice and iron fertilization may further enhance $O_{2,\mathrm{dis,bio}}$, while weaker latitudinal temperature gradients could reduce the effect of sea ice on $O_{2,\mathrm{dis,phy}}$.

The "reverse" set of experiments, where the LGM state was perturbed by PIC conditions, allow us to assess the robustness of different processes in their effect on any given O_2 component. Processes that elicit a response of opposite signs in the two sets of perturbation experiments are regarded as robust, as most are found to be (Fig. 4). The exceptions are $O_{2,\mathrm{eq}}$ and $O_{2,\mathrm{dis,bio}}$ in the circulation experiment, and $O_{2,\mathrm{dis,phy}}$ and $O_{2,\mathrm{soft}}$ in the "All" experiment. Crucially, in both sets of experiments, $O_{2,\mathrm{dis,bio}}$ is the primary driver of O_2 changes resulting from sea ice and iron fertilization, supporting our conclusion that these processes play a leading role in glacial deoxygenation.

Implications for estimates of ocean carbon storage during the LGM

The development of quantitative oxygen proxies opens up the powerful possibility of better constraining glacial ocean carbon storage using the Apparent Oxygen Utilization (AOU) method, the most widely used approach for estimating the inventory of respired carbon in the ocean. AOU is the difference between the saturation concentration $O_{2,\mathrm{sat}}$ of oxygen in a water sample (estimated from its temperature and salinity) and its *in situ* concentration. Assuming that the water was in solubility equilibrium when it was last at the surface of the ocean, this difference is typically attributed to oxygen consumed during soft-tissue regeneration (C_{soft}) as the water is transported from the surface into the interior [11]. Observed higher levels of AOU in the deep ocean during the LGM relative to present day have been used to conclude that the ocean contained more C_{soft} during the glacial period, leading to a drawdown in atmospheric CO_2 [27, 29, 8, 4]. Air-sea disequilibrium complicates this straightforward interpretation of AOU in two ways.

First, oxygen disequilibrium, shown here to be greater during the LGM, violates a key assumption of the AOU method. For instance, if surface waters are undersaturated, the true oxygen utilization will be smaller than that predicted by AOU, leading to an overestimate of C_{soft} [14, 18, 19, 10] (by as much as 50% in the global inventory according to a recent study [10]). Second, it has long been recognized that disequilibrium of CO_2 amplifies the direct effect of C_{soft} on ocean carbon storage [13]. This biologically-mediated component of DIC, $C_{\mathrm{dis,bio}}$, has been shown to be also much larger during the LGM [10, 44]. It is therefore more appropriate to define total biological carbon storage, $\mathrm{C_{bio}}$, as a sum of $\mathrm{C_{soft}}$ and $\mathrm{C_{dis,bio}}$. While both aspects have been acknowledged as a source of uncertainty in AOU-based estimates of glacial biological carbon storage, it has been argued that, if anything, in the presence of disequilibrium AOU systematically underestimates $\mathrm{C_{bio}}$ [8, 4]. Here, we combine our oxygen decomposition with a previous carbon one [10] to show that the extent to which proxy-based estimates of AOU capture true glacial biological carbon storage depends sensitively on the mechanisms involved.

The change in biological carbon storage is estimated from AOU according to: $\Delta\mathrm{C_{bio}(AOU)} = R_{\mathrm{C:-O_2}} \times \Delta\mathrm{AOU}$, where $R_{\mathrm{C:-O_2}}$ is a constant carbon-to-oxygen stoichiometric ratio. ΔAOU can be expressed in terms of its components as (see Methods):

$$\Delta\mathrm{AOU} \approx -\Delta\mathrm{O_{2,soft}} - \Delta\mathrm{O_{2,dis,bio}} - \Delta\mathrm{O_{2,dis,phy}}, \tag{2}$$

demonstrating the explicit dependence of $\Delta\mathrm{C_{bio}(AOU)}$ on the disequilibrium components.

Fig. 5 shows how the cumulative sum of the oxygen terms in equation 2 is related to that of the corresponding carbon components, $\Delta\mathrm{C_{soft}}$, $\Delta\mathrm{C_{dis,bio}}$ and $\Delta\mathrm{C_{dis,phy}}$, respectively, for the various perturbation experiments (see Figs. S25–Fig. S26 for the reverse experiments). By construction, $\Delta\mathrm{C_{soft}}$ and $\Delta\mathrm{O_{2,soft}}$, which are both diagnosed from the regenerated phosphate concentration, are exactly proportional to each other via the Redfield (stoichiometric) ratio $-R_{\mathrm{C:-O_2}}$. When the biological disequilibrium term is added, this relationship remains strong for the "solely" biological iron fertilization and SI-bio experiments because $\Delta\mathrm{C_{dis,bio}}$ and $\Delta\mathrm{O_{2,dis,bio}}$ roughly follow the Redfield line (Fig. S25). The latter relationship becomes weaker in SI-gasx, causing $\Delta\mathrm{C_{soft}} + \Delta\mathrm{C_{dis,bio}}$ to deviate from the Redfied relationship with $\Delta\mathrm{O_{2,soft}} + \Delta\mathrm{O_{2,dis,bio}}$. (The full sea ice experiment is intermediate between SI-gasx and SI-bio.) In the circulation experiment, $\Delta\mathrm{C_{dis,bio}}$ and $\Delta\mathrm{O_{2,dis,bio}}$ are almost orthogonal to the Redfield line, causing a large deviation from the Redfield estimate of AOU change and deep carbon change. The "All" experiment, which can be regarded as a sum of the iron fertilization, sea ice and circulation experiments, also falls close to the Redfield line.

ΔAOU also contains a physical disequilibrium component, $\Delta\mathrm{O_{2,dis,phy}}$, which can impact its relationship with $\Delta\mathrm{C_{bio}}$. In particular, in the sea ice experiment, which shows the largest effect on O_2 of any single parameter examined, both $O_{2,\mathrm{dis,bio}}$ and $O_{2,\mathrm{dis,phy}}$ are enhanced (become more negative) leading to a large decrease in deep ocean oxygen, despite reduced consumption. On the other hand, sea ice has a much smaller effect on glacial carbon storage because physical air-sea disequilibrium serves to decrease DIC, whereas biologically-mediated disequilibrium serves to increase DIC by preventing outgassing of carbon-rich upwelled waters, such that there is a cancellation of much of the effect of sea ice on CO_2 air-sea gas exchange [10]. This breaks down the relationship between AOU and biological carbon storage, such that AOU overestimates the change in biological carbon storage by over a factor of three (ΔC_{bio}=99 PgC; ΔC_{bio} (AOU)=334 PgC) in this experiment. A similar overestimation is found in the circulation experiment ($\Delta C_{\mathrm{bio}}=-102$ PgC; ΔC_{bio} (AOU)$=-253$ PgC).

Interestingly, in the "All" experiment ΔAOU appears to be a good proxy for ΔC_{bio}. But we note that this is because the change in $C_{\mathrm{dis,phy}}$ is quite small due to compensating effects from circulation, temperature and sea ice [10]. We believe that while the effect of different processes on individual oxygen and carbon components in our model is qualitatively quite robust, quantitative changes in those components and their interactions are likely to be model- and state-dependent (cf. the "reverse" experiments Fig. S26). Such a cancellation, and hence the ability of AOU to quantify changes in C_{bio}, is therefore unlikely to be robust.

To summarize, the simulated deep ocean deoxygenation in the LGM is consistent with proxy data. Oxygen concentrations decrease despite a reduction in modeled export production in the glacial ocean, which leads to a reduction in respired carbon (and thus O_2 consumption), i.e., a less efficient biological carbon pump as conventionally defined. Previous studies [5, 9] have instead interpreted the same proxy-based evidence of glacial deoxygenation as implying an increase in the efficiency of the soft-tissue pump. We find instead that greater air-sea O_2 disequilibrium during the LGM, caused by an expansion in sea ice cover in the Southern Ocean, along with increased iron fertilization, provides a better explanation for lower oxygen concentrations in the glacial deep ocean.

Our results also suggest that the observed increase in AOU in the LGM was primarily caused by biologically-mediated disequilibrium, compounded by physical disequilibrium. The latter can decouple AOU from biological carbon storage, implying that caution must be exercised in interpreting quantitative oxygen proxies in terms of carbon storage.

Our model likely does not capture the complex nature of gas exchange in regions such as the Southern Ocean, where it may be altered by, for example, the presence of leads in sea ice and seasonal polynyas [19, 26, 40]. To refine our understanding of glacial–interglacial changes in ocean carbon and oxygen distributions, more extensive seasonal observations of O_2 gas exchange, especially in the Southern Ocean, are required. The magnitude of disequilibrium should also be investigated both in models that do not base respired carbon estimates on AOU and that incorporate recent developments in using flexible stoichiometry [45, 46]. The results of recent studies with such models suggest that this may enhance glacial C_{bio} storage [47, 46] and may slightly reduce the quota of O_2 required to respire C_{soft} [46], which could alleviate deoxygenation.

Methods

Model description

The model set up used for this study is described in [10] and references therein. Briefly, the biogeochemical model used is the Model of Ocean Biogeochemistry and Isotopes (MOBI), which has the limiting nutrients dissolved nitrogen, phosphorus and iron, two phytoplankton functional groups, one zooplankton class, dissolved and particulate organic matter and dissolved inorganic carbon (DIC), O_2 and alkalinity [21]. All components of the model track carbon and nitrogen isotopes. The interactive iron cycle is driven externally from atmospheric dust, sediments and hydrothermal vent inputs [48]. Monthly climatologies of atmospheric soluble iron fluxes are used that were generated using monthly dust flux climatologies of both preindustrial control (PIC) and Last Glacial Maximum (LGM) [49], using a constant iron dust content of 3.5% [50] and using a fitted function of iron flux and iron solubility [48]. The dust flux climatologies were constructed by interpolation of Holocene and glacial dust flux data from terrestrial and marine sediments, and ice cores, primarily from the DIRTMAP 3 database [49]. In the Southern Ocean south of 35°S, the LGM soluble iron flux is multiplied by 10, placing the estimate in line with Antarctic ice cores [42] and marine sediment cores [43] and resulting in a substantially better fit [22] between simulated and observed δ^{15}N and glacial-interglacial export production changes (Fig. S3). Sedimentary release of dissolved iron is proportional to the flux of organic carbon at the ocean bottom [48]; the LGM the sub-grid bathymetry used to calculated this is adjusted for the 110 m glacial sea level drop [51]. MOBI is coupled to the Transport Matrix Method (TMM) [52, 53, 54], a framework for computationally efficient offline tracer simulations.

MOBI-TMM is driven by surface winds, circulation, temperature, salinity and sea ice from UVic ESCM (version 2.9) [20], a 3-D ocean general circulation model (1.8°×3.6°×19 layers) coupled to a 1-layer atmospheric energy-moisture balance, dynamic-thermodynamic sea ice, and land surface models. Preindustrial control (PIC) and Last Glacial Maximum (LGM) simulations used were tuned to a suite of modern biogeochemical and LGM sedimentary isotope (δ^{13}C, $\Delta^{14}C$ and δ^{15}N) records, as previously described [55, 22]. Briefly, the LGM simulation was forced with atmospheric CO_2 and orbital parameters in accord with 19ka BP, addition of a multimodel mean LGM anomaly wind field stress from the Paleoclimate Intercomparison Project Phase 3 (PMIP3) to the present day climatological field, a PMIP3 reconstruction of the continental ice sheet [56], and a global addition of 1-PSU (Practical Salinity Unit) to salinity consistent with glacial sea level drop. The consistency of simulated large-scale tracer distributions with observations have been demonstrated previously for the equilibrium solutions [22, 10]. The characteristics of the model's LGM state are consistent with observational studies, namely, colder global mean temperature (ΔT=-2.5°C compared to -2.6°C from ice core noble gas measurements [57]) and patterns of sea surface temperature change [34, 35]; a weaker (by ∼50%) and shallower Atlantic Meridional Circulation (AMOC) (as implied by the δ^{13}C distribution and ∼600 year-older $\Delta^{14}C$ deep ocean ages [58, 59]); 50% more sea ice than in PIC such that Southern Ocean maximum (winter) cover is 3×10^{13} m^2, slightly less than reconstructions (4×10^{13} m^2) [39]; and enhanced surface iron fluxes to the Southern Ocean (required to reproduce observed δ^{13}C [22] and δ^{15}N data).

Oxygen decomposition

To track O_2 through the model, total O_2 is expressed as the sum of preformed O_2 ($O_{2,\mathrm{pre}}$) and O_2 consumed from the respiration of soft-tissue ($O_{2,\mathrm{soft}}$) (equation 3).

$$O_2 = O_{2,\mathrm{pre}} + O_{2,\mathrm{soft}} \tag{3}$$

A preformed tracer is a conservative tracer whose value is set at the surface of the ocean and is passively transported into the interior by the circulation. $O_{2,\mathrm{soft}}$ is negative as respiration removes O_2, whereas respired carbon (C_{soft}) is positive as it is released when soft-tissue is regenerated. $O_{2,\mathrm{soft}}$ and C_{soft} are calculated as:

$$\begin{aligned} O_{2,\mathrm{soft}} &= (-1/R_{\mathrm{C}:-\mathrm{O}_2}) \times C_{\mathrm{soft}} && (4)\\ C_{\mathrm{soft}} &= R_{\mathrm{C:P}} \times PO_{4,\mathrm{reg}} && (5)\\ PO_{4,\mathrm{reg}} &= PO_4 - PO_{4,\mathrm{pre}}, && (6) \end{aligned}$$

where we relate $O_{2,\mathrm{soft}}$, C_{soft} and regenerated phosphate ($PO_{4,\mathrm{reg}}$) via a fixed Redfield stoichiometry for C:P:O_2. The phosphate inventory is fixed in the ocean model, and to calculate $PO_{4,\mathrm{reg}}$ we simulate a preformed phosphate ($PO_{4,\mathrm{pre}}$) tracer for each experiment by propagating the seasonally-varying surface ocean phosphate field into the interior using the TMM. The difference between PO_4 and $PO_{4,\mathrm{pre}}$ at the end of each run is the regenerated phosphate (equation 6).

To simulate $O_{2,\mathrm{pre}}$ we similarly propagate the seasonally-varying surface ocean oxygen field into the interior. $O_{2,\mathrm{pre}}$ is further decomposed into equilibrium and disequilibrium components by simulating an additional tracer, $O_{2,\mathrm{eq}}$, by propagating the surface theoretical equilibrium oxygen into the interior. $O_{2,\mathrm{pre}}$ and $O_{2,\mathrm{eq}}$ are simulated for each experiment and the disequilibrium component $O_{2,\mathrm{dis}}$ of preformed O_2 is the difference between the two.

The O_2 decomposition in equation 3 is thus more completely described by:

$$O_2 = \underbrace{O_{2,\mathrm{eq}} + O_{2,\mathrm{dis,phy}} + O_{2,\mathrm{dis,bio}}}_{O_{2,\mathrm{pre}}} + \underbrace{(-R_{-\mathrm{O}_2:\mathrm{P}}) \times PO_{4,\mathrm{reg}}}_{O_{2,\mathrm{soft}}} \tag{7}$$

For every experiment we also run a parallel simulation where the physical forcings (circulation, temperature, salinity, winds, etc) are the same, but the source/sink terms in the biogeochemical model are switched off. Nutrients, DIC and O_2 are all transported by the TMM but do not get used in biological processes. As such, this parallel simulation gives us a reference point for the ocean without any biological activity. $O_{2,\mathrm{eq}}$, which only depends on temperature and salinity, is identical in the full physical-biogeochemical simulation and physics-only simulation. The disequilibrium component of preformed oxygen in the physics-only experiment, $O_{2,\mathrm{pre,phy}}$, is then purely a result of physical processes (e.g., temperature gradients, sea ice blocking gas exchange) for the conditions of that simulation (equation 8). In the parallel full physical-biogeochemical simulations, biological processes will change the distribution of DIC and O_2, and thus change O_2 disequilibrium. We attribute any difference in disequilibrium between the full and physics-only experiments to biological processes (equation 9).

$$O_{2,\mathrm{dis,phy}} = O_{2,\mathrm{pre,phy}} - O_{2,\mathrm{eq}} \tag{8}$$

$$O_{2,\mathrm{dis,bio}} = O_{2,\mathrm{dis}} - O_{2,\mathrm{dis,phy}} \tag{9}$$

Equilibrium and perturbation experiments

All equilibrium and perturbation tracer simulations were run for 10,000 years to steady-state. The procedure of running parallel sets of physics-only and full simulations is carried out for the PIC and LGM equilibrium experiments, as well as all perturbation experiments. In the physics-only simulations for the perturbation experiments the model starts from the steady state of the corresponding physics-only base run (e.g., PIC for PIC→LGM perturbations), while for the full physical-biogeochemical perturbation simulations the model starts from the steady state of the corresponding full base run. The perturbations applied are the same in both cases. At the end of each perturbation run, the decomposition is performed as explained above and differences from the respective base states give us the perturbation effect on each oxygen component. The “All” perturbation experiment, in which temperature, circulation, sea ice, iron fertilization and salinity (to account for the 110 m drop in LGM sea level) are simultaneously perturbed, does not exactly reproduce the LGM equilibrium simulation as it still uses the PIC conditions for light, freshwater fluxes and subgrid bathymetry, which affects sedimentary release of organic carbon.

Decomposition of Apparent Oxygen Utilization (AOU) into oxygen components

We express AOU in terms of its components:

$$\begin{aligned}
\mathrm{AOU} &= \mathrm{O}_{2,\mathrm{sat}} - \mathrm{O}_2 \\
&= \mathrm{O}_{2,\mathrm{sat}} - \left[\mathrm{O}_{2,\mathrm{eq}} + \mathrm{O}_{2,\mathrm{soft}} + \mathrm{O}_{2,\mathrm{dis,bio}} + \mathrm{O}_{2,\mathrm{dis,phy}}\right] \\
&\approx \mathrm{O}_{2,\mathrm{sat}} - \left[\mathrm{O}_{2,\mathrm{sat}} + \mathrm{O}_{2,\mathrm{soft}} + \mathrm{O}_{2,\mathrm{dis,bio}} + \mathrm{O}_{2,\mathrm{dis,phy}}\right] \\
&= -\left[\mathrm{O}_{2,\mathrm{soft}} + \mathrm{O}_{2,\mathrm{dis,bio}} + \mathrm{O}_{2,\mathrm{dis,phy}}\right],
\end{aligned}$$

where we have approximated $\mathrm{O}_{2,\mathrm{eq}}$ by $\mathrm{O}_{2,\mathrm{sat}}$. Thus, a change in AOU can be written as:

$$\Delta\mathrm{AOU} \approx -\Delta\mathrm{O}_{2,\mathrm{soft}} - \Delta\mathrm{O}_{2,\mathrm{dis,bio}} - \Delta\mathrm{O}_{2,\mathrm{dis,phy}}.$$

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Author Contributions

SK and AS designed the study; SK carried out the experiments; all authors analyzed the results; EC wrote the manuscript with input from SK and AS.

Competing Interests

The authors declare no conflicts of interest.

Data availability

The model output that support the findings of this study are available from `http://doi.org/10.5281/zenodo.4078981`. World Ocean Atlas data were obtained from `https://www.nodc.noaa.gov/OC5/woa18/`, and float data from the SOCCOM website `https://soccom.princeton.edu/`.

Code availability

Model codes are available from https://github.com/samarkhatiwala/tmm.

	O_2	$O_{2,\mathrm{eq}}$	$O_{2,\mathrm{dis,phy}}$	$O_{2,\mathrm{dis,bio}}$	$O_{2,\mathrm{soft}}$
PIC (Pmol)	266	458	-12	-49	-127
PIC (mmol m^{-3})	196	337	-9	-36	-94
LGM	233	482	-9	-132	-104
LGM (mmol m^{-3})	172	355	-7	-97	-77
LGM-PIC (Pmol)	-33	+24	+3	-83	+23
LGM-PIC (mmol m^{-3})	-24	+18	+2	-61	+17

Table 1: Results of the O_2 decomposition for PIC and LGM equilibrium runs are shown in terms of the total inventory (Pmol) and global mean concentration (mmol m^{-3}). Negative values indicate a deficit of O_2 resulting from incomplete equilibration or consumption during respiration. The differences between the LGM and PIC inventory values are also shown, with positive (negative) values indicating more (less) O_2 in the LGM than PIC.

Figure 1: Comparison of surface O_2 saturation from a compilation of World Ocean Atlas 2018 (WOA18; [60]) and float data (University of Washington Argo O_2 reanalysis [61], and quality-controlled data from the SOCCOM program [62]). Data were spatially binned into $1^\circ \times 1^\circ$WOA grid boxes, and a seasonal climatology was made by binning data temporally by month. Grid boxes without any measurements were discarded. Results shown here are for northern hemisphere winter/southern hemisphere summer (December-January-February; left) and northern summer/southern winter (June-July-August; right). Surface O_2 saturation values are shown for observations (top) and the model preindustrial control simulation interpolated to the locations where observations are available (middle row). The bottom row shows a comparison of zonal mean surface O_2 saturation in the observations and model at the location of observations with one standard deviation of the zonal data shaded. Note that observations for the Southern Ocean are sparse, particularly in the winter months, as are those in the Arctic, where large model-data differences are seen and may be influenced by sampling biases in conditions without or with thin sea ice because research vessels are limited in accessing regions with thick sea ice cover.

Figure 2: Schematic of the O_2 decomposition used in this study. Top panel shows the standard decomposition (see Methods) of O_2 into preformed O_2 ($O_{2,\mathrm{pre}}$), set at the surface and subsequently transported conservatively into the interior by the circulation, and $O_{2,\mathrm{soft}}$, O_2 consumed during respiration of organic matter (which is therefore negative) [14, 18]. The sum of these terms gives total O_2. The bottom panel shows the extended decomposition that incorporates surface disequilibrium which causes deviation from the equilibrium preformed concentration ($O_{2,\mathrm{eq}}$). Physical disequilibrium ($O_{2,\mathrm{dis,phy}}$) is caused by surface heat fluxes. Biological processes can also cause disequilibria ($O_{2,\mathrm{dis,bio}}$) by photosynthesis at the surface, creating a positive disequilibrium, or as a result of the upwelling of waters depleted in O_2 due to respiration, leading to a negative disequilibrium. Waters upwelling in the Southern Ocean have a short surface exposure time so can have significant $O_{2,\mathrm{dis,bio}}$, which may be enhanced by sea ice blocking gas exchange.

Figure 3: The components of O_2 in the preindustrial (PIC) and LGM relative to PIC. Oxygen decomposition for the preindustrial control (PIC) equilibrium simulation (a) and the difference between the Last Glacial Maximum (LGM) and PIC equilibrium simulations (b) are shown as inventory values in Pmol O_2 and mmol m^{-3}. The equivalent deep ocean inventory decomposition plots are in Fig. S5. Zonal mean sections of LGM-PIC ΔO_2 are shown for the Atlantic (c) and Pacific (d) oceans. Proxy-based reconstructions of ΔO_2 from the LGM to holocene have been included. Blue (red) circles indicate a qualitative decrease (increase) in O_2 from the holocene (5-10 kyr bp) to the LGM (20-22 kyr bp) [3, 6, 29, 25, 28, 26, 31, 8]. Diamonds represent a quantitative O_2 change [27, 29, 30, 4] using results of the infaunal-epifaunal foraminifera $\delta^{13}C$ method that were within the range of a previously published calibration [27] and are shaded using the same color scale as the color bar. The quantitative data point shown in the southern Atlantic was calculated using the modern O_2 concentration at the core site as data was not available for the Holocene [25] and recalculated per ref. [63]. See the Supplement for further comparison of model and reconstructions.

Figure 4: Top row: Response of PIC O_2 components to LGM perturbations. (a) Change in inventory due to a perturbation in circulation; sea ice; temperature; iron; all perturbations in which LGM temperature, circulation, sea ice, iron fertilization, salinity (1-PSU increase consistent with 110 m sea level drop) and winds were used to perturb the PIC. Note that the "All" experiment does not exactly reproduce the LGM equilibrium simulation as it still uses the PIC conditions for light, freshwater fluxes and subgrid bathymetry, which affects sedimentary release of organic carbon. (b) Change in inventory due to perturbation of sea ice; SI-gasx: effect of sea ice on O_2 gas exchange; SI-bio: sea ice effect on light limitation for biology. The corresponding spatial distribution of these changes are shown in Figs. S10- S22. Bottom row: Assessment of robustness of response of O_2 components to perturbations. Vertical bars are the average of the two sets of perturbation experiments (Equation S1) and the vertical lines are the differences (Equation S2), with the sign of the LGM to PIC ones reversed in both cases. The bars thus indicate whether the response is of the same or opposite sign in the two directions, while the lines show the average magnitude of the perturbation for the two experiment sets, such that if a line crosses the x axis, it implies a non-robust response to the perturbation (see Supplement for details). Those experiments are marked with an asterisk. (c) and (d) Changes due to perturbations corresponding to those in (a) and (b), respectively.

Figure 5: Relationship between ΔO_2, ΔAOU and biological carbon storage. a) Schematic showing how use of AOU can lead to over- or underestimation of biological carbon storage. For a given ΔC_{bio} ($= \Delta C_{\mathrm{soft}} + \Delta C_{\mathrm{dis,bio}}$), the ratio of carbon to oxygen disequilibrium relative to the Redfield C:$-O_2$ ratio (dashed grey line) controls whether AOU under- or over-estimates the change in true biological carbon storage. In a plot of ΔAOU versus ΔC_{bio}, for points that plot in the red (blue) region below (above) the Redfield line, ΔC_{bio}(AOU) over- (under-) estimates ΔC_{bio}. Only for points that fall on the line does ΔC_{bio}(AOU) accurately quantify biological carbon storage change. Physical disequilibrium can cause further deviation from the Redfield line which affects ΔAOU. b) ΔO_2 versus ΔC in the deep ocean (below 1000 m) for the perturbation experiments where an LGM condition is imposed on the preindustrial configuration. (For the relationship between the individual components see Fig. S25 and for reverse experiments with PIC perturbations on the LGM state see Fig. S26.) Changes are shown for the following perturbations: "All" (black); sea ice (green) which is further separated into the gas exchange effect (SI-gasx, yellow), and biological light limitation effect (SI-bio, light blue); iron fertilization (pink); temperature (red); and circulation (dark blue). For each perturbation three components of the carbon-oxygen system are shown: soft-tissue components ($\Delta O_{2,\mathrm{soft}}$ and ΔC_{soft}) (stars); soft-tissue and biological disequilibrium components ($\Delta O_{2,\mathrm{soft}} + \Delta O_{2,\mathrm{dis,bio}}$ and ΔC_{bio}) (triangles); total O_2 and C change from soft-tissue, biological and physical disequilibrium (ΔAOU and $\Delta C_{\mathrm{bio}} + \Delta C_{\mathrm{dis,phy}}$).