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Impact of brine-induced stratification on the glacial carbon cycle

N. Bouttes¹, D. Paillard¹, and D. M. Roche¹,²

¹Laboratoire des Sciences du Climat et de l’Environnement, IPSL-CEA-CNRS-UVSQ, UMR 8212, Centre d’Etudes de Saclay, Orme des Merisiers bat. 701, 91191 Gif Sur Yvette, France
²Faculty of Earth and Life Sciences, Section Climate Change and Landscape dynamics, Vrije Universiteit Amsterdam, De Boelelaan, 1085, 1081 HV Amsterdam, The Netherlands

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Abstract. During the cold period of the Last Glacial Maximum (LGM, about 21 000 years ago) atmospheric CO₂ was around 190 ppm, much lower than the pre-industrial concentration of 280 ppm. The causes of this substantial drop remain partially unresolved, despite intense research. Understanding the origin of reduced atmospheric CO₂ during glacial times is crucial to comprehend the evolution of the different carbon reservoirs within the Earth system (atmosphere, terrestrial biosphere and ocean). In this context, the ocean is believed to play a major role as it can store large amounts of carbon, especially in the abyss, which is a carbon reservoir that is thought to have expanded during glacial times. To create this larger reservoir, one possible mechanism is to produce very dense glacial waters, thereby stratifying the deep ocean and reducing the carbon exchange between the deep and upper ocean. The existence of such very dense waters has been inferred in the LGM deep Atlantic from sediment pore water salinity and δ¹⁸O inferred temperature. Based on these observations, we study the impact of a brine mechanism on the glacial carbon cycle. This mechanism relies on the formation and rapid sinking of brines, very salty water released during sea ice formation, which brings salty dense water down to the bottom of the ocean. It provides two major features: a direct link from the surface to the deep ocean along with an efficient way of setting a strong stratification. We show with the CLIMBER-2 carbon-climate model that such a brine mechanism can account for a significant decrease in atmospheric CO₂ and contribute to the glacial-interglacial change. This mechanism can be amplified by low vertical diffusion resulting from the brine-induced stratification. The modeled glacial distribution of oceanic δ¹³C as well as the deep ocean salinity are substantially improved and better agree with reconstructions from sediment cores, suggesting that such a mechanism could have played an important role during glacial times.

1 Introduction

Proxy data suggest that the climate of the Last Glacial Maximum (LGM, about 21 000 years ago) was very cold (~2 to −6°C in the Southern Ocean surface (MARGO Project Members, 2009)) with huge Northern Hemisphere ice sheets (Peltier, 2004). The associated carbon cycle was characterized by low atmospheric CO₂ concentrations of ~190 ppm (Monnin et al., 2001) and very negative deep ocean δ¹³C. The latter is based on the stable carbon isotopic composition (δ¹³C) of benthic foraminifera which is assumed to reflect the δ¹³C of total dissolved inorganic carbon (DIC) in bottom waters.

The Atlantic δ¹³C reached low values down to −0.8‰ in the deep ocean participating in a higher upper to deep oceanic gradient (Duplessy et al., 1988; Curry and Oppo, 2005; Köhler and Bintanja, 2008). The mean upper (~2000 m to 0 m) to deep (~5000 m to −3000 m) gradient in the Atlantic, (noted Δδ¹³C Atl), was about 1.2‰ in the Atlantic, compared to only 0.4‰ during the pre-industrial.

LGM climate can be explained by the extended ice sheets in connection with a different orbital configuration (Berger, 1978) and lower CO₂ (Jahn et al., 2005). To explain the crucial question of the low glacial CO₂ numerous hypotheses have been proposed. Some of them imply changes of physical mechanisms such as modifications of sea ice coverage (Stephens and Keeling, 2000) or winds (Toggweiler et al., 2006). Many have focused on enhancing

Correspondence to: N. Bouttes (nathaelle.bouttes@lsce.ipsl.fr)
or making more efficient the marine biology, for example through higher C/P ratio (Broecker and Peng, 1982), iron fertilization (Martin, 1990), a shift of dominant plankton species (Archer and Maier-Reimer, 1994), larger nutrients availability (Matsumoto et al., 2002), or modified rain ratio (Brovkin et al., 2007). Other studies have involved coral reef fluctuations (Berger, 1982; Opdyke and Walker, 1992), or oceanic chemistry with carbonate compensation (Broecker and Peng, 1987). But most only have a small impact on CO₂ compared to the glacial-interglacial change, or would require unrealistic modifications to become dominant (Archer et al., 2000, 2003; Kohfeld et al., 2005; Menviel et al., 2008b). Moreover, it has remained especially difficult to correctly simulate simultaneously the very negative δ¹³C in the deep ocean inferred from marine sediment cores, although part of the change is due to the glacial reduced terrestrial biosphere which releases light ¹²C leading to a reduction of the global mean oceanic δ¹³C (Köhler et al., 2010). Additionally, the strong link between Antarctic temperatures and atmospheric CO₂ variations (Luthi et al., 2008) suggests that mechanisms closely tied to Southern Ocean surface processes are likely to be dominant in controlling atmospheric CO₂ variability.

The general consensus is that the ocean is at the core of the solution regarding LGM CO₂. It is the biggest carbon reservoir active on the short time scale studied (a few thousand years) and the only one that could increase during glacial times, since the other two reservoirs, i.e., the atmosphere (Monnin et al., 2001) and terrestrial biosphere (Bird et al., 1994; Crowley, 1995), were both reduced. Observations indicate that the deep glacial ocean was much saltier and colder than today (Adkins et al., 2002), thus more stratified in the abyss. Such a deep stratification has important impacts on the ocean’s circulation and carbon cycle, as pointed out by climate models of different complexities (Toggweiler, 1999; Paillard and Parrenin, 2004; Köhler et al., 2005a; Bouttes et al., 2009; Tagliabue et al., 2009). In particular, deep stratification is required to reconcile δ¹³C (Bouttes et al., 2009; Tagliabue et al., 2009). However, only box models could significantly reduce atmospheric CO₂ when prescribing a reduced Southern ventilation (Watson and Garabato, 2005). With models of higher complexity (Bouttes et al., 2009; Tagliabue et al., 2009) the induced CO₂ drop remained too small which highlights the need of another mechanism that would still maintain the benefits of deep stratification (deep negative δ¹³C values) while reducing CO₂ more drastically.

Here we test the impact of the formation and rapid deep sinking of brines, i.e. very salty waters rejected during sea ice formation, on the glacial carbon cycle. The role of brines has been previously proposed as an explanation for the reduced Southern ventilation (Paillard and Parrenin, 2004; Köhler et al., 2005a; Watson and Garabato, 2005), but they were not explicitly simulated. Instead, the proposed effect of reducing the ventilation was tested by imposing lower mixing in box models only. Here we directly test this mechanism with a more complex model which physically includes advection and diffusion in the ocean and thus is able to reproduce the dynamical effect of brines. Because they are enriched in salt, these “pockets of water” are very dense. In the modern Antarctic they are generally mixed with fresh water from ice shelf melting (Joughin and Padman, 2003). However, during the glacial periods the sea level progressively fell (down to about 120 m at the Last Glacial Maximum) and the northward Antarctic ice sheet extent resulted in a progressive reduction of the shelf slope (Ritz et al., 2001) where modern waters are mixed. Tidal dissipation, which is important in today’s mixing, would then seriously decrease. Accordingly, the brine signal, which is diluted today, would be more preserved at the LGM. Furthermore, the sea ice formation location would also shift northward and closer to the continental shelf break. The preserved brine-dense water, whose volume was increased because of enhanced sea ice formation, would arrive at the shelf break and then flow quickly down the slope (helped by thermobaricity and supercritical flux properties) (Foldvik et al., 2004). This mechanism (referred herein thereafter as the brine mechanism) provides two major features: a direct link from the surface to the deep ocean and an effective physical way of achieving a strong stratification. In this study we test its impact on the carbon cycle and compare the modeled results to atmospheric CO₂, oceanic δ¹³C and salinity data inferred from ice core and marine sediment cores.

2 Methods

2.1 CLIMBER-2 model

The brine mechanism has been implemented and tested in CLIMBER-2, an intermediate complexity climate model (Petoukhov et al., 2000) well suited for the long term simulations we run. Indeed, the simulations are run for 20 000 years to ensure the equilibrium of the carbon cycle. Moreover we realize an ensemble of about 100 simulations to test the mechanism, which would be unfeasible with a general circulation model (GCM) in a reasonable amount of time. The intermediate complexity model, although simpler than a state of the art OGCM, includes the main known processes and mechanisms and computes the dynamics of the oceanic circulation contrary to box models. Furthermore, like GCMs, CLIMBER-2 does not exhibit box model sensitivity to high-latitude sea ice or presumably stratification (Archer et al., 2003). Additionally, the model compares favourably with a state of the art OGCM and gives the same response in terms of carbon cycle when the circulation is arbitrarily modified (Tagliabue et al., 2009).

CLIMBER-2 has a coarse resolution of 10° in latitude by 51° in longitude in the atmosphere, and 21 depth levels by 2.5° latitude in the zonally averaged ocean, which is precise enough to take into account geographical changes, while
allowing the model to be fast enough to run the long simulations considered. The model is composed of various modules simulating the ocean, the atmosphere, and the continental biosphere dynamics. No sediment model is included, the model thus does not take into account the carbonate compensation mechanism. CLIMBER-2 has already been used and evaluated in previous studies (Ganopolski et al., 2001a; Brovkin et al., 2002a,b, 2007; Bouttes et al., 2009). As the model version used explicitly computes the evolution of the carbon cycle and carbon isotopes (such as δ13C) in every reservoir, it allows us to compare the model output with data from sediment cores. In the glacial simulations three boundary conditions are simultaneously imposed: the ice sheets (Peltier, 2004), the solar insolation (Berger, 1978), and the atmospheric CO2 concentration for the radiative forcing (190 ppm, not used in the carbon cycle part of the model) (Munin et al., 2001). To account for the glacial sea level fall of about 120 m, salinity and nutrients (NO3 and PO4) mean concentrations are increased by 3.3%.

2.2 Implementation of brines in the CLIMBER-2 model

When sea ice is formed, a flux of ions is released into the ocean as sea ice is mostly composed of fresh water (Wakatsuchi and Ono, 1983; Rysgaard et al., 2007, 2009). Because the underlying water is then enriched in salt it becomes denser and can thus sink and transport salt to deeper waters. The rejection of salt by sea ice formation plays an important role in the formation of deep water, as it is the case for the Antarctic Bottom Water (AABW) which has been studied for a few decades (Foster and Carmack, 1976; Whitworth and Nowlin, 1987; Foldvik et al., 2004; Nicholls et al., 2009). The brine mechanism has been mostly observed in details in the Northern Hemisphere oceans (Haarpaintner et al., 2001; Shcherbina et al., 2003; Skogseth et al., 2004, 2008), where measures are easier than in the Southern Ocean. For instance, measures in the Arctic fjords indicate that approximately 78% of the brine-enriched shelf water was released out of the fjord in the Norwegian Sea (Haarpaintner et al., 2001), i.e. around 62% of the salt flux rapidly released by sea ice formation (the first rapid salt release is ~82% of the total salt flux rejected by sea ice formation). The impact of the brine formation on the concentration of other geochemical variables, especially dissolved inorganic carbon (DIC) has also been studied and it has been shown that DIC is rejected together with brine from growing sea ice (Rysgaard et al., 2007, 2009). Besides, numerical studies of this local mechanism show that the topography plays an important role in the transport of salt (Kikuchi et al., 1999).

Thus although today the brine formation around Antarctica does not affect the bottom waters (Toggweiler and Samuels, 1995), the formation and sinking of brines is a mechanism that can be observed and studied in some places of the modern ocean and that strongly depends on local conditions. The inferred higher salinity in the glacial Southern Ocean seems to indicate that enhanced brine formation and sinking could well have taken place around Antarctica during glacial conditions, which should be tested.

In order to assess the potential impact of the sinking of brines on the carbon cycle we need to use a global carbon-climate model. Yet the spatial resolution of such models, even state of the art GCMs, is too large to resolve the brine sink, requesting a parameterization. We thus develop a simple parameterization for this mechanism. The simplicity of the scheme used permits a first evaluation of such a mechanism and allows a separation of the different processes to understand the reasons of the changes observed.

The sinking of brines initially depends on the amount of salt rejected which is determined by the rate of sea ice formation. In CLIMBER-2, sea ice formation is computed by a one layer thermodynamic sea ice model with a simple parameterization for horizontal ice transport (Brovkin et al., 2007). The sea ice extent is increased in winter in agreement with proxy data (Gersonde et al., 2005) although during summer sea ice extent is also increased contrary to the data which indicate a sea ice covered area similar to the modern one.

During the formation of sea ice, in the standard version of CLIMBER-2 only the flux of salt (FS) was considered. It is usually a good approximation on the first order, yet the release of other ions and dissolved gases could be of importance for this study. Hence we have added the same process as the release of salt for the other ions and dissolved gases simulated in the model (dissolved inorganic carbon (DIC), alkalinity (ALK), nutrients, dissolved organic carbon, oxygen, DI13C, DI14C). As a first approximation the surface oceanic cell is enriched in these geochemical variables in the same proportion as salt as it has been observed to be not very different on the first order (Rysgaard et al., 2007, 2009). The flux (FX) of any geochemical variable X rejected during sea ice formation to the surface ocean is then:

\[ F_X = \frac{F_S}{S_{surface}} \cdot X_{surface} \]  

(1)

With FS the flux of salt, Ssurface the surface salinity, and Xsurface the surface concentration of any geochemical variable.

This process is active in all simulations, though it has a small impact on the standard pre-industrial and LGM simulations (atmospheric CO2 is changed by less than 5 ppm).

In the standard version of CLIMBER-2 when sea ice is formed all the salt is released in the corresponding surface oceanic cell, which is relatively large according to the coarse resolution of the model and thus dilutes the brine signal. In the brine simulations, a fixed fraction (frac) of this salt flux (and of the other ions flux) will form the sinking brines (Fig. 1a). This fraction frac can be set to 0 when none of the salt sinks to the bottom of the ocean (standard version of the model) and 1 when all the salt is used in the brine mechanism. The very salty (thus dense) brine water sinks to the bottom of the ocean where it modifies the concentration of
any geochemical variable $X$ (salinity, DIC, ALK, nutrients, dissolved organic carbon, oxygen, DI$^{13}$C and DI$^{14}$C) as following:

$$V_{\text{bottom}} \frac{dX_{\text{bottom}}}{dt} = \frac{\text{frac}}{1} \cdot F_X \cdot \text{area}$$

(2)

With $V_{\text{bottom}}$ the volume of the bottom cell, $X_{\text{bottom}}$ the concentration of $X$ at the bottom and area the area of the surface cell. At the surface the rest of the ion flux from sea ice formation not sinking with brines ($(1 - \frac{\text{frac}}{1}) \cdot F_X$) is diluted in the surface cell. The geochemical variables are thus modified as following:

$$V_{\text{surface}} \frac{dX_{\text{surface}}}{dt} = (1 - \frac{\text{frac}}{1}) \cdot F_X \cdot \text{area}$$

(3)

Even if this brine mechanism is idealized, it reflects the impact of intense Antarctic sea ice formation during the LGM. As the glacial Antarctic ice sheet extends close to the limit of the continental shelf, sea ice formation enhanced by the strong katabatic winds happens close to the continental slope. The brines formed by the coeval salt rejection can then rapidly sink along the continental slope down to the deep ocean. Unlike convection, the brine mechanism directly transports this fraction of salt and other ions ($\frac{\text{frac}}{1} \cdot F_X$) to the deep ocean, and thus represents a direct link from the surface to the bottom of the ocean. Because of the salt transport to the deep ocean this mechanism leads to enhanced stratification of the ocean as the density gradient between the deep and upper ocean increases (Fig. 1b).

We present model results and compare them to the main carbon data available for the LGM, e.g. atmospheric CO$_2$ concentration and $\delta^{13}$C distribution in the ocean, which constitute a major constraint with which to validate this mechanism. We also compare model results to the glacial deep ocean salinity and $\Delta^{14}$C.

3 Results and discussion

3.1 Standard simulation

The CLIMBER-2 version used here has a closed carbon cycle i.e. the total (fixed) amount of carbon is interactively distributed between the three reservoirs (atmosphere, terrestrial biosphere and ocean) (Brovkin et al., 2002a), and the model does not include carbonate compensation. From the pre-industrial value of 280 ppm, atmospheric CO$_2$ rises to 296 ppm for the standard glacial simulation (LGM-std, Fig. 2a). This CO$_2$ rise is due to the prevailing effect of increased ocean salinity and terrestrial vegetation decline (of approximately 700 GtC) which increase CO$_2$, despite increased nutrient concentration (linked to sea level drop) and colder sea surface temperatures which decrease CO$_2$. This modeled 16 ppm increase adds to the observed 90 ppm
3.2 Atmospheric CO$_2$ drawdown induced by the brine mechanism

The sinking of brines can have a very large effect on atmospheric CO$_2$ concentration in our simulations (Fig. 2a). Atmospheric CO$_2$ progressively decreases when the fraction of salt frac that sinks to the abyss increases. The frac = 0 simulation (no brine mechanism) corresponds to the standard LGM simulation (LGM-std), where CO$_2$ is 296 ppm. The maximum effect of the brines is obtained for frac = 1, i.e., when all the salt released by sea ice formation sinks to the bottom of the ocean with the brine mechanism. The latter gives a maximum CO$_2$ drop of about 52 ppm (CO$_2$ is 244 ppm). In this case it takes approximately 3000 years for the model to gain steady state oceanic circulation. The brines seem to be a good candidate as they will bring saline water to the abyss which will increase deep water salinity. In the following we will assess the impact of the brines and compare with data to either validate or reject such a possibility.

Fig. 2. (a) Atmospheric CO$_2$ concentration, (b) $\Delta\delta^{13}$C$_{at}$ (mean upper (-2000 m to 0 m) to deep (-3000 m to -3000 m) gradient in the Atlantic) and (c) salinity in the deep Southern ocean (Atlantic sector, 50 degrees South, 3626 m depth) as a function of the fraction of salt released by sea ice formation used for the brine mechanism (fraction of salt frac, $0 \leq \text{frac} \leq 1$). frac = 0 corresponds to the standard simulations without any brine mechanism (all the salt and ions are diluted in the surface cell where sea ice is formed). When frac = 1 all the released salt and other ions sink with the brine mechanism down to the abyss. The Last Glacial Maximum (LGM) and Pre-industrial (PI) data are from Monnin et al., 2001; Curry and Oppo, 2005; Köhler and Bintanja, 2008; Adkins et al., 2002.

Fig. 3. (a) Atmospheric CO$_2$ change ($\Delta$CO$_2$) and (b) $\Delta\delta^{13}$C$_{at}$ change ($\Delta\delta^{13}$C$_{at}$) due to the transport of salt (S), dissolved inorganic carbon (DIC) and alkalinity (ALK), nutrients, and dissolved organic carbon (DOC, too small too be visible, less than 1 ppm). In all simulations the transport of salt is activated. In the “S transport” experiment only salt is transported, in “DIC+ALK transport” salt, DIC and ALK are transported, in “Nutrients transport” salt and nutrients are transported. “All” is the effect of the simultaneous transport of all variables. $\Delta$CO$_2$ is the difference between the modeled CO$_2$ and the standard modeled CO$_2$ (LGM std, CO$_2$ = 296 ppm). $\Delta(\Delta\delta^{13}$C$_{at}$) is the difference between the modeled $\Delta\delta^{13}$C$_{at}$ and the standard modeled $\Delta\delta^{13}$C$_{at}$ (LGM std).
again after the onset of the sinking of brines, as the ocean circulation has to adapt to the induced change of density distribution (Fig. 1b).

To understand the reasons of the atmospheric CO$_2$ drawdown, we first assess which variable transport is a major contributor to these changes (Fig. 3a). We explore the impact of the sinking of salt alone, then we add either dissolved inorganic carbon (DIC) and alkalinity (ALK), nutrients (phosphate and nitrate) or dissolved organic carbon (DOC). The transport of salt is activated in all simulations as it is the initial reason for the sinking of the brines.

First we consider only the transport of salt to the deep ocean; the other variables do not sink with the brines. The salt sink accounts for the largest part of the CO$_2$ drop (approximately 60% of the CO$_2$ drawdown due to the brine mechanism, Fig. 3a). The increased salinity of the bottom waters results in higher upper to deep ocean density difference (Fig. 1b). Hence the deep stratification is enhanced and the oceanic circulation modified (Fig. 4). In the standard glacial simulation the Atlantic meridional overturning circulation is slightly different from the pre-industrial one. The upper branch is shallower while the lower branch more intense and penetrates farther north (Fig. 4a and b). With the sinking of salt the vertical density gradient is higher. This leads to a more reduced upper branch while the lower branch expands upwards (Fig. 4c and d). The ventilation of the lower branch is reduced resulting in a decoupling between upper and deep waters. The carbon enriched Antarctic Bottom Water (AABW) is less mixed with the surrounding waters and constitutes a greater volume of water. The trapping of CO$_2$ released from the remineralization of organic matter in the deep ocean is then more efficient. The deep carbon reservoir has thus expanded thanks to the change of circulation induced by the salt transport alone.

The transport of dissolved inorganic carbon (DIC) and alkalinity (ALK) by brines also plays a role as it further decreases atmospheric CO$_2$ (Fig. 3). The direct transport of DIC and ALK to the abyss helps building an increased deep oceanic carbon reservoir as carbon is brought to the deep ocean but can not escape because of the stratification set by the increased density. In these sensitivity experiments, salt, DIC and ALK are transported. If only DIC and ALK were transported, the CO$_2$ change would be much greater, but with the salt transport the DIC and ALK concentrations in the surface are already depleted so that the effect of transporting DIC and ALK is not as effective.

The transport of nutrients has an opposite effect, as their transport to the abyss decreases their surface concentrations and thus the biological activity (Fig. 3). The biological pump being less efficient, less atmospheric CO$_2$ is taken up by the ocean. Yet this effect is smaller than the two previous ones. Additionally the transport of DOC is negligible compared to the other mechanisms (less than 1 ppm).

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**Fig. 4.** Simulated meridional overturning stream function (Sv) in the Atlantic for (a) the Pre-industrial (PI) simulation, (b) the standard LGM simulation (LGM-std) with $frac=0$ (no impact of brines), (c) the LGM simulation with $frac=0.5$ (medium impact of brines), (d) the LGM simulation with $frac=1$ (maximum impact of brines).
Now that we have seen that the salt sink is the main driver of the CO$_2$ drop and that the DIC and ALK transport can also play a role, we investigate how they impact the atmospheric CO$_2$. Because of the direct effect of the salt sink (transport from the surface to the bottom) and indirect effect (change of oceanic circulation because of the stratification) the distribution of salinity, DIC and ALK in the ocean is modified (especially the repartition between surface and deep waters). The changed surface concentrations modify the oceanic dissolved CO$_2$ which ultimately drives atmospheric CO$_2$.

Because of the salt transport by brines, salinity is increased in the deep ocean (Fig. 2c) and decreased in the surface. As the solubility of CO$_2$ increases when salinity decreases it results in an atmospheric CO$_2$ drawdown. To quantify this impact we have run the geochemical module of CLIMBER-2 alone forced by the standard distribution of all variables (from the LGM-std simulation without brines) except salinity. For the latter we prescribe the distribution obtained in the simulation with brines for frac=0 to 1. This allows us to get the CO$_2$ change only due to the salinity distribution change. It appears that the modification of the salinity distribution generally accounts for around 1/4 to a 1/3rd of the total CO$_2$ decrease (Fig. 5).

Similarly, DIC and ALK are increased in the deep ocean and decreased in the surface (Fig. 6), both because of the salt transport induced stratification (we have seen that this is the main process) and the direct transport of DIC and ALK by brines. To assess the impact of the change of DIC and ALK distribution we realize the same test as for salinity. With the geochemical module of CLIMBER-2 we evaluate the impact of the change of distribution of DIC and ALK alone for frac=0 to 1. It shows that the DIC and ALK distribution modification can generally explain between 1/2 and 2/3rd of the oceanic pCO$_2$ decrease (Fig. 5). Indeed, as the brines sink and make the deep ocean saltier, increased vertical stratification results. Southern convection (formation of Antarctic Bottom Water, AABW) is greatly reduced and very little exchange exists from the deep ocean to the surface, creating a deep isolated water mass that is enriched in DIC and ALK (while the surface is depleted, Fig. 6). With respect to oceanic pCO$_2$, DIC and ALK changes have opposite effects (reduced surface DIC decreases pCO$_2$, reduced ALK increases pCO$_2$), but the DIC change prevails and results in a net oceanic pCO$_2$ decrease.

### 3.3 Impact of brines on oceanic $\delta^{13}$C

$\delta^{13}$C is usually used to track oceanic circulation, since their changes reflect the changes in ventilation of the different water masses (Duplessy et al., 1988; Curry and Oppo, 2005; Köhler and Bintanja, 2008). In the brine simulations, the modeled $\Delta\delta^{13}$C$_{atl}$ in the Atlantic Ocean is increased when the fraction of salt frac increases (Fig. 2b), which improves the results compared to proxy data. Several mechanisms can affect $\Delta\delta^{13}$C$_{atl}$, as biology and circulation both impact the distribution of $\delta^{13}$C. Indeed, the vertical gradient of $\delta^{13}$C is primarily due the biological activity which preferentially incorporates $^{12}$C during photosynthesis. This tends to deplete the upper waters of $^{12}$C and hence increase $\delta^{13}$C. On the opposite, when organic matter is remineralized deeper in the ocean it releases $^{12}$C thus decreases the deep $\delta^{13}$C. This process is then modulated by the oceanic circulation which transports and mixes water masses with different $\delta^{13}$C signatures and thus modifies the $\delta^{13}$C distribution. With the brine mechanism these two processes are involved as the salt transport alters circulation, the DIC, ALK and DOC transport directly modifies the upper and deep $\delta^{13}$C values, and the nutrients transport impacts the biological activity.

To assess the role of the salt, DIC and ALK, nutrients and DOC transport on the increase of $\Delta\delta^{13}$C$_{atl}$ we analyze the same simulations as for CO$_2$, when considering the transport of each of the variables (Fig. 3b). As for the CO$_2$ decrease, the salt transport plays an important role. The $\Delta\delta^{13}$C$_{atl}$ increase is explained entirely by the salt transport. Because of the brine-induced stratification and resulting modified circulation (Fig. 4) the waters are less mixed. Hence the effect of the biological pump becomes...
more important compared to the mixing. The biological pump increases the vertical δ^{13}C gradient. On the contrary the mixing lowers this gradient. Because the mixing is less intense the vertical gradient increases with lower deep δ^{13}C and higher upper δ^{13}C.

The DIC and ALK transport as well as nutrient transport have an opposite yet minor effect. The DIC and ALK transport brings high surface δ^{13}C values down to the bottom and tends to lower the Δδ^{13}C_{atl}, but it has only a small impact of generally less than 0.1‰. The transport of nutrients lowers the surface nutrient concentration which decreases the biological production. As the latter is responsible for the initial Δδ^{13}C_{atl} it also lowers Δδ^{13}C_{atl}. However this effect is negligible (less than 0.1‰). Finally the effect of DOC transport is too small to be seen.

It appears that the salt transport is clearly the main process driving the Δδ^{13}C_{atl} increase. On the contrary the other variables have only a small impact and tend to decrease Δδ^{13}C_{atl}. The Δδ^{13}C_{atl} is thus improved due to the change of circulation.

3.4 Amplifications by low vertical diffusion

In the previous simulations, only the impact of brines on convection and advection was taken into account via salinity changes. But it is highly probable that such changes would also reduce vertical diffusion. CLIMBER-2 prescribes vertical diffusion as a fixed vertical profile, whereas in theory it depends on the vertical density profile in the ocean. The brine induced stratification would therefore also change.
diffusion, as the more stratified the water becomes, the less vertical diffusion there would be (it requires more energy to mix well stratified water masses). To test this impact on CO$_2$, we conduct a series of simulations with the brine mechanism where three low vertical diffusion profiles (Kz1, Kz2 and Kz3) are prescribed (Fig. 7). The impact of such low diffusion profiles alone in CLIMBER-2 has been previously studied (Bouttes et al., 2009) which showed that it helps reconcile the deep glacial $\delta^{13}$C though with a small impact on atmospheric CO$_2$ (10 ppm decrease only). Here we test these low diffusion profiles when the brine mechanism is activated in the model. We run a set of simulations by varying the $\text{frac}$ value between 0 and 1 for the three diffusion profiles.

The effect of low diffusion alone, that was previously analyzed, resulted in a very small impact on atmospheric CO$_2$, which is the case for the $\text{frac}=0$ simulations. When combined with brines, the brine induced CO$_2$ decline is amplified and it leads to a further significant CO$_2$ decrease (Fig. 8a). It shows a clear amplification of the brine mechanism. Indeed, the low diffusion prevents even more the mixing between the carbon enriched bottom waters and the surface. Therefore it amplifies the trapping of carbon in the deep ocean and results in the supplementary simulated CO$_2$ drawdown.

The amplification also applies for $\delta^{13}$C, especially for $\Delta \delta^{13}$C$_{\text{at}}$ which is increased (Fig. 8b). Indeed, when low diffusion is added, the deep $\delta^{13}$C becomes even more negative. The deep (below $\sim 3000 \text{ m}$) ocean $\delta^{13}$C distribution thus compares far better with the data than in our standard simulation (LGM-std) where the values were too high (Figs. 9 and 10). The upper (above $\sim 2000 \text{ m}$) values are greater, resulting in the stronger upper to deep gradient. Hence $\delta^{13}$C strongly supports the brine mechanism amplified by low diffusion. Yet even though the Antarctic Bottom Water (AABW) expands and the Glacial North Atlantic Deep Water (GNADW) shoals, the $\delta^{13}$C values are still not negative enough in the intermediate south. This suggests that either GNADW should be further reduced and confined to the northern Atlantic, or that another southern water mass existed at intermediate depths (e.g. a Glacial Antarctic Intermediate Water).

3.5 Impact of brines and low diffusion on oceanic $\Delta^{14}$C

The oceanic distribution of $\Delta^{14}$C can be modified by two different processes with the brine mechanism. The change of oceanic circulation induced by the transport of salt to the deep ocean alters the mixing of water masses. The mixing is lowered which tends to increase the vertical gradient and
lower $\delta^{14}C$ in the deep ocean. On the opposite, the DI$^{14}C$ transport during the sinking of brines brings DIC with high $^{14}C$ from the surface to the bottom. It then increases the deep $\Delta^{14}C$ values and lower the vertical gradient. The change of circulation is the prevailing effect and the deep $\Delta^{14}C$ values become very low (Fig. 11a, c and d). Yet only with the very extreme and probably unrealistic $frac$ value ($frac=1$) can the circulation capture the increased deep-water ages present in the data (Robinson et al., 2005; Skinner et al., 2010).

The low diffusion enhances the vertical gradient as the deep ocean becomes even more isolated. The deep $\Delta^{14}C$ data values can then be reached with lower $frac$ values. With very low diffusion profiles (Kz2 and 3, Fig. 12), the deep water $\Delta^{14}C$ become too low showing that the diffusion should be lowered but not as much.

### 3.6 Glacial-interglacial carbon cycle changes

Previous studies with simple box models showed that a reduced Southern ocean vertical mixing rate, which is imposed in the model, can reduce atmospheric CO$_2$ (Paillard...
Fig. 10. $\delta^{13}$C (‰) distribution in the Atlantic. The dots represent the LGM data (Curry and Oppo, 2005; Köhler and Bintanja, 2008). (a), (b), (c), (d), (e), (f) Modelled $\delta^{13}$C distribution: (a), (c), (e) with the low diffusion profile $Kz2$ (Fig. 7); (b), (d), (f) with the low diffusion profile $Kz3$ (Fig. 7). (a), (b) $frac = 0$ (no impact of brines), (c), (d) $frac = 0.5$ (medium impact of brines), (e), (f) $frac = 1$ (maximum impact of brines).

and Parrenin, 2004; Köhler et al., 2005). It also decreases the deep Southern $\delta^{13}$C (Köhler et al., 2005). More complex models of intermediate complexity and general circulation showed that changes in the oceanic circulation impacts the $\delta^{13}$C distribution in the ocean. Reducing the strength of the meridional overturning circulation by adding fresh water fluxes to the North Atlantic tends to decrease the simulated $\delta^{13}$C of the deep ocean in line with data (Tagliabue et al., 2009). Alternatively, imposing a lower vertical mixing by changing the vertical diffusion profile also increases the upper to deep oceanic $\delta^{13}$C in agreement with data (Bouttes et al., 2009). However in both cases the associated atmospheric CO$_2$ drawdown remains small compared to the glacial-interglacial change (less than 10 ppm compared to $\sim 90$ ppm).

With the sinking of brines, the necessary change of circulation which leads to an increase of the oceanic vertical $\delta^{13}$C gradient is simulated with a more physical mechanism (no artificial fresh water flux is added). Moreover the CO$_2$ drawdown simulated is much more significant. With the maximum effect of the sinking of brines ($frac = 1$) the CO$_2$ drawdown is 52 ppm. With less extreme values of $frac$ around 0.5, the CO$_2$ decrease is around 30 ppm, which can be further amplified by 5 to 15 ppm with vertical low diffusion. $frac$ values around 0.5 are the most plausible values as they are both supported by the comparisons of model results with data and modern observations. Indeed, comparisons between the modelled salinity and $\Delta \delta^{13}$C with data are in better agreement for $frac$ values around 0.5 with the low diffusion profile $Kz1$ (Fig. 8), as well as $\Delta ^{14}$C (Fig. 11). Such a $frac$ value is also close to 0.62 which corresponds to the observed $\sim 62\%$ of the salt flux rapidly released by sea ice formation that is released out of the fjord in the Norwegian Sea (Haarpainter et al., 2001). Yet, though the simulated CO$_2$ drop is important it is still not enough indicating the need for other processes.
Fig. 11. $\Delta^{14}C$ (‰) distribution in the Atlantic simulated by the model (where $\Delta^{14}C = 1000 \times (\frac{D^{14}C}{DIC} - 1)$). The dots represent the LGM data (Robinson et al., 2005; Skinner et al., 2010). (a), (c), (e) with the standard diffusion profile $Kz0$ (Fig. 7); (b), (d), (f) with the low diffusion profile $Kz1$ (Fig. 7). (a), (b) $frac = 0$ (no impact of brines), (c), (d) $frac = 0.5$ (medium impact of brines), (e), (f) $frac = 1$ (maximum impact of brines).

Hence, although the brine mechanism has the potential to decrease significantly atmospheric CO$_2$, additional mechanisms are also very likely to be involved. In particular, within the already tested mechanisms, the addition of carbonate compensation is a likely candidate, since it would further decrease CO$_2$ by around 30 ppm (Broecker and Peng, 1987; Brovkin et al., 2007). Additionally, modifications to the biological pump (linked to dust reconstructions and phytoplankton stoichiometry) can provide an additional 10–25 ppm (Bopp et al., 2003; Tagliabue et al., 2009), as well as increasing carbon export in line with proxy reconstructions. Overall, a combination of low diffusion, carbonate compensation and enhanced biological pump added to the brine mechanism could yield the full range of glacial to interglacial variability of CO$_2$.

4 Conclusions

In conclusion, the brine mechanism can lead to a large atmospheric CO$_2$ drop supported by the concomitant simulated changes in oceanic carbon isotope distribution, in agreement with proxy data. We have shown that this CO$_2$ decline is primarily due to the salt transport although the DIC and ALK sink also play a role. Because of the salt transport to the deep ocean the oceanic circulation is modified and the deep ocean becomes more stratified and decoupled from the surface. The abyss is enriched in carbon which is trapped because of the reduced mixing with other water masses. This decrease can be amplified if the simultaneous impact on oceanic vertical diffusion is accounted for. The low diffusion would further reduce the mixing between the deep and upper ocean, hence
Fig. 12. $\Delta^{14}C$ (‰) distribution in the Atlantic simulated by the model (where $\Delta^{14}C = 1000 \cdot (\frac{DI^{14}C}{DIC}) - 1$)). The dots represent the LGM data (Robinson et al., 2005; Skinner et al., 2010). (a), (c), (e) with the low diffusion profile $Kz2$ (Fig. 7); (b), (d), (f) with the low diffusion profile $Kz3$ (Fig. 7). (a), (b) $frac=0$ (no impact of brines), (c), (d) $frac=0.5$ (medium impact of brines), (e), (f) $frac=1$ (maximum impact of brines).

decreasing atmospheric CO$_2$ and increasing the $\Delta^{13}C_{at}$ in line with data. We hypothesize that a combination of the already known carbonate compensation mechanism, iron fertilization, brine mechanism and low diffusion would be sufficient to reach the glacial value of 190 ppm. The brine mechanism provides two major features: a physical way of setting the needed glacial deep ocean stratification and a direct connection from surface to deep waters, which is crucial to create a very large deep ocean carbon reservoir. Beyond the understanding of past climate, this mechanism sheds new light on ocean dynamics. Brines have a crucial role in the formation of deep water and should therefore be better accounted for in climate models.

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