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## RESEARCH ARTICLE

10.1002/2014PA002720

## Key Points:

- We simulate salinity and water isotopes for conditions during the last glacial
- Large errors for past quantitative salinity with actual  $\delta^{18}\text{O}$ -salinity relation
- Use water isotopologues reduce uncertainties on quantitative paleosalinity

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## Modeling water isotopologues during the last glacial: Implications for quantitative paleosalinity reconstruction

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**Abstract** Quantitative paleosalinity reconstructions with reasonable uncertainties remain a challenge in paleoceanography. In this study, we focus on stable isotope-based methods ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) to derive paleosalinity. We use the water isotopes-enabled fully coupled atmosphere/ocean/vegetation/land surface three-dimensional model of intermediate complexity iLOVECLIM to simulate the climate and water isotopes during the Last Glacial Maximum (LGM) and Heinrich event 1. We investigate how the isotopes in water can be used as reliable proxies to quantitatively reconstruct past changes in seawater salinity. Our results demonstrate that a quantitative salinity reconstruction during glacial conditions based on present-day regional  $\delta^{18}\text{O}$ -salinity relationships can lead to considerable errors (up to 25 g/kg in certain regions). However, we show that these eventual uncertainties on paleosalinity reconstruction can be reduced by allowing for model-derived regional  $\delta^{18}\text{O}$ -salinity relationships to vary through time. Our results indicate a rather stable dependence between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in surface seawater during the LGM. This suggests that quantitative reconstruction of salinity based on the  $\delta^2\text{H}$  measurement of alkenones ( $\delta^2\text{H}_a$ ) might be possible if the slope and the intercept of the regression between the fractionation factor  $\delta^2\text{H}_a$ - $\delta^2\text{H}_{\text{sw}}$  and salinity can be sufficiently tightly constrained in open ocean conditions. We confirm that pairing water isotopologues has a strong potential to reduce uncertainties on quantitative paleosalinity reconstructions, also under glacial boundary conditions.

### 1. Introduction

Salinity can be easily measured during oceanographic cruises [Boyer and Levitus, 1994] and by satellite observations [Le Vine et al., 2010], but studies of past ocean sea surface salinity are dependent on indirect measurements or so-called proxy reconstructions. Estimates of sea surface salinity variations are not only important for the understanding of past oceanic dynamics [Duplessy et al., 1991] and past hydrological cycles as, for example, monsoon intensity [Duplessy, 1982; Weldeab et al., 2007] but also are critical for evaluating climate models used to predict future climate changes. While there exist qualitative proxies for sea surface salinity, quantitative reconstructions with reasonable uncertainties remain a challenge in paleoceanography.

Some tools that exist include the potential of using morphological variations of phytoplankton in reconstructing salinity [Bollmann and Herrle, 2007]. However, there are issues with this method such as taphonomic processes [Bollmann et al., 2009]. Another tool for the quantitative reconstruction of paleosalinity is transfer functions of dinoflagellate or diatom assemblages, which can be used in specific marine environments [Rochon et al., 1999; DeSève, 1999; De Vernal et al., 1994, 2001] with an accuracy of  $\pm 1.8$  g/kg (absolute salinity ( $S_A$ )) for the present day [De Vernal et al., 2001]. This method assumes that each species lives in a given range of climatic and environmental conditions. However, these methods cannot be extrapolated unambiguously to a global scale because of nonanalogue situations in the past. Another more recent quantitative method has established the Ba/Ca ratio of foraminiferal  $\text{CaCO}_3$  as a proxy for river runoff with a calibration established using the modern Ba/Ca-salinity relationship [Carroll et al., 1993; Moore, 1997; Weldeab et al., 2007]. Apart from being limited to coastal regions with river runoff, this approach assumes that the Ba/Ca ratio in planktonic foraminifer shells is dominated by the Ba/Ca concentration of seawater and not by other factors and that the present-day calibration is applicable into the past.

The most common method presently used is the calibration of stable oxygen isotope ratios measured on carbonate microfossils (foraminifera) with salinity [Craig and Gordon, 1965; Shackleton, 1974; Duplessy et al., 1991; Malaizé and Caley, 2009]. Unfortunately, this method rarely permits meaningful quantitative salinity reconstructions because of the large uncertainties associated [Rohling and Bigg, 1998; Schmidt, 1999; Rohling, 2000; Legrande and Schmidt, 2011].

Yet another method uses hydrogen isotope changes. Culture experiments found a constant offset between the hydrogen isotopic composition of water and of alkenones synthesized in that water [Paul, 2002; Englebrecht and Sachs, 2005]. Recently, Schouten et al. [2006] demonstrated that this offset was not constant, but dependent on salinity (biological fractionation). The hydrogen isotopic composition of the alkenones reflects mainly this biological fractionation but also the hydrogen isotopic composition of the water. This biological fractionation makes it impossible to simply reconstruct the hydrogen isotopic composition of the water and, even if it would be possible, this method suffers from the same large uncertainties as the oxygen isotopes of water. An alternative approach is to use the biological fractionation factor between the hydrogen isotopic composition of alkenones and water that is linked to salinity [Schouten et al., 2006]. However, that method requires information on the hydrogen isotope ratio of seawater ( $\delta^2\text{H}$ :  $\delta$  in permil units =  $(\text{Ratio}_{\text{sample}}/\text{Ratio}_{\text{standard}} - 1) * 1000$ ) and its relationship with oxygen isotope ratio of seawater over time that could suffer from large uncertainties.

It has been also suggested that pairing information from water isotopes,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  (isotopologues), could yield better estimates for paleosalinity [Rohling, 2007; Leduc et al., 2013]. A numerical modeling experiment for the Holocene period has demonstrated that this combination of water isotopologues may indeed allow for a better estimation of paleosalinity variability [Legrande and Schmidt, 2011]. However, similar modeling experiments under different boundary conditions such as glacial periods do not exist.

In this paper, we focus on stable isotope-based methods to derive paleosalinity. In order to investigate how water isotopes can be used as reliable proxies to quantitatively reconstruct past changes in seawater salinity, we use a water isotope enabled fully coupled atmosphere/ocean/vegetation/land surface three-dimensional model of intermediate complexity *i*LOVECLIM (v1.0) [Roche, 2013; Roche and Caley, 2013; Caley and Roche, 2013]. We simulate the climate and water isotopes during the LGM and Heinrich event 1, and we address the stability of the slope of the  $\delta^{18}\text{O}$ -salinity relationship spatially and temporally. There are two ways to define a slope between water isotopes and salinity, either fixing a point in time and looking at the spatial relationship between the two, hereafter the “spatial slope,” or anchoring a point in space and consider the variation of the two elements in time, the “temporal slope.”

The stability of the  $\delta^{18}\text{O}$ - $\delta^2\text{H}$  slope together with the potential improvement of paleosalinity reconstructions using the combination of water isotopologues was investigated for glacial conditions. In the light of these results, future directions of quantitative stable isotope-based salinity reconstructions are proposed.

## 2. Methods

### 2.1. Water Isotopes in *i*LOVECLIM

The *i*LOVECLIM (version 1.0) model is a derivative of the LOVECLIM-1.2 climate model extensively described in Goosse et al. [2010]. We retained the atmospheric (ECBilt), oceanic (CLIO), vegetation (VECODE), and land surface (LBM) components of the original model, integrating a complete, conservative, water isotope cycle through these components. A detailed description of the method used to compute the oxygen isotopes in *i*LOVECLIM can be found in Roche [2013], and the validation of model results can be found in Roche and Caley [2013] and Caley and Roche [2013]. With regards to water isotopes, a key development involves the atmospheric component (approximately  $5.6^\circ$  resolution in latitude and longitude), in which evaporation, condensation, and existence of different phases (liquid and solid) all affect the isotopic conditions of the water isotopes. In the ocean component (approximately  $3^\circ$  resolution in latitude and longitude), the water isotopes act as passive tracers, ignoring the small fractionation implied by the presence of sea ice [Craig and Gordon, 1965]. For the land surface component, the implementation follows a similar procedure as for the water except that equilibrium fractionation is assumed during phase changes. An important differentiation is that in this module water accumulates on land until a certain threshold; once this is exceeded, water is routed instantaneously to the ocean.

Although not discussed previously, hydrogen isotopes were implemented at the same time in the water cycle. Hydrogen isotopes are treated nearly identical to the oxygen isotopes described in Roche [2013], except for differences in the fractionation coefficients. For deuterium, we use the liquid-vapor fractionation formula proposed by Majoube [1971b] and the solid-vapor fractionation formula of Majoube [1971a].

## 2.2. LGM Boundary Conditions

The details of the model in simulating the present-day oxygen isotopes are presented by Roche [2013], Roche and Caley [2013], and Caley and Roche [2013]. We use the boundary conditions defined in/by the Palaeoclimate Modelling Intercomparison Project Phase 2 (PMIP2, [Braconnot et al., 2007a, 2007b]) protocol to simulate the LGM climate as described in Caley et al. [2014]. Lowered levels of atmospheric greenhouse gas concentrations ( $\text{CO}_2 = 185$  ppm,  $\text{CH}_4 = 350$  ppb, and  $\text{NO}_2 = 200$  ppb) are used in agreement with ice core measurements [Fluckiger et al., 1999; Dällenbach et al., 2000; Monnin et al., 2001]. Ice sheet topographic changes are taken from Peltier [2004], and the surface albedo is set accordingly. Orbital parameters correspond to 21,000 years before present [Berger and Loutre, 1992]. To account for the  $\sim 130$  m decrease in sea level relative to present day, the land-sea mask (migration of coastlines) and the ocean bathymetry are modified [Lambeck and Chappell, 2001]. Some variations exist among the PMIP-2 simulations, mainly for the Northern Hemisphere, in how to handle changes in the river basins [Weber et al., 2007], i.e., changes in river routing due to the presence of ice sheets. In our LGM simulation, we included changes in the water routing from the Laurentide ice sheet over North America and from the Fennoscandian ice sheet over Eurasia. These forcings were applied to the model and integrated over 5000 years until a new equilibrium was reached.

Our choice of using the PMIP-2 boundary conditions instead of the more recent (The Paleoclimate Modelling Intercomparison Project (PMIP), 2013, <http://pmip3.lscce.ipsl.fr>) protocol arise from several considerations: (1) having a state readily comparable to the already published LGM state of an earlier version of the model [Roche et al., 2007] and (2) the possibility in a future study to intercompare our atmospheric results to already published PMIP-2 LGM atmospheric general circulation model.

The behavior of the water oxygen isotope under glacial conditions has been evaluated in Caley et al. [2014] and found to be, in general, good agreement with available proxy data.

## 2.3. Heinrich Event Simulation Setup

Freshwater hosing is used to mimic Heinrich event 1 as described in Roche et al. [2014]. We start from the LGM conditions described previously and applied a freshwater flux equal to 0.16 Sv in the Labrador Sea. With our model sensitivity, this freshwater flux leads to the best agreement between isotopic data and model results during Heinrich 1, as evaluated in detail in Roche et al. [2014]. In terms of water oxygen isotopes, the additional freshwater is applied to the surface ocean with a  $\delta^{18}\text{O}$  water value of  $-30$  per mil. Since the freshwater perturbation is supposed to originate from icebergs coming from the Laurentide ice sheet, a very depleted content is expected (the glacial ice in the neighboring Greenland ice sheet is around  $-36$  per mil).

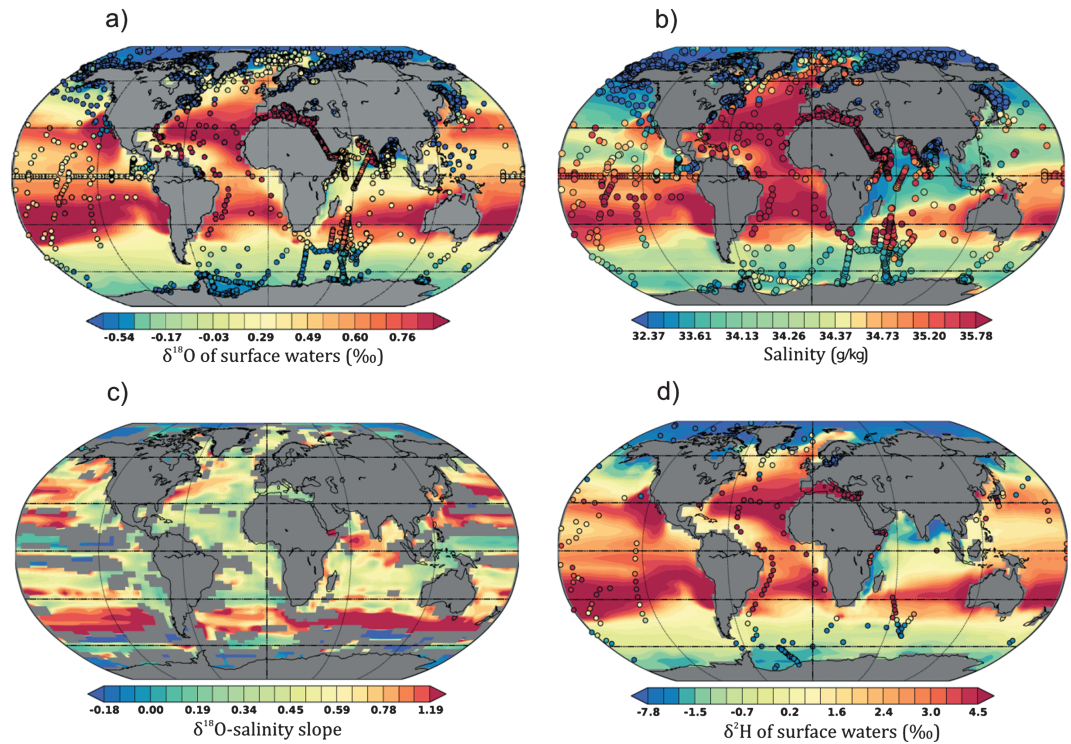
## 3. Quantitative Paleosalinity: Methods and Evaluation

### 3.1. Stable Oxygen Isotopes ( $\delta^{18}\text{O}$ )

#### 3.1.1. Basis of the Method

The method uses the regional linear relationship between seawater stable oxygen isotopes and salinity [Craig and Gordon, 1965; Duplessy et al., 1991]. The seawater oxygen isotope composition ( $\delta^{18}\text{O}$ :  $\delta$  in per mil units =  $(\text{Ratio}_{\text{sample}}/\text{Ratio}_{\text{standard}} - 1) * 1000$ ) can be reconstructed by measuring the oxygen isotopic composition of carbonaceous microfossils (foraminifera) and by correcting for the effect of temperature on stable oxygen isotope fractionation using temperatures derived from Mg/Ca ratios measured on the same shells [Shackleton, 1974; Duplessy et al., 1991; Malaizé and Caley, 2009]. Unfortunately, this method rarely permits meaningful quantitative salinity reconstructions because of the large uncertainties associated [Rohling and Bigg, 1998; Schmidt, 1999; Rohling, 2000]. Numerical modeling results indicate that the relationship of oxygen isotopes with salinity strongly changes with time resulting in large uncertainties (reconstructed salinity change using the  $\delta^{18}\text{O}_{\text{sw}}$  to salinity slope can be 2–4 times the simulated salinity change) [Legrande and Schmidt, 2011], in addition to the  $\approx 0.8$ – $1.8$  g/kg structural/analytical error [Schmidt, 1999]. However, such a numerical modeling experiment have been conducted for the Holocene, a period when climate was primarily driven by orbital changes [Legrande and Schmidt, 2011]. Drivers of climate





**Figure 1.** (a) Near-surface ocean  $\delta^{18}\text{O}$  of seawater in *i*LOVECLIM compared to the Goddard Institute for Space Studies (GISS) database [Schmidt *et al.*, 1999] (colored circles). (b) Near-surface ocean salinity in *i*LOVECLIM compared to the GISS database [Schmidt *et al.*, 1999] (colored circles). (c) Slope of the  $\delta^{18}\text{O}_{\text{sw}}$ -salinity relation in near-surface as simulated with *i*LOVECLIM in the control experiment. The masked areas indicate that the coefficient of determination of the linear regression is lower than 0.4 ( $R^2 < 0.4$ ). (d) Near-surface ocean  $\delta^2\text{H}$  of seawater in *i*LOVECLIM compared to the GISS database [Schmidt *et al.*, 1999] (colored circles).

change over glacial to interglacial time scales (atmospheric greenhouse gas concentrations, ice sheet topography, and sea level changes) may produce a different pattern of temporal slopes [LeGrande and Schmidt, 2011]. For example, a study in the northern Indian Ocean under Last Glacial Maximum (LGM) conditions shows that there is a higher probability that the  $\delta^{18}\text{O}$ -salinity slopes were stable and reduced error on paleosalinity [Delaygue *et al.*, 2001].

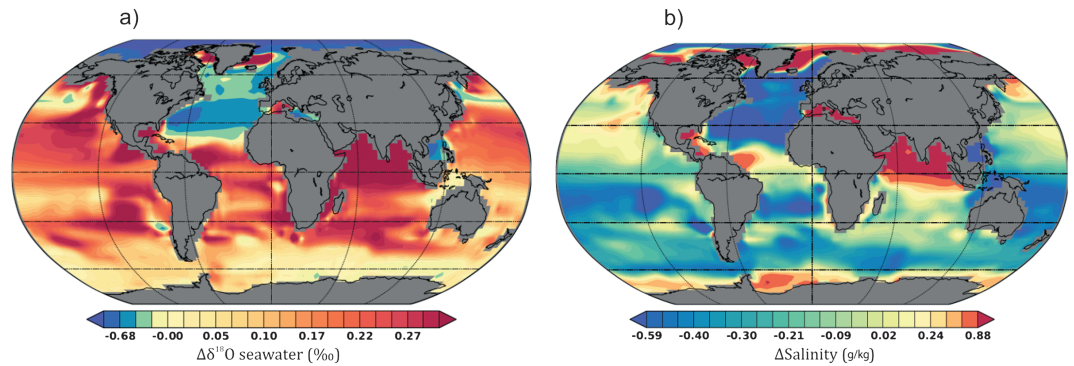
### 3.1.2. Model Results

Salinity and  $\delta^{18}\text{O}$  simulated with *i*LOVECLIM for the preindustrial compare well with present-day data [Schmidt *et al.*, 1999] (Figure 1), although a notable mismatch occurs in the western Indian Ocean where the simulated near surface ocean values are much lower than those observed in reality [Roche and Caley, 2013].

Simulated regional spatial  $\delta^{18}\text{O}$ -salinity slopes (defined regionally in different regions of the globe) for the present day are in good agreement with observations [LeGrande and Schmidt, 2006] (Figure 1). The  $\delta^{18}\text{O}$ -salinity slopes at midlatitudes are greatest ( $>0.5\text{‰}/1\text{ g/kg}$  of salinity) because of a small amount of very depleted water vapor that leaves the tropics at a midtroposphere level [LeGrande and Schmidt, 2009] combined with depleted end-members from river input [Craig and Gordon, 1965; Fairbanks *et al.*, 1992; LeGrande and Schmidt, 2006]. In the tropics, the slopes are shallowest (0.1 to  $0.3\text{‰}/1\text{ g/kg}$  of salinity) as a result of vigorous water recycling [Fairbanks *et al.*, 1992; LeGrande and Schmidt, 2006].

At high latitudes, sea ice preferentially incorporates  $^{18}\text{O}$  and excludes salt, yielding a (slightly) negative  $\delta^{18}\text{O}$ -salinity relationship. This process is not taken into account in our simulation, but the effect is small [Craig and Gordon, 1965].

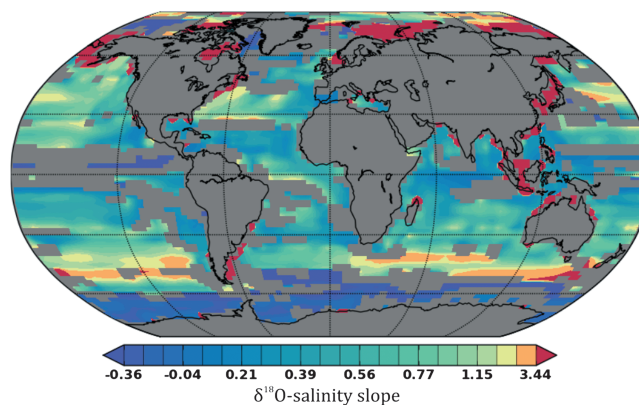
We now turn to the LGM simulated in this study. A previous study has demonstrated that modeled surface water  $\delta^{18}\text{O}$  differences between the LGM and present day exhibit negative values in the North Atlantic



**Figure 2.** (a) Simulated surface water  $\delta^{18}\text{O}$  difference (LGM-CT) in iLOVECLIM. (b) Simulated surface salinity difference (LGM-CT) in iLOVECLIM. The LGM ice sheet contribution (1‰) is not taken into account.

region (between 30°N and 60°N) as a consequence of changes in ice sheets distribution and their impact on surface water  $\delta^{18}\text{O}$  through depleted water discharges from rivers [Caley et al., 2014] (Figure 2). The change from present-day seasonal sea ice to LGM permanent sea ice conditions was responsible for positive differences at both sides of the Greenland ice sheet [Caley et al., 2014]. The rest of the oceans (tropical area) was mainly marked by slightly positive differences, probably reflecting more  $\delta^{18}\text{O}$  enriched precipitation signal during the LGM [Caley et al., 2014] (Figure 2). Concerning surface salinity changes, we observe some differences in comparison to water  $\delta^{18}\text{O}$  changes. For example, southern hemisphere salinity differences between the LGM and present-day range from 0.0 to  $-0.6\text{ g/kg}$ , significantly more negative than what is observed for  $\delta^{18}\text{O}$  differences (which range from 0.0 to  $+0.4\text{‰}$ ) (Figure 2). The changes observed during the LGM climate for the surface water  $\delta^{18}\text{O}$  and salinity create differences in spatial slopes during the LGM when compared to present day (Figure 3).

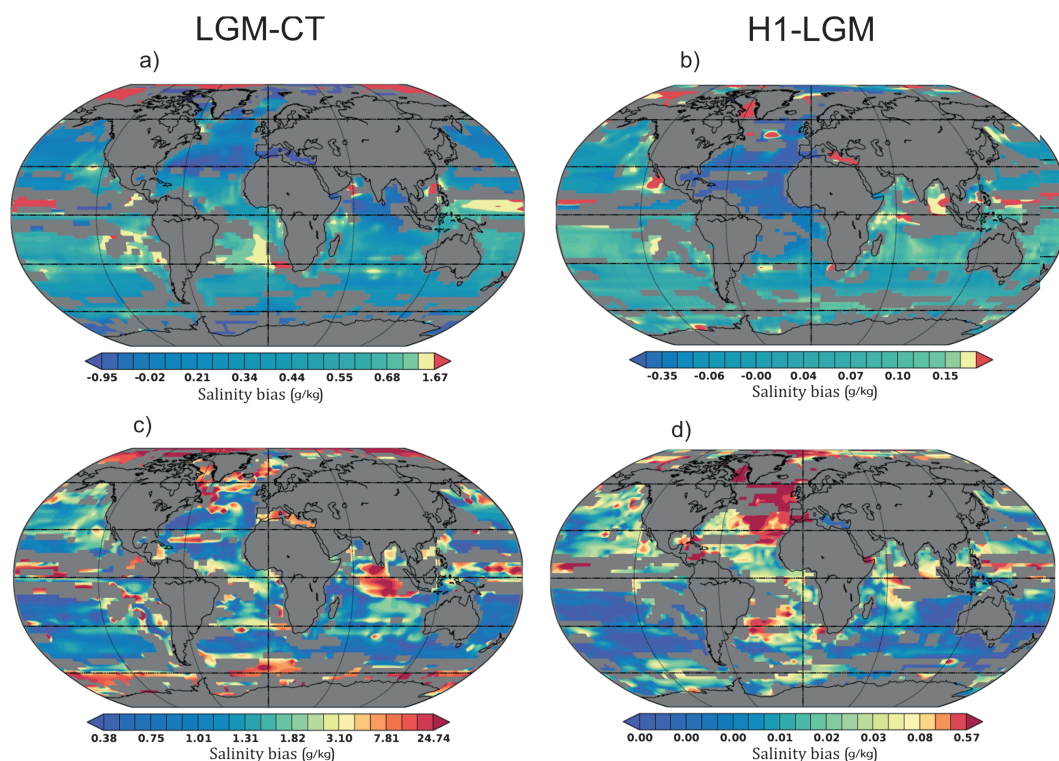
We first calculate the errors linked to the use of the present-day spatial slopes to reconstruct LGM salinity (Figure 4a). These errors are generally smaller than  $1.5\text{ g/kg}$ . However, the use of such spatial slopes is not permissible for reconstructing records of paleosalinity. The temporal slope must be considered. Local variations in  $\Delta S$  and  $\Delta\delta^{18}\text{O}$  of salinity and isotope, between modern and the last glacial climate, are related by  $\Delta S = \Delta\delta^{18}\text{O}/a'$ , but inferred as  $\Delta S = \Delta\delta^{18}\text{O}/a$  (where  $a'$  denotes the LGM spatial slope and  $a$  the modern one). The spatial slopes for the modern and LGM periods have been calculated for each near-surface ocean grid point of the iLOVECLIM model. To do so, a linear regression was performed between water



**Figure 3.** Slope of the  $\delta^{18}\text{O}_{\text{sw}}$ -salinity relation in near-surface as simulated with iLOVECLIM for the LGM. The masked areas indicate that the coefficient of determination of the linear regression is lower than 0.4 ( $R^2 < 0.4$ ). The red areas indicate the locations where the land-sea mask and the oceanic bathymetry are modified to account for the  $\sim 130\text{ m}$  decrease in sea level relative to present day.

isotopes and salinity, considering each grid point and the eight closest grid points around (nine grid points containing  $\delta^{18}\text{O}$  and salinity values are used per linear regression). Only linear regressions with coefficients of determination higher than 0.4 ( $R^2 > 0.4$ ) are conserved and used in this study.

The error on the inferred  $\Delta S$  can therefore be calculated as  $\sigma = \Delta\delta^{18}\text{O} (a-a')/(aa)$ . Results indicate larger errors in the tropics and high latitudes ( $> 2\text{ g/kg}$  with a maximum value of  $25\text{ g/kg}$ ) whereas errors in the midlatitudes are smaller (between 0 and  $2\text{ g/kg}$ ) (Figure 4c). Therefore, this indicates that the major uncertainties in paleosalinity reconstruction between the LGM and present are related to the temporal slopes.



**Figure 4.** (a) Bias linked to the use of the present-day  $\delta^{18}\text{O}_{\text{sw}}$ -salinity spatial slopes to reconstruct LGM salinity. (b) Bias linked to the use of the LGM  $\delta^{18}\text{O}_{\text{sw}}$ -salinity spatial slopes to reconstruct salinity during Heinrich 1 conditions. (c) Absolute bias of salinity linked to temporal evolution of the  $\delta^{18}\text{O}_{\text{sw}}$ -salinity slope between the LGM and present with iLOVECLIM. (d) Absolute bias of salinity linked to temporal evolution of the  $\delta^{18}\text{O}_{\text{sw}}$ -salinity slope between the Heinrich 1 conditions and LGM with iLOVECLIM.

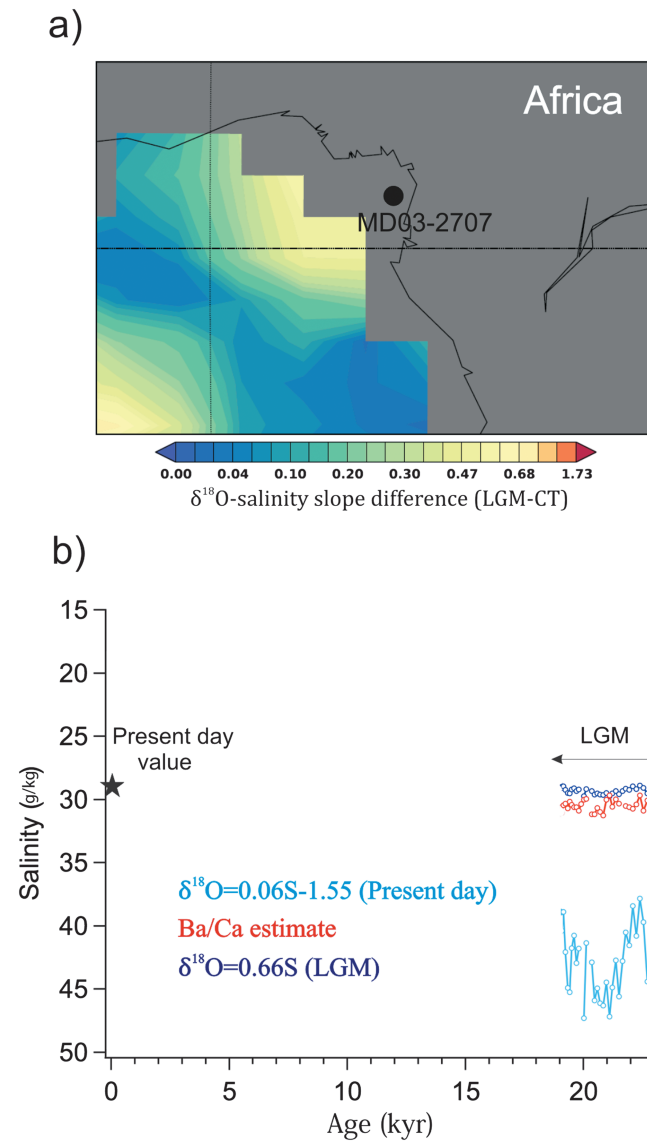
We also calculate the errors linked to the use of the LGM spatial slopes to reconstruct salinity during Heinrich event 1 (Figures 4b and 4d). These errors are small ( $<0.5$  g/kg) and of the same order of magnitude as errors associated with temporal slopes. The largest errors for both the spatial and temporal slopes are located in the North Atlantic Ocean (Figures 4b and 4d). These errors must be added to the large errors associated with the temporal slopes between the LGM (Figures 4a and 4c) and present to obtain the final uncertainties associated with the use of actual spatial slopes for reconstructing paleosalinity during Heinrich event 1.

### 3.1.3. Perspectives

Assuming that the model results are robust (i.e., in a perfect model sense), it may be possible to use the model-derived temporal slopes directly in the calculation to reduce uncertainties on the paleosalinity reconstructions during glacial conditions. To test this approach we use the published results of a marine sediment core (MD03-2707) located in Gulf of Guinea and influenced by West African monsoon hydrology [Weldeab *et al.*, 2007] (Figure 5). We calculate the temporal slopes evolution of the  $\delta^{18}\text{O}$ -salinity relationship with the iLOVECLIM model for this region (Figure 5a). Ocean salinity at this core location was reconstructed using Ba/Ca in planktonic foraminiferal (*G. ruber pink*) calcite (Figure 5b). In addition, a record of  $\delta^{18}\text{O}_{\text{sw}}$ , obtained by correcting for the effect of temperature on stable oxygen isotope fractionation using temperatures derived from Mg/Ca ratios measured on the same shells, is also available. This is therefore an ideal location to test if the temporal slopes evolution obtained with our model can reduce uncertainties on paleosalinity reconstruction during last glacial conditions.

We use the present-day  $\delta^{18}\text{O}$ -salinity relationship of the eastern equatorial Atlantic ( $\delta^{18}\text{O} = 0.06\text{S} - 1.55$  Leduc *et al.* [2013] from Legrande and Schmidt [2006]) to reconstruct past salinity using  $\delta^{18}\text{O}_{\text{sw}}$ . The modern annual SSS value at 10 to 25 m water depth over the core site is 29 g/kg [Weldeab *et al.*, 2007] in agreement with the Ba/Ca estimate at  $\sim 360$  years. Using the present-day  $\delta^{18}\text{O}_{\text{sw}}$ -salinity relationship with a salinity of 29 g/kg leads to a  $\delta^{18}\text{O}_{\text{sw}}$  of  $\sim 0.2\text{‰}$ , in good agreement with the estimate of  $\sim 0.3\text{‰}$  at  $\sim 360$  years [Weldeab *et al.*, 2007]





**Figure 5.** (a) Location of core MD03-2707 in Gulf of Guinea and change of  $\delta^{18}\text{O}_{\text{sw}}$ -salinity slope between the LGM and present as simulated with iLOVECLIM. (b) Quantitative salinity reconstructions during the LGM from core MD03-2707 located in Gulf of Guinea using  $\delta^{18}\text{O}_{\text{sw}}$ -salinity relationship for the present day, the  $\delta^{18}\text{O}_{\text{sw}}$ -salinity relationship when applying the change of slope of  $\sim 0.6$  between the LGM and present and Ba/Ca estimate.

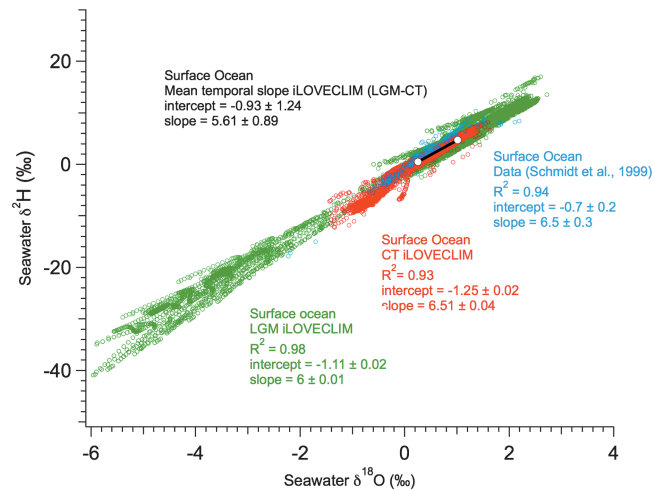
(a + 0.6‰ was added to the calculated  $\delta^{18}\text{O}_{\text{sw}}$  to account for *G. ruber pink* vital effect [Deuser and Ross, 1989]). We therefore use this relation to reconstruct paleosalinity during the LGM (19–23 ka), correcting the effect of global  $\delta^{18}\text{O}_{\text{sw}}$  and salinity changes from sea level and  $\delta^{18}\text{O}_{\text{sw}}$  estimation derived from model experiments [Bintanja et al., 2005]. The results are shown in Figure 5. The disagreement between salinity derived from Ba/Ca and salinity derived from  $\delta^{18}\text{O}_{\text{sw}}$  during the LGM is extremely large ( $\sim 15$  g/kg). Applying the change of slope of  $\sim 0.6$  between the LGM and present that we compute for the eastern equatorial Atlantic (Figure 5a) leads to a much better agreement between the two approaches to reconstruct paleosalinity (Figure 5b). This suggests that (1) the Ba/Ca-derived salinity estimation, that is based on the modern seawater Ba/salinity relationship, may be valid during the LGM; (2) quantitative salinity reconstructions based on present-day regional  $\delta^{18}\text{O}$ -salinity relationships are not possible in areas with increased/enlarged uncertainties linked to temporal slopes changes; and (3) the use of model-derived temporal slopes directly in the calculation result in a better fit between the two proxies approach for paleosalinity reconstruction during glacial conditions.

For areas where the errors are not substantial, the present-day relationship can potentially be used. For example, a study adjacent to the Manche paleoriver outlet combined quantitative salinity reconstructions derived from dinocyst and planktonic foraminiferal analyses (assuming that the present-day  $\delta^{18}\text{O}_{\text{sw}}$ -salinity spatial relationship can be used in the past) during the last glacial [Eynaud et al., 2012]. A high similarity in the amplitude and timing of paleosalinity changes was found. Based on our model results, the studied region is indeed marked by weak uncertainties associated to spatial and temporal changes of the  $\delta^{18}\text{O}_{\text{sw}}$ -salinity relationship (Figure 3). Nonetheless, model-derived temporal slopes can contain some uncertainties and so complementary approaches must be developed to quantitatively reconstruct paleosalinity as described below.

### 3.2. Stable Hydrogen Isotopes ( $\delta^2\text{H}$ )

#### 3.2.1. Basis of the Method

Culture experiments have indicated a significant relationship between the hydrogen isotopic composition of alkenones ( $\delta^2\text{H}_a$ ) and salinity [Schouten et al., 2006]. The biological fractionation between the alkenones and the water is linked to salinity, species, and to a lesser extent growth rate [Schouten et al., 2006]. This



**Figure 6.** Regression between surface seawater  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  for the present and LGM time period with iLOVECLIM. The present-day regression for surface seawater (first 50 m) was calculated using the GISS database [Schmidt et al., 1999].

fractionation factor  $\alpha$ -salinity relationship can be used to reconstruct paleo sea surface salinities [Van der Meer et al., 2007, 2008]:

$$S = \frac{(1000 + \delta^2\text{H}_a) - b}{a}$$

where  $a$  and  $b$  refer to the slope and the intercept of the relation between the fractionation factor  $\alpha$ -salinity and salinity, respectively.

Schwab and Sachs [2011] found that there was no relationship between the fractionation factor  $\alpha$ -salinity and salinity in a natural salinity gradient in the Chesapeake Bay estuary. Instead, the authors suggested, in a similar line of reasoning to Nelson and Sachs

[2014], that there might be differences in the sensitivity of hydrogen isotopic fractionation to salinity between different haptophytes, i.e., open marine environments than in producers from continental interior sites. Although recent studies do not support this hypothesis and confirm that hydrogen isotope fractionation of all alkenone-producing species is strongly related to salinity, while there may also be a growth rate effect, and different species may fractionate differently in absolute values [Chivall et al., 2014; M'Boile et al., 2014]. Large differences in  $\delta^2\text{H}$  between the C37:2 and C37:3 alkenones of up to 45‰ have been reported within the literature [D'Andrea et al., 2007; Schwab and Sachs, 2009; Wolhowe et al., 2009]. Recent studies recommend analyzing the combined C37 alkenones, which reflect a more primary signal related to internal cell water and salinity [van der Meer et al., 2013; Chivall et al., 2014].

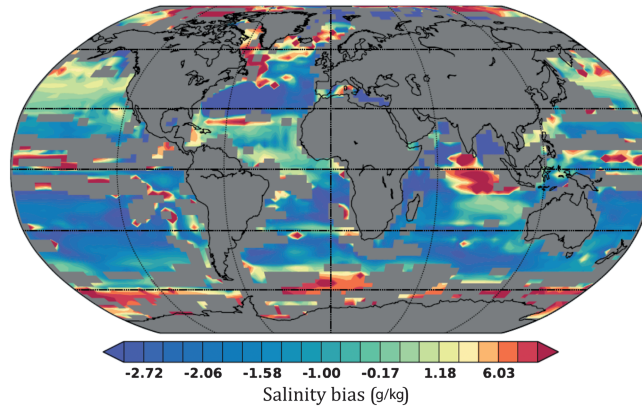
In order to reconstruct paleo-sea surface salinities using this method, information on the hydrogen isotope ratio of seawater is required ( $\delta^2\text{H}_{\text{sw}}$ ). Schouten et al. [2006] considered that the  $\delta^2\text{H}_{\text{sw}}$  might be constrained by using the so-called meteoric water line (MWL), which determines a proportional dependence between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in precipitation that can be approximated by  $\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 10$  today (8 is the slope of the relationship and 10 is the intercept that is called deuterium excess) [Craig, 1961; Craig and Gordon, 1965]. However, Rohling [2007] reasoned that the formula that needs to be used to reconstruct the hydrogen isotope ratio of seawater is not the MWL but the formula that corresponds to that of the surface seawater (Figure 6). There is great uncertainty about both the past slope and the past intercept of the regression that might be used to calculate  $\delta^2\text{H}_{\text{sw}}$  from  $\delta^{18}\text{O}_{\text{sw}}$ .

### 3.2.2. Model Results and Perspectives

$\delta^2\text{H}$  simulated with iLOVECLIM for the preindustrial compare well with present-day data [Schmidt et al., 1999] (Figure 1), although the same notable mismatch observed for the  $\delta^{18}\text{O}$  occurs in the western Indian Ocean where the simulated near surface ocean values are much lower than those observed in reality [Roche and Caley, 2013].

We simulated the  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  relationship with iLOVECLIM for the preindustrial surface seawater and compare the results with present-day data [Schmidt et al., 1999] (Figure 6). Both the slope ( $\sim 6.5$ ) and the intercept ( $\sim -1$ ) of the regression for simulated and observed values compare well. We have then investigated the stability of the spatial and temporal  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  slope for surface seawater between the LGM and present. Results indicate that the global regression is rather stable (Figure 6). Therefore, the present-day  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  formula could be used to calculate  $\delta^2\text{H}_{\text{sw}}$  from  $\delta^{18}\text{O}_{\text{sw}}$  and reconstruct paleosalinity.

As an example of the approach, we reconstruct salinity during the LGM from a core near the coast of South Africa. Oxygen isotopes analysis revealed a  $\delta^{18}\text{O}_{\text{sw}}$  of  $\sim 1.4\text{‰}$  while  $\delta^2\text{H}_a$  is  $\sim -173\text{‰}$  [Kasper et al., 2014]. Applying the present-day regression between  $\delta^2\text{H}_{\text{sw}}$  and  $\delta^{18}\text{O}_{\text{sw}}$  and using the recent calibration between



**Figure 7.** Difference between the salinity biases (LGM/present) obtained with two different approaches with *i*LOVECLIM: (1) temporal variation of the  $\delta^{18}\text{O}_{\text{sw}}$ -salinity relation and (2) isotopologues method. Positive values indicate the reduction of errors associated with the method of water isotopologues.

the fractionation factor  $\alpha$ -salinity and salinity of *M'Boule et al.* [2014] (slope of 0.0021 and intercept of 0.74) leads to an estimate of LGM salinity of  $\sim 38 \pm 23$  g/kg. The error on the reconstructed salinity was calculated following *Rohling* [2007]:

$$\sigma_s = \sqrt{\left(\frac{\partial S}{\partial \delta^2 \text{H}_a} \sigma_{\delta^2 \text{H}_a}\right)^2 + \left(\frac{\partial S}{\partial \delta^2 \text{H}_{\text{sw}}} \sigma_{\delta^2 \text{H}_{\text{sw}}}\right)^2 + \left(\frac{\partial S}{\partial a} \sigma_a\right)^2 + \left(\frac{\partial S}{\partial b} \sigma_b\right)^2}$$

with  $\sigma_{\delta^2 \text{H}_a} = 2\text{‰}$ ,  $\sigma_{\delta^2 \text{H}_{\text{sw}}} = 0$ ,  $\sigma_a = 0.001$ , and  $\sigma_b = 0.03$ .

With a present-day sea surface salinity of 35.5 g/kg, the amplitude change between LGM and present appears realistic ( $\sim 2.5$  g/kg). However, there are important uncertainties associated with the slope and the intercept of the regression between the fractionation factor  $\alpha$  and salinity that are not yet sufficiently tightly constrained [*Rohling*, 2007]. A better calibration for open ocean conditions is necessary to significantly improve quantitative salinity reconstruction with this approach.

### 3.3. Water Isotopologues ( $\delta^{18}\text{O}$ and $\delta^2\text{H}$ )

#### 3.3.1. Basis of the Method

Water isotopologues in seawater ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ :  $\delta$  in permil units =  $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$ ) are intrinsically linked to salinity through the local freshwater budget, being regionally linearly related.

In a theoretical framework proposed by *Rohling* [2007] this new approach uses the fact that isotopologues in surface seawater are affected by the freshwater budget and that the fractionation during phase changes of the water is not completely the same for oxygen 18 and deuterium. The freshwater budget then determines the change in surface salinity [*Rohling*, 2007].

Coupling water isotopologues has been shown through a numerical modeling experiment on the Holocene period to have the potential to improve estimations of paleosalinity variability [*Legrande and Schmidt*, 2011]. However, validation of this methodology by modeling experiments under different boundary conditions, such as glacial periods, has not yet been performed.

#### 3.3.2. Model Results and Perspectives

We, thus apply the relationship described by *Rohling* [2007] to reconstruct paleosalinity:

$$\Phi_s = S_0 \times \left( \frac{\Phi_{\delta^2 \text{H}_{\text{sw}}} - \lambda \Phi_{\delta^{18} \text{O}_{\text{sw}}}}{\delta^2 \text{H}_{\text{sw}0} - \lambda \delta^{18} \text{O}_{\text{sw}0} - d} \right)$$

We use the simulated present surface salinity ( $S_0$ ), present surface  $\delta^2\text{H}$  ( $\delta^2\text{H}_{\text{sw}0}$ ), present surface  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O}_{\text{sw}0}$ ), change in surface seawater  $\delta^2\text{H}$  ( $\Phi_{\delta^2 \text{H}_{\text{sw}}}$ ), and change in surface seawater  $\delta^{18}\text{O}$  ( $\Phi_{\delta^{18} \text{O}_{\text{sw}}}$ ) and assume a present meteoric water line slope of 8 ( $\lambda$ ) with a deuterium excess of 13 ( $d$ ). We then calculate the estimated salinity change between the LGM and present and compare it with the simulated salinity change. Finally, we subtract the absolute errors calculated for the temporal slopes of the relation  $\delta^{18}\text{O}$ -salinity (Figure 4) from the absolute errors calculated with the isotopologues approach. Positive values on Figure 7 indicate the



reduction of errors associated with the method of water isotopologues. The uncertainties are strongly reduced at high latitudes and in tropical regions. Errors increase slightly at midlatitudes where the errors based on the  $\delta^{18}\text{O}$ -salinity relationship were small or zero.

These results must be considered as a conceptual approach to investigate the potential reduction of the error but cannot be used as the exact reduction of the error associated with the use of water isotopologues. Indeed, we assumed a fixed present meteoric water line slope of 8 ( $\lambda$ ) with a deuterium excess of 13 ( $d$ ) that is in fact regionally variable. Furthermore, some disagreement between modeled seawater  $\delta^{18}\text{O}$  and measured seawater  $\delta^{18}\text{O}$  exist for the present day [Roche and Caley, 2013] (Figure 1). This could introduce supplementary errors when a calculation is realized in comparison to the LGM period (errors in the difference). Nonetheless, our conceptual approach suggests that pairing information from water isotopologues could yield better estimates for paleosalinity as was also observed by Legrande and Schmidt [2011] under different boundary conditions. This convergence of results obtained with two different models strongly suggests that pairing water isotopologues has a strong potential to reduce uncertainties on quantitative paleosalinity reconstructions over different boundary conditions.

## 4. Summary

### 4.1. Using iLOVECLIM Results in a Perfect Model Sense

Reconstructing quantitative sea surface salinity variations is important for the understanding of past oceanic dynamics, past hydrological cycles and to evaluate climate models used to predict future climate changes. These quantitative paleosalinity reconstructions with reasonable uncertainties remain very challenging in paleoceanography. We have focused on stable isotope-based methods ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) to derive paleosalinity. In order to investigate how water isotopes can be used as reliable proxies to quantitatively reconstruct past changes in seawater salinity we used the isotope-enabled fully coupled atmosphere/ocean/vegetation/land surface three-dimensional model of intermediate complexity iLOVECLIM [Roche, 2013; Roche and Caley, 2013; Caley and Roche, 2013]. We simulated the climate and water isotopes during the LGM and Heinrich event 1, and we addressed the stability of the spatial and temporal  $\delta^{18}\text{O}$ -salinity slopes.

Our results, used in a perfect model sense, demonstrate that quantitative salinity reconstruction during glacial conditions based on present-day  $\delta^{18}\text{O}$ -salinity spatial slope can lead to very large errors (up to 25 g/kg in certain regions). We also demonstrate that the use of model-derived temporal slopes directly in the calculation allows to reduce the eventual uncertainty on paleosalinity reconstruction.

We then investigated the stability of the  $\delta^{18}\text{O}$ - $\delta^2\text{H}$  slope in surface seawater together with the potential improvement of paleosalinity reconstruction using the combination of water isotopologues during glacial conditions. Our results suggest that quantitative reconstruction of salinity based on the  $\delta^2\text{H}$  measurement of alkenones ( $\delta^2\text{H}_a$ ) might be possible if the slope and the intercept of the relation between the fractionation factor  $\alpha$  between the water and the alkenones and salinity can be sufficiently tightly constrained. We also confirm that pairing water isotopologues has a strong potential to reduce uncertainties on quantitative paleosalinity reconstructions.

### 4.2. Outlook

Simulations of water isotopes with various climate models of different complexities are necessary. An intercomparison study using several coupled climate models for some reference time periods, such as the LGM, could reinforce our conclusion regarding the errors on quantitative salinity reconstruction when using the modern  $\delta^{18}\text{O}$ -salinity relationship. Such intercomparison would also allow for better constraints on error reduction and uncertainties when using model-derived temporal slopes.

Studies of the impacts of species composition and growth phase on the use of alkenones  $\delta^2\text{H}$  to reconstruct relative shifts in paleosalinity are necessary [Wolhowe et al., 2009; Chivall et al., 2014; M'Boule et al., 2014]. It will be crucial to know in which growth phase the alkenones that end up in the geological record are produced [Chivall et al., 2014]. An open ocean calibration (core-tops) of the fractionation factor  $\alpha$  versus salinity is therefore necessary to understand the effect of growth phase on the hydrogen isotopic composition of alkenones in nature and, thereby, to significantly improve quantitative salinity

reconstruction based on hydrogen isotopic composition of alkenones. Pairing water isotopologues has a strong potential to reduce uncertainties on quantitative paleosalinity reconstructions. Further climate model simulations for different boundary conditions could reinforce this conclusion. The use of water isotopologues in paleoclimate marine records is currently limited [Rohling, 2007; Leduc et al., 2013] because of the large number of analyses required to obtain reasonable uncertainties and because of unconstrained uncertainties. Indeed, there could be ecological biases introduced by combining two different proxy archives (zooplankton for the foraminifera and phytoplankton for the coccoliths) and differences in dissolution and bioturbation at a core site. New results in comparison with independent quantitative salinity reconstruction (as Ba/Ca, i.e. multiproxy approach) can help to much better constrain some of the uncertainties that we face.

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