

1 Sudden freshening and cooling of western North Atlantic slope water at the onset of the Little  
2 Ice Age based on Magnesium-to-Calcium ratio and oxygen stable isotope record.

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14 **ABSTRACT**

15 The Little Ice Age (LIA, ~1400–1850 CE) was characterized by colder winters and more  
16 frequent extreme weather events in the Northern Hemisphere. While changes in ocean  
17 circulation likely contributed to global cooling, the specific mechanisms remain poorly  
18 understood. Here, we investigate how ocean circulation changed before, during, and after the  
19 LIA using marine sediment cores from the Laurentian Channel in the Lower St. Lawrence  
20 Estuary. We first established a Mg/Ca-temperature calibration for *Globobulimina auriculata*  
21 using instrumental temperature data and a century-old box core. Applying this calibration to a  
22 longer piston core, we reconstructed bottom-water temperatures during the LIA. Coupling  
23 these results with existing  $\delta^{18}\text{O}$  calcite data allowed us to isolate the  $\delta^{18}\text{O}$  seawater signal,  
24 which reflects changes in the relative contributions of the Labrador Current and Gulf Stream.  
25 Our results indicate an increase of fresh and cold Labrador Sea-derived waters around 1500  
26 CE. Throughout most of the LIA we observed a slow and steady warming of the bottom  
27 water associated with a gradual increase in the proportion of Atlantic-derived waters until  
28 ~1850 CE. The ~1800–1950 CE interval shows high-amplitude variability, including a  
29 sudden freshening event at the LIA's end. After 1950 CE, regional warming dominates,  
30 consistent with previous studies documenting increased Atlantic influence over the Canadian  
31 shelf.

32

33 **KEYWORDS**

34 Mg/Ca ratio, foraminifera, oxygen isotope, St Lawrence Estuary, temperature reconstruction,  
35 Little Ice Age, Labrador Current, Gulf Stream, AMOC, Paleoceanography

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## 38 **1. INTRODUCTION**

39 The Little Ice Age (LIA) is a relatively short climate anomaly (~1400-1850 CE, with variable  
40 onset timing depending on the region), was characterized by abrupt cooling and glacier  
41 expansion, following the warming in Medieval Climate Anomaly (MCA) (Brönnimann et al.,  
42 2019; Wanner et al., 2022). The LIA is the coldest period in the last 8,000 years, being 0.7 to  
43 1°C cooler in the Northern Hemisphere than in the 2000 CE (Lean and Rind, 1999). It is also  
44 associated with a higher frequency of extreme weather and more extreme seasonal  
45 temperatures. Due to the higher land coverage, the Northern Hemisphere was suggested to be  
46 more affected than the Southern Hemisphere (Wanner et al., 2022). The socio-economic  
47 impacts of the LIA have been relatively well documented (e.g., Behringer 1999; Fan 2023;  
48 Putnam et al. 2016), making it a valuable period for understanding how abrupt climate  
49 change may affect our livelihoods. It also provides valuable insights into ocean-climate  
50 interactions as its late occurrence provided us with relatively high resolution in the  
51 sedimentary records. While the dominating factors causing the onset of LIA are still not fully  
52 resolved, previous studies suggest that sea ice-ocean and atmosphere-ocean feedbacks may  
53 have played a significant role (e.g., Moffa-Sánchez et al., 2019).

54

55 One key part of the ocean-climate feedback is the Atlantic Meridional Overturning  
56 Circulation (AMOC), which is a branch of the thermohaline circulation in the North Atlantic  
57 Ocean (Broecker et al., 1985; Stommel, 1961), The Gulf Stream and the Labrador Current are  
58 two major ocean currents that play key roles in the AMOC and in shaping the dynamics of  
59 the North Atlantic subtropical and subpolar gyres. (Figure 1). The Gulf Stream is a  
60 northeastward-flowing warm surface current originating in the Gulf of Mexico, bringing heat

61 up the meridians, while the Labrador Current is a cold surface current flowing southward  
62 along the North Atlantic coast under the Coriolis force. Their respective strengths have been  
63 used to assess changes in the AMOC strength across different intervals, such as the Holocene  
64 and modern times (Ezer, 2015; Rashid et al., 2017; Thibodeau et al., 2018, 2010). While the  
65 strength of the AMOC has experienced large amplitude variations during Earth's history,  
66 slight variations are often overlooked, which may be as informative about the potential  
67 consequences of global warming for the AMOC (Galaasen et al., 2020; Thibodeau et al.,  
68 2025).

69

70 During the LIA, changes in the subpolar gyre and/or AMOC may have impacted meridional  
71 heat transport to higher latitudes, thereby influencing the climate of the North Atlantic and  
72 subpolar regions (e.g., Moffa-Sánchez et al., 2014). Multiple studies have attempted to  
73 characterize changes in AMOC and identify its drivers during this period (Table S1); two  
74 different mechanisms have been proposed to explain changes in AMOC, i.e., wind forcing  
75 and freshwater forcing. In the wind forcing scenario, it was suggested that the negative North  
76 Atlantic Oscillation caused weaker northwestern wind and more frequent Southern wind,  
77 leading to a weaker Labrador Current and associated northward shift in the Gulf Stream  
78 (Jutras et al., 2023; Sicre et al., 2014), thus resulting in a weaker AMOC. On the other hand,  
79 in the freshwater forcing scenario, the increase in storminess (Dawson et al., 2007) during  
80 LIA led to more sea ice formation, break-off, and rafting, which eventually melted and  
81 contributed to the Labrador Current. The large quantity of freshwater decreased the salinity,  
82 lowering the density gradient and thus weakening Labrador Sea convection and the subpolar  
83 gyre convection, resulting in a decrease in AMOC (Alonso-Garcia et al., 2017; Holliday et  
84 al., 2020; Moffa-Sánchez et al., 2014; Moffa-Sánchez and Hall, 2017; Rashid et al., 2023;

85 Thibodeau et al., 2018, 2010; Thornalley et al., 2018).

86

87 Previous reconstructions of northwestern Atlantic oceanography have described a sharp  
88 cooling from the MCA to the LIA (Keigwin, 1996) and a progressive increase in the relative  
89 contribution of Atlantic-derived water in the Laurentian Channel toward the end of the LIA,  
90 as evidenced by oxygen isotope records from benthic foraminifera (Thibodeau et al. 2018).  
91 More recent work also suggested a gradual replacement of Labrador-derived water  
92 throughout the LIA based, again, on  $\delta^{18}\text{O}_{\text{calcite}}$  measurements and end-member mixing  
93 calculations (Keigwin et al., 2025). However, disentangling the temperature and  $\delta^{18}\text{O}_{\text{seawater}}$   
94 solely from the  $\delta^{18}\text{O}_{\text{calcite}}$  is complex and relies on a set of assumptions, notably the  
95 consistency of the endmembers over time. One way to elucidate the  $\delta^{18}\text{O}_{\text{seawater}}$  from the  
96  $\delta^{18}\text{O}_{\text{calcite}}$  is to reconstruct temperature, which is possible from measurements of magnesium-  
97 to-calcium ratio .

98

99 The magnesium-to-calcium ratio (Mg/Ca) in perforate foraminiferal tests is governed by both  
100 biological processes (Bentov and Erez, 2006; Erez, 2003) and the physicochemical properties  
101 of ambient seawater (Alkhatib et al., 2022; Katz, 1973; Mucci, 1987; Rosenthal et al., 1997).  
102 Since both are strongly temperature-dependent, Mg/Ca serves as a widely used  
103 paleothermometer (e.g., Elderfield and Ganssen, 2000). The solubility of calcite decreases  
104 with increasing temperature (Segnit et al., 1962), and more  $\text{Mg}^{2+}$  is incorporated into  
105 inorganically precipitated calcite with increasing temperature. Temperature also enhances  
106 ATP hydrolysis, the chemical process that converts ATP to ADP and releases energy. Since  
107 ATP molecules can bind free  $\text{Mg}^{2+}$  ions, enhanced ATP hydrolysis results in less ATP  
108 available and thus fewer  $\text{Mg}^{2+}$  ions to be bound by ATP. This process increases the

109 concentration of free  $Mg^{2+}$  ions in the cellular environment, thus increasing the Mg/Ca ratio  
110 (Bentov and Erez, 2006; Romani and Maguire, 2002). Another factor governing the Mg/Ca  
111 ratio in calcite is the diffusion constant of  $Mg^{2+}$  ions, which increases with temperature,  
112 facilitating diffusion between ambient seawater and the vacuole of the foraminifers (Bentov  
113 and Erez, 2006).

114

115 The Laurentian Channel serve as a recorder of NW Atlantic subsurface conditions due to its  
116 depth of about 350m (Thibodeau et al., 2010). The proportion of Labrador Subarctic Slope  
117 Water (LSSW) versus Atlantic Temperate Slope Water (ATSW) entering the Laurentian  
118 Channel is primarily controlled by the strength of the northern recirculation gyre (Hogg et al.,  
119 1986), which itself depends on the intensity of deep water formation in the Labrador Sea and  
120 the associated deep western boundary current (Zhang et al., 2007). When Labrador Sea  
121 convection is vigorous and the AMOC is strong, the recirculation gyre keeps the Gulf Stream  
122 path well separated from the coast, allowing greater southward penetration of cold, oxygen-  
123 rich LSSW along the continental shelf edge and into the Laurentian Channel (Thibodeau et  
124 al., 2018). Conversely, during periods of weak convection — characteristic of modern  
125 conditions — the recirculation gyre weakens, the Gulf Stream shifts northward, and a larger  
126 proportion of warm, oxygen-poor ATSW enters the channel. This mechanism explains why  
127 the proportion of LSSW in the Laurentian Channel bottom water decreased from  
128 approximately 72% to 53% over the twentieth century, driving a bottom water warming of  
129 about 1.7 °C that is ultimately linked to the ongoing weakening of the AMOC (Thibodeau et  
130 al., 2018; Thornalley et al., 2018).

131

132 In this paper, we used in-solution ICP-MS measurements from individual foraminifer tests to

133 establish a Mg/Ca-temperature calibration curve for *Globobulimina auriculata* in the lower  
134 St. Lawrence Estuary. By removing the temperature signal from published oxygen isotopic  
135 data, we then reconstructed the relative proportions of Labrador Current and Atlantic water  
136 entering the Laurentian Channel to better understand the dynamics of these water masses  
137 during the LIA. We thus aim to provide new insights into oceanographic changes in the NW  
138 Atlantic during the LIA and thus contribute to a better understanding of the relationship  
139 between AMOC, the subpolar gyre, and climate.

140

## 141 **2. METHODOLOGY**

### 142 **2.1 Sediment core and subsampling**

143 Two sediment cores obtained from the St. Lawrence Estuary were used for this study (Figure  
144 S1). Core CR02-23 is a 0.12 m<sup>2</sup> x 0.5 m long and was collected at 48°42.008'N, 68°38.894'W  
145 at 345m, during an expedition of the *R/V Coriolis II* in 2002 CE. The age-depth model of the  
146 core was previously established using Pb-210 (Thibodeau et al., 2018, 2010, 2006). A 1.8-yr  
147 age uncertainty was calculated in the age model (Figure S2). Five cm<sup>3</sup> of wet sediment was  
148 taken at 1-cm intervals from 0 to 30 cm, with an additional sampling at 0.5 cm depth. The  
149 depth corresponded to 1933 – 2001 CE. The average sediment rate was 0.42 cm/yr. Analyses  
150 of this CR02-23 core were used to establish a Mg/Ca–temperature calibration equation.

151 Core MD99-2220 is 51.6 m long and was collected at 48°38.32N, 68°37.93W, at 320 m of  
152 water depth during an expedition of the *R/V Marion Dufresne* in 1999. The upper 14 cm of  
153 the core was missing due to handling disturbances (St-Onge et al., 2003). The  
154 lithostratigraphy of the core had been divided into two units, Unit 1 from the base of the core  
155 to 1497 cm), and Unit 2 from 1497 cm to the surface. Unit 1 consists of grey to dark grey  
156 laminated to massive clays, while Unit 2 consists of postglacial bioturbated silty clay (St-

157 Onge et al., 2003). The age-depth model was established using radiocarbon dating (St-Onge  
158 et al., 2003), with a  $2\sigma$  uncertainty of  $\pm 100$  yr. For our study of the LIA interval, 5 cm<sup>3</sup> of wet  
159 sediment was taken from the core at 1-cm intervals from 0 cm to 75.5 cm, with an additional  
160 sample at 0.5 cm depth. The study interval spans from 1396 to 1975 CE, which covers the  
161 LIA (Figure S2). According to the age model of St-Onge et al. (2003), sedimentation rates are  
162 approximately 0.74 cm/yr for the upper 20 cm, 0.28cm/yr from 20 to 30 cm, and 0.15 cm/yr  
163 from 30 to 75 cm (Figure S2).

164 For all sample, wet sediment was sieved through a 63- $\mu$ m mesh sieve to remove silt and clay.  
165 In the coarse fraction ( $>125\mu$ m), foraminifera were examined under the Leica EZ4W  
166 Stereomicroscope, and adult specimens of *Globobulimina auriculata* were identified and  
167 hand-picked. In most samples, four intact foraminifer shells were selected from each depth as  
168 replicates (Trejos et al., 2003).

169

## 170 **2.2 Cleaning**

171 The tests were cleaned according to the protocol of Barker et al. (2003), but without the  
172 reductive cleaning step to remove the Mn-oxide coatings (Martin and Lea, 2002). Previous  
173 studies observed a 10-15% Mg/Ca ratio decrease after reductive cleaning (Barker et al., 2003;  
174 Martin and Lea, 2002). However, only a 0.03 mmol/mol (i.e.,  $\sim 1\%$ ) decrease in Mg/Ca is  
175 expected if all Mn-Fe oxide coating is removed (Barker et al., 2003). Given that the Mg/Ca  
176 ratio in this foraminifer species is low, averaging 3.65 mmol/mol, we did not perform a  
177 reductive cleaning step to avoid excessive Mg/Ca loss.

178

## 179 **2.3 Single-foraminifer ICP-MS Analysis**

180 All measurements were performed using an Agilent 7900 ICP-MS at the Chinese University  
181 of Hong Kong. We used JCp-1, a certified coral reference material developed by the  
182 Geological Survey of Japan commonly used for other foraminiferal studies (e.g. Zhou et al.,  
183 2022; Yoshimura et al., 2011), as an internal standard. A self-made multi-element solution  
184 (MeRC) was served as a reference material, comprising a mixture of pure Ca, Mg, Sr, Mn,  
185 and Fe solutions and 2% nitric acid. The accuracy and precision of JCp-1 and MeRC were  
186 measured multiple times every run with ICP-MS and were consistently within 5% of  
187 expected values, if not the samples were run again if possible. Each run of the ICP-MS  
188 analysis was composed of 2% nitric acid blank acquisition at the start and end of the run.  
189 Every five foraminiferal sample acquisitions were accompanied by a set of reference material  
190 and 2% nitric acid blank for recalibration and brief cleaning of the machine. Details of the  
191 ICP-MS setup are reported in the supplementary information.

192 Raw data were obtained from the ICP-MS Data Analysis window software (Agilent  
193 Technologies, 2014). Because ICP-MS can be relatively unstable, frequent recalibration of  
194 the instrument against reference materials is required (Jackson and Sylvester, 2008). Re-  
195 calibration was done with MeRC correction, in which the cps of each elemental isotope in the  
196 first MeRC acquisition of each run was used as the baseline. These baseline cps values were  
197 then compared against the subsequent MeRC acquisitions within the same run. Variations  
198 between MeRC acquisition and the baseline were computed to define the linear slope. The  
199 samples in between acquisitions were corrected with the respective slope. To mitigate the  
200 effects of omitting a reductive cleaning step, data exceeding the elimination thresholds  
201 determined from our location data were considered contaminated and removed (see Table  
202 S2).

203

204 *2.3.1 CR02-23 Calibration Curve and Temperature Reconstruction Comparison*

205 The downcore comparison of MeRC-corrected  $^{24}\text{Mg}/^{48}\text{Ca}$  data and instrumental temperature  
206 compiled by Thibodeau et al. (2010), led to the establishment of our calibration curves, which  
207 was tested with both linear fit and exponential fit. The  $^{24}\text{Mg}/^{48}\text{Ca}$  data led to the  
208 reconstruction of the bottom water temperature (*t in Celsius*), and were compared using the  
209 following calibration equations:

210

211 Eq.1) Lear et al. (2002), which used benthic foraminifera belonging to *Cibicidoides* from  
212 core-tops:

$$213 \quad \text{Mg/Ca (mmol/mol)} = (0.867 \pm 0.049) e^{((0.109 \pm 0.007)t)}$$

214

215 Eq.2) Weldeab et al. (2016), which used the genus *Globobulimina*:

$$216 \quad \text{Mg/Ca (mmol/mol)} = (0.36 \pm 0.02)t + 2.22 \pm 0.19$$

217

### 218 2.3.2 Salinity Effect

219 The salinity impact on the Mg/Ca ratio in foraminifera is under debate, especially for benthic  
220 foraminifera (e.g. Mathien-Blard and Bassinot 2009; Weldeab, Arce, and Kasten 2016). To  
221 investigate the effect of salinity on our Mg/Ca data, two approaches were used. 1) Mg/Ca  
222 data were analysed against the instrumental salinity data at 300 m depth in the study area  
223 (Galbraith et al., 2018); 2) Differences between our Mg/Ca data and back-calculated Mg/Ca  
224 from the Weldeab et al. (2016) equation in *Globobulimina* (Eq.2) were compared against  
225 instrumental salinity.

226

## 227 2.4 MD99-2220 Parent Water Mass Reconstruction

228 The calibration curve from the core CR02-23 Mg/Ca data was applied to reconstruct bottom-  
 229 water temperature from core MD99-2220. Using the  $\delta^{18}\text{O}_{(\text{calcite})}$  data previously obtained for  
 230 MD99-2220 (Thibodeau et al., 2018), we could calculate the  $\delta^{18}\text{O}_{(\text{seawater})}$  signal from the  
 231 equation of Marchitto et al. (2014), which assumes a 0.9‰ offset for vital effect as measured  
 232 for *Globobulimina affinis* (Hoogakker et al., 2010):

$$233 \quad t (^{\circ} \text{C}) = \frac{0.245 - \sqrt{0.045461 + 0.0044(\delta^{18}\text{O}_{(\text{calcite})} - \delta^{18}\text{O}_{(\text{seawater})})}}{0.0022}$$

234 Given that the Atlantic Temperate Slope Water (ATSW) and Labrador Sea Slope Water  
 235 (LSSW) have distinct  $\delta^{18}\text{O}$  signals, we can track the change of contribution from  $\delta^{18}\text{O}_{(\text{seawater})}$   
 236 changes (Thibodeau et al. 2018, 2010). In the  $\delta^{18}\text{O}_{(\text{seawater})}$  reconstruction, a positive signature  
 237 represents a dominant ATSW (proxy for Gulf Stream) and a negative signature represents a  
 238 dominant LSSW (proxy for Labrador Current). A 95% confidence interval was applied for all  
 239 statistical analyses, and all results were corrected to two decimal places, apart from cps, R-  
 240 squares, and equations. All analyses and graphs were produced on GraphPad Prism 9.0 and  
 241 Excel, while maps were produced via the use of Ocean Data View.

242

### 243 3. RESULT

#### 244 3.1 CR02-23

245 In core CR02-23, measurements were made in a total of 75 samples of foraminifera. All  
 246 elemental isotopes measured exceeded the limits of detection (LOD) and quantification  
 247 (LOQ), indicating quantifiable concentrations.

248

##### 249 3.1.1 Mg/Ca Ratio

250 After applying the elimination threshold (Table S2), 43 measurements remained for analysis.

251 The  $^{24}\text{Mg}/^{48}\text{Ca}$  ranges from 1.72 to 9.01 mmol/mol (Table S3). The p-value for the linear

252 regression model of isotope ratios was  $< 0.05$ , representing a significant relationship between  
253 bottom water temperature and Mg/Ca ratio (Figure 2a). For both linear and non-linear  
254 (exponential) models, the R-squared values were  $> 0.7$ , indicating a significant correlation  
255 between temperature and the Mg/Ca ratio (Table S4). The exponential equation is chosen  
256 because it yielded a higher R-squared ( $R^2=0.76$ ) than that of the linear model ( $R^2=0.74$ ).

257

### 258 *3.1.2 Salinity Effect and Contamination*

259 No statistically significant relationship was observed between salinity and Mg/Ca (p-value  
260  $>0.05$ , R-square  $<0.02$ ; Figure 2b and Table S5). However, the lack of correlation could result  
261 from the small sample size ( $n=8$ ) and the narrow salinity range (32.34 to 34.94 psu). No  
262 significant correlation was observed between Mn/Ca or Fe/Ca with Mg/Ca (Figure 3). A low  
263 but significant correlation was observed between Al/Ca and Mg/Ca, suggesting minimal  
264 contamination.

265

## 266 **3.2 MD99-2220**

267 A total of 286 foraminiferal samples were analysed. After applying the elimination threshold,  
268 100 measurements remained for data analysis.

269 The average Mg/Ca ratio in MD99-2220 across depths 0 cm to 76 cm ranged from 1.14 to  
270 9.16 mmol/mol. Reconstruction yielded bottom-water temperatures of 1.58-7.18°C (Figure  
271 4a). We observed a stepwise increase in temperature from ~1396 to 1905 CE, followed by a  
272 decrease from ~1905 CE onwards with large fluctuations in the 20<sup>th</sup> century. The seawater  
273 isotope signal declined from the base of the record until ~1500 CE, then increased stepwise  
274 until ~1800 CE, after which a sharp decrease was recorded (Figure 4b). Because of the

275 relatively high standard deviation of our measurements, we remained cautious when  
276 discussing small-amplitude variations in our record.

277

## 278 **4. DISCUSSION**

### 279 **4.1 Calibration of Mg/Ca vs temperature in the St. Lawrence Estuary**

#### 280 *4.1.1 Comparisons of Calibrations*

281 We compared the CR02-23 Mg/Ca ratio with previously established calibrations for  
282 temperature estimates from Mg/Ca, thereby testing the applicability of published equations  
283 (Lear et al., 2002; Weldeab et al., 2016) for *G. auriculata* at our study location. The  
284 temperature reconstructions using published equations yield a wide range of values (-1 to 28  
285 °C), well outside the study environment's range (3 to 6 °C). This highlights the need for a  
286 regional calibration curve using *Globobulimina auriculata*.

287

#### 288 *4.1.2 Calibration Equation for Globobulimina auriculata in the Lower St. Lawrence Estuary*

289 The calibration equation was established as the best-fit exponential equation from  $^{24}\text{Mg}/^{48}\text{Ca}$   
290 data after MeRC correction and instrumental temperature from the St. Lawrence bottom  
291 water (Thibodeau et al., 2018):

$$292 \quad \text{Mg/Ca (mmol/mol)} = 0.6341e^{(0.3740t)}$$

293 *where t represents water temperature in Celsius*

294

295 This equation yielded a range of bottom-water temperatures of 3.0 to 5.5°C, with an R-square  
296 of 0.76 between instrumental and estimated values. It is important to note that this calibration  
297 used Mg/Ca values from the sediment core and instrumental temperature records on a  
298 calendar-year scale. Therefore, the correlation may be affected by uncertainty in the core

299 chronology. Moreover, because we used the local temperature gradient over time, the  
300 calibration covers only a 3 °C temperature range. While this calibration can provide a fine-  
301 scale reconstruction, the narrow temperature range may have amplified uncertainty in the  
302 relationship between the actual and reconstructed data, resulting in a relatively low  
303 coefficient of correlation. Finally, assuming that carbonate ion concentration mainly affects  
304 the Mg/Ca ratio at bottom-water temperatures < 3 °C (Elderfield et al. 2006), we did not  
305 account for the effect of carbonate ion, which may be an additional caveat. Regardless of  
306 these potential limitations, the calibration equation tailored to *Globobulimina auriculata* in  
307 the Lower St. Lawrence Estuary appears robust for regional reconstructions of temperature  
308 through time. However, it is important to note that the most recent part of the record includes  
309 data that are outside our calibration range, which may explain the higher variability observed,  
310 notably in the most recent part of the cores where temperatures are expected to be warmer.

311

#### 312 **4.2 Little Ice Age temperature reconstruction**

313 Changes in bottom-water temperature reconstructed from our Mg/Ca data followed a pattern  
314 similar to our expectation based on literature, namely a cooling at the beginning of the LIA  
315 following by a gradual warming throughout the LIA (Figure 4a) (e.g., Forman et al., 2025;  
316 Keigwin, 1996; Keigwin et al., 2025; Thibodeau et al., 2018). Our calculated  $\delta^{18}\text{O}_{\text{seawater}}$  was  
317 characterized by similar pattern than the temperature (Figure 4b) supporting previous  
318 interpretation suggesting that the dominant factor controlling temperature changes is likely  
319 related to the mixing proportions of parent water masses in the bottom water of the lower St.  
320 Lawrence Estuary.

321 Non-parametric Mann-Kendall Trend Test was applied to identify significant trends. A  
322 positive trend characterized the ~1490 to ~1850 CE interval for both  $\delta^{18}\text{O}_{\text{seawater}}$  and

323 temperature (Table S6). Transitions were thus identified at 1490 and 1850 CE, yielding three  
324 time-intervals in the study sequence (Figure 5), which are discussed hereafter with reference  
325 to potential drivers of change in the dynamics of western North Atlantic circulation during  
326 the LIA. This segmentation is aligned with previous studies suggesting the onset of the LIA  
327 in this region to be around 1500 CE (e.g., Keigwin et al., 2025).

328

#### 329 *4.2.1 Transition from MCA to LIA (pre 1500 CE)*

330 This time interval was characterized by a relatively constant signal, followed by a relatively  
331 sharp decrease in both temperature and seawater  $\delta^{18}\text{O}$  in the latter half of the 15<sup>th</sup> century  
332 suggesting increased influence of Labrador-derived water at our site. This cooling is  
333 synchronous with an increase in the size of sortable silt from Southeast Grand Banks,  
334 suggesting an increase in Labrador Current flow speed since ~1450 CE (Rashid et al., 2023),  
335 before the rise in the contribution of LSSW as reconstructed herein. This may have been  
336 caused by an increase freshwater transport into the Labrador Sea slope waters as suggested  
337 by modern observational data (Lazier and Wright, 1993). Increased freshwater release in the  
338 Labrador Sea has been reconstructed for the LIA, which may originate from meltwater  
339 produced during the warm Medieval Climate Anomaly (MCA) (Alonso-Garcia et al., 2017;  
340 Lapointe and Bradley, 2021; Moffa-Sánchez et al., 2014). This freshwater discharge has been  
341 observed from TEX<sub>86</sub>-T and higher presence of Polar waters at Eirik Drift (Rashid et al.,  
342 2023). These evidences also aligns with relatively cool condition in the Sargasso Sea  
343 (Keigwin, 1996) and relatively low  $\delta^{18}\text{O}$ , indicating fresh and cold condition, in the Jordan  
344 Basin (Keigwin et al., 2025) This explains the cooling observed from ~1470 CE in our core  
345 (Figure 4a), and the higher presence of stronger Labrador Sea current-derived waters (Figure  
346 4b). This is also coherent with a weaken Gulf stream (Caesar et al., 2018; Rahmstorf et al.,

347 2015), and reduced northward heat transport (Lund et al., 2006) reducing the relative  
348 contribution of the ATSW as estimated from our record (Figure 4).

349

#### 350 4.2.2 The Little Ice Age (~1500 to 1850 CE)

351 In the study region, the LIA was characterized by a significant increasing trend of oxygen  
352 isotope signature and bottom water temperature (Table S6). The coldest and freshest  
353 subsurface water in the Labrador Sea was recorded right at the beginning of the 16<sup>th</sup> century,  
354 as indicated by our Mg/Ca ratios, which is coherent with  $\delta^{18}\text{O}$  values in *Neogloboquadrina*  
355 *pachyderma* (Moffa-Sánchez et al., 2014). Gradually during the LIA, more saline waters  
356 were observed until around 1800 CE (Lund et al., 2006) and can be attributed to drier  
357 conditions in the West Atlantic (Saenger et al., 2011). The increased salinity of the Gulf  
358 Stream, resulting in a higher oxygen isotope composition of the ATSW, might have  
359 contributed to the rise in  $\delta^{18}\text{O}_{\text{seawater}}$  in our reconstruction (Figure 4b).

360 The end of LIA (~1810-1850 CE) coincides with the early stage of the industrial era (~1830  
361 CE onwards), during which air temperature and sea surface temperature recorded a  $<0.2$  °C  
362 and  $<0.5$  °C increase, respectively (Abram et al., 2016). However, climate-related warming  
363 cannot account for the  $\sim 2$  °C increase observed in bottom water temperature. (Figure 5)  
364 Therefore, we hypothesize that the regional warming was mainly caused by the enhanced  
365 contribution of ATSW relative to LSSW. The timing of the peak matched the end of the large-  
366 scale ice-rafting events in  $\sim 1800$  CE (Alonso-Garcia et al., 2017) and the end of the series of  
367 volcanic eruptions ( $\sim 1835$  CE) (Brönnimann et al., 2019). A decrease in the deep western  
368 boundary current (DWBC) was also inferred from sortable silt (Thornalley et al., 2018),  
369 which may reduce the amount of  $\delta^{18}\text{O}$ -depleted water reaching this site and thus explains the

370 maximum oxygen isotopic signal observed during this interval. This is also consistent with  
371 other studies suggesting a gradual northward displacement of the Gulf Stream in the later  
372 stage of the LIA (Forman et al., 2025).

373

#### 374 *4.2.3 Post-LIA (post 1850 CE)*

375 This beginning of this interval has lower resolution, mostly due to contaminated samples, and  
376 thus the comparison with other records is not straightforward. Moreover, we observed very  
377 high variability, especially in the 20<sup>th</sup> century. The start of this interval was marked by an  
378 important cooling of approximately 3°C of bottom-water temperature between ~1850 CE and  
379 ~1925 CE. While this cooling seems to align with a resurgence of LSSW at our site and a  
380 strengthening of the AMOC (Figure 5), this cooling is only recorded in two samples and thus  
381 should be interpreted with caution. Moreover, this cooling is immediately followed by a 3°C  
382 warming between ~1925 CE and ~1934 CE. The following two decades are then  
383 characterised by a cooling of about 2.5°C, followed by a similar warming of >2°C in the  
384 second half of the 20<sup>th</sup> century (~1954 CE to the end of our record). Interestingly, the  
385 observed cooling at the beginning of this period coincides with a short-lived peak in  
386 hematite-stained grain abundance in the Labrador Sea, indicating a sudden and significant  
387 increase in Arctic sea-ice export through the Eastern Greenland Current (Alonso-Garcia et al.,  
388 2017). Therefore, the drop in  $\delta^{18}\text{O}_{\text{seawater}}$  may be caused by an increase in Labrador-derived  
389 water, but also by the freshening of this endmember. The latter could also explain why this  
390 cooling seems at odds with other interpretations of regional  $\delta^{18}\text{O}$  records that suggested a  
391 warming from the beginning of the 20<sup>th</sup> century (Keigwin et al., 2025; Thibodeau et al.,  
392 2018). However, a transient cooling of about 2°C was also observed in the Jordan basin deep  
393 water with coldest condition around 1920 CE (Keigwin et al., 2025). Moreover, while the

394 Gulf Stream was strengthening as well after the end of the LIA, its  $\delta^{18}\text{O}_{\text{seawater}}$  also dropped  
395 by  $\sim 0.3\text{‰}$  (Lund et al., 2006). Therefore, evidence of lower  $\delta^{18}\text{O}_{\text{seawater}}$  values in both  
396 endmembers composing the Laurentian bottom water suggests that the isotopic signal may  
397 have been primarily controlled by changes in the isotopic composition of these water masses  
398 due to freshwater input following the LIA rather than temperature as suggested by previous  
399 studies. In the second half of the 20th century, we reconstructed a  $2^\circ\text{C}$  warming, coherent  
400 with multiple observations in the region and that was attributed to an increased influence of  
401 Atlantic-derived water over the Canadian shelf, which is also present in our reconstruction of  
402 seawater  $\delta^{18}\text{O}$  (Genovesi et al., 2011; Gilbert et al., 2005; Keigwin et al., 2003; Keigwin et  
403 al., 2025; Thibodeau et al., 2006, 2010, 2013, 2018).

404

## 405 5. CONCLUSION

406 In this paper, we used single foraminifer ICP-MS to establish an exponential Mg/Ca-  
407 temperature calibration curve for *Globobulimina auriculata* at the Lower St. Lawrence  
408 Estuary, i.e.  $\text{Mg/Ca} (\text{mmol/mol}) = 0.6341e^{(0.3740t)}$ . This bottom-water temperature  
409 reconstruction curve applies to a temperature range of  $3.0\text{--}5.5^\circ\text{C}$ . Despite its narrow  
410 temperature range, it provides a species- and region-specific curve for relatively accurate  
411 temperature reconstruction in future studies. Using the newly established calibration curve  
412 and Mg/Ca data from the MD99-2220 core, we reconstructed the bottom-water temperature  
413 in the Lower St. Lawrence Estuary during the LIA. Constrained by  $\delta^{18}\text{O}_{\text{calcite}}$  data, we  
414 calculated the change in  $\delta^{18}\text{O}_{\text{seawater}}$  and used it as a proxy for the change in the contribution  
415 of the parent water mass. Our results, taken together with previous evidence, indicate that the  
416 transition from MCA to LIA was characterized a sharp decrease in temperature and oxygen  
417 isotope values, likely due to increased Labrador Sea-derived water. During the LIA, there  
418 was an increasing trend in oxygen isotope signal and bottom water temperature, with a shift

419 from LSSW to ATSW dominance. The post-LIA period began with a sharp decrease in  
420 bottom water temperature, followed by a significant warming trend in the late 20th century,  
421 attributed to an increased influence of Atlantic-derived water masses over the Canadian  
422 continental shelf.

423

#### 424 **6. AUTHOR CONTRIBUTIONS**

425 **Wai Ching Rachel Chu:** Methodology, Formal analysis, Investigation, Data Curation,  
426 Writing-Original Draft, Writing – Review & Editing, Visualization. **Anne de Vernal:**  
427 Resources, Writing – Review & Editing. **Tiffany Audet:** Resources, Writing – Review &  
428 Editing. **Benoit Thibodeau:** Conceptualization, Resources, Data Curation, Visualization,  
429 Supervision, Project administration, Funding acquisition, Writing – Review & Editing.

430

#### 431 **7. DATA AVAILABILITY**

432 Data produced for this paper are available at <https://doi.org/10.48668/HLKYR>.

433

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442

443 **9. DECLARATION OF COMPETING INTEREST**

444 Declaration of Interest Statement

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

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448

449

450 **10. REFERENCES**

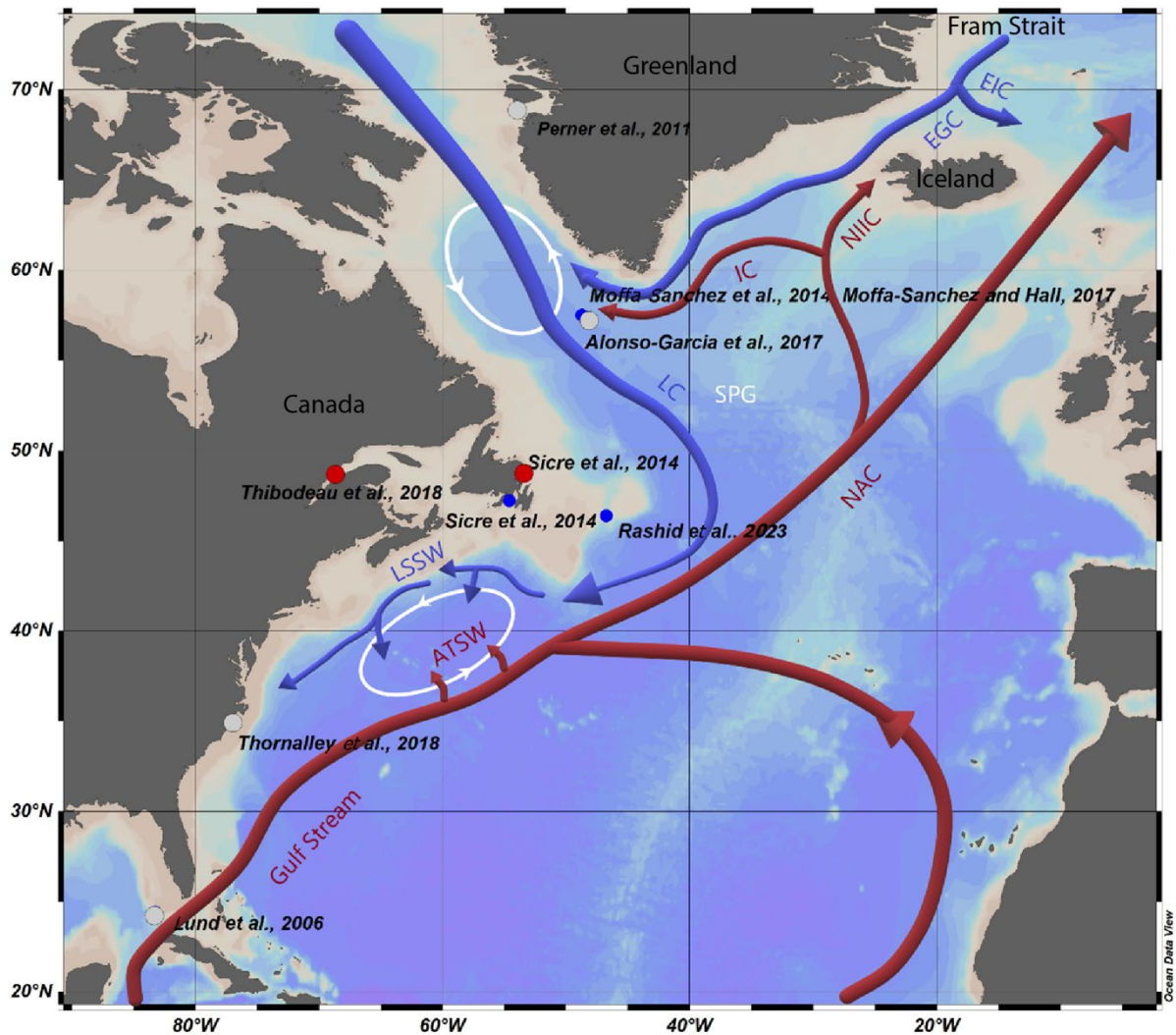
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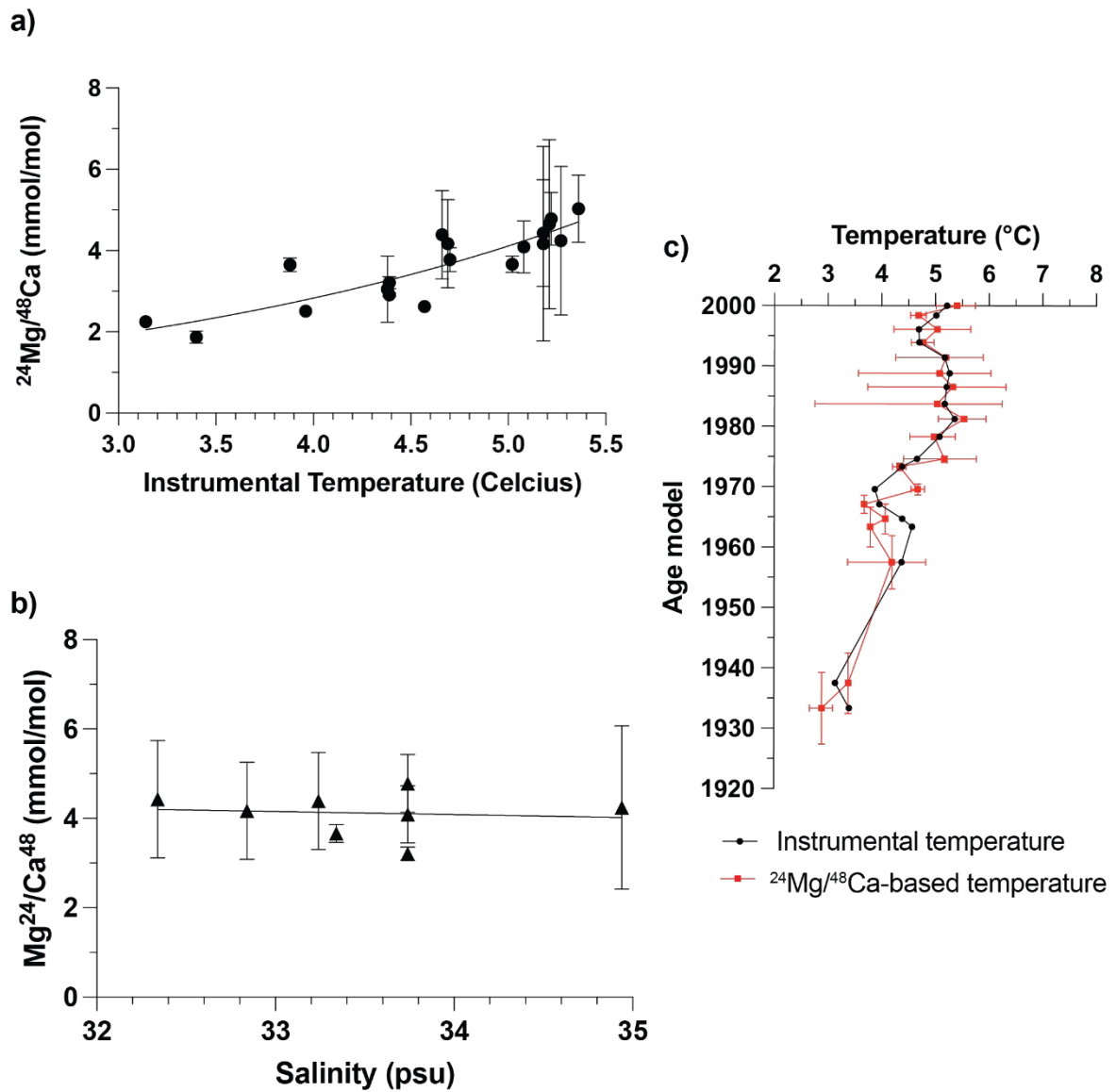


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668 Figure 1 Map of the North Atlantic, ocean currents and locations of study cores listed in  
 669 Table 1. Red dots refer to studies indicating a warming during LIA, blue dots refer to studies  
 670 indicating a cooling during LIA, and grey dots refer to studies using non-temperature-related  
 671 proxies. Abbreviations on the map are: ATSW= Atlantic Temperate Slope Water; EIC= East  
 672 Iceland Current; EGC= East Greenland Current; IC= Irminger Current; LC= Labrador  
 673 Current; LSSW: Labrador Sea Slope Water; NAC= North Atlantic Current; NIIC= North  
 674 Iceland Irminger Current; SPG= sub-polar gyre; The two white circles indicate convection;  
 675 the upper one refers to Labrador Sea Convection while the lower one refers to Northern  
 676 Recirculation Gyre. Figure made with Ocean Data View (Schlitzer, 2018)

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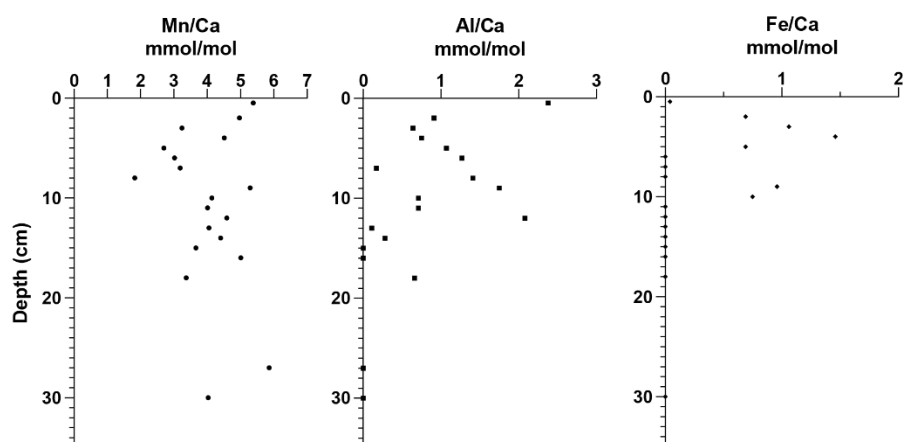
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679 Figure 2 Best-fit curve for the MeRC-corrected  $^{24}\text{Mg}/^{48}\text{Ca}$  data against a) instrumental temperature  
 680 and b) instrumental salinity, respectively. Error bars represent the standard deviation of replicate  
 681 measurements. In panel c) we plot instrumental temperature and reconstructed temperature from core  
 682 CR02-23 based on MeRC-corrected  $^{24}\text{Mg}/^{48}\text{Ca}$  data best fit. Error bars represent standard deviation  
 683 from replication measurement (temperature, x-axis) and error from  $^{210}\text{Pb}$  CRS-model (year, y-axis).  
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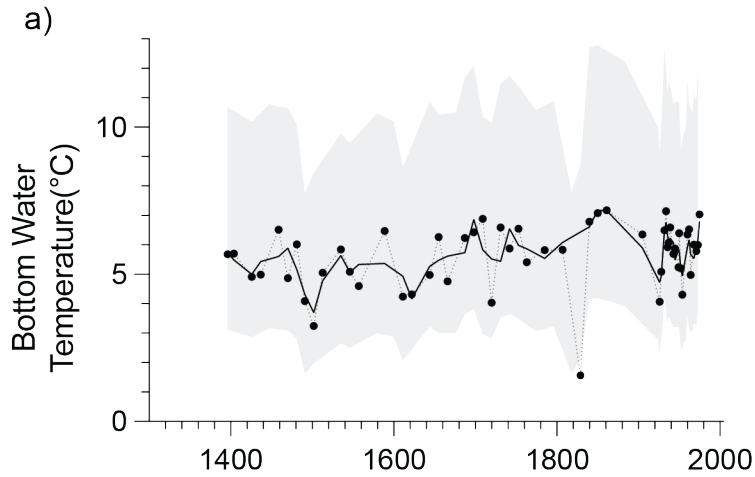


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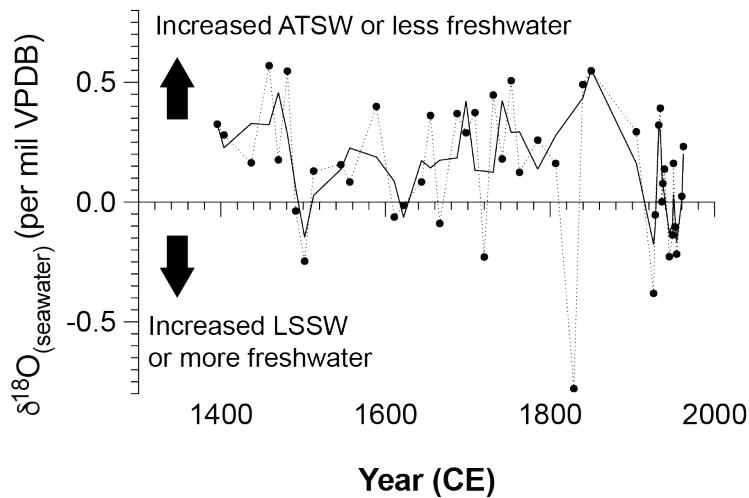
688 Figure 3 Ratio of contaminant (Mn, Al and Fe) on Ca downcore of CR02-23

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b)



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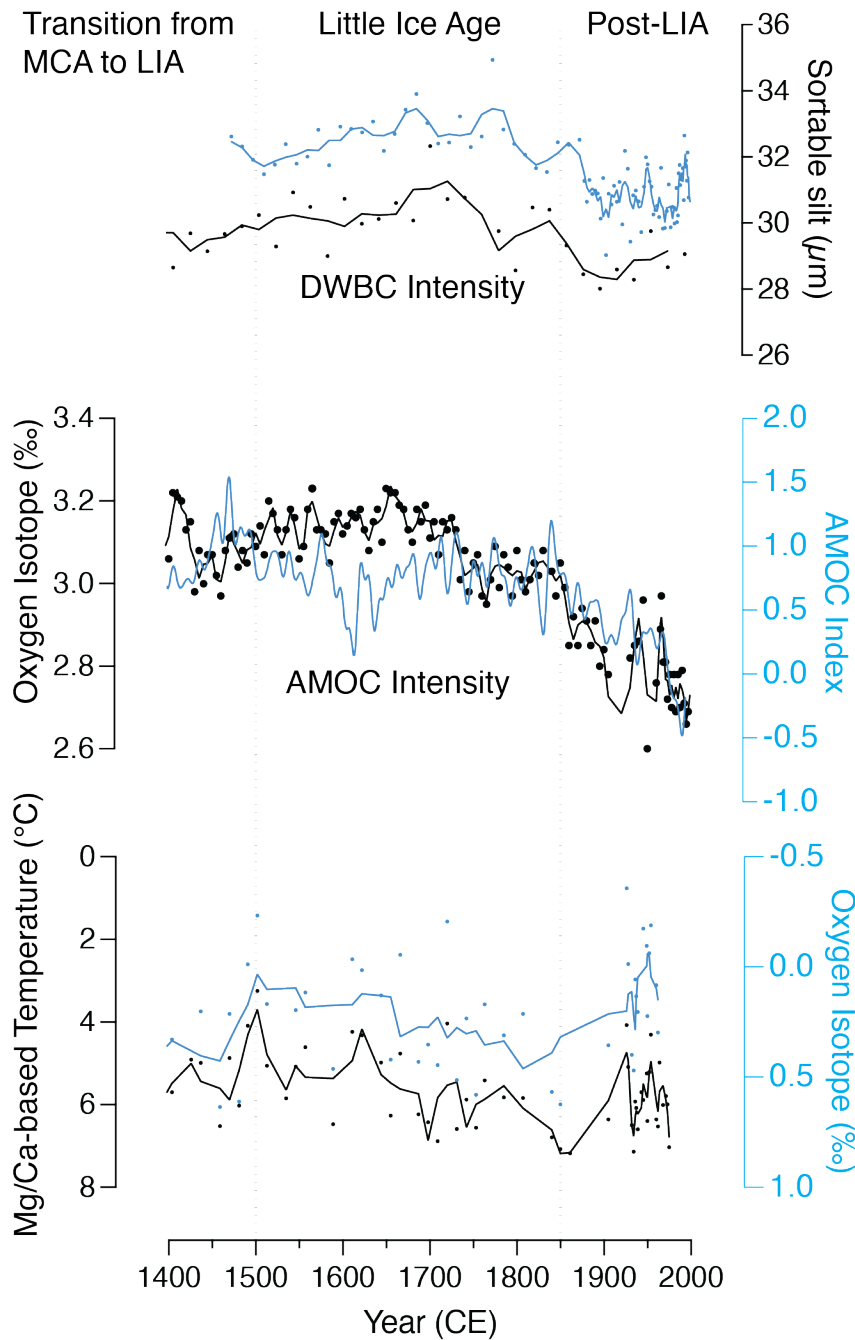
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693 Figure 4. a) Bottom Water Temperature Reconstruction and b) seawater oxygen isotope

694 reconstruction of the St. Lawrence Estuary from 1396 to 1975 CE. The thick lines correspond

695 to a 3-point moving average. Temperature uncertainty was set at 95% of the confidence

696 interval of the equation fit of the 3-point moving average, excluding the outlier at 1829 CE.



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Figure 5 Comparison of selected LIA records with our result. Upper panel display sortable silt in core KNR-178-48JPC in blue KNR-178-56JPC in black which is used as a proxy of flow speed of deep western boundary current (Thornalley et al., 2018). Middle panel display AMOC index in blue (Rahmstorf et al. 2015) and  $\delta^{18}\text{O}$  of *G. auriculata* in core MD99-2220 (Thibodeau et al., 2010, 2018). Bottom panel display bottom water reconstruction Mg/Ca of *G. auriculata* from core MD99-2220 (this study) in black and reconstructed seawater  $\delta^{18}\text{O}$  (this study) in black. The black vertical dashed lines indicate the suggested separation between different time intervals.