



Dynamique des températures dans le système du Saint-Laurent durant l'Holocène

MÉMOIRE PRÉSENTÉ

dans le cadre du programme de maîtrise en océanographie
en vue de l'obtention du grade de maître ès en sciences

PAR

© MARIE ENGEL

Novembre 2025

Composition du jury :

Mathilde Jutras, présidente du jury, Université du Québec à Rimouski

Stephanie Kusch, directrice de recherche, Université du Québec à Rimouski

El Mahdi Bendif, codirecteur de recherche, Université du Québec à Rimouski

André Pellerin, codirecteur de recherche, Université du Québec à Rimouski

Anne de Vernal, examinatrice externe, Université du Québec à Montréal

Dépôt initial le 8 août 2025

Dépôt final le 4 novembre 2025

UNIVERSITÉ DU QUÉBEC À RIMOUSKI

Service de la bibliothèque

Avertissement

La diffusion de ce mémoire ou de cette thèse se fait dans le respect des droits de son auteur, qui a signé le formulaire « *Autorisation de reproduire et de diffuser un rapport, un mémoire ou une thèse* ». En signant ce formulaire, l'auteur concède à l'Université du Québec à Rimouski une licence non exclusive d'utilisation et de publication de la totalité ou d'une partie importante de son travail de recherche pour des fins pédagogiques et non commerciales. Plus précisément, l'auteur autorise l'Université du Québec à Rimouski à reproduire, diffuser, prêter, distribuer ou vendre des copies de son travail de recherche à des fins non commerciales sur quelque support que ce soit, y compris l'Internet. Cette licence et cette autorisation n'entraînent pas une renonciation de la part de l'auteur à ses droits moraux ni à ses droits de propriété intellectuelle. Sauf entente contraire, l'auteur conserve la liberté de diffuser et de commercialiser ou non ce travail dont il possède un exemplaire.

REMERCIEMENTS

First, I would like to thank my supervisor, Steph, for everything. Thank you for introducing me to organic geochemistry, for generously sharing your knowledge, and for your endless optimism and patience. I'm also grateful for all the time and support you've given me, not only for this project, but also for the opportunities to explore new ideas and work on side projects (and for your support when I was a bit of a nervous wreck).

I would also like to thank my co-supervisors, Mahdi and André, for their invaluable input and encouragement. Mahdi, thank you for sharing your inspiring passion for phytoplankton (or rather haptophytes) and for giving me the chance to incorporate more of this into my project. I'm super excited for all the haptophyte projects still to come. André, thank you for your contagious enthusiasm and curiosity about everything. I'm also grateful to Mathilde Jutras and Anne de Vernal for taking the time to read and assess this thesis.

A huge thank you to Daphnée, the other half of this project, for all the lipid extractions, shared frustrations and laughter along the way. We made a great team! Many thanks as well to Dominique, our enthusiastic intern, for bringing joy to our lab work, to Laury-Ann for your constant support and expertise and to Haluka, for welcoming me into your paleogenomics research. I'd also like to thank all the members of the Isotope Biogeochemistry Lab for the important discussions (including our very serious debates about superpowers), the vegan treats, and most of all, the good company and mental support. My sincere thanks also go to the good souls of ISMER and UQAR – Martine, Éricka, Mélanie, Dominique, Mathieu, Quentin, Pascal and Steeven – for always being ready to help and for patiently answering my endless questions.

I'm grateful to ISMER and Geotop for their financial support, and to UQAR and IFQM for their mobility scholarships, which allowed me to attend the GRC Organic Geochemistry Conference and carry out a research visit at the Station Biologique de Roscoff. Many thanks

as well to Ian and the entire Roscoff Culture Collection team for the amazing experience.

Thank you to everyone who made my life in Rimouski so wonderful. A special mention to Tommy-Loup (aka Timoula) for this amazing friendship and for all those hours spent playing pool – though it's a bit sad to admit how bad I still am. Nao, thank you for always being there for me, for keeping me company with your daily podcasts, and for patiently listening to mine, that means so much! Thanks to Jojo for not only being an awesome flat- and labmate, but also a great friend. Thanks also to all my NEMO friends and the (past and current) 'le pont occupants', as well as everyone else who came by the pont but weren't officially part of it – I count you in anyway.

I would also like to thank my family and friends far away who have always supported me in my decisions and been there for me, no matter the distance. And thanks to all the inspiring and kind people I've met along the way – thank you for shaping this journey and helping me get to where I am today.

Merci pour tout ♥

RÉSUMÉ

L'estuaire maritime du Saint-Laurent est confronté à une hypoxie des eaux de fond, majoritairement en raison des changements climatiques qui impactent la circulation océanique. L'apport des eaux froides et bien oxygénées du courant du Labrador est remplacé par l'arrivée des eaux chaudes et pauvres en oxygène du Gulf Stream, ce qui accentue la perte d'oxygène lors de la respiration microbienne de la matière organique. Ici, nous reconstituons l'histoire spatio-temporelle de la température et de la ventilation au cours de l'Holocène afin d'en faire un analogue du réchauffement actuel et futur ainsi que pour mieux comprendre la variabilité naturelle de ce système. Nous présentons les données de température de surface dérivées de l'indice $U_{37}^{K'}$ basé sur les alcénones produits par des haptophytes et des données de l'indice TEX_{86} à base de lipides tétraéther d'archées, qui représentent les températures des eaux de fond le long du chenal Laurentien. Dans l'ensemble, les deux traceurs montrent un réchauffement au début de l'Holocène, suivi d'un refroidissement après environ 7,5 ka BP, plus prononcé dans les eaux de surface. Cette différence entraîne un changement distinct dans l'écart relatif entre les deux traceurs, ce qui suggère des changements transitoires dans la dynamique de la circulation/l'approvisionnement en eau de fond. Après correction du biais dans les températures de surface dérivées par $U_{37}^{K'}$ causé par les conditions saumâtres résultant de l'événement de fonte des glaces il y a 8,2 ka BP, l'écart de température relatif entre les eaux de surface et les eaux de fond semble indiquer une contribution croissante des eaux de fond provenant du Gulf Stream après 7,0 ka BP ou des changements dans les propriétés des eaux entrant dans le système. Après 4,0 ka BP, l'écart entre les températures de surface et des eaux de fond est plutôt stable, ce qui indique des changements mineurs dans l'approvisionnement en eau profonde. Nos données montrent donc que le lien actuel entre les changements de circulation et l'hypoxie pourrait être sans précédent au cours de l'Holocène.

Mots clés : Système du Saint-Laurent, hypoxie, changement de circulation, Gulf Stream, Holocène, biomarqueurs lipidiques.

ABSTRACT

The Lower St. Lawrence Estuary is facing bottom water hypoxia mostly due to climate-driven changes in ocean circulation. A decrease in the inflow of cold, oxygen-rich bottom waters from the Labrador Current in favor of warm and oxygen-poor bottom waters from the Gulf Stream exacerbates oxygen loss during microbial respiration of organic matter. Here, we spatiotemporally reconstruct the Holocene temperature and ventilation history as an analog of current and future warming and to better understand the natural variability of this system. We present sea surface temperature (SST) data derived from the haptophyte-based alkenone proxy ($U_{37}^{K'}$) and the archaeal tetraether lipid-based TEX₈₆ proxy recording bottom water temperatures along the Laurentian Channel. Both proxies overall show warming of water temperatures during the early Holocene followed by cooling after around 7.5 ka BP, but the cooling trend is much more pronounced for SSTs. This difference results in a distinct change in the relative temperature offset between the two proxies, which suggest transient changes in circulation dynamics/bottom water sourcing. After correcting for a temperature bias in the $U_{37}^{K'}$ -derived SSTs caused by the brackish conditions resulting from the 8.2 ka BP meltwater event, the relative temperature offset between surface and bottom waters seems to indicate increasing bottom water contributions from the Gulf Stream after 7.0 ka BP or changes in the properties of the waters entering the system. After 4.0 ka BP, the relative temperature offset is rather stable, indicating minor changes in bottom water sourcing. Our data thus show that the current link between circulation changes and hypoxia may be unprecedented over the Holocene.

Keywords : St. Lawrence system, hypoxia, circulation changes, Gulf Stream, Holocene, lipid biomarkers.

TABLE DES MATIÈRES

LISTE DES FIGURES	xii
LISTE DES ABRÉVIATIONS	xiv
INTRODUCTION GÉNÉRALE	1
LA DÉSOXYGÉNATION DANS LE SAINT-LAURENT	1
LA DÉGLACIATION DE L'INLANDSIS LAURENTIDIEN	5
LES BIOMARQUEURS LIPIDIQUES	9
OBJECTIFS ET HYPOTHÈSES	14
ARTICLE 1	
BIOMARKER-BASED RECONSTRUCTION OF HOLOCENE WATER TEMPERATURES IN THE ST. LAWRENCE INDICATES CHANGES IN CIRCULATION DYNAMICS	16
1 ABSTRACT	16
2 INTRODUCTION	17
3 STUDY AREA	20
4 MATERIAL AND METHODS	22
4.1 Materials	22
4.2 Elemental analyses	23
4.3 Biomarker analyses	23
4.4 Proxy calculations	25
5 RESULTS	26
5.1 Elemental analyses	26
5.2 Alkenones	27
5.3 GDGTs	31
6 DISCUSSION	33
6.1 Chronology	33
6.2 Proxy appraisal	34
6.2.1 Alkenones	34

6.2.2	GDGTs	38
6.3	Holocene temperature-inferred circulation dynamics	40
6.3.1	Spatio-temporal surface and bottom water temperature evolution in the St. Lawrence system	40
6.3.2	Potential ecological effects controlled by freshwater and sea level dynamics	45
7	SUMMARY & CONCLUSION	50
	CONCLUSION GÉNÉRALE	52
	ANNEXE I	
	AGE MODELS	54
	ANNEXE II	
	DISCUSSION – COMPOSITE CALIBRATION FOR ALKENONES	57
	RÉFÉRENCES	59

LISTE DES FIGURES

INTRODUCTION GÉNÉRALE

I	Système du Saint-Laurent et les courants.	2
II	Stratification dans le Saint-Laurent.	4
III	Insolation au solstice d'été à 48°N depuis 25 ka BP.	6
IV	Retrait de l'inlandsis laurentidien.	7
V	Reconstruction de l'intensité de l'AMOC depuis le dernier maximum glaciaire.	8
VI	Structures et ions moléculaires des alcénones et calibration globale.	11
VII	Structures et ions moléculaires des isoGDGTs et calibration de TEX ₈₆	13

ARTICLE 1

1	Map of the St. Lawrence system with location of three sediment cores and instrumental temperature data from years 1873 to 2024.	21
2	Total organic carbon content and C/N ratios in cores COR0602-36PC, COR-0602-42PC, COR0503-36PC.	27
3	U ₃₇ ^{K'} -derived SSTs and TEX ₈₆ ^L -derived bottom water temperatures in cores COR0602-36PC, COR0602-42PC and COR0503-36PC and the absolute temperature difference (ΔT) between U ₃₇ ^{K'} and TEX ₈₆ ^L -derived water temperatures.	28
4	Relative proportions and abundances of C _{37:2} , C _{37:3} and C _{37:4} alkenones in cores COR0602-36PC, COR0602-42PC and COR0503-36PC.	30
5	BIT index, #rings _{tetra} , GDGT-0/crenarchaeol, GDGT-2/crenarchaeol & methane index in cores COR0602-36PC, COR0602-42PC and COR0503-36PC.	32

6	Insolation at 48°N; global and regional sea level changes; <i>N. pachyderma</i> $\delta^{18}\text{O}$ on the Laurentian Fan; Bottom water temperatures in the Labrador Sea based on benthic Mg/Ca; $\delta^{18}\text{O}$ and SSTs in COR0602-42PC & at Dry Tortugas; dinocyst-derived SSTs at Orphan Knoll and in COR0602-42PC; alkenone-derived SSTs on the Laurentian Fan and at the Scotian Margin; $U_{37}^{K'}$ & TEX_{86} in COR0503-36PC.	39
7	Alkenone-derived SST composite ($U_{37}^{K'}$ and $U_{37}^{K''}$ based on $C_{37:4}/C_{37:3}$) and TEX_{86}^L -derived water temperatures in cores COR0602-36PC, COR0602-42PC and COR0503-36PC and the absolute temperature difference (ΔT) between the composite alkenone SSTs and TEX_{86}^L -derived water temperatures.	46

ANNEXES

ANNEXE I – AGE MODELS

S1	Age-models for COR0602-36PC with different sedimentation rates overlain. .	55
S2	Age-model for COR0602-36PC.	55
S3	Age-model for COR0602-42PC.	56
S4	Age-model for COR0503-36PC.	56

ANNEXE II – COMPOSITE CALIBRATION FOR ALKENONES

S5	$C_{37:4}/C_{37:3}$ -alkenones with a threshold set at 1.5 and the comparison between $U_{37}^{K'}$ and $U_{37}^{K''}$	58
----	--	----

LISTE DES ABRÉVIATIONS

AMOC Atlantic meridional overturning circulation

B/A Bølling-Allerød interstadial

BIT Index Branched and isoprenoid tetraether index

brGDGT Branched glycerol dialkyl glycerol tetraethers

BWT Bottom water temperatures

cal ka BP Calibrated kiloannum before present

CIL Cold Intermediate Layer

DCM Dichloromethane

GC-MS/FID Gas chromatography - mass spectrometry/flame ionization detector

GDGT Glycerol dialkylglycerol tetraether

Hex Hexane

H1 Heinrich event 1

IPA Isopropyl alcohol

isoGDGT Isoprenoid glycerol dialkyl glycerol tetraethers

LC-MS Liquid chromatography - mass spectrometry

LGM Last glacial maximum

MeOH Methanol

MI Methane index

NADW North Atlantic deep water

TEX₈₆ TetraEther indeX of 86 carbon atoms

TOC Total organic carbon

SST Sea surface temperatures

Sv Sverdrup ($10^6 \text{ m}^3 \text{ s}^{-1}$)

U₃₇^{K'} Unsaturated ketones with 37 carbon atoms

YD Younger Dryas

INTRODUCTION GÉNÉRALE

LA DÉSOXYGÉNATION DANS LE SAINT-LAURENT

À travers le monde, les océans et les mers sont de plus en plus confrontés à des phénomènes d'hypoxie (Breitburg et al., 2018). Le seuil d'hypoxie est défini à $62,5 \mu\text{mol L}^{-1}$ de dioxygène (O_2) dissous et correspond à la concentration d' O_2 où la vie et la reproduction animale sont impactées (Diaz et al., 1995; Rabalais et al., 2001). Une baisse globale de plus de 2 % de la teneur en O_2 a été observée depuis 1960 (Schmidtke et al., 2017), et les simulations numériques suggèrent une baisse supplémentaire de 1 à 7 % au cours du siècle prochain (Keeling et al., 2010). Une partie de cette désoxygénation est saisonnière dans les zones côtières et résulte de l'eutrophisation, augmentant la consommation d' O_2 par les organismes (Levin et al., 2009). La désoxygénation peut également être observée dans l'océan ouvert en raison de l'augmentation des températures, entraînant une diminution de la solubilité de l' O_2 , une stratification croissante et ainsi une ventilation réduite (Schmidtke et al., 2017; Levin, 2018).

Outre ces effets directs, des modifications de la circulation océanique à grande échelle peuvent influencer les concentrations d' O_2 (Yamamoto et al., 2015; Palter and Trossman, 2018; Frölicher et al., 2020). Par exemple, Yamamoto et al. (2015) proposent une diminution de l' O_2 dans l'Atlantique Nord à cause de l'affaiblissement de la circulation méridienne de retournement de l'Atlantique (AMOC). En déplaçant de grandes masses d'eau à travers les océans, l'AMOC redistribue non seulement de l' O_2 , mais aussi du carbone, des nutriments et de la chaleur (Ganachaud and Wunsch, 2000; Buckley and Marshall, 2016; Lynch-Stieglitz et al., 2024). L'AMOC influence le climat terrestre en transportant les eaux chaudes des tropiques vers le nord, où elles se refroidissent, deviennent plus denses et plongent pour former les eaux profondes de l'Atlantique Nord (NADW) qui circulent ensuite vers le sud (Srokosz and Bryden, 2015). Un affaiblissement significatif de l'AMOC a été envisagé depuis le petit âge glaciaire (~1850 CE), principalement à cause de l'apport accru en eau douce (Rahm-

storf et al., 2015; Thornalley et al., 2018). Cette arrivée d'eau douce résulte de la fonte des glaces de l'Arctique et de la calotte glaciaire du Groenland. Elle augmente la stratification de surface, réduit la formation d'eau profonde (Rahmstorf et al., 2015; Bakker et al., 2016; Thornalley et al., 2018), et impacte ainsi l'approvisionnement d'O₂ en profondeur (Portela et al., 2024). Cependant, l'affaiblissement de l'AMOC reste controversé (Latif et al., 2022; He and Clark, 2022; Kelson et al., 2022).

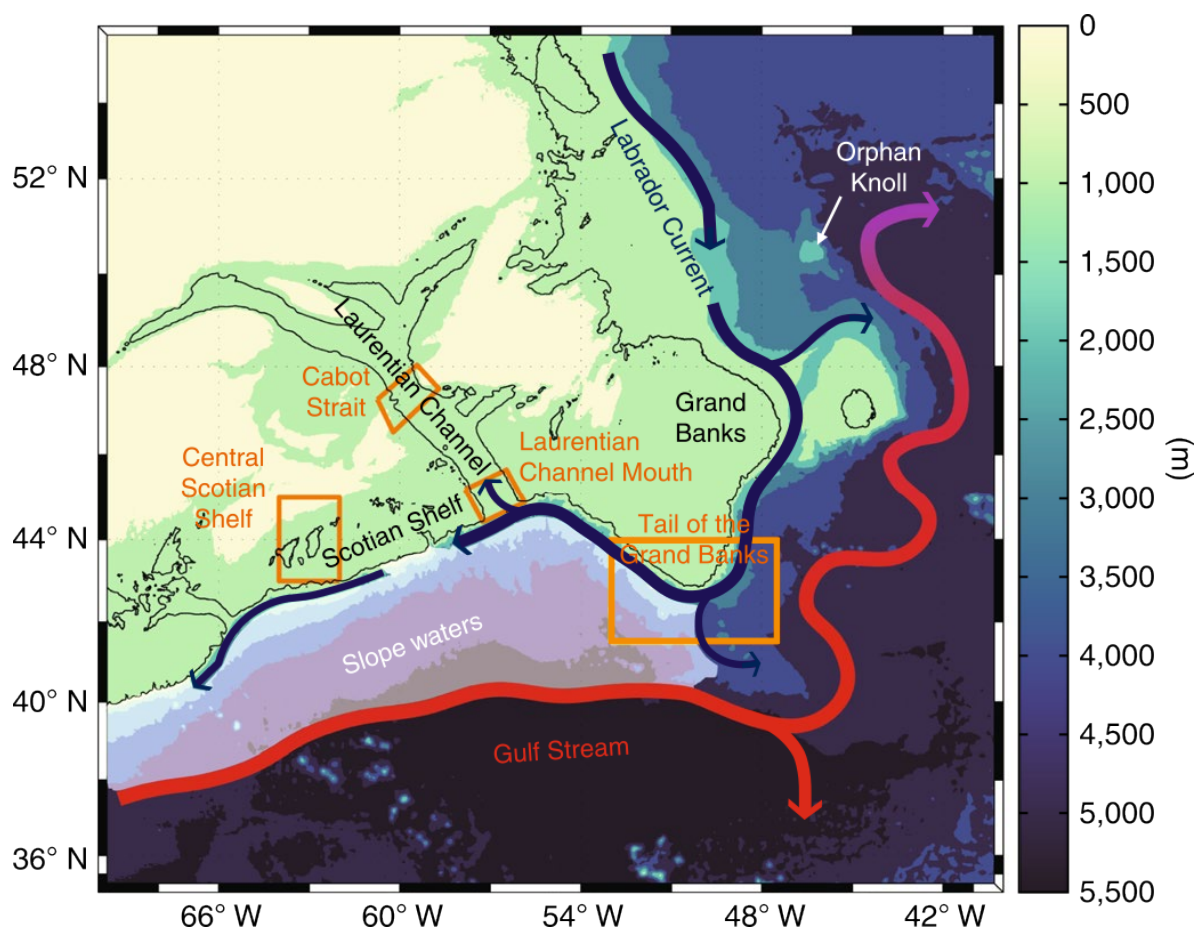


FIGURE I – Système du Saint-Laurent et les courants (Claret et al., 2018).

Ce potentiel affaiblissement de l'AMOC peut également avoir des impacts régionaux, comme dans le système du Saint-Laurent, où l'on observe un changement significatif dans l'approvisionnement des eaux de fond (Claret et al., 2018). En effet, cette région est directement

influencée par deux masses d'eaux avec différentes caractéristiques (Fig. I). D'une part, des eaux plus froides et plus oxygénées provenant de la mer du Labrador, qui longent le plateau continental, puis se dirigent vers l'ouest, en direction des Grands Bancs de Terre-Neuve. D'autre part, les eaux centrales de l'Atlantique Nord, transportées par le Gulf Stream, sont plus chaudes, plus salées et moins oxygénées (Fig. I; Claret et al., 2018). Il y a quelques décennies, ces deux masses d'eaux se mélangeaient et formaient alors les eaux profondes du Saint-Laurent qui entraient dans le système par le détroit de Cabot et remontaient le chenal laurentien (Gatien, 1976; Bugden, 1991; Gilbert et al., 2005; Jutras et al., 2023b). Un affaiblissement potentiel de l'AMOC au cours des dernières décennies aurait pu entraîner une diminution notable du débit du courant du Labrador dans le détroit de Cabot (Gilbert et al., 2005; Thibodeau et al., 2006; Genovesi et al., 2011; Claret et al., 2018) : actuellement, près de la totalité des eaux de fond entrant dans le système du Saint-Laurent proviennent du Gulf Stream (Jutras et al., 2020, 2023b), accentuant la perte d'O₂ par respiration microbienne de la matière organique durant le transport le long du système vers la tête du chenal laurentien (Oschlies et al., 2018). L'hypoxie dans le Saint-Laurent est donc en partie causée par un changement d'approvisionnement des eaux profondes (Thornalley et al., 2018; Thibodeau et al., 2018). Outre les changements de circulation, la perte d'O₂ est amplifiée par l'eutrophisation, qui augmente la respiration aérobie dans la colonne d'eau et les sédiments, et la hausse des températures, qui accélère le métabolisme des organismes et augmente leur consommation en O₂ (Thibodeau et al., 2006; Genovesi et al., 2011; Mucci et al., 2011). Cette hypoxie se manifeste de manière permanente, en raison de la stratification en trois couches distinctes dans ce système : la couche de surface, la couche intermédiaire froide et la couche profonde (Fig. II; Banks, 1966; Galbraith, 2006).

L'hypoxie dans le Saint-Laurent s'est étendue à la fois en superficie et en épaisseur : la couche hypoxique est passée de 1300 km² en 2003 à 9400 km² en 2021 (Gilbert et al., 2005; Jutras et al., 2023b) et son épaisseur a doublé, passant d'environ 75 m en 1995 à plus de 150 m depuis les dix dernières années (Jutras et al., 2023b). Les données instrumentales montrent une forte corrélation entre la diminution de la teneur en O₂ et l'augmentation des températures

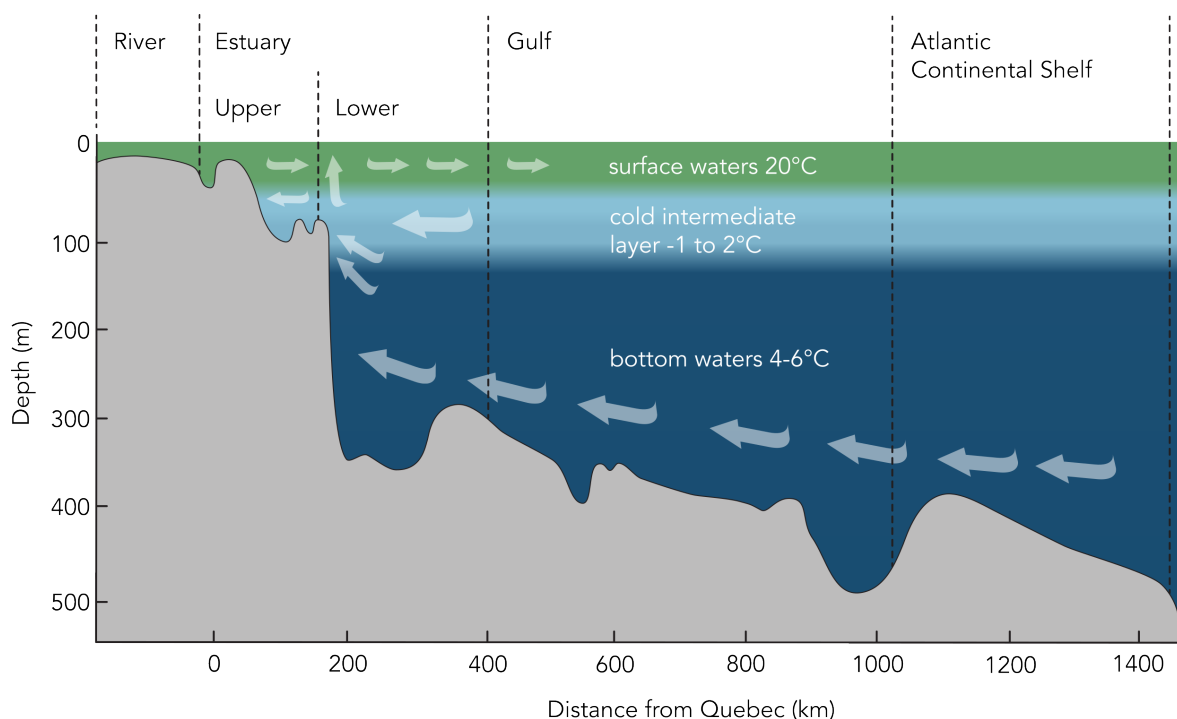


FIGURE II – Stratification dans le Saint-Laurent reproduit et adapté de Koutitonsky and Bugden (1991) par Stephanie Kusch.

des eaux de fond, due au flux des eaux du Gulf Stream (Gilbert et al., 2005; Jutras et al., 2023b). Les eaux de fond du système Saint-Laurent se sont réchauffés d'environ 3 °C en 1930, à 7 °C en 2021 (Jutras et al., 2023b). Les taux d'O₂ sont passés d'environ 125 μmol L⁻¹ en 1930 à des concentrations hypoxiques inférieures à 62,5 μmol L⁻¹ après 1984, puis ont chuté davantage en 2020, pour atteindre des niveaux d'environ 35 μmol L⁻¹ (Jutras et al., 2023b).

Cependant, les données instrumentales disponibles pour le système du Saint-Laurent ne permettent pas de remonter à des périodes antérieures aux années 1870 (Galbraith et al., 2024) et la variabilité naturelle de ce système n'est donc pas connue. Des études montrent que les apports actuels d'eaux atlantiques centrales et la tendance à la désoxygénation n'ont jamais atteint de tels niveaux au cours des 1000 à 2000 dernières années (Thibodeau et al., 2010; Sherwood et al., 2011; Thibodeau et al., 2018). Pour l'ensemble de l'Holocène, aucune étude

fait le lien entre la dynamique des températures de surface/de fond ou alors des concentrations d'O₂, qui permettrait de mieux comprendre l'évolution de la circulation. Le changement climatique naturel par les variations de l'orbite terrestre, peut servir d'analogie récente aux changements climatiques anthropiques actuels. Dans le contexte actuel de changement de courants et d'hypoxie, il est nécessaire de mieux comprendre la variabilité naturelle du système et d'analyser la dynamique de circulation des eaux profondes du système du Saint-Laurent.

LA DÉGLACIATION DE L'INLANDSIS LAURENTIDIEN

Bien que cette étude se concentre sur l'Holocène, un aperçu depuis le dernier maximum glaciaire est présenté afin de replacer les résultats dans un contexte plus large. L'insolation, qui correspond à la quantité d'énergie solaire reçue par la Terre, est influencée par des variations périodiques qui affectent l'orbite terrestre, connues sous le nom de cycles de Milankovitch (Fig. III ; Bennett, 1990; Berger and Loutre, 1991). Les périodes glaciaires sont liées à ces variations orbitales et le minimum d'ensoleillement estival boréal à 24 ka BP (Fig. III) a ainsi favorisé le dernier maximum glaciaire (~26,5-19 ka ; Clark et al., 2009). Conséquemment, une grande partie de l'Amérique du Nord était recouverte par l'inlandsis laurentidien (Fig. IV ; Dalton et al., 2020).

Avec l'augmentation de l'insolation, l'inlandsis laurentidien a commencé à diminuer (Fig. IV). L'histoire de sa déglaciation est marquée par plusieurs événements majeurs (Stokes, 2017). Des instabilités dans l'inlandsis laurentidien ont causé une phase de décharge d'icebergs massive de ~19,3-15,3 ka, appelée l'événement Heinrich 1 (H1 ; Hemming, 2004; Heath et al., 2018). Ensuite, au cours de l'interstadial Bølling-Allerød (B/A ; 14,7-12,9 ka), une période caractérisée par une fonte accrue de l'inlandsis laurentidien due à une augmentation des températures globales, le système du Saint-Laurent s'est déglacé (~14 cal ka BP ; Shaw et al., 2006; Dalton et al., 2020; Naughton et al., 2023). Cette fonte a également formé

le lac proglaciaire Agassiz dont la superficie et le volume ont beaucoup évolué au cours du retrait de l'inlandsis (Teller et al., 2002). Son extension vers l'est a ensuite formé le lac Agassiz-Ojibway, le plus grand lac proglaciaire associé à l'inlandsis laurentidien (Teller et al., 2002; Teller and Leverington, 2004). Le déversement de ce lac a déclenché quatre voies de drainage principales, dont une vers le fleuve Mississippi, une vers la baie d'Hudson, une vers le fleuve Mackenzie et une passant à travers le système du Saint-Laurent (Leverington and Teller, 2003; Teller, 2013). Le drainage de ces lacs ont causés l'effondrement de l'AMOC, conduisant à une période de refroidissement, appelée le Dryas récent (~12,9-11,5 ka; Broecker et al., 1989).

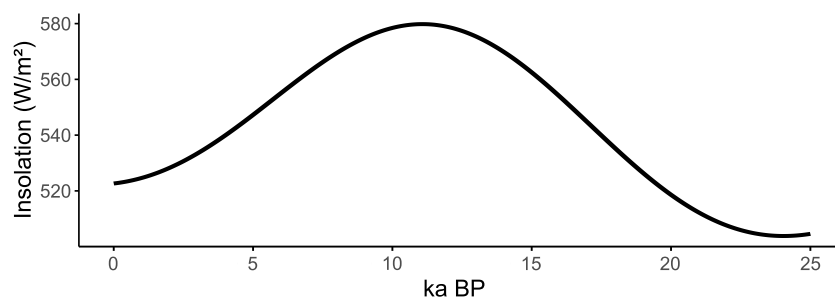


FIGURE III – Insolation au solstice d'été à 48°N dans le système du Saint-Laurent depuis 25 ka BP (Berger and Loutre, 1991).

Le début de l'Holocène (~11,7 ka) était caractérisé par un maximum d'ensoleillement estival boréal, entraînant un réchauffement important (Fig. III; Berger and Loutre, 1991). Environ 9500 km³ d'eau de fonte se sont déversés par le système du Saint-Laurent à partir de ~10,8 ka BP (Dyke, 2004), ce qui a affecté le niveau de la mer, l'hydrologie et la dynamique sédimentaire dans ce système (Casse et al., 2017; Leydet et al., 2018). Vers 8,2 ka, une décharge soudaine des lacs Agassiz-Ojibway vers l'Atlantique s'est produite (Barber et al., 1999; Carlson et al., 2008). Plus de 100 000 km³ d'eau de fonte se sont déversés dans la mer du Labrador, ayant entraîné un important rafraîchissement des eaux de surface dans la mer du Labrador (Barber et al., 1999; Clarke et al., 2004). La stratification qui en résultait a réduit la formation d'eaux profondes dans la mer du Labrador et diminué la formation d'eaux centrales dans l'At-

lantique Nord, ce qui a affaibli l'AMOC (Hillaire-Marcel et al., 2001b; Solignac et al., 2004; Hoogakker et al., 2015). Les conditions de surface dans la mer du Labrador (température et salinité) se sont stabilisées vers 7,5 ka. En augmentant la densité des eaux de surface, cette stabilisation a permis la reprise de la convection hivernale et instauré la circulation moderne (Hillaire-Marcel et al., 2001a,b; Solignac et al., 2004; Lochte et al., 2019).

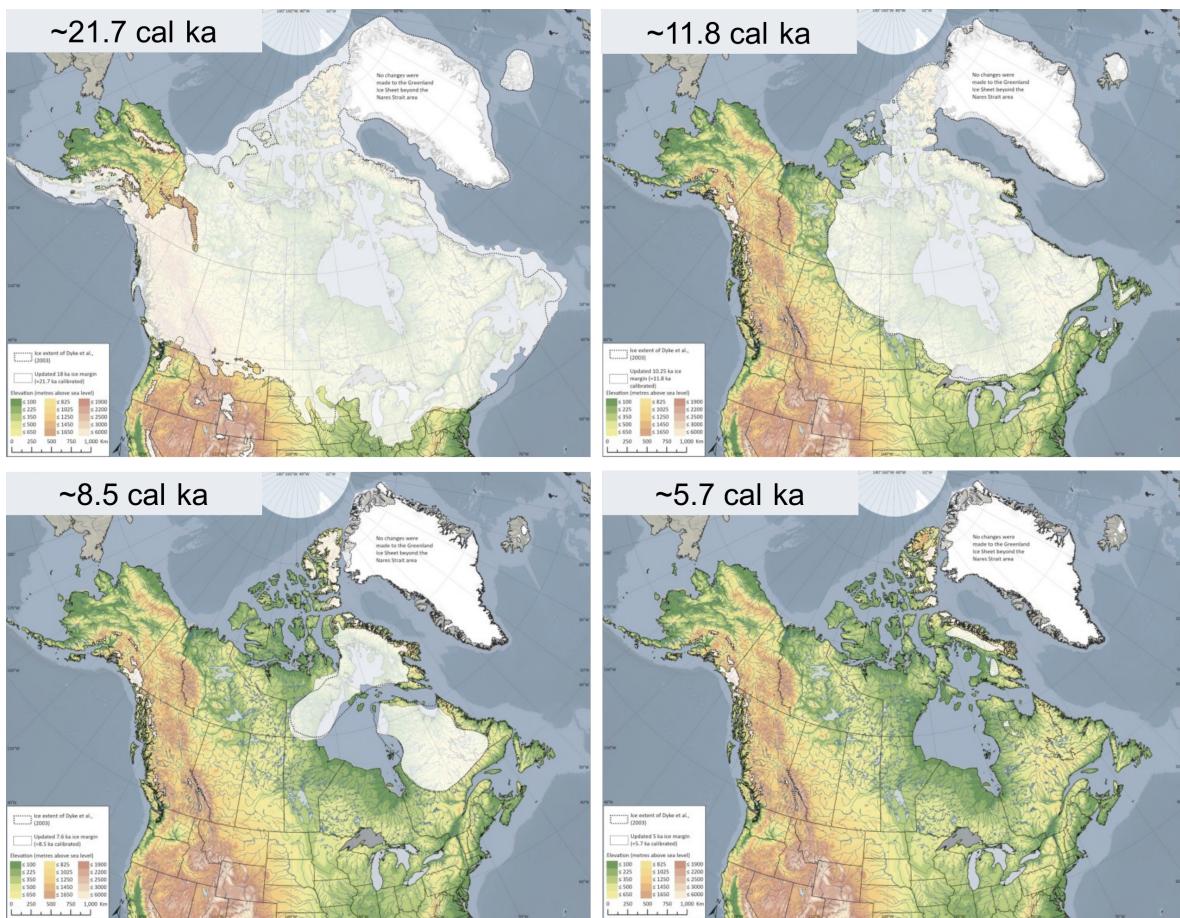


FIGURE IV – Retrait de l'inlandsis laurentidien depuis environ 21,7 cal ka (Dalton et al., 2020)

Ritz et al. (2013) ont simulé les variations de l'AMOC depuis le dernier maximum glaciaire. Des effondrements de l'AMOC ont eu lieu lors des événements climatiques Heinrich 1 et le Dryas récent, avec une diminution de 14 et 12 Sverdrup (Sv), respectivement (Fig. V). En re-

vanche, pendant l'Holocène, l'AMOC n'a pas subi d'effondrement, mais des affaiblissements (Fig. V ; McManus et al., 2004; Ritz et al., 2013). Par contre, l'impact des changements d'intensité passés de l'AMOC sur le système du Saint-Laurent n'est pas connu. Ce système est donc d'une zone d'intérêt pour étudier le climat durant l'Holocène, en raison de sa proximité avec le courant du Labrador et le Gulf Stream, ainsi que des changements d'insolation, de la diminution de l'inlandsis laurentidien et de l'impact de l'eau de fonte (Cohmap Members, 1988; Smith and Schwing, 1991; Levac, 2001).

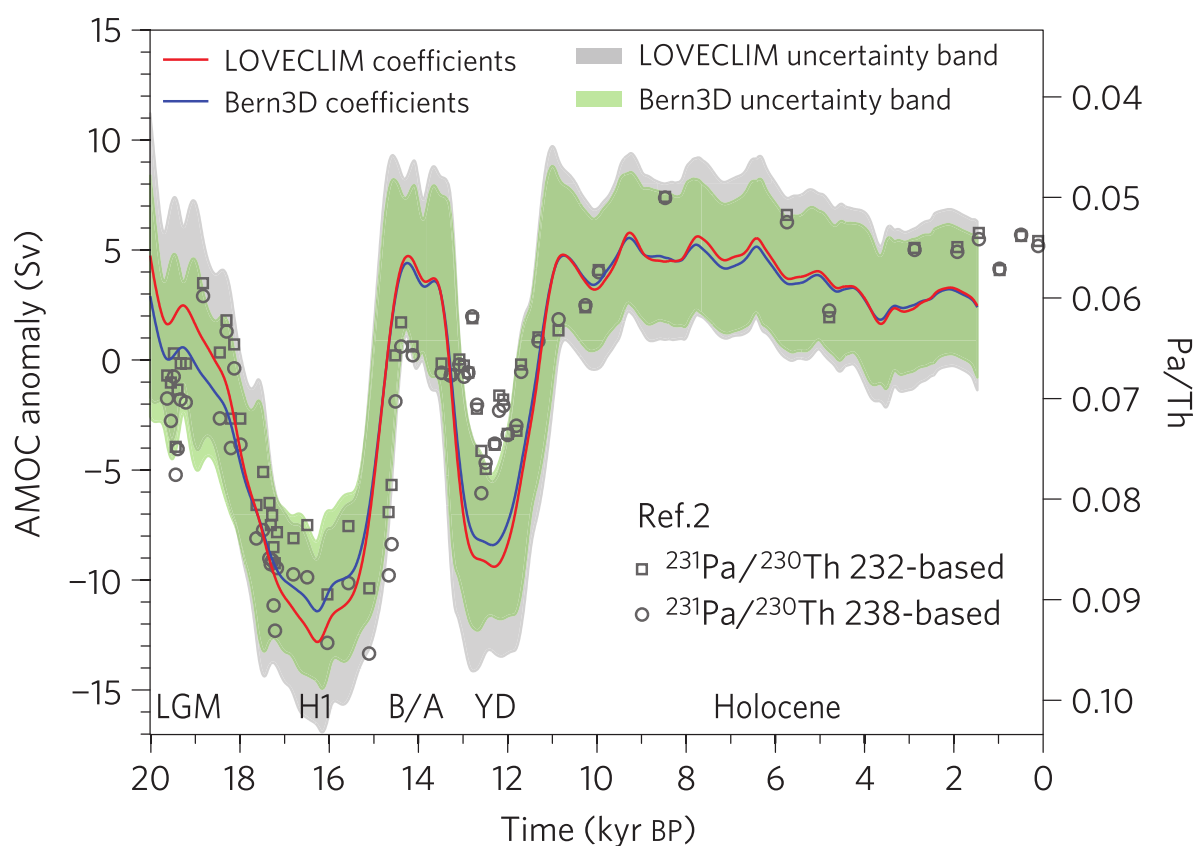


FIGURE V – Modélisations de l'intensité de l'AMOC depuis le dernier maximum glaciaire (basée sur deux modèles différents : LOVECLIM & Bern3D), avec le dernier maximum glaciaire (LGM), le stade Heinrich 1 (H1), l'interstade du Bølling-Allerød (B/A), le stade Dryas récent (YD) et l'Holocène (Ritz et al., 2013). Les symboles gris correspondent à une reconstruction à partir du traceur $^{231}\text{Pa}/^{230}\text{Th}$ sédimentaire (McManus et al., 2004). Plus de ^{231}Pa s'accumule dans les sédiments quand l'AMOC est affaibli, ce qui augmente donc le rapport $^{231}\text{Pa}/^{230}\text{Th}$. Tirée de Ritz et al. (2013).

Thibodeau et al. (2013) propose que le nord-est du golfe du Saint-Laurent a connu des conditions hypoxiques au cours de l'Holocène moyen (~6,0-4,0 cal ka BP) en se basant sur la présence de *Brizalina subaenariensis*, une espèce de foraminifère que l'on trouve dans des concentrations faibles en O₂. L'augmentation simultanée de la température des eaux profondes, reconstituée à partir des valeurs $\delta^{18}\text{O}$ des tests de foraminifères, indique un afflux accru d'eau provenant de l'Atlantique pendant cette période (Thibodeau et al., 2013). Cette étude souligne que les conditions de circulation pourraient avoir changé au cours de l'Holocène, mais les preuves sont spatialement limitées au chenal d'Esquiman et leur résolution temporelle est relativement faible en raison des faibles taux de sédimentation. Aucun indice de changements de circulation a pu être observé dans le chenal laurentien (Wu et al., 2023). De nouvelles approches peuvent donc être utilisées pour comprendre les dynamiques de circulation dans l'estuaire maritime et le golfe du Saint-Laurent durant l'Holocène. Bien que certaines études reconstruisent les conditions de surface à l'aide de microfossiles durant l'Holocène sur le plateau continental, au large de Terre-Neuve (Levac, 2001, 2003; Solignac et al., 2011; Balestra et al., 2013) et dans le système du Saint-Laurent (de Vernal et al., 1993; Lemay-Tougas, 2014; Wu et al., 2022, 2023), aucune reconstruction des températures par biomarqueurs lipidiques n'a été réalisée auparavant dans ce système. Cette approche permet de combler le manque de distinction claire, tant sur le plan spatial que temporel, entre la dynamique des eaux de surface et des eaux profondes, qui peut être liée à l'évolution de la circulation dans ce système.

LES BIOMARQUEURS LIPIDIQUES

Les biomarqueurs lipidiques sont des composés moléculaires spécifiques, stables dans le temps, provenant d'origine biologique. Leurs structures fournissent des informations sur les sources biologiques et les conditions environnementales, ce qui nous permet de reconstituer les environnements passés en analysant des archives environnementales (Eglinton and Eglinton, 2008; Summons et al., 2022). Dans ce projet de maîtrise, les alcénones et les glycérols

dialkylglycérols tétraéthers isoprénoïdes (isoGDGTs) sont utilisés pour reconstituer les températures des eaux de surface et de fond, respectivement.

Alcénones Les alcénones sont produits par des haptophytes, de l'ordre des Isochrysidales, qui sont présents dans la zone euphotique supérieure (Müller et al., 1998). Les alcénones sont une classe de méthyle et d'éthylcétones insaturés qui peuvent avoir des chaînes de carbones variant entre 35 et 42 carbones avec une à quatre insaturations (De Leeuw et al., 1980; Volkman et al., 1980; Marlowe et al., 1984). $U_{37}^{K'}$ est l'un des indices basée sur des biomarqueurs le plus ancien. Il est utilisé pour reconstruire les températures de surface de l'eau, et le principe repose sur la proportion d'alcénones di- et tri-insaturées ($C_{37:2}$ et $C_{37:3}$; Fig. VIa), laquelle est influencée par la température de croissance des Isochrysidales (Brassell et al., 1986; Prahl and Wakeham, 1987; Eglinton and Eglinton, 2008). La production d'alcénones uniquement par les Isochrysidales et la bonne préservation de ces molécules dans les sédiments en fait un traceur de températures très performant, qui peut remonter jusqu'au Pléistocène/à l'Éocène moyen et même jusqu'au Crétacé (Marlowe et al., 1984; Farrimond et al., 1986; Marlowe et al., 1990; Herbert, 2006). Les haptophytes sont des producteurs primaires importants, qui sont non seulement présents dans les océans mais aussi dans les environnements saumâtres et lacustres (Cranwell, 1985; Coolen et al., 2004; Zhao et al., 2014). Au sein des Isochrysidales, trois grands groupes phylogénétiques délimités par la salinité ont été définis, chacun présentant des signatures d'alcénones différentes, ce qui peut avoir une incidence sur la reconstitution des températures (Theroux et al., 2010). Le groupe I correspond aux Isochrysidales d'eaux douces, qui pour l'instant n'ont pas pu être cultivés (Longo et al., 2016; D'Andrea et al., 2006; Kaiser et al., 2019). Le groupe II est composé par des espèces des régions côtières et lacustres saumâtres à hypersalins, telles que *Tisochrysis lutea*, *Isochrysis galbana* et *Ruttenella lamellosa* (Theroux et al., 2010; Liao et al., 2020). Le groupe III comprend les espèces de l'océan ouvert, comme *Gephyrocapsa huxleyi* (Brassell et al., 1986; Prahl and Wakeham, 1987; Müller et al., 1998).

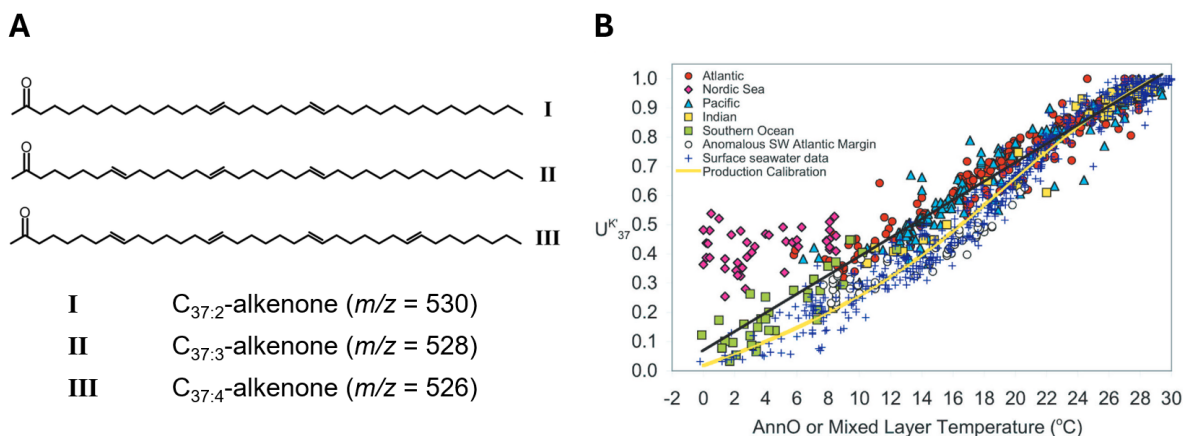


FIGURE VI – **A**) Structures moléculaires et ions moléculaires des alcénones à 37 atomes de carbones avec deux, trois et quatre insaturations. Tirée de Freitas et al. (2017). **B**) Calibration globale de $U_{37}^{K'}$ en fonction des températures de surface moyennes annuelles et de la couche de mélange. Tirée de Conte et al. (2006).

Les alcénones sont obtenus par extraction des lipides sédimentaires totaux à l'aide de solvants organiques. Les lipides sont ensuite saponifiés, puis fractionnés par colonne de silice (Kusch et al., 2010). La méthode exacte est décrite dans le manuscrit (section 4.3). Les alcénones se retrouvent dans la fraction des cétones, qui est analysée par chromatographie en phase gazeuse couplée à un ionisateur de flamme (GC-FID). Les proportions d'alcénones C_{37:2} sont produites en plus grande quantité dans des eaux plus chaudes, tandis que les proportions d'alcénones C_{37:3} sont produites dans des eaux plus froides. L'indice $U_{37}^{K'}$ est donc calculé à partir des proportions relatives des aires sous la courbe des alcénones C_{37:2} et C_{37:3} (équation 1) obtenus dans le chromatogramme, puis converti en température de surface à l'aide de calibrations pré-établies basées sur des sédiments de surface et des températures instrumentales modernes (Fig. VIb ; Müller et al., 1998).

$$U_{37}^{K'} = \frac{C_{37:2}}{(C_{37:2} + C_{37:3})} \quad (\text{Pahl and Wakeham, 1987}) \quad (1)$$

GDGTs Les glycérol dialkylglycérol tétraéthers isoprénoïdes (isoGDGTs) sont des lipides membranaires des Thaumarchaeota, qui font partie du domaine des archées (De Rosa and Gambacorta, 1988; Brochier-Armanet et al., 2008). Les isoGDGTs sont composés de deux chaînes d'alkyle reliés à un squelette de glycérol par une liaison éther, formant une structure tétraéther (Fig. VIIa; Schouten et al., 2002, 2013). Le nombre d'unités cyclopentanes varie avec la température de croissance des Thaumarchaeota. Le traceur TEX₈₆, basée sur le nombre d'unités de cyclopentanes, a donc été mis en place pour reconstruire les températures passées (Schouten et al., 2002). L'omniprésence et la bonne préservation des isoGDGTs dans les sédiments les rends particulièrement utile et permet des reconstructions jusqu'au Jurassique (Jenkyns et al., 2012). Cependant, des incertitudes de reconstructions de températures plus importantes sont trouvés dans les régions polaires (Fig. VIIb; Ho et al., 2014; Tierney and Tingley, 2015). Comme les Thaumarchaeota sont présents dans l'ensemble de la colonne d'eau (Karner et al., 2001), la profondeur correspondante à la température reconstruite a beaucoup été discuté (Zhang and Liu, 2018). Certaines études montrent que les températures reconstruites par TEX₈₆ reflètent le mieux les températures de surface (Schouten et al., 2002; Kim et al., 2008), alors que d'autres montrent qu'elles représentent plutôt des températures sous la surface jusqu'à des profondeurs de 200 m (Fig. VIIb; Tierney and Tingley, 2015; Ho and Laepple, 2016; Hurley et al., 2018). Kim et al. (2015) montrent même l'importance des GDGTs qui proviennent des eaux profondes. Cependant, les Thaumarchaeota sont des oxydants de l'ammoniac en nitrite et se retrouvent préférentiellement dans le maximum d'ammonium, sous la zone euphotique (Francis et al., 2005; Könneke et al., 2005; Beman et al., 2008). Dans le cadre de ce projet de maîtrise, les températures résultant de cet indice seront donc considérées comme correspondant à des températures situées à environ 200-300 mètres de profondeur, soit dans la couche d'eau profonde du système du Saint-Laurent (Fig. II) et la profondeur à laquelle les concentrations de nitrates deviennent plus importantes dans le Saint-Laurent (Bluteau et al., 2021).

Pour analyser les GDGTs, les lipides sont extraits, saponifiés puis fractionnés par colonne de silice, de la même manière que pour les alcénones. Cependant, pour les GDGTs, c'est

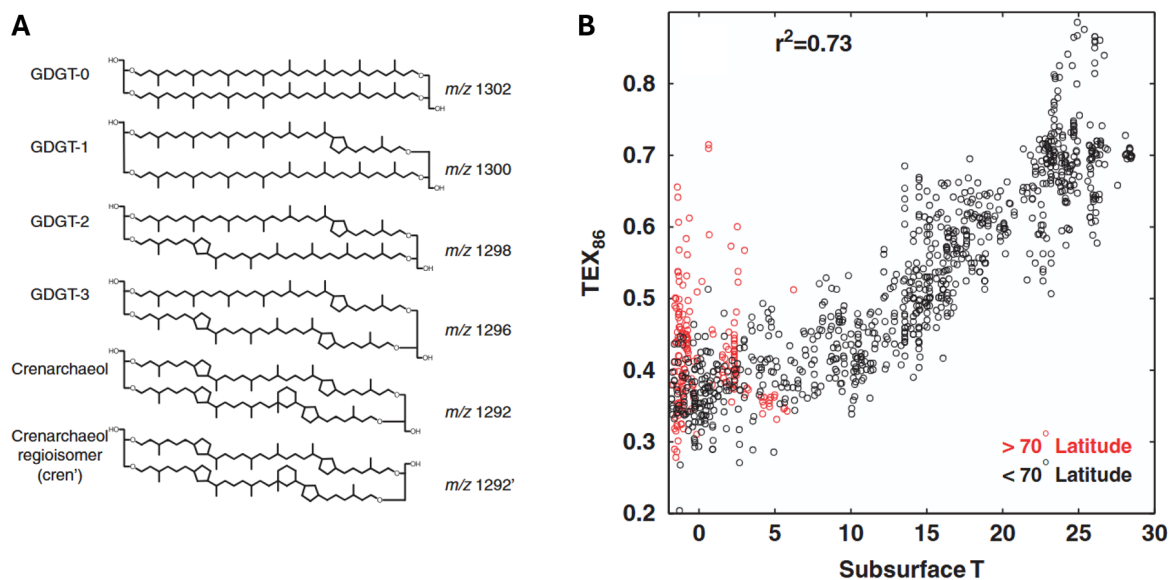


FIGURE VII – **A)** Structures moléculaires des isoGDGTs utilisés dans le proxy TEX₈₆. **B)** Calibration de TEX₈₆ en fonction des températures sous la surface (0-200 m). Tirées de Tierney and Tingley (2015).

la fraction des alcools qui est analysée par chromatographie en phase liquide couplée à un spectromètre de masse (LC-Orbitrap) afin de séparer et d'obtenir les concentrations des différentes molécules d'isoGDGTs. La méthode exacte est décrite dans le manuscrit (section 4.3). Dans les eaux plus chaudes, les Thaumarchaeota produisent des isoGDGTs contenant plus d'unités cyclopentanes, qui diminuent dans les eaux plus froides. L'indice TEX₈₆ peut ainsi être calculé à partir de ces proportions (équation 2), puis converti en température à l'aide de différentes calibrations basées sur les sédiments de surface et les températures instrumentales modernes (Fig. VIIb; Tierney and Tingley, 2015).

$$\text{GDGT index-1} = \log\left(\frac{[\text{GDGT-2}]}{([\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}])}\right) \quad (\text{Kim et al., 2010}) \quad (2)$$

OBJECTIFS ET HYPOTHÈSES

L'objectif de ce projet est de reconstruire les changements de circulation dans le système du Saint-Laurent durant l'Holocène en analysant les températures de surface et des eaux de fond. Une approche par biomarqueurs lipidiques est utilisée pour reconstituer l'évolution spatio-temporelle de la température et de la dynamique de la circulation dans le système du Saint-Laurent, afin de la relier à l'histoire de sa désoxygénation.

Hypothèse 1 L'hypothèse principale est que des changements de circulation peuvent être observés en comparant les variations des températures de surface et des eaux de fond qui se superposent aux effets d'insolation. En utilisant les indices $U_{37}^{K'}$ et TEX_{86} pour reconstruire les températures de surface et celles des eaux profondes respectivement, il est possible d'analyser les écarts entre les différentes masses d'eaux (ΔT). Pour des changements induits par l'insolation, un enregistrement simultanément par les deux traceurs devrait donner des valeurs avec un écart constant. En revanche, les changements de circulation devraient provoquer un écart variable entre les températures de surface et celles des eaux de fonds. Des périodes d'augmentation de l'apport des eaux du Gulf Stream, telles qu'observées au cours du dernier millénaire (Thibodeau et al., 2010; Sherwood et al., 2011; Thibodeau et al., 2018), devraient donc entraîner un écart réduit des températures entre $U_{37}^{K'}$ et TEX_{86} . De même, une diminution des apports du Gulf Stream devrait amplifier cet écart.

Hypothèse 2 Les changements de circulation devraient pouvoir être liés à des épisodes passés d'hypoxie, qui sont reconstitués indépendamment à l'aide de proxies élémentaires, isotopiques et lipidiques. Si des périodes d'hypoxie se sont produites par le passé, elles pourraient être associées à une eutrophisation accrue ou à un apport plus important d'eaux du Gulf Stream. Ces conditions correspondraient alors à des températures plus élevées en profondeur et à une réduction de l'écart thermique entre les eaux de surface et les eaux de fond (ΔT). En revanche, un apport plus important des eaux du courant du Labrador, qui se traduirait par

un ΔT plus important, ne devrait pas conduire à une période hypoxique. Cette approche est menée en collaboration avec Daphnée Laliberté, qui travaille sur les mêmes échantillons et carottes sédimentaires.

Ce mémoire est écrit sous forme d'article scientifique intitulé « Biomarker-based reconstruction of Holocene water temperatures in the St. Lawrence system indicates changes in circulation dynamics ». Il sera soumis au journal *JGR : Biogeosciences* à l'automne 2025. En tant que première autrice, j'ai réalisé les travaux en laboratoire, les analyses par GC-FID et LC-Orbitrap, le traitement et l'interprétation des données, ainsi que la rédaction du manuscrit. Daphnée Laliberté a contribué de manière égale aux travaux en laboratoire. Mathieu Babin a apporté un soutien technique pour la LC-Orbitrap, le développement méthodologique et l'extraction des données. Stephanie Kusch a proposé l'idée du projet, participé au développement méthodologique, ainsi qu'à l'interprétation des données et à la rédaction du manuscrit.

ARTICLE 1

BIOMARKER-BASED RECONSTRUCTION OF HOLOCENE WATER TEMPERATURES IN THE ST. LAWRENCE INDICATES CHANGES IN CIRCULATION DYNAMICS

Marie Engel, Daphnée Laliberté, Mathieu Babin, Stephanie Kusch

Institut des Sciences de la Mer, Université du Québec à Rimouski, Rimouski, Canada

1 ABSTRACT

The Lower St. Lawrence Estuary is facing bottom water hypoxia mostly due to climate-driven changes in ocean circulation. A decrease in the inflow of cold, oxygen-rich bottom waters from the Labrador Current in favor of warm and oxygen-poor bottom waters from the Gulf Stream exacerbates oxygen loss during microbial respiration of organic matter. Here, we spatiotemporally reconstruct the Holocene temperature and ventilation history as an analog of current and future warming and to better understand the natural variability of this system. We present sea surface temperature (SST) data derived from the haptophyte-based alkenone proxy ($U_{37}^{K'}$) and the archaeal tetraether lipid-based TEX₈₆ proxy recording bottom water temperatures along the Laurentian Channel. Both proxies overall show warming of water temperatures during the early Holocene followed by cooling after around 7.5 ka BP, but the cooling trend is much more pronounced for SSTs. This difference results in a distinct change in the relative temperature offset between the two proxies, which suggest transient changes in circulation dynamics/bottom water sourcing. After correcting for a temperature bias in the $U_{37}^{K'}$ -derived SSTs caused by the brackish conditions resulting from the 8.2 ka BP meltwater event, the relative temperature offset between surface and bottom waters seems to indicate

increasing bottom water contributions from the Gulf Stream after 7.0 ka BP or changes in the properties of the waters entering the system. After 4.0 ka BP, the relative temperature offset is rather stable, indicating minor changes in bottom water sourcing. Our data thus show that the current link between circulation changes and hypoxia may be unprecedented over the Holocene.

2 INTRODUCTION

The world's oceans and seas are becoming increasingly hypoxic. A global oxygen decline of 2% has been observed since 1960 (Schmidtke et al., 2017), and models predict an additional oxygen decline of 1-7% over the next century (Keeling et al., 2010). Much of the observed oxygen loss in coastal ocean settings globally results from eutrophication and occurs seasonally (Levin et al., 2009). However, hypoxia in the St. Lawrence system (Fig. 1a) is permanent and formed in large parts through changes in the bottom water composition (Gilbert et al., 2005; Claret et al., 2018; Thibodeau et al., 2018; Thornalley et al., 2018). Shelf and offshore Labrador Current waters flow along the continental shelf of the Labrador Sea and then westwards towards the Grand Banks of Newfoundland, carrying colder, more oxygenated waters. In contrast, the North Atlantic Central Waters, carried by the Gulf Stream, are warmer, saltier, and less oxygenated (Claret et al., 2018; Thornalley et al., 2018). These waters mix on the continental slope and form the bottom water of the St. Lawrence system entering through Cabot Strait to slowly move up the Laurentian Channel (Gatien, 1976; Bugden, 1991; Gilbert et al., 2005; Jutras et al., 2023b). At present almost 100% of the bottom water entering the St. Lawrence system is supplied via the Gulf Stream (Gilbert et al., 2005; Claret et al., 2018; Jutras et al., 2020, 2023b). One possible explanation for these changes is the weakening of the Atlantic Meridional Overturning Circulation (AMOC) over recent decades (Claret et al., 2018; Arellano-Nava et al., 2025), which may have led to a substantial reduction in the Labrador Current-derived inflow through the Cabot Strait. However, the weakening of the AMOC is debated (Latif et al., 2022; He and Clark, 2022; Kelson et al.,

2022). The change in bottom water composition accentuates the loss of oxygen during microbial respiration of organic matter along the estuary towards the head of the Laurentian Channel (Oschlies et al., 2018), which is further augmented by an increased oxygen demand in the water column and sediments caused by eutrophication and higher respiration rates of organisms at higher temperatures (Benoit et al., 2006; Thibodeau et al., 2006; Genovesi et al., 2011; Mucci et al., 2011). Instrumental data show a strong correlation between decreasing oxygen content and increasing bottom water temperatures due to the influx of Gulf Stream waters (Gilbert et al., 2005; Jutras et al., 2023b). Mean bottom water temperatures from May to November in the Gulf of St. Lawrence have been increasing from 3.4 °C in 1930 to 6.6 °C in 2024 while surface waters have only been increasing from 10.2 °C in 1930 to 11.7 °C in 2024 (Fig. 1b; Galbraith et al., 2024). Although bottom water temperatures are increasing because of the changing circulation dynamics, surface waters are not impacted by bottom water warming due to thermal isolation via the cold intermediate layer (CIL; Banks, 1966). However, due to the interannual temperature variability in surface and bottom water temperatures, the warming trend in surface and bottom water temperatures is similar, leading to a relatively stable – but slightly decreasing – offset between surface and bottom temperatures (ΔT ; Fig. 1b).

As instrumental data for the St. Lawrence system only partly go back to the 1870s (Fig. 1b; Galbraith et al., 2024), and few studies have reconstructed circulation regime shifts through temperature and oxygen dynamics over longer time scales it is difficult to assess the relationship between temperature and oxygen levels and whether there were significant variations in circulation prior to the recently observed changes. Some paleoceanographic studies cover the last 1-2 millennia and show that the recent influx of Atlantic waters and the trend towards deoxygenation are unprecedented over this time scale (Thibodeau et al., 2010; Sherwood et al., 2011; Thibodeau et al., 2018). Thibodeau et al. (2013) inferred that the NE Gulf of St. Lawrence, more specifically the Esquiman Channel, may have experienced low-oxygen conditions during the middle Holocene (~6.0-4.0 cal ka BP) based on the presence of *Brizalina subaenariensis*, a foraminiferal species found at low oxygen concentrations. The

simultaneous increase in bottom water temperature, reconstructed using the $\delta^{18}\text{O}$ values of foraminiferal tests of *Globobulimina auriculata*, indicate an increased influx of water from the Atlantic during this period (Thibodeau et al., 2013). This study highlights that ventilation/redox conditions may have changed during the Holocene, but the evidence is spatially confined to the Esquiman Channel and has relatively poor temporal resolution due to low sedimentation rates, whereas Wu et al. (2023) shows no evidence for hypoxia based on benthic foraminiferal data in the St. Lawrence Estuary. No comparable data exists for the Laurentian Channel or for the early Holocene because of high sedimentation rates and poor foraminifera preservation.

Other approaches can be used to reconstruct circulation/ventilation dynamics in the Lower St. Lawrence Estuary and Gulf of St. Lawrence during the Holocene. Here, we use lipid biomarker thermometry to spatiotemporally reconstruct water temperatures and, by inference, circulation changes in the St. Lawrence system during the Holocene. We use alkenones (U_{37}^{K}) and isoprenoid glycerol dialkyl glycerol tetraethers (isoGDGTs; TEX_{86}) to reconstruct surface and bottom water temperatures, respectively. Alkenones are an unusual class of unsaturated methyl and ethyl ketones with carbon chains ranging from 35 to 42 carbon atoms and 1 to 4 unsaturations (Volkman et al., 1980; Marlowe et al., 1984; Farrimond et al., 1986), which show an empirical relationship with growth temperature (Brassell et al., 1986). Alkenones are produced by haptophyte microalgae of the order Isochrysidales and, thus, record upper euphotic zone sea surface temperatures (Müller et al., 1998). The TEX_{86} index is based on GDGTs, the membrane lipids of Thaumarchaeota (De Rosa and Gambacorta, 1988; Schouten et al., 2002; Brochier-Armanet et al., 2008). These molecules form a lipid bilayer membrane with isoprenoid carbon chains linked to glycerol backbones by ether bonds. They can have 0 to 8 cyclopentane moieties, whose number correlates with growth temperatures (Schouten et al., 2002, 2013), with the exception of polar regions having larger uncertainties (Ho et al., 2014). GDGT-producing Thaumarchaeota are ammonia oxidizers that preferentially inhabit the subsurface ammonia maximum in the thermocline (Francis et al., 2005; Könneke et al., 2005; Beman et al., 2008). However, the habitat depth of these molecules in the water column

may vary spatially and temporally (Zhang and Liu, 2018) and other confounding ecological factors may also influence TEX₈₆-derived water temperatures, like oxygen content, pH and nutrient stress (Qin et al., 2015, 2017, 2018; Guo et al., 2021; Rattanasriampaipong et al., 2025).

In this study, we use three sediment cores along the Laurentian Channel to reconstruct surface and bottom water temperatures of the St. Lawrence system during the Holocene based on alkenones and GDGTs, respectively. Our data show a warming of mean annual temperatures for surface and bottom waters in the early Holocene. The relative offset between the surface and bottom water temperatures decreases significantly at around 7.5 cal ka BP, when surface waters are cooling more than bottom water temperatures, potentially indicating past circulation changes.

3 STUDY AREA

The St. Lawrence Estuary (Fig. 1a) is one of the largest estuaries in the world, with a freshwater flow of approximately $1.1 \times 10^4 \text{ m}^3 \text{ s}^{-1}$ (El-Sabh and Silverberg, 1990; Bourgault and Koutitonsky, 1999). This system is connected to the Atlantic through Cabot Strait, which has a maximum depth of 480 m and a width of 104 km, and Belles Isle Strait, which has a depth of less than 60 m and a width of just 15 km (Koutitonsky and Bugden, 1991). The Laurentian Channel is an important topographical feature in this system, extending 300 to 400 m in depth over 1000 km from the North Atlantic through the Cabot Strait to the Upper St. Lawrence Estuary at Tadoussac (Koutitonsky and Bugden, 1991). The circulation in this system is estuarine. Fresh surface waters from the St. Lawrence River flow downstream, while the bottom waters entering the system at Cabot Strait/Belles Isle Strait flow upstream along the Laurentian Channel to its head (Saucier et al., 2003; Gilbert, 2004). Bottom water transport to the head of the Laurentian Channel is sluggish and Bugden (1991) and Gilbert (2004) proposed a bottom water transport to the head of the Laurentian Channel of 4 to 7 years at a propagation speed of 0.95 cm s^{-1} . More recent studies, however, suggest a

transit time of 1.7 to 4.7 years (Stevens et al., 2024) and 3.2 ± 0.7 years (Rousseau et al., 2025). Sea ice generally forms from December to March in the coastal areas of the estuary (Galbraith et al., 2024). During these winter months, the St. Lawrence water column is stratified into two layers, the surface (variable depths of ~40 m to 150 m) and the deep/bottom water layer (Galbraith, 2006). As the water begins to warm up in spring, temperature and salinity differences cause additional stratification of the surface waters, resulting in three distinct water layers (Banks, 1966; Galbraith, 2006): the surface layer with large seasonal temperature variations ($\sim 7.2^\circ\text{C}$; May to November mean from 1991-2020 in the estuary), the cold intermediate layer, which results from the winter freeze out ($< 1^\circ\text{C}$), and the deep layer ($\sim 5.1^\circ\text{C}$, May to November mean from 1991-2020 in the estuary; Galbraith et al., 2024).

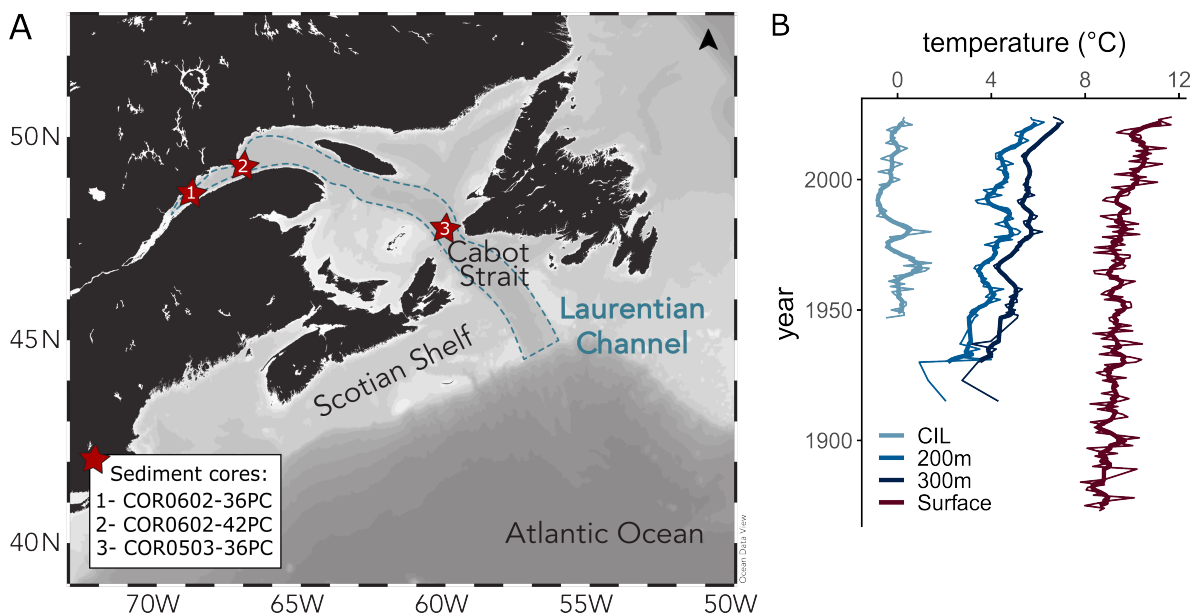


Figure 1 – **A)** St. Lawrence system with location of the three investigated sediment cores. **B)** Mean instrumental temperatures in the Gulf of St. Lawrence from May to November for surface waters (for the period 1873-1982 inferred from air temperatures, from 1982-2024 obtained empirically), the cold intermediate layer (CIL; 1947-2024 by direct measurement), and bottom waters at 200 m and 300 m (1915-2024 obtained empirically; Galbraith et al., 2024).

4 MATERIAL AND METHODS

4.1 Materials

Piston cores were collected during R/V Coriolis II missions in June 2005 and 2006 (Fig. 1a). COR0602-36PC (48° 24.0700 N; 69° 14.2400 W, 315 m water depth, 6.97 m core length) and COR0602-42PC (49° 07.1800 N; 67° 16.8000 W, 332 m water depth, 7.53 m core length) were obtained in the Lower St. Lawrence Estuary and COR0503-36PC (47° 40.2860 N; 59° 59.9850 W, 544 m water depth, 7.71 m core length) was collected in the Gulf of St. Lawrence, near Cabot Strait. All cores were stored in a cold room at 4 °C at UQAR-ISMER until analysis.

Previously published radiocarbon ages for cores COR0602-36PC, COR0602-42PC and COR0503-36PC (Barletta et al., 2010; Wu et al., 2023) were calibrated with the Marine20 calibration curve (Heaton et al., 2020) using the rbacon package ('tofu()' command) from Blaauw and Christen (2011). A reservoir age correction (ΔR) of 25 ± 72 years was applied following Wu et al. (2023). An additional age tie point, obtained via wiggle matching of magnetic susceptibility profiles with core MD99-2221, was added to core COR0602-36PC following Casse et al. (2017). To fit this tie point into the age-depth model, a change in the sedimentation rate was added at a depth of 520 cm (model input 0.2 cm yr^{-1} to 0.05 cm yr^{-1}), the transition to glaciomarine sediments. Different accumulation rates ($0.1\text{-}0.5 \text{ cm yr}^{-1}$; Fig. S1) were tested to constrain the model and the resulting probability density functions were overlain to find the best fit scenario consistent with the lithological and paleoenvironmental evidence.

4.2 Elemental analyses

Subsamples of each core were taken roughly every 15 cm and freeze-dried, corresponding to intervals of ~100 to 300 years. Approximately 100 mg of sediment per subsample were decarbonized using 12N HCl. Carbon and nitrogen contents were analyzed with a COSTECH ECS 4010 elemental analyzer equipped with a Zero Blank autosampler. An in-house sediment standard was analyzed regularly to assess reproducibility (relative error of ± 0.07 for carbon and ± 0.01 for nitrogen).

4.3 Biomarker analyses

The total lipid extract (TLE) was obtained using a modified Bligh and Dyer (1959) protocol with 10-40 g of dry sediment (Kusch et al., 2018). A mixture of methanol (MeOH), dichloromethane (DCM) and water (2:1:0.8) was added to the freeze-dried sediments, followed by 10 min ultrasonication, shaking for an hour, and centrifugation. This step was repeated twice but only DCM was added during the third extraction step. The combined TLE was transferred into a separatory funnel to which DCM and water was added (1:1) to perform a liquid-liquid extraction until colorless. The TLE was dried and then saponified with 0.5M KOH in 90% MeOH for two hours at 80 °C. Neutral lipids were liquid-liquid extracted ~3-5 times into hexane (Hex) and fatty acids were extracted ~3-5 times into DCM following adjustment of the pH to 1 with 6N HCl. The neutral lipid fraction was further separated by silica column chromatography with 1% deactivated SiO₂ in Hex. A polarity gradient was used to separate hydrocarbons (~4 ml Hex), ketones (~4 ml 2:1 DCM:Hex) and alcohols (~4 ml MeOH).

Ketones were taken up in a defined volume of DCM and analyzed with an Agilent gas chromatography-mass spectrometry system (8890 GC and 5977B MS) operated in FID mode and equipped with a Restek Rxi-5ms column and helium as carrier gas. The inlet was op-

erated in pulsed splitless mode with a temperature of 320 °C. The oven parameters were set to an initial temperature of 70 °C, increasing 20 °C min⁻¹ until 200 °C, and increasing 3 °C min⁻¹ until 320 °C with a final hold time of 25 min. The data were analyzed using Agilent MassHunter Qualitative Analysis 10.0 software. Alkenone concentrations were calculated against an external alkane standard and should be considered semi-quantitative.

Alcohols were dissolved in a defined volume of 95:5 Hex:isopropyl alcohol (IPA), spiked with an internal C₄₆ GDGT standard (Huguet et al., 2006), and analyzed with a Thermo LC-Orbitrap system. The Accela HPLC was equipped with two Waters Acquity BEH HILIC columns (1.7 μm, 150 mm × 2.1 mm) mounted in series, the autosampler temperature set at 4 °C, column temperature set at 30 °C, and solvent flow rate set at 200 μL min⁻¹. GDGTs were separated following Hopmans et al. (2016) with mobile phase A 100% Hex and mobile phase B 90:10 Hex:IPA mixed using a solvent gradient (82% A isocratic for 25 min, ramp to 65% A at 50 min, ramp to 0% A at 80 min). Re-equilibration with 82% A started at 85 min for 20 min. The Thermo Orbitrap LTQ Discovery high-resolution mass spectrometer was operated in positive ion mode using an atmospheric pressure chemical ionisation (APCI) ion probe with a set voltage of 6 kV and vaporizer temperature of 350 °C. Nitrogen was used as sheath, auxiliary and sweep gas at 50, 5 and 5 (arbitrary units), respectively. Capillary temperature was set to 275 °C. Scan range was from 60 to 1500 m/z and GDGTs abundances were determined based on their individual [M+H]⁺ ions. High-Resolution Mass Spectrometry data analysis was performed with Xcalibur 2.0 software from Thermo with a 10 ppm mass tolerance.

4.4 Proxy calculations

Alkenone sea surface temperatures (SSTs) were calculated using the peak areas and the following equations:

$$U_{37}^{K'} = \frac{C_{37:2}}{(C_{37:2} + C_{37:3})} \quad (\text{Prahl and Wakeham, 1987}) \quad (1)$$

$$\text{Alkenone SST} = \frac{(U_{37}^{K'} - 0.044)}{0.033} \quad (\text{Müller et al., 1998}) \quad (2)$$

The TEX_{86}^L water temperatures were calculated as follows:

$$\text{GDGT index-1} = \log\left(\frac{[\text{GDGT-2}]}{([\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}])}\right) \quad (\text{Kim et al., 2010}) \quad (3)$$

$$\text{TEX}_{86}^L \text{ temperatures} = 67.5 \times [\text{GDGT-Index-1}] + 46.9 \quad (\text{Kim et al., 2010}) \quad (4)$$

To assess potential biases in the GDGT records, the branched and isoprenoid tetraether (BIT) index, $\#rings_{tetra}$ and the methane index (MI) were calculated according to the following equations.

$$\text{BIT Index} = \frac{([\text{Ia}] + [\text{IIa}] + [\text{IIa}'] + [\text{IIIa}] + [\text{IIIa}'])}{([\text{Ia}] + [\text{IIa}] + [\text{IIa}'] + [\text{IIIa}] + [\text{IIIa}'] + [\text{cren}])} \quad (\text{Hopmans et al., 2004}) \quad (5)$$

$$\#rings_{tetra} = \frac{([\text{Ib}] + 2 \times [\text{Ic}])}{([\text{Ia}] + [\text{Ib}] + [\text{Ic}])} \quad (\text{Sinninghe Damsté, 2016}) \quad (6)$$

$$\text{MI} = \frac{([\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}])}{([\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}] + [\text{cren}] + [\text{cren}'])} \quad (\text{Zhang et al., 2011}) \quad (7)$$

The ratios of GDGT-0/crenarchaeol and GDGT-2/crenarchaeol were also calculated (Blaga et al., 2009).

5 RESULTS

5.1 Elemental analyses

Fig. 2a shows the total organic carbon (TOC) content of cores COR0602-36PC, COR0602-42PC and COR0503-36PC. From the base of core COR0602-36PC until ~6.5 cal ka BP, the TOC fluctuates between 0.2% and 0.3%, increasing to approximately 0.5% around 5.0 cal ka BP and further to 0.8% in the uppermost sample. The C/N ratio in the same sediment core varies between 5 and 8 in the lower part of the core (9.4-8.6 cal ka BP), with a minimum value of 4.8 at 8.9 cal ka BP. In the top part of the core (5.8-0.1 cal ka BP), values shift around 10.0-12.0, with a maximum value of 13.0 in the uppermost sediment sample (Fig. 2b). In core COR0602-42PC, the TOC content increases relatively consistently from a minimum of 0.2% at 8.2 cal ka BP to a maximum of 0.9% at 0.8 cal ka BP (Fig. 2a). In contrast, the C/N values of core COR0602-42PC are relatively stable throughout the core, mostly around 9.0–10.0, with minimum and maximum values of 6.8 (7.7 cal ka BP) and 11.4 (7.9 cal ka BP), respectively (Fig. 2b). The TOC content of the Cabot Strait core COR0503-36PC ranges from 0.4% at 10.1 cal ka BP to 1.6% at 0.8 cal ka BP (Fig. 2a) and values mostly increase towards the uppermost sample. The C/N values in this core range from 6.7 to 9.3, showing a gradual increase towards the present (Fig. 2b).

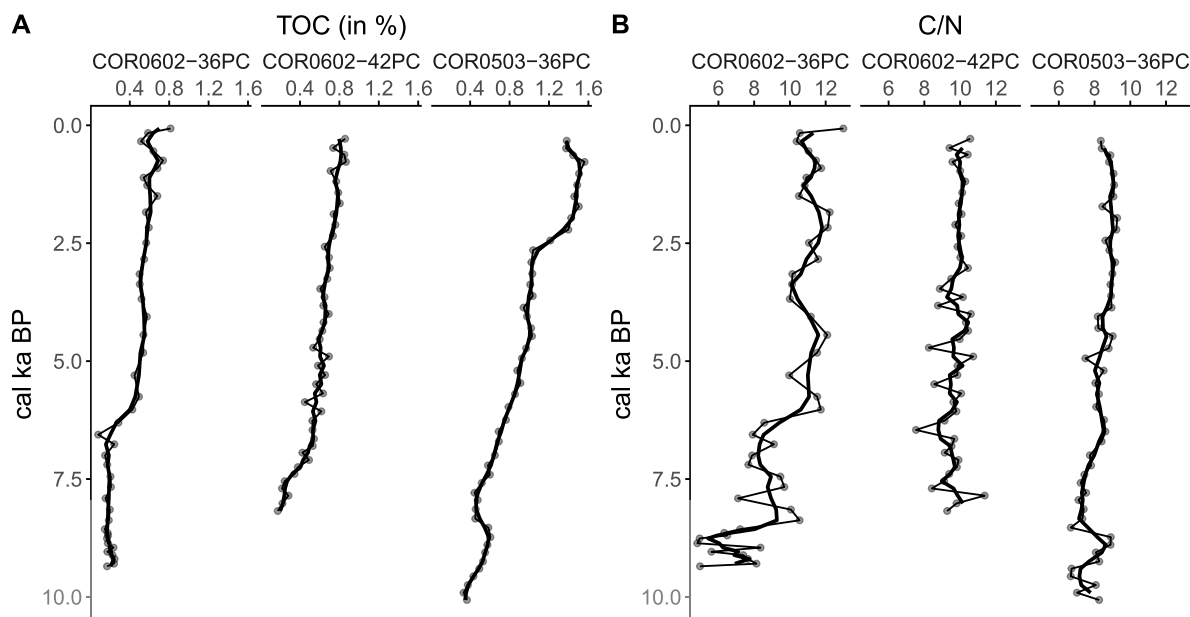


Figure 2 – **A)** Total organic carbon (TOC) in cores COR0602-36PC, COR0602-42PC and COR0503-36PC. The bold line represents the 3-point moving average. The grey axis indicates glaciomarine sediments, where the age model is not well constrained. **B)** C/N ratio in cores COR0602-36PC, COR0602-42PC and COR0503-36PC. The bold line represents the 3-point moving average. The grey axis indicates glaciomarine sediments, where the age model is not well constrained.

5.2 Alkenones

Fig. 3a shows the reconstructed $U_{37}^{K'}$ and TEX_{86}^L -derived temperatures. The $U_{37}^{K'}$ values in all cores range from 0.23 to 0.91, corresponding to surface temperatures from 5.5 °C to 26.3 °C respectively. Core COR0602-36PC has $U_{37}^{K'}$ values between 0.30 and 0.91, corresponding to surface temperatures between 7.9 °C and 26.3 °C. Core COR0602-42PC has $U_{37}^{K'}$ values from 0.28 to 0.55, corresponding to surface temperatures from 7.1 °C to 15.2 °C. The $U_{37}^{K'}$ values in core COR0503-36PC range from 0.23 to 0.57, corresponding to surface temperatures from 5.5 °C to 15.8 °C. Overall, there is a general surface temperature cooling trend across the Holocene in all sediment cores. While core COR0602-36PC shows a surface temperature decrease of ~18 °C, cores COR0602-42PC and COR0503-36PC show a cooling of ~8 °C

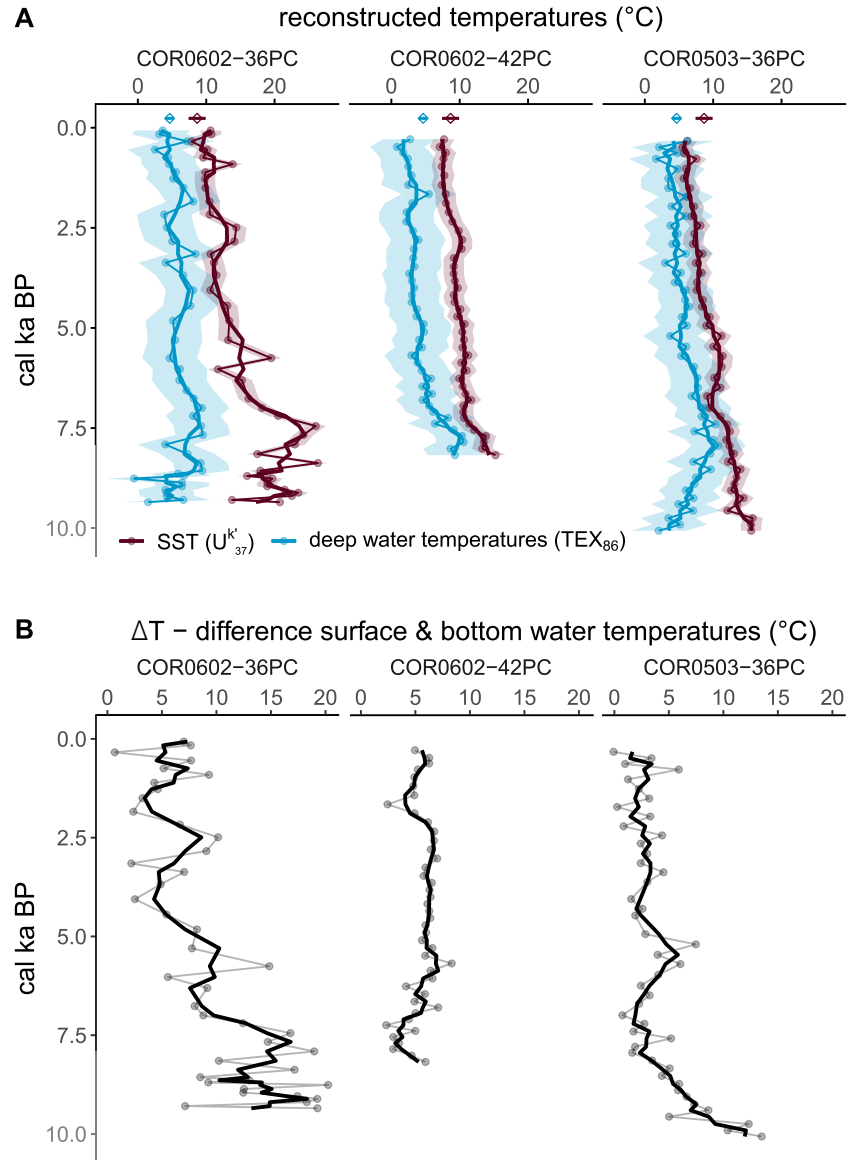


Figure 3 – **A)** $U_{37}^{K'}$ -derived SSTs and TEX_{86}^L -derived water temperatures for cores COR0602-36PC, COR0602-42PC and COR0503-36PC. The bold line represents the 3-point moving average. The lightly colored area in each curve shows the uncertainty associated with each calibration. The single SST data point shown above the 0 cm depth interval indicates the instrumental mean surface temperature from May-Nov for the period from 1982 to 2024 in the estuary, the NW gulf and Cabot Strait (Galbraith et al., 2024). The single deep water temperature data point represents the temperature mean of waters at 200 m depth from 1982 to 2024 in the estuary, the NW gulf and Cabot Strait (Galbraith et al., 2024). The grey axis indicates glaciomarine sediments, where the age model is not well constrained. **B)** Absolute temperature difference (ΔT) between $U_{37}^{K'}$ and TEX_{86}^L -derived water temperatures in cores COR0602-36PC, COR0602-42PC, COR0503-36PC. The bold line represents the 3-point moving average. The grey axis indicates glaciomarine sediments, where the age model is not well constrained.

and $\sim 10^{\circ}\text{C}$, respectively. Core COR0602-36PC generally shows higher surface temperature variability than cores COR0602-42PC and COR0503-36PC, which show a steady decrease in temperatures over the Holocene. A decreasing trend in ‘core-top’ surface temperature can also be observed spatially along the estuary, from 10.6°C in core COR0602-36PC to 7.7°C and 6.2°C in cores COR0602-42PC and COR0503-36PC, respectively.

In addition to the $\text{C}_{37:2}$ and $\text{C}_{37:3}$ alkenones, we also observe $\text{C}_{37:4}$ alkenones at variable relative abundance downcore (Fig. 4a). At the base of the cores (~ 10.0 - 7.0 cal ka BP), $\text{C}_{37:2}$ and $\text{C}_{37:4}$ alkenones dominate the C_{37} alkenone assemblage, ranging from $\sim 20\%$ to $\sim 60\%$, while $\text{C}_{37:3}$ alkenones only constitute ~ 5 - 20% in all cores. This changes around 9.0 - 7.5 cal ka BP, where the $\text{C}_{37:3}$ -alkenone become the most abundant C_{37} -alkenone. The proportions of $\text{C}_{37:3}$ increase to up to 45% , 62% and 68% in the uppermost sediment samples of cores COR0602-36PC, COR0602-42PC and COR0503-36PC, respectively.

Fig. 4b shows the concentrations of alkenones in cores COR0602-36PC, COR0602-42PC and COR0503-36PC. In core COR0602-36PC $\text{C}_{37:2}$ -alkenone concentrations range from 2.3 - 61.9 ng g^{-1} TOC, $\text{C}_{37:3}$ alkenones range from 1.9 - 95.4 ng g^{-1} TOC and $\text{C}_{37:4}$ range from 0.9 - 66.1 ng g^{-1} TOC. From 9.4 to 7.0 cal ka BP $\text{C}_{37:2}$ and $\text{C}_{37:4}$ alkenone concentrations are very similar and higher than $\text{C}_{37:3}$ alkenone concentrations. Afterwards, $\text{C}_{37:4}$ alkenones are generally lowest, followed by $\text{C}_{37:2}$ and then highest concentrations are found in $\text{C}_{37:3}$. An increasing concentration of $\text{C}_{37:2}$ and $\text{C}_{37:3}$ alkenones can be observed from 6.8 cal ka BP to the uppermost samples. In core COR0602-42PC, the concentrations in $\text{C}_{37:2}$ alkenones range from 28.7 - 195.2 ng g^{-1} TOC, $\text{C}_{37:3}$ alkenones range from 44.5 - 388.3 ng g^{-1} TOC and $\text{C}_{37:4}$ alkenones range from 10.1 - 67.5 ng g^{-1} TOC. In this core, the alkenone concentrations of all alkenones co-vary, with only minor changes in proportions. $\text{C}_{37:4}$ alkenones always have the lowest concentration and $\text{C}_{37:3}$ alkenones dominate. The same pattern is found in core COR0503-36PC, except from 10.1 to 9.7 cal ka BP, where $\text{C}_{37:2}$ and $\text{C}_{37:3}$ alkenone concentrations are lower than $\text{C}_{37:4}$ concentrations. In this core, the concentrations range from 5.9 - 209.5 ng g^{-1} TOC for $\text{C}_{37:2}$ alkenones, from 4.7 - 442.7 ng g^{-1} TOC for $\text{C}_{37:3}$ -alkenone,

and from 3.2-68.0 ng g⁻¹ TOC for C_{37:4} alkenones.

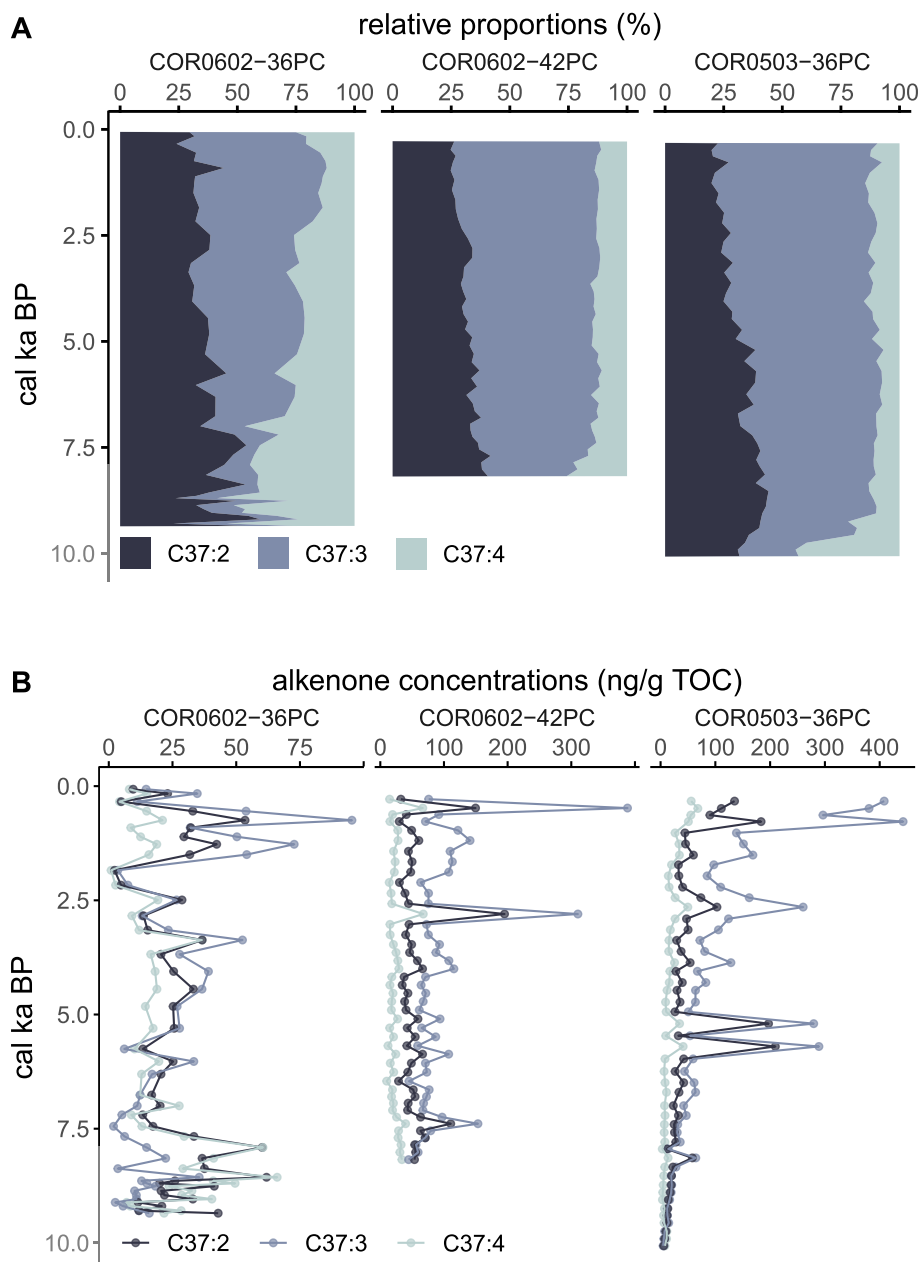


Figure 4 – **A)** Relative proportions and **B)** absolute abundances of C_{37:2}, C_{37:3} and C_{37:4} alkenones in the estuary core COR0602-36PC, the NW gulf core COR0602-42PC and the Cabot Strait core COR0503-36PC. The grey axis indicates glaciomarine sediments, where the age model is not well constrained.

5.3 GDGTs

TEX₈₆^L values in all cores range from -0.70 to -0.54 corresponding to water temperatures of -0.6 °C to 10.8 °C (Fig. 3a). The TEX₈₆^L-temperatures increase from the bottom of all sediment cores and reach maximum values of 9.5 °C, 10.6 °C and 10.8 °C around 8.0-7.5 cal ka BP in cores COR0602-36PC, COR0602-42PC and COR0503-36PC, respectively. Afterwards, the reconstructed water temperatures decrease steadily and reach minimum values of 0.8 °C at ~0.5 cal ka BP in core COR0602-42PC and 1.6 °C at ~0.8 cal ka BP in core COR0503-36PC, respectively. Overall, water temperatures also decrease towards the core-top in COR0602-36PC, but water temperatures remain above the lowest value of -0.6 °C at ~12.0 cal ka BP. The total amplitude of TEX₈₆^L-derived water temperatures is 5 °C to 8 °C from the maximum value to the core-top. In contrast to the U₃₇^{K'}-derived temperatures, core-top water temperatures overall increase along the St. Lawrence system towards Cabot Strait, from 3.6 °C in core COR062-36PC to 2.8 °C in core COR0602-42PC and 6.3 °C in core COR0503-36PC.

Fig. 5 shows the BIT index, #rings_{tetra}, GDGT-0/crenarchaeol, GDGT-2/crenarchaeol, and the methane index. In core COR0602-36PC (Fig. 5a), the BIT index values range from 0.37 to 0.57. The lowest values are found between 8.5 and 6.5 cal ka BP, and the highest values are found at 9.4-8.8 cal ka BP and at 0.9-0.1 cal ka BP, respectively. The #rings_{tetra} values show the opposite trend, ranging from 0.20 to 0.31, with the highest value at around 7.5 cal ka BP. GDGT-0/crenarchaeol values range from 1.1 to 1.6 and show a general increase throughout the Holocene. GDGT-2/crenarchaeol values increase from 0.02 to 0.05 until ~7.5 cal ka BP and decrease afterwards. The methane index values vary in parallel with GDGT-2/crenarchaeol, with values ranging from 0.10 to 0.15. The BIT index of core COR0602-42PC (Fig. 5b) gradually increases from 0.21 at 8.2 cal ka BP to a value of 0.34 at 0.3 cal ka BP. The BIT index remains below 0.38 throughout the core. The #rings_{tetra} values decrease from 0.55 at 8.2 cal ka BP to 0.35 at 0.3 cal ka BP in core COR0602-42PC. GDGT-0/crenarchaeol values are relatively stable between 1.31 and 1.63; however, the #rings_{tetra}

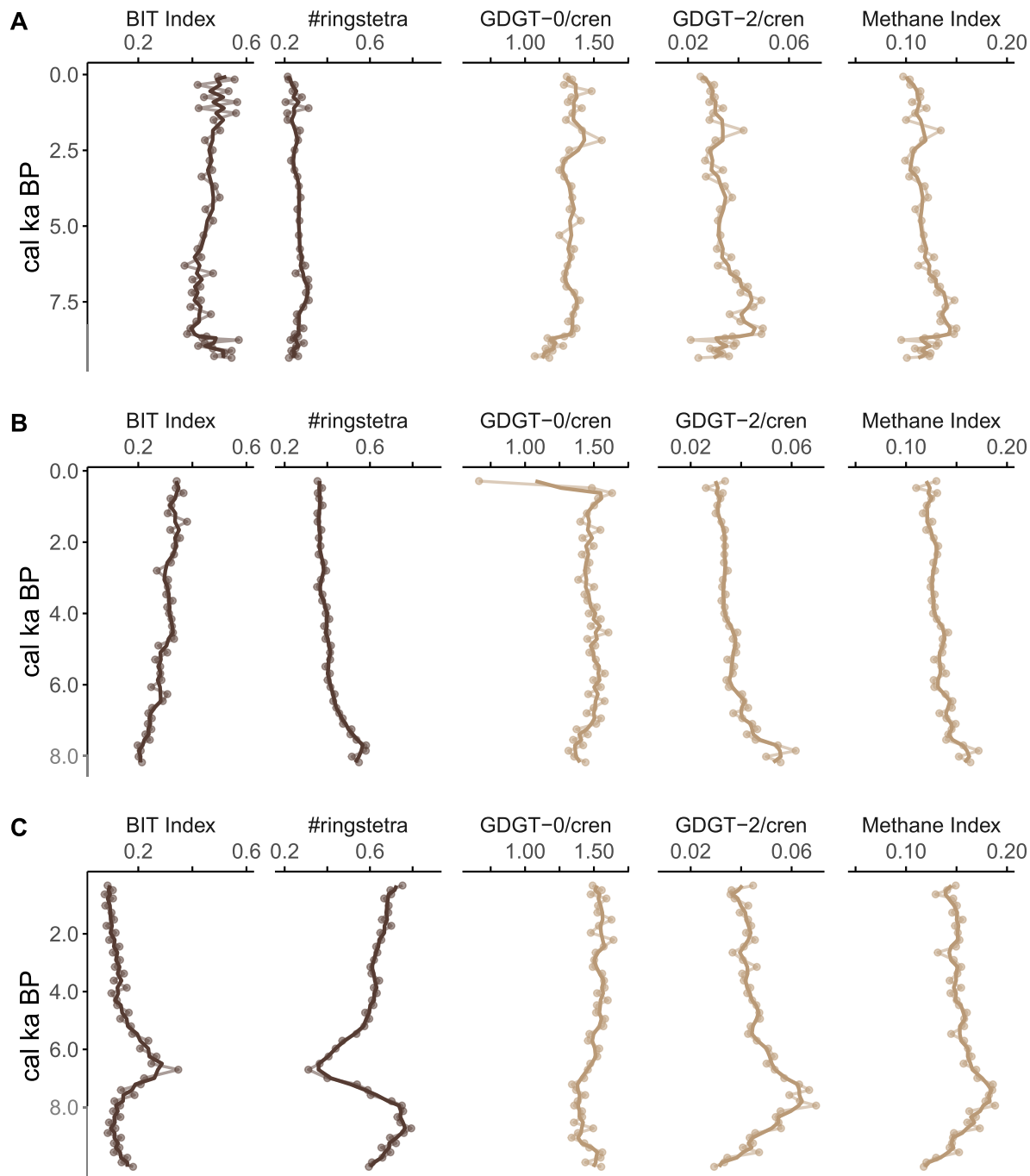


Figure 5 – BIT index, #ring_{stetra}, GDGT-0/crenarchaeol, GDGT-2/crenarchaeol, methane index in cores **A)** COR0602-36PC, **B)** COR0602-42PC, **C)** COR0503-36PC. The bold line represents the 3-point moving average. The grey axis indicates glaciomarine sediments, where the age model is not well constrained.

value in the uppermost sample decreases to 0.67. GDGT-2/crenarchaeol values gradually decrease throughout the core from 0.06 to a minimum of 0.02. The methane index follows the same trend, decreasing from 0.17 to 0.11. The BIT index of COR0503-36PC (Fig. 5c) has values between 0.1 and 0.2 between 10.0 and 7.5 cal ka BP and shows an increase to up to 0.35 at around 6.7 cal ka BP. After this peak, values decrease until around 4.0 cal ka BP and further to around 0.1 in the uppermost sample. The opposite trend is observed for $\#rings_{tetra}$, which has a minimum value of 0.31 at 6.7 cal ka BP and otherwise has values up to 0.79. The cut-off value 0.7 is exceeded between around 7.7 cal ka BP and 9.2 cal ka BP. Individual samples also exceed this value at around 1.7 cal ka BP and in the uppermost sediment sample. GDGT-0/crenarchaeol shows lower values (1.3-1.4) from approximately 9.0 to 7.0 cal ka BP, reaching its maximum value of 1.6 at 2.2 cal ka BP. The opposite trend is observed for GDGT-2/crenarchaeol and the methane index, which increase from 0.03 and 0.12, respectively, to maximum values of 0.07 and 0.19 at 7.5 cal ka BP and then decrease towards the core-top.

6 DISCUSSION

6.1 Chronology

The original age models for cores COR0602-36PC, COR0503-36PC, and COR0602-36PC were published by Barletta et al. (2010) who fitted a third-order polynomial function to the ages of COR0602-36PC, a linear fit to COR0602-42PC, and an interpolation function to COR0503-36PC. New age models were published by Casse et al. (2017) for COR0602-36PC and COR0503-36PC, using rbacon with the Marine13 calibration curve and by Wu et al. (2023) for COR0602-42PC, using the Marine20 calibration curve. We update the age models of the cores COR0602-36PC and COR0503-36PC using the Marine20 calibration curve (Fig. S2 and S4; Heaton et al., 2020). In both cores, the oldest ^{14}C tie point was not obtained at the base of each core due to the absence of carbonaceous material. We use a Bayesian

model (Blaauw and Christen, 2011) to extrapolate below 457 cm in core COR0602-36PC and below 620 cm depth in core COR0503-36PC. Accordingly, the age-depth relationship for these depths are associated with larger uncertainties.

The age-depth models of cores COR0602-42PC and COR0503-36PC indicate quite linear sedimentation throughout each core (Figs. S3 and S4). At lengths of 771 cm and 753 cm, and basal ages at ~ 10.1 cal ka BP and ~ 8.2 cal ka BP, respectively, the resulting sedimentation rates are ~ 0.08 cm yr⁻¹ and ~ 0.09 cm yr⁻¹. The age-depth model of core COR0602-36PC shows more variable sedimentation over time, with a basal age at 9.4 cal ka BP constrained by a tie point at the transition between postglacial sediments and glaciomarine sediments (released during the decay of the Laurentide Ice Sheet; Casse et al., 2017). Sedimentation rates are 0.20 cm yr⁻¹ from the base of the core up to 520 cm depth, and from there they decrease to 0.06 cm yr⁻¹. Much higher sedimentation rates prior to 8.5 cal ka BP (during the deposition of glaciomarine sediments) are consistent with observations from core COR0503-CL05-37PC, a sediment core recovered between COR0503-36PC and Anticosti Island (Barletta et al., 2010) and the establishment of modern sedimentation in the St. Lawrence system at ~ 8.5 cal ka BP (Casse et al., 2017). The age of the lithological transition also agrees well with the corresponding transition from glaciomarine to postglacial sediments in cores COR0602-42PC and COR0503-36PC, which are observed at ~ 8.0 cal ka BP.

6.2 Proxy appraisal

6.2.1 Alkenones

6.2.1.1 Comparison with instrumental data and published sedimentary records

To assess potential biases in the $U_{37}^{K'}$ -derived sea surface temperatures, we first compare our proxy data with the instrumental record of Galbraith et al. (2024) followed by a comparison with other regional Holocene water temperature records. The uppermost sediment samples

have SSTs of 10.6 °C (COR0602-36PC, estuary), 7.7 °C (COR0602-42PC, estuary-NW gulf) and 6.2 °C (COR0503-36PC, gulf) respectively (Fig. 3a). Mean instrumental data from May to November from the years 1991-2020 from Galbraith et al. (2024) show $7.2\text{ °C} \pm 0.6$ in the estuary, $8.5\text{ °C} \pm 0.6$ in the NW gulf and $9.7\text{ °C} \pm 0.6$ in the gulf and Cabot Strait. Overall, these $U_{37}^{K'}$ -derived SSTs agree well with the instrumental data since the Müller et al. (1998) calibration has a calibration error of $\pm 1.5\text{ °C}$. The instrumental data of the NW gulf compared to the temperature of the uppermost sediment sample from core COR0602-42PC falls within the calibration error. In contrast, the reconstructed temperature is 3.4 °C higher than the instrumental data in core COR0602-36PC and 3.5 °C colder in core COR0503-36PC than the 1991-2020 mean instrumental surface water temperature. However, the uppermost sample in core COR0602-36PC has an age of ~0.1 cal ka BP and the uppermost sample in cores COR0602-42PC and COR0503-36PC have ages of ~0.3 cal ka BP. Water temperatures have increased significantly in recent decades (Galbraith et al., 2024), thus we assume the offset results – at least in part – from this warming effect. For core COR0602-36PC, the instrumental SSTs in the uppermost sample are lower than the $U_{37}^{K'}$ -derived SSTs, but this core also shows much higher general variability of $U_{37}^{K'}$ -derived SSTs (Fig. 3a), which might also explain the offset. In addition to the overall good agreement of our data and the instrumental data, the downcore trends in our records are also very similar.

Moreover, our alkenone data also agree well with alkenone records obtained on sediment cores from the Scotian Margin, Laurentian Fan and Virginia Slope (Fig. 6i; Keigwin et al., 2005; Sachs, 2007), both in downcore trend and amplitude. Keigwin et al. (2005) and Sachs (2007) reported a strong decrease in temperatures during the Holocene, from ~18 °C in the early Holocene to 8 °C at present offshore the Laurentian Fan, which also fits well with $\delta^{18}\text{O}$ and abundance of the warm water planktonic foraminifera *Globigerinoides ruber* (Keigwin et al., 2005). Likewise, Solignac et al. (2004) showed temperatures based on dinoflagellate cyst assemblages at Orphan Knoll (Fig. 6g) and at the Greenland Rise, which have similar trends. August values at Orphan Knoll reached ~18 °C and higher during the early Holocene between 11.0 and 8.0 cal ka BP and decreased sharply to ~8 °C from 8.0 to 7.4 cal ka BP

(Solignac et al., 2004). The dinoflagellate cyst-derived August SST values from Greenland Rise show a similar trend with an SST amplitude from $\sim 15^{\circ}\text{C}$ to $\sim 8^{\circ}\text{C}$. Levac (2001) and Levac (2003) show temperatures of around 5°C warmer than today from 8.5 to 10.5 cal ka BP on the Scotian Shelf and from 8.6 to 6.8 cal ka BP at Bay of Islands, western Newfoundland. Diatom-derived SSTs from north-eastern Newfoundland show a cooling trend from $\sim 7^{\circ}\text{C}$ at 7.2 cal ka BP to $\sim 4^{\circ}\text{C}$ at present (Orme et al., 2021).

Despite this good agreement with other regional SST records, dinocyst assemblages in core COR0602-42PC differ substantially from those trends (Wu et al., 2023). Reconstructed summer SSTs were between 9°C and 10°C at 8.0 cal ka BP, increased to $11\text{--}12^{\circ}\text{C}$ from around 7.5 to 6.5 cal ka BP, and then varied between $\sim 10^{\circ}\text{C}$ and 12°C until present (Fig. 6h). Similar summer SST trends, based on dinocyst and coccolith assemblages, have been shown by Balestra et al. (2013) on the Laurentian Fan, i.e., temperatures around 10°C from 12.0 to 11.0 cal ka BP and values around 15°C since 11.0 cal ka BP. These trends are also very similar to the results obtained by de Vernal et al. (1993) at Cabot Strait and in the Esquiman and Anticosti channels. While alkenone and dinocyst proxies indicate different SST trends in the region, the overall picture indicates a cooling trend throughout the Holocene, which is reflected in our data. Dinocyst transfer functions have been shown to be affected by several processes, including ecological aspects such as salinity and nutrient shifts but also seasonality and lateral transport (Marret and de Vernal, 2024). However, alkenone SSTs might also be seasonally biased and impacted by salinity, nutrient changes and haptophyte community composition (Theroux et al., 2010; Epstein et al., 1998; Prahl et al., 2003) as well as preferential degradation (Rontani et al., 2008) and lateral transport (Mollenhauer et al., 2003).

6.2.1.2 Potential ecological biases in the alkenone records

The extent of the U_{37}^{K} -derived SST change – especially in core COR0602-36PC – warrants further inspection. Balestra et al. (2013) observed a change in coccolith microfossil assemblages in Laurentian Fan sediments over time, which might indicate a change in the haptophyte community composition, which in turn may impact the alkenone signatures (Fig. 4a).

Indeed, the relative abundance of $C_{37:4}$ alkenones is much higher in the lower sections of all of our cores. $C_{37:4}$ alkenones are known to be mostly found in cold waters with low salinity (Bendle et al., 2005; Blanz et al., 2005; Rosell-Melé, 1998; Sicre et al., 2002). More recently, it has been shown that $C_{37:4}$ alkenones seem to correlate with sea ice coverage rather than salinity (Liao and Huang, 2022; Liao et al., 2023) and their tentative producers are ice-algae (group 2i Isochrysidales; Wang et al., 2021, 2024). The production of $C_{37:4}$ alkenones seems to be intrinsic to the group 2i Isochrysidales and does not seem to be linked to environmental conditions such as temperature. Although $C_{37:4}$ is not included in the $U_{37}^{K'}$ proxy, group 2i Isochrysidales seem to also produce $C_{37:2}$ and $C_{37:3}$ alkenones (Liao and Huang, 2022), which could bias $U_{37}^{K'}$ -derived SSTs if they substantially contribute to the sedimentary $C_{37:2}$ and $C_{37:3}$ alkenone pool. Yet, it is thus far unknown whether the $C_{37:2}$ and $C_{37:3}$ alkenones produced by group 2i Isochrysidales ‘record’ ambient seawater temperature or whether their relative abundance is controlled by other environmental or physiological factors. If $C_{37:4}$ alkenones in our cores are derived from ice algae, their increased abundance until approximately 9.0-8.0 cal ka BP would either imply greater and/or longer ice coverage during the year or, alternatively, generally lower production of alkenones by non-ice algae. De Vernal et al. (1993) showed that sea ice coverage in the St. Lawrence system was similar to today after 10.0 cal ka BP and individual downcore alkenone concentrations (Fig. 4b) indicate that their absolute abundances change in parallel in cores COR0602-42PC and COR0503-36PC. This implies that the relative shifts are controlled by rather minor individual concentration changes. Indeed, core COR0503-36PC has the highest $C_{37:4}$ concentrations in the uppermost samples rather than at its base. Only core COR0602-36PC has higher $C_{37:4}$ concentrations in the lower core section. The highest concentrations of $C_{37:4}$ in COR0602-36PC occur between 9.4 cal ka BP and 7.0 cal ka BP, where SSTs range from 13.8 to 26.0 °C. If any, we expect an ice-algae bias on $U_{37}^{K'}$ -derived SSTs in this interval. While we cannot correct for the potential bias based on our data, we expect SSTs in this interval to only be slightly biased towards warmer SSTs since independent evidence (de Vernal et al., 1993) indicates no significant change in sea ice conditions during that time.

6.2.2 GDGTs

Analogous to our alkenone data, we compare our TEX₈₆-derived water temperatures with the instrumental bottom water temperature data from Galbraith et al. (2024) to determine the likely water depth of GDGT production and to assess the accuracy of the calibration. Moreover, we use the BIT index, GDGT-0/crenarchaeol, GDGT-2/crenarchaeol, and methane index to identify any potential biases in the isoGDGT assemblages.

Isoprenoid GDGTs are the predominant membrane lipids of Thaumarchaeota, which typically thrive in the ammonium maximum in the thermocline (Francis et al., 2005). Given the shallow water depths in the St. Lawrence and the bottom water layer starting at around 150 m (Galbraith et al., 2024), GDGT-derived water temperatures should be representative of bottom water temperatures, where the nitracline is found (Bluteau et al., 2021). The TEX₈₆-derived water temperatures agree well with the instrumental temperature data at 200 m depth from Galbraith et al. (2024). The instrumental 1991-2020 mean temperature from May to November was 4.0 °C in the estuary, 4.4 °C in the NW gulf and 5.2 °C in the gulf at Cabot Strait, approximately 3-4.5 °C colder than SSTs. The TEX₈₆^L-derived water temperatures in the uppermost sediment intervals are 3.6 °C in the estuary, 2.8 °C in the NW gulf and 6.3 °C in the gulf at Cabot Strait. The difference between the instrumental 1991-2020 mean bottom water temperatures and our proxy-derived water temperatures falls well within the uncertainty of the TEX₈₆^L calibration (± 4 °C; Kim et al., 2010). Within calibration error, TEX₈₆^L-derived water temperatures also agree with instrumental data at a depth of 300 m (1991-2020 mean temperature from May to November at 300 m depth are 5.1 °C in the estuary, 5.4 °C in the NW gulf and 6.4 °C at Cabot Strait; Galbraith et al., 2024). We thus assume that our TEX₈₆^L-derived temperatures reflect the water temperatures at depths of 200 to 300 m.

However, isoGDGT records can be influenced by *in-situ* production by sedimentary methanogenic and methanotrophic Euryarchaeota (Blaga et al., 2009; Weijers et al., 2011; Kim and Zhang, 2023). The thresholds for GDGT-0/crenarchaeol and GDGT-2/crenarchaeol

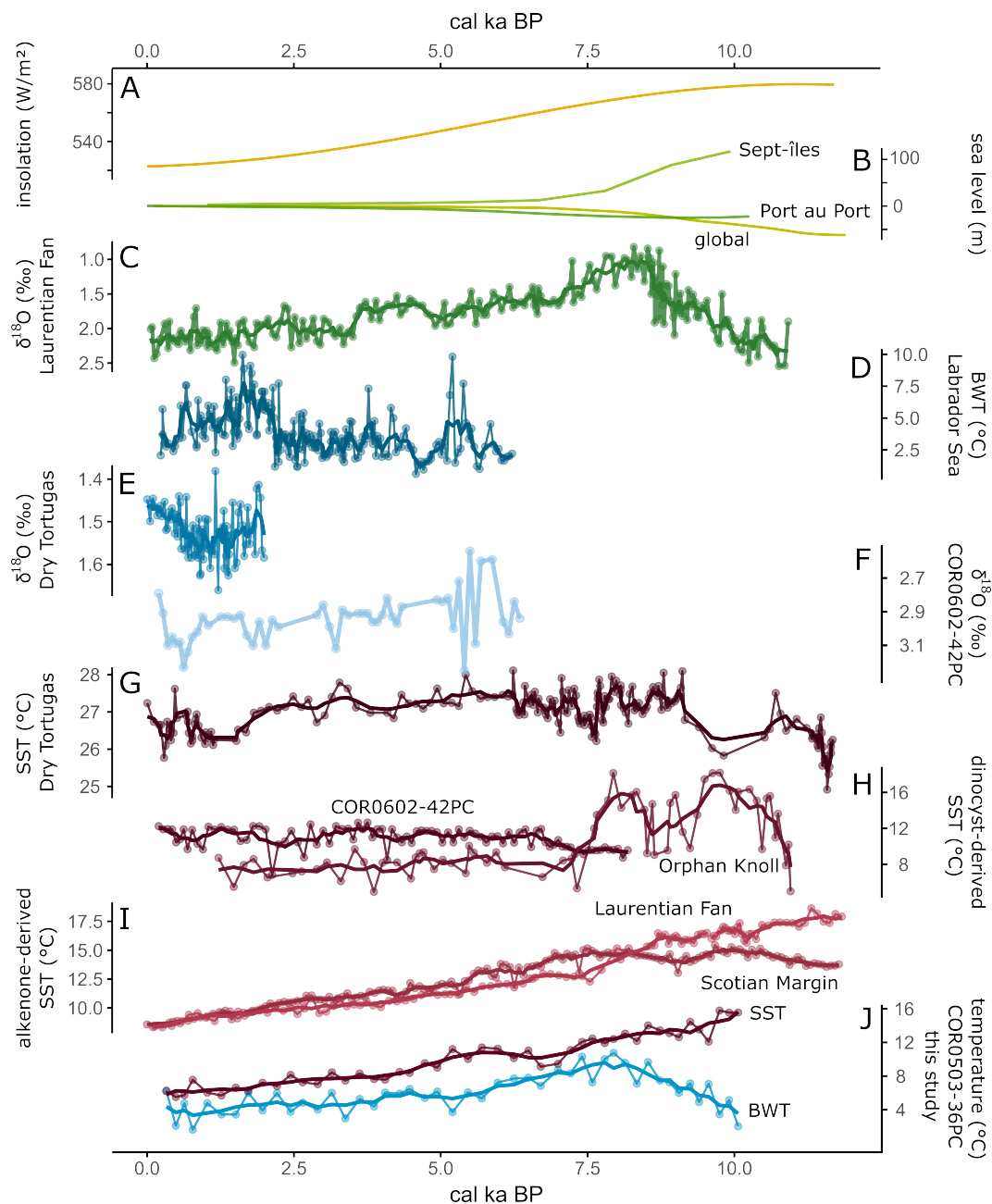


Figure 6 – **A)** Holocene summer solstice insolation at 48°N (Berger and Loutre, 1991). **B)** Sea level changes – Global (Lambeck et al., 2014); Port au Port and Sept-îles (Shaw et al., 2002). **C)** $\delta^{18}\text{O}$ of *N. pachyderma* on the Laurentian Fan (Keigwin et al., 2005). **D)** Bottom water temperatures (BWT) based on Mg/Ca of the benthic foraminifera *N. labradorica* (Lochte et al., 2020). **E)** $\delta^{18}\text{O}$ of benthic foraminifera at Dry Tortugas at 540 m depth (Gulf Stream; Lund et al., 2006). **F)** $\delta^{18}\text{O}$ of *B. marginata* in COR0602-42PC. **G)** SST at Dry Tortugas derived from $\delta^{18}\text{O}$ and Mg/Ca in *G. ruber* (Gulf Stream; Lund and Curry, 2006; Schmidt and Lynch-Stieglitz, 2011; Schmidt et al., 2012). **H)** Dinocyst-derived SSTs at Orphan Knoll (Solignac et al., 2004) and in core COR0602-42PC (Wu et al., 2023). **I)** Alkenone-derived SSTs on the Laurentian Fan & the Scotian Margin (Sachs, 2007). **J)** U_{37}^K and TEX_{86} -inferred temperatures in COR0503-36PC from this study.

indicating such overprint are 2 and 0.2, respectively, which are never exceeded in our data set. This conclusion is confirmed by the methane index indicating substantial contributions from methanotrophic archaea at values >0.5 (Zhang et al., 2011). In coastal environments, sedimentary isoGDGT populations may also be biased by contributions of terrestrial isoGDGTs produced by soil archaea. A BIT index of 0.4 has been identified as the threshold at which TEX₈₆-derived water temperatures may become substantially biased (Hopmans et al., 2004). In our data set (Fig. 5a), most samples in the estuarine core COR0602-36PC exceed this threshold (ranging from 0.37 to 0.57). Since the #rings_{tetra} index values are below the 0.7 threshold, the brGDGTs controlling the BIT index are mainly of terrestrial origin rather than produced *in-situ*. This interpretation is further supported by the coastal setting of the core and the notably high C/N ratios, which are indicative of terrestrial organic matter (Fig. 2b). While the BIT index values in core COR0602-36PC are above the threshold, the downcore trend is relatively stable and the good agreement of TEX₈₆-derived water temperatures in the uppermost samples with instrumental data suggests limited bias by terrestrial isoGDGTs. Moreover, the consistent offset between TEX₈₆^L- and U₃₇^K-derived temperatures throughout the late Holocene indicates limited effects since alkenone SSTs are not affected by terrestrial biases. Given the good agreement between instrumental bottom water temperatures and our proxy-derived water temperatures, we exclude any strong bias in our TEX₈₆^L-derived temperatures through terrestrial input in core COR0602-36PC and consider our GDGT TEX₈₆^L-derived SST records representative of the bottom waters.

6.3 Holocene temperature-inferred circulation dynamics

6.3.1 Spatio-temporal surface and bottom water temperature evolution in the St. Lawrence system

Circulation dynamics in the St. Lawrence system are linked to the AMOC and Labrador Sea circulation. Evidence suggests that the AMOC may have been gradually weakening since the

end of the Little Ice Age (~1850 CE), possibly due to enhanced freshwater fluxes from melting glaciers, which could have reduced deep-water convection in the Labrador Sea (Rahmstorf et al., 2015; Thornalley et al., 2018). This results in an increased input of North Atlantic Central Waters into the St. Lawrence system, leading to hypoxia in its bottom waters (Gilbert et al., 2005). High boreal summer insolation during the early Holocene led to the decay of the Laurentide Ice Sheet (Fig. 6a), thus, natural climate change during the early Holocene can serve as a recent analog for current anthropogenic climate change. In response to the early Holocene insolation increase, global temperatures rose, culminating in the Holocene Thermal Maximum at around 6.5 ka (Kaufman et al., 2004, 2020). Any potential ventilation-driven temperature dynamics recorded in our sediment records (related to changes in AMOC) will consequently be superimposed on these insolation-driven temperature dynamics.

Instrumental data of surface and bottom water temperatures in the St. Lawrence system since the 1870s from (Fig. 1b; Galbraith et al., 2024), show a general increasing trend (around +2-3 °C) for both surface and bottom water. This results in a relatively constant temperature offset between surface and bottom waters, although the composition of bottom waters has significantly changed over the last few decades, i.e., from 20%–50% of Labrador current water entering the St. Lawrence system several years ago to nearly 0% at present (Jutras et al., 2023b). Thus, changes in the composition of the bottom water could have occurred without necessarily being visible in the temperature offset, ΔT . However, Lochte et al. (2020) show that bottom water temperatures in the Labrador Sea have indeed decreased during the last ~1,500 yrs (Fig. 6d). The Gulf Stream temperatures, in contrast, have increased in the last ~1,000 yrs, shown by decreasing $\delta^{18}\text{O}$ values based on benthic foraminifera (Fig. 6e) and the SSTs derived from $\delta^{18}\text{O}$ and Mg/Ca in *G. ruber* at Dry Tortugas (Fig. 6g; Lund et al., 2006; Lund and Curry, 2006; Schmidt and Lynch-Stieglitz, 2011; Schmidt et al., 2012). Accordingly, we would expect a divergence of the surface and bottom water temperature trends if the Labrador Current were still entering this system as a dominant bottom water source, resulting in an increasing temperature offset (ΔT) between surface and bottom waters. Unfortunately, we cannot directly compare and cross-validate our proxy data with the annual/decadal reso-

lution of the instrumental records since the uppermost sediments analyzed in our study have ages of around 100 and 300 years, i.e., the most recent seawater warming trend is not captured by our proxy data. Thus, we use the temperature offset between surface and bottom waters ΔT (Fig. 3b), inferred by $U_{37}^{K'}$ and TEX_{86}^L respectively, to assess potential changes in circulation superimposed on insolation-driven absolute seawater temperature changes in the past. Assuming the background temperature signal of surface and bottom water temperatures in the St. Lawrence system follows the boreal summer insolation curve during the Holocene (Fig. 6a; Berger and Loutre, 1991), we expect both $U_{37}^{K'}$ and TEX_{86}^L -derived temperatures to either change in parallel, reflected in a relatively stable ΔT , or to record a slightly increasing ΔT if surface waters warm more strongly than bottom waters in the absence of circulation changes. In contrast, a decrease in ΔT likely indicates changes in water mass sourcing and, by inference, circulation dynamics (increased sourcing from the North Atlantic).

The overall water temperature trends show that cooling was more pronounced in surface waters than in deep waters, leading to a significant decrease in the relative offset between the two proxies (Fig. 3b). Cores COR0602-36PC and COR0503-36PC show a general decrease in ΔT during the early Holocene. In core COR0602-36PC ΔT decreases from up to 19 °C at 9.4 cal ka BP to 9 °C at 7.0 cal ka BP. After cooling of surface temperatures at ~7.0 cal ka BP, ΔT generally does not exceed 10 °C and gradually decreases towards the present. This indicates enhanced warming of bottom waters relative to surface waters. Similarly, in core COR0503-36PC ΔT decreases from around 14 °C to 2 °C throughout the record. We do not observe a decreasing ΔT in COR0602-42PC due to the resulting basal age of 8.2 cal ka BP. However, we note that the lowermost samples record contrasting trends in $U_{37}^{K'}$ and TEX_{86}^L -derived water temperatures and ΔT , which may continue in deeper sediments.

By analogy with recent observations (Galbraith et al., 2024), the downcore ΔT trends suggest that the St. Lawrence system is mainly influenced by the Labrador Current in the early Holocene due to a larger offset between surface and bottom water temperatures. The decreasing offset around 8.0 to 7.0 cal ka BP indicates that the North Atlantic Central Waters,

carried by the Gulf Stream, may have increasingly contributed to the bottom waters of the St. Lawrence system, bringing warmer bottom waters into the system and muting the deep water cooling relative to surface water cooling. This observation agrees with data from Thibodeau et al. (2013) that show lower benthic foraminiferal $\delta^{18}\text{O}$ values at 6.0-4.0 cal ka BP in the Esquiman Channel, which are not observed in the Laurentian Channel (Wu et al., 2023). This evidence suggests that the bottom waters in the Esquiman Channel were warmer during that time period, explained by a larger proportion of North Atlantic Central Waters entering the system. Also, a study at Hamilton Bank on the Labrador Shelf, based on pollen assemblages, shows that the Labrador Current was deflected eastwards at 6.0 ka BP. This led to warmer waters from the North Atlantic penetrating the continental shelf to southern Newfoundland (Fillon, 1976). This hypothesis has been supported by foraminiferal assemblages on the Scotian Shelf (Vilks and Rashid, 1976), which suggest that the deflection of the Labrador Current offshore was driven through lower sea level leading to an input of more brackish waters. Also, Rashid et al. (2017) inferred an intensification of the Labrador Current from 9.2 to 5.0 cal ka BP based on increasing mean sortable silt size, with maximum current speed between 5.0 and 3.1 cal ka BP. The strength of the Labrador Current over the Labrador Shelf is anti-correlated with that west of the Grand Banks. That means that an intensification of the Labrador Current over the shelf should lead to a weaker inflow of these waters into the St. Lawrence system during that time (Han et al., 2014; Jutras et al., 2023a; Gonçalves Neto et al., 2023).

However, the hypothesis that more North Atlantic Central Waters are entering the St. Lawrence system at around 8.0 to 7.5 cal ka BP contradicts proxy interpretations in previous studies (Balsam and Heusser, 1976; Balsam, 1981; Rahman and de Vernal, 1994; Levac, 2001; Sachs, 2007; Rashid et al., 2017). Sachs (2007) argues that the $U_{37}^{K'}$ -derived SST cooling on the Virginia slope, the Scotian margin and the Laurentian Fan (Fig. 6i) is too high to be solely driven by insolation and suggests that an increase in convection in the Labrador Sea and a shift of the Gulf Stream towards the equator could have exacerbated this Holocene cooling. Rahman and de Vernal (1994) suggest, based on nannofossil assemblages, that at 10.7 ka

BP, the warm waters of the North Atlantic predominantly influenced the southern Labrador Sea, and that the Labrador Current intensified after 9.0 ka BP, becoming fully developed by 8.4 ka BP. SST reconstructions based on a transfer function using foraminifera off the coast of Chesapeake Bay show an abrupt temperature rise of around 10 °C, which led to the onset of interglacial conditions around 12.0 ka BP (Balsam and Heusser, 1976). They explain this temperature increase through a northward movement of the Gulf Stream around this time with a maximum influence around 8.0 ka BP. Based on the analysis of planktonic foraminifera assemblages, Balsam (1981) suggests that maximum SSTs occurred between 8.0 and 6.0 cal ka BP in the North Atlantic after Gulf Stream waters increasingly entered slope waters. Gradual cooling began at 6.0 cal ka BP, which was explained through the decreasing influx of Gulf Stream waters into the slope waters. The $\delta^{18}\text{O}$ values of *N. pachyderma* on the Laurentian Fan (Fig. 6c; Keigwin et al., 2005) and of *B. marginata* in the St. Lawrence Estuary (Fig. 6f; Wu et al., 2023) show similar trends to our bottom water temperatures, not indicating past hypoxia in the Laurentian Channel.

While our data (decreasing ΔT) agree with the results of Fillon (1976) and Vilks and Rashid (1976), i.e., increased Gulf Stream waters entering the St. Lawrence system around 6.0 cal ka BP, our absolute U_{37}^{K} -derived SSTs and the TEX_{86} -derived bottom water temperature trends can individually also be explained by the same mechanism as inferred by Sachs (2007) and Rahman and de Vernal (1994), i.e., warmer SSTs and bottom waters until around 8.0-7.0 cal ka BP due to a northward shift and thus a greater influence of the North Atlantic Central Waters, and then a gradual cooling because of the strengthening of the Labrador Current (Balsam and Heusser, 1976; Balsam, 1981; Rahman and de Vernal, 1994). In this scenario, general water temperatures, would be decreasing from 7.5 cal ka BP through the strengthening of the Labrador Current, and the decreasing ΔT must result from different processes. During the deglacial and early Holocene, the decay of the Laurentide Ice Sheet and sea level changes significantly impacted regional hydrology and AMOC circulation, which could have led to ecological shifts in the St. Lawrence Isochrysidales and Thaumarchaeota populations. This will be further discussed in the following section.

6.3.2 Potential ecological effects controlled by freshwater and sea level dynamics

The decay of the Laurentide Ice Sheet in response to the high boreal summer insolation (Berger and Loutre, 1991) during the early Holocene, led to meltwater drainage via the St. Lawrence system starting ~10.8 ka BP (Teller, 2013; Fisher, 2020; Dyke, 2004) and eventually catastrophic drainage of Lakes Agassiz and Ojibway at 8.2 cal ka BP (Barber et al., 1999; Carlson et al., 2008). $\delta^{18}\text{O}$ values of the planktonic foraminifera *Neogloboquadrina pachyderma* from the Laurentian Fan show a substantial decrease to values around 1‰ at ~8.2 cal ka BP resulting from the inflow of meltwater (Fig. 6c; Keigwin et al., 2005). Consequently, the freshwater release affected sea level (due to glacio-isostatic rebound), hydrology and sediment dynamics in the St. Lawrence system (Casse et al., 2017; Leydet et al., 2018) as well as the Labrador Sea, which was fed via the Hudson Strait meltwater conduit. Studies have shown freshening of surface waters in the Labrador Sea, which decreased Labrador Sea Water formation and reduced the strength of the AMOC (Hillaire-Marcel et al., 2001b; Solignac et al., 2004; Hoogakker et al., 2015). The input of meltwater to the system made the environment more brackish; Wu et al. (2023) reconstructed salinity based on dinocyst assemblages in core COR0602-42PC and showed that salinity was lowest around 8.0 to 7.0 cal ka BP and subsequently increased until ~2.0 cal ka BP. This change in salinity may have affected the microbial communities.

The three main phylogenetic groups of alkenone producers inhabit different salinity conditions and can have different alkenone signatures and U_{37}^K -SST relationships (Zheng et al., 2019). In culture, Chivall et al. (2014) observed higher $C_{37:4}$ concentrations in group II species when grown at higher salinities (with a concomitant minor decrease in U_{37}^K values), whereas no clear correlation of $C_{37:4}$ with temperature or salinity could be observed in marine core-top sediments, which are likely dominated by group III Isochrysidales (Sikes and Sicre, 2002). Larger haptophyte community changes between group II and III Isochrysidales in response to changes in salinity have been observed elsewhere during the Holocene. In the Baltic Sea, Warden et al. (2016) demonstrated a shift in haptophyte community com-

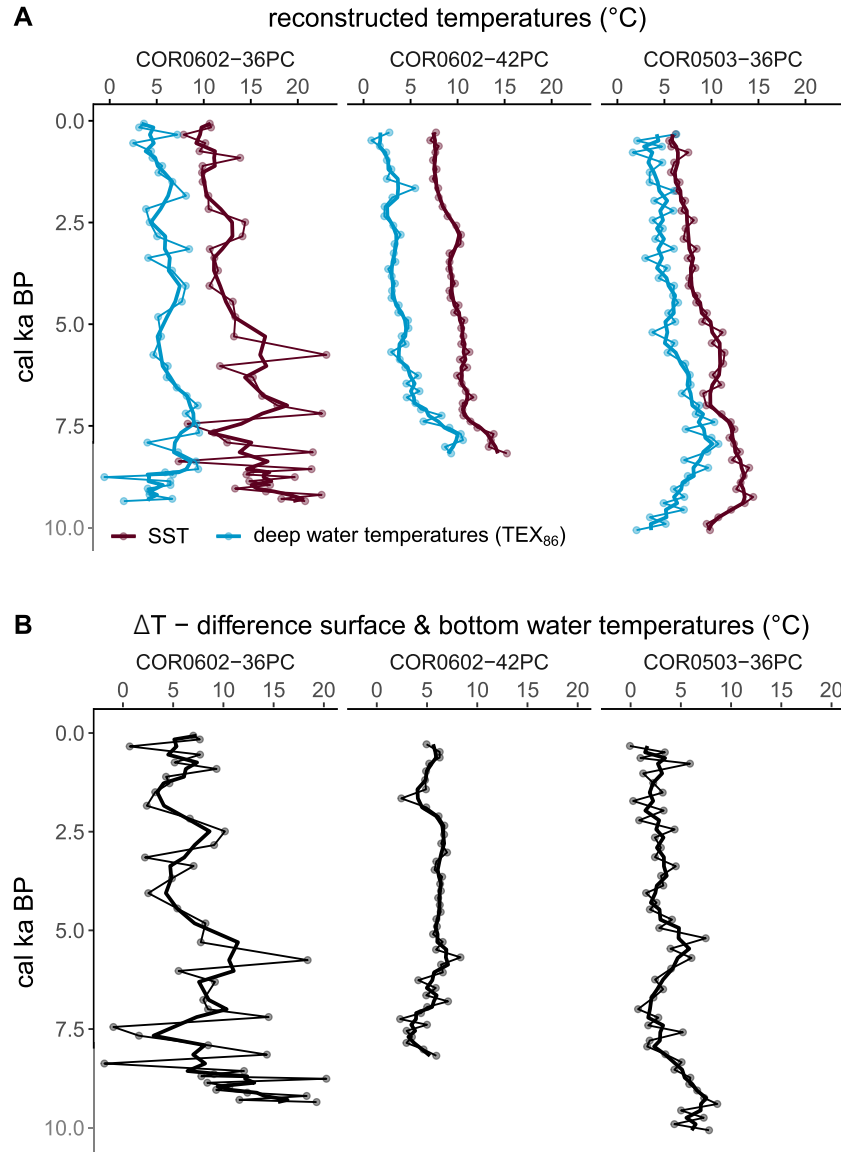


Figure 7 – **A)** Alkenone-derived SSTs and TEX₈₆^L-derived water temperatures in cores COR0602-36PC, COR0602-42PC and COR0503-36PC. The alkenone SSTs represent a composite of SSTs calibrated using U_{37}^K for samples with $C_{37:4}/C_{37:3} < 1.5$ and U_{37}^K for samples with $C_{37:4}/C_{37:3} > 1.5$. The bold line represents the 3-point moving average. The grey axis indicates glaciomarine sediments, where the age model is not well constrained. **B)** Absolute temperature difference (ΔT) between the composite alkenone SSTs and TEX₈₆^L-derived water temperatures in cores COR0602-36PC, COR0602-42PC, COR0503-36PC. The bold line represents the 3-point moving average. The grey axis indicates glaciomarine sediments, where the age model is not well constrained.

position between its freshwater lake phase (high abundance of $C_{37:4}$) and brackish phase, which influenced $U_{37}^{K'}$. Likewise, Coolen et al. (2009) observed a species effect on $U_{37}^{K'}$ in the Black Sea due to changes in salinity. *Isochrysis* spp. dominated during brackish conditions (sapropel deposition) from around 7.5 to 5.3 cal ka BP, characterized by low concentrations of $C_{37:3}$ alkenones and unreliable SST shifts (ranging from 5 °C to 30 °C). Subsequently, *Gephyrocapsa huxleyi* became the dominant alkenone producer, which resulted in more stable and consistent SSTs. The coastal setting and meltwater dynamics during the early Holocene may have led to similar community changes in our sediment records. Zheng et al. (2016) proposed the $U_{37}^{K''}$ calibration for lacustrine and estuarine settings, that excludes $C_{37:2}$ alkenones. They suggested that the SST relationship in group II haptophytes such as *Rutitera lamellosa* and *Isochrysis galbana* is stronger for $C_{37:4}$ and $C_{37:3}$. To test the potential influence of meltwater-driven community changes on our SST reconstruction, we calculated $U_{37}^{K''}$ -temperatures as well as the ratio of $C_{37:4}$ to $C_{37:3}$ alkenones (Fig. S5a). The resulting plots show that $C_{37:4}/C_{37:3} > 1.5$ occur in cores COR0602-36PC and COR0503-36PC during the time of major meltwater perturbation (Fig. S5a) and the corresponding $U_{37}^{K''}$ -derived SSTs are substantially lower than $U_{37}^{K'}$ -temperatures (Fig. S5b). We, thus, infer a change in haptophyte community composition during those intervals, but acknowledge that further analyses should be carried out to support this hypothesis, e.g., through the sequencing of ancient sedimentary DNA.

Based on our hypothesis, we reconstructed a composite alkenone SST record using the $U_{37}^{K''}$ calibration for samples with $C_{37:4}/C_{37:3} > 1.5$ and $U_{37}^{K'}$ for samples with $C_{37:4}/C_{37:3} < 1.5$ (Fig. 7). The composite SST record (Fig. 7a) for core COR0602-36PC has a greater temperature variability at the base of the core with overall lower SSTs and lower ΔT between 9.0 to 7.5 cal ka BP. While ΔT based only on $U_{37}^{K'}$ fluctuates between 10 °C and 17 °C (Fig. 3b), the ΔT based on the composite SST records, fluctuate from 3 °C to 13 °C (Fig. 7b). At 8.4 cal ka BP, we observe a distinct SST minimum (7.3 °C), which might correspond to the meltwater pulse recorded in $\delta^{18}O$ values by Keigwin et al. (2005) and de Vernal and Hillaire-Marcel (2006). ΔT further decreases until 7.4 cal ka BP, but returns to pre-meltwater values exceeding 10 °C

around 7.0 cal ka BP. This shift in ΔT to higher values may correspond to a period of recovery following the meltwater pulse (re-establishment of circulation). This also results in a smaller offset between surface and bottom water temperatures, leading to a more stable ΔT over time (Fig. 7b). However, despite the reduction in the ΔT from around 8.5 to 7.5 cal ka BP, the ΔT still exceeds 10 °C from 9.4 to 8.6 cal ka BP, which is comparable to the ΔT from 7.0 to 5.0 cal ka BP. In the Cabot Strait core COR0503-36PC, only the three lowermost samples are characterized by $C_{37:4}/C_{37:3} > 1.5$ (Fig. S5a) and the composite SST record results in a smaller offset between surface and bottom waters from 10.1 to 9.7 cal ka BP ($\Delta T \sim 6$ °C, Fig. 7b instead of $\Delta T \sim 11$ °C, Fig. 3b). Despite the changes in ΔT resulting from the composite alkenone SST records, ΔT in both cores COR0602-36PC and COR0503-36PC is still larger prior to 4.0 cal ka BP than after 4.0 cal ka BP, indicating warming of bottom waters relative to surface waters. Based on the analogy with recent observations (Galbraith et al., 2024), our composite alkenone SST-based ΔT record would be best explained by a change in circulation dynamics, i.e., an increasing but more transient contribution of Gulf Stream waters after 7.0 cal ka BP or changes in the properties of the Gulf Stream waters. The spatial variations of alkenone temperatures are also surprising. A surface temperature decreasing trend can be observed along the system, which is the opposite to current temperatures, that are increasing towards the Gulf (Galbraith et al., 2024), which is determined by the estuarine circulation in this system (Saucier et al., 2003; Gilbert, 2004). This variation could also be biased by haptophyte community composition, which might have a higher proportion of lacustrine and brackish species in the estuary.

Analogous to alkenones, brackish conditions might have also impacted the thaumarchaeal community and/or physiology (Polik et al., 2018) and, thus, TEX_{86} . For example, the input of meltwater could have disrupted the nutrient regime in the St. Lawrence system. Rattanasriampaipong et al. (2025) showed that nitrate concentrations are negatively correlated with TEX_{86} temperatures, resulting in elevated TEX_{86} . In the absence of proxies that allow reconstructing past nitrate or ammonium concentrations, we can only infer potential changes in nutrient dynamics through terrestrial input. The BIT index values in core COR0602-36PC do

not indicate substantial changes in terrestrial/soil organic matter supply during the Holocene. However, BIT index values can be biased by changes in sea level, i.e., a shift in the proximity of the runoff source relative to the core location. At 10.0 cal ka BP, the sea-level was 120 m higher in the lower estuary (Fig. 6b) and 20 m lower in the gulf due to glacio-isostatic rebound (Clark et al., 1978; Shaw et al., 2002; Casse et al., 2017). In theory, this sea level shift should have led to an increased supply of terrestrial organic matter and nutrients due to the decreasing distance to the input source and thus, if any, we would expect a bias towards lower TEX₈₆ values/water temperatures (Rattanasriampaipong et al., 2025). While we consider runoff-controlled nutrient effects unlikely, the meltwater dynamics and changes in sea level could have impacted the habitat depth of the thaumarchaeal community and altered the export depth of the TEX₈₆ signal over if water column stratification or nitracline depth changed. However, the effect on our TEX₈₆ records are difficult to test in the absence of independent data constraining stratification and nitracline depth. We argue that the good agreement in absolute TEX₈₆-derived water temperature between all three core locations indicates little to no biases though sea level change and, if any, only brief changes during meltwater pulses. Since our early Holocene ΔT values do not imply changes in water mass composition beyond the state observed after 4.0 cal ka BP, we also do not expect an influence of oxygen concentrations in the bottom waters on TEX₈₆ values either (Guo et al., 2021; Qin et al., 2015). This is also consistent with the benthic foraminiferal data reported by Wu et al. (2023).

Overall, our data indicate that U₃₇^{K'}-derived SSTs may be biased by haptophyte community change due to more brackish conditions imposed by meltwater input (Marshall et al., 2021a,b), but we find no evidence for ecological effects on the thaumarchaeal community and TEX₈₆.

7 SUMMARY & CONCLUSION

In this study we reconstruct surface and bottom water temperatures in three sediment cores of the St. Lawrence Estuary and Gulf of St. Lawrence using $U_{37}^{K'}$ and TEX_{86} . Our data show a general cooling trend of around 7-10 °C for $U_{37}^{K'}$ -derived SSTs throughout the Holocene and an insolation-driven warming for TEX_{86} -derived bottom waters in the early Holocene, followed by a cooling starting of around 6-8 °C around 7.5 cal ka BP until today. Based on the trend recorded in instrumental data, we use the relative temperature offset between surface and bottom waters, ΔT , as a proxy to trace changes in circulation dynamics/bottom water sourcing. ΔT decreases substantially from 10.0 to 7.0 cal ka BP, which seems to suggest a change in circulation dynamics, i.e., an increasing contribution of Gulf Stream waters entering the St. Lawrence system. After 4.0 cal ka BP, ΔT remains relatively stable, suggesting only minor changes in the proportions of Gulf Stream and Labrador Current waters entering the system. Since this observation contradicts previous studies and given the large SST change recorded by $U_{37}^{K'}$, we inspected the alkenone and GDGT lipid composition in more detail to identify potential ecological biases. While no substantial biases can be identified in the GDGT record, high proportions of $C_{37:4}$ alkenones between 10.0 and 7.0 cal ka BP indicate a shift in the haptophyte community towards species adapted to brackish conditions. We corrected for this potential bias using the $U_{37}^{K''}$ for SST calibration in the respective intervals and obtained a composite SST record. The temperature offset between surface and bottom waters, ΔT , resulting from the composite SST record is lower during the early to middle Holocene compared to the initial ΔT curve based on $U_{37}^{K'}$ only. Although the new ΔT record indicates more transient changes over time, ΔT is still higher during the early Holocene than the late Holocene, with a notable change occurring only in response to the meltwater event. ΔT values similar to early instrumental observations are established after 4.0 cal ka BP. The rather stable ΔT values since 4.0 cal ka BP imply that bottom water sourcing has been relatively stable since, which suggests the dominance of Gulf Stream waters at present is unprecedented over the Holocene. Thus, we assume that the current circulation changes and their control

on hypoxia may also be unprecedented over the Holocene. However, additional data tracing redox conditions, such as benthic foraminiferal assemblages, trace metals as paleoredox proxies and redox-sensitive biomarkers should be obtained in this system to directly investigate past hypoxic conditions. Moreover, further research is needed to investigate changes in the haptophyte community composition over time. Paleogenomics could confirm that the high proportions of $C_{37:4}$ indeed stem from species adapted to brackish conditions and help assess how these impact the alkenone signatures in our sediment cores.

CONCLUSION GÉNÉRALE

L'étude réalisée dans le cadre de ce mémoire a permis de reconstituer les températures de surface et des eaux profondes dans l'estuaire et le golfe du Saint-Laurent, afin de mieux comprendre l'évolution de la circulation au cours de l'Holocène. Trois carottes sédimentaires prélevées le long du chenal laurentien ont été analysées à l'aide de biomarqueurs lipidiques jamais utilisés auparavant dans cette région : les traceurs $U_{37}^{K'}$ pour les eaux de surface et TEX_{86} pour les eaux profondes. Cette étude repose sur deux hypothèses principales.

Notre première hypothèse est que les changements de température dus à l'insolation peuvent être distingués des changements de circulation dans les eaux profondes du Saint-Laurent, en observant l'écart de température relatif entre la surface et les eaux profondes (ΔT). Bien qu'il y ait un réchauffement de 3.2 °C dans les températures des eaux profondes entre 1930 et 2024 contre 1.5 °C dans les eaux de surface (Galbraith et al., 2024), la variabilité interannuelle est trop importante pour pouvoir distinguer clairement un réchauffement plus significatif dans les eaux profondes, conduisant à un écart relativement stable entre la surface et le fond (ΔT). Cependant, en tenant compte de la tendance des eaux de fond du Labrador à se refroidir depuis environ 1000 ans, on s'attendrait à une augmentation du ΔT si ce courant entrainait en plus grande quantité, et à une diminution du ΔT avec la tendance des eaux du Gulf Stream à se réchauffer (Lund et al., 2006; Lochte et al., 2020). Nos données montrent un refroidissement important de 7 à 10 °C pour les températures de surface tout au long de l'Holocène, ainsi qu'un refroidissement de 6 à 8 °C pour les eaux profondes entre 7,5 ka BP et aujourd'hui. ΔT diminue considérablement entre 10,0 et 7,0 cal ka BP, ce qui semble indiquer un changement dans la dynamique de circulation, avec une contribution croissante des eaux du Gulf Stream entrant dans le système du Saint-Laurent. Les eaux profondes ne se sont pas autant refroidies que les eaux de surface, ce qui pourrait s'expliquer par un approvisionnement accru d'eaux plus chaudes dans les eaux de fonds provenant du Gulf Stream. Après 4,0 cal ka BP, ΔT reste relativement stable, ce qui suggère seulement de légers changements dans les proportions des

eaux du Gulf Stream et du courant du Labrador entrant dans le système.

Cette conclusion contredit certaines études, ce qui pourrait soulever des biais dans les biomarqueurs utilisés. Nous avons donc analysé plus en détail la composition lipidique des alcénones et des GDGTs afin d'identifier d'éventuels biais écologiques. Bien qu'aucun biais substantiel ne puisse être identifié dans les GDGTs, des proportions élevées d'alcénones $C_{37:4}$ entre 10,0 et 7,0 cal ka BP pourraient indiquer un changement dans la communauté d'Isochrysidales. Ce changement de communauté pourrait s'expliquer par l'événement de fonte de glaces à 8,2 cal ka BP, qui aurait rendu les conditions dans le Saint-Laurent plus saumâtres. Pour confirmer ce changement de communauté, des analyses de paléogénomique sont en cours afin de vérifier si les proportions élevées de $C_{37:4}$ proviennent effectivement d'espèces adaptées à ces conditions. Nous avons ainsi corrigé ce biais potentiel pour les intervalles respectifs en utilisant la calibration $U_{37}^{K''}$, proposé par Zheng et al. (2016) pour des conditions saumâtres. Bien que la surestimation des températures de surface par l'indice $U_{37}^{K'}$ puisse influencer les résultats de cette étude, l'utilisation de $U_{37}^{K''}$ indique une diminution des températures en raison de l'apport d'eau de fonte, sans remettre en cause notre conclusion. Une proportion du courant du Labrador plus importante serait donc entrée dans le système entre 10,0 et 7,0 cal ka BP. Un approvisionnement plus important par le Gulf Stream aurait commencé vers de 7,0 cal ka BP. A cause de la constance du ΔT on considère que ce changement de circulation n'aurait toutefois pas entraîné de période hypoxique. Mais ceci ne peut pas être entièrement exclu sur la base des données de température de notre première hypothèse.

Dans le contexte de désoxygénation, notre deuxième hypothèse est que des changements de circulation devraient pouvoir être liés à des épisodes passés d'hypoxie. La collaboration avec Daphnée Laliberté, qui reconstruit les conditions redox dans les mêmes échantillons sédimentaires grâce à des biomarqueurs lipidiques et des isotopes ne donnent aucun signe d'une période hypoxique persistante dans le passé. Cela renforce donc notre conclusion selon laquelle les changements de circulation qui se sont produits à l'Holocène moyen et supérieur n'ont pas été aussi importants.

ANNEXE I

AGE MODELS

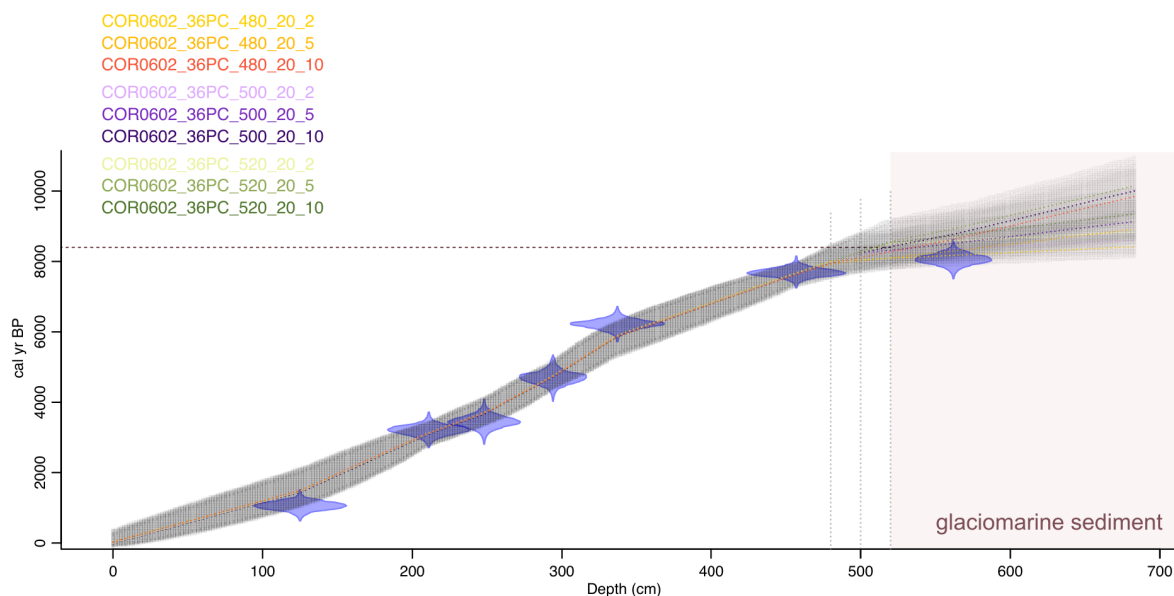


FIGURE S1 – Core COR0602-36PC calibrated with the Marine20 calibration with bayesian model made with rbacon (Blaauw and Christen, 2011), based on six ^{14}C ages (Barletta et al., 2010) and one paleomagnetic tie point (Casse et al., 2017), with a ΔR of 25 ± 72 years based on Wu et al. (2023). Different sedimentation rate changes ($0.1\text{-}0.5 \text{ cm yr}^{-1}$) were overlain at 480 cm, 500 cm and 520 cm.

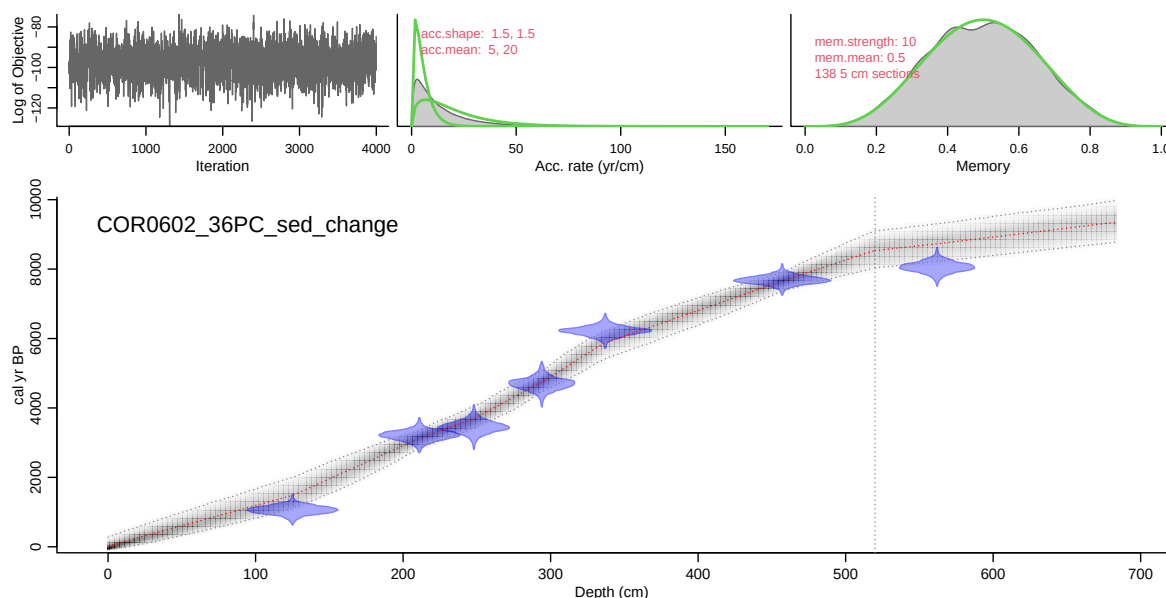


FIGURE S2 – Core COR0602-36PC calibrated with the Marine20 calibration with bayesian model made with rbacon (Blaauw and Christen, 2011), based on six ^{14}C ages (Barletta et al., 2010) and an age from Casse et al. (2017), with a ΔR of 25 ± 72 years based on Wu et al. (2023). A sedimentation rate change from 0.2 cm yr^{-1} to 0.05 cm yr^{-1} was defined at 520 cm.

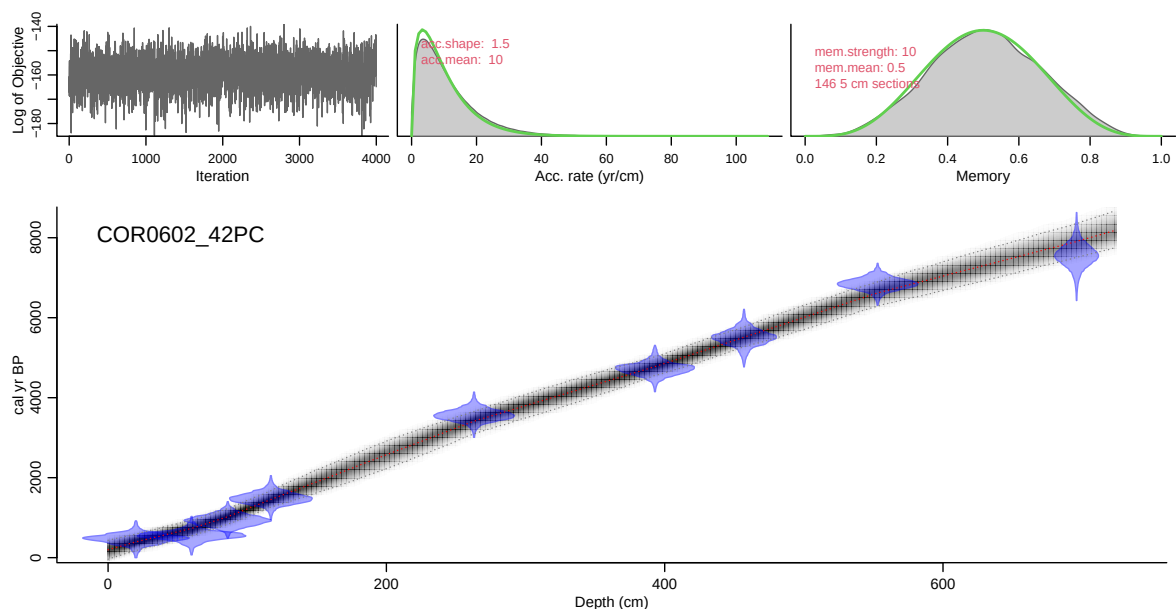


FIGURE S3 – Core COR0602-42PC calibrated with the Marine20 calibration with bayesian model made with rbacon (Blaauw and Christen, 2011), based on nine ^{14}C ages (Barletta et al., 2010; Wu et al., 2023), with a ΔR of 25 ± 72 years based on Wu et al. (2023).

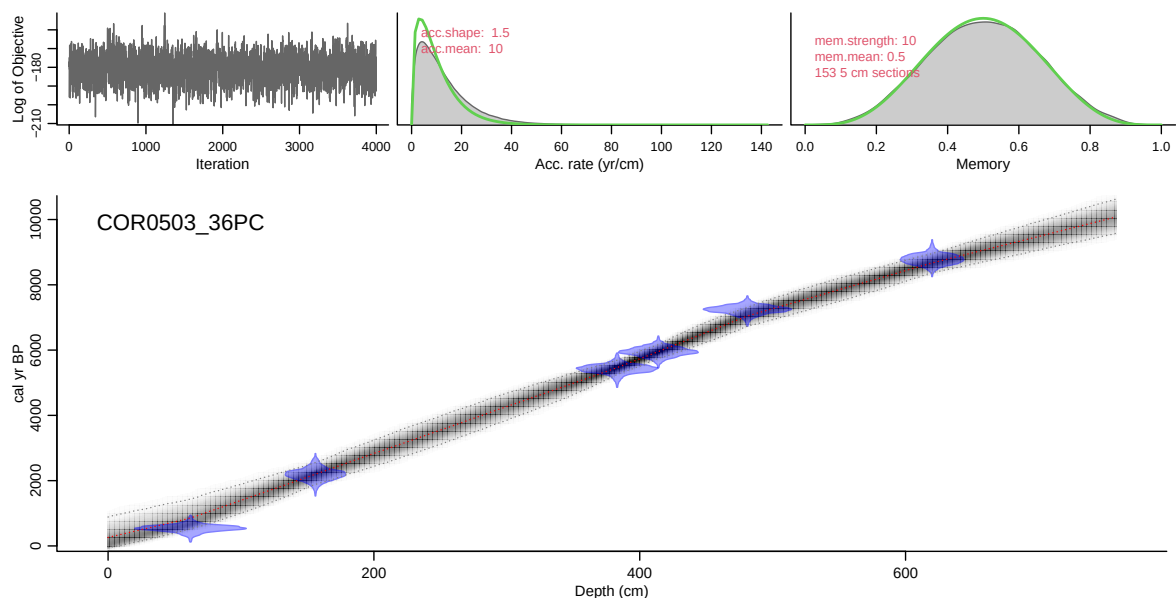


FIGURE S4 – Core COR0503-36PC calibrated with the Marine20 calibration with bayesian model made with rbacon (Blaauw and Christen, 2011), based on six ^{14}C ages (Barletta et al., 2010), with a ΔR of 25 ± 72 years based on Wu et al. (2023).

ANNEXE II

DISCUSSION – COMPOSITE CALIBRATION FOR ALKENONES

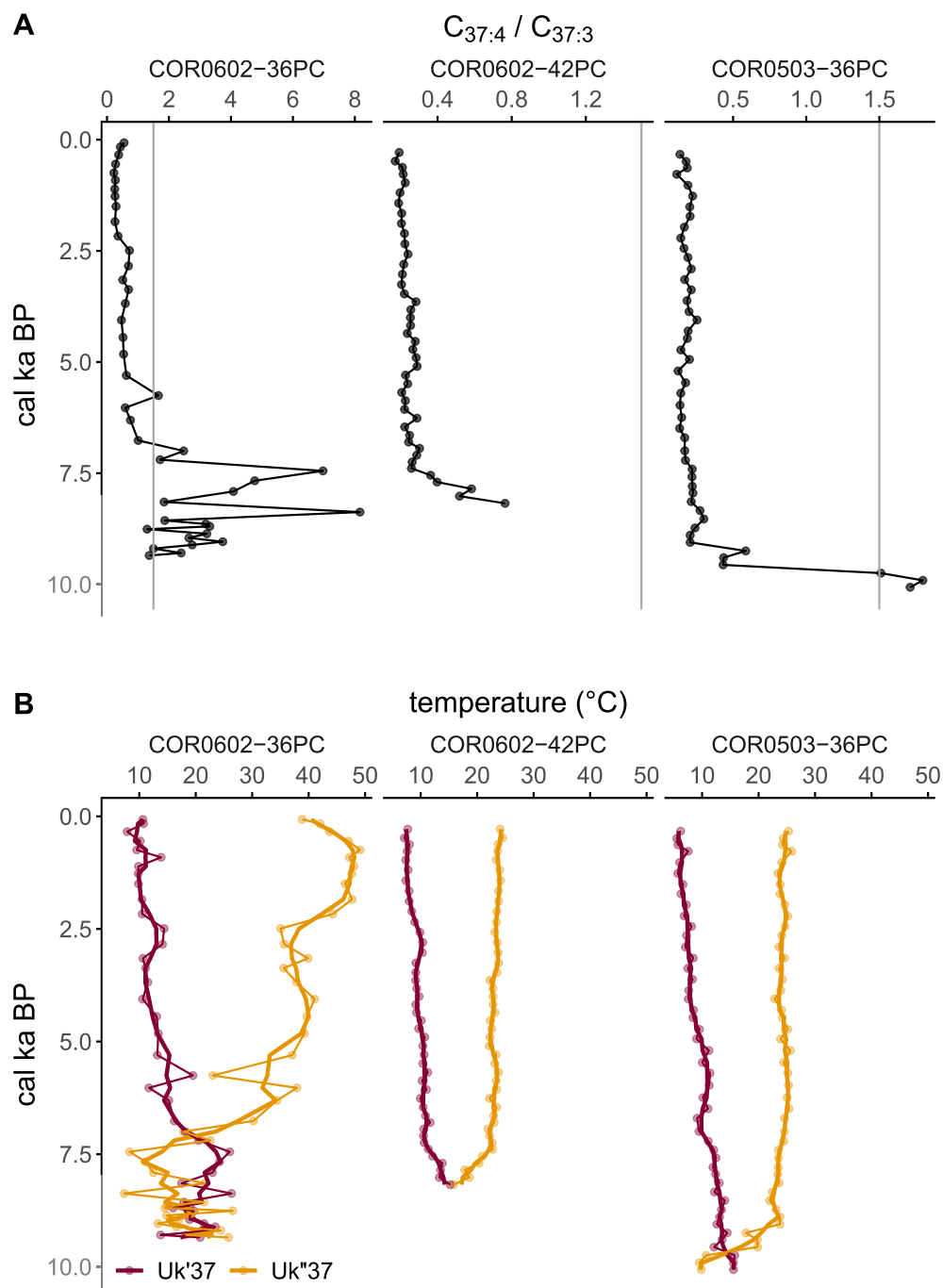


FIGURE S5 – **A**) Ratio of $C_{37:4}$ -alkenones over $C_{37:3}$ -alkenones. Threshold set at 1.5. The grey axis indicates glaciomarine sediments, where the age model is not well constrained. **B**) Comparison between $U_{37}^{K'}$ (Müller et al., 1998) and $U_{37}^{K''}$ (Zheng et al., 2016). The bold line represents the 3-point moving average. The grey axis indicates glaciomarine sediments, where the age model is not well constrained.

RÉFÉRENCES

- Arellano-Nava, B., Lenton, T.M., Boulton, C.A., Holmes, S., Scourse, J., Butler, P.G., Reynolds, D.J., Trofimova, T., Poitevin, P., Román-González, A., et al., 2025. Recent and early 20th century destabilization of the subpolar North Atlantic recorded in bivalves. *Science Advances* 11, eadw3468.
- Bakker, P., Schmittner, A., Lenaerts, J., Abe-Ouchi, A., Bi, D., Van Den Broeke, M., Chan, W.L., Hu, A., Beadling, R., Marsland, S., et al., 2016. Fate of the Atlantic Meridional Overturning Circulation: Strong decline under continued warming and Greenland melting. *Geophysical Research Letters* 43, 12–252.
- Balestra, B., Bertini, A., de Vernal, A., Monechi, S., Reale, V., 2013. Late Quaternary sea surface conditions in the Laurentian Fan: Evidence from coccolith and dinocyst assemblages. *Palaeogeography, Palaeoclimatology, Palaeoecology* 387, 200–210.
- Balsam, W., 1981. Late Quaternary sedimentation in the western North Atlantic: Stratigraphy and paleoceanography. *Palaeogeography, Palaeoclimatology, Palaeoecology* 35, 215–240.
- Balsam, W.L., Heusser, L.E., 1976. Direct correlation of sea surface paleotemperatures, deep circulation, and terrestrial paleoclimates: Foraminiferal and palynological evidence from two cores off Chesapeake Bay. *Marine Geology* 21, 121–147.
- Banks, R., 1966. The cold layer in the Gulf of St. Lawrence. *Journal of Geophysical Research* 71, 1603–1610.
- Barber, D.C., Dyke, A., Hillaire-Marcel, C., Jennings, A.E., Andrews, J.T., Kerwin, M.W., Bilodeau, G., McNeely, R., Southon, J., Morehead, M.D., et al., 1999. Forcing of the cold event of 8,200 years ago by catastrophic drainage of Laurentide lakes. *Nature* 400, 344–348.
- Barletta, F., St-Onge, G., Stoner, J., Lajeunesse, P., Locat, J., 2010. A high-resolution Holocene paleomagnetic secular variation and relative paleointensity stack from eastern Canada. *Earth and Planetary Science Letters* 298, 162–174.
- Beman, J.M., Popp, B.N., Francis, C.A., 2008. Molecular and biogeochemical evidence for ammonia oxidation by marine Crenarchaeota in the Gulf of California. *The ISME Journal* 2, 429–441.
- Bendle, J., Rosell-Melé, A., Ziveri, P., 2005. Variability of unusual distributions of alkenones in the surface waters of the Nordic seas. *Paleoceanography and Paleoclimatology* 20, 1–15.
- Bennett, K.D., 1990. Milankovitch cycles and their effects on species in ecological and evolutionary time. *Paleobiology* 16, 11–21.

- Benoit, P., Gratton, Y., Mucci, A., 2006. Modeling of dissolved oxygen levels in the bottom waters of the Lower St. Lawrence Estuary: Coupling of benthic and pelagic processes. *Marine Chemistry* 102, 13–32.
- Berger, A., Loutre, M.F., 1991. Insolation values for the climate of the last 10 million years. *Quaternary Science Reviews* 10, 297–317.
- Blaauw, M., Christen, J.A., 2011. Flexible paleoclimate age-depth models using an autoregressive gamma process. *Bayesian Analysis* 6, 457 – 474.
- Blaga, C.I., Reichart, G.J., Heiri, O., Sinninghe Damsté, J.S., 2009. Tetraether membrane lipid distributions in water-column particulate matter and sediments: a study of 47 European lakes along a north–south transect. *Journal of Paleolimnology* 41, 523–540.
- Blanz, T., Emeis, K.C., Siegel, H., 2005. Controls on alkenone unsaturation ratios along the salinity gradient between the open ocean and the Baltic Sea. *Geochimica et Cosmochimica Acta* 69, 3589–3600.
- Bligh, E.G., Dyer, W.J., 1959. A rapid method of total lipid extraction and purification. *Canadian Journal of Biochemistry and Physiology* 37, 911–917.
- Bluteau, C.E., Galbraith, P.S., Bourgault, D., Villeneuve, V., Tremblay, J.É., 2021. Winter observations alter the seasonal perspectives of the nutrient transport pathways into the Lower St. Lawrence Estuary. *Ocean Science* 17, 1509–1525.
- Bourgault, D., Koutitonsky, V.G., 1999. Real-time monitoring of the freshwater discharge at the head of the St. Lawrence Estuary. *Atmosphere-Ocean* 37, 203–220.
- Brassell, S.C., Eglinton, G., Marlowe, I., Pflaumann, U., Sarnthein, M., 1986. Molecular stratigraphy: a new tool for climatic assessment. *Nature* 320, 129–133.
- Breitburg, D., Levin, L.A., Oschlies, A., Grégoire, M., Chavez, F.P., Conley, D.J., Garçon, V., Gilbert, D., Gutiérrez, D., Isensee, K., et al., 2018. Declining oxygen in the global ocean and coastal waters. *Science* 359, eaam7240.
- Brochier-Armanet, C., Boussau, B., Gribaldo, S., Forterre, P., 2008. Mesophilic Crenarchaeota: proposal for a third archaeal phylum, the Thaumarchaeota. *Nature Reviews Microbiology* 6, 245–252.
- Broecker, W.S., Kennett, J.P., Flower, B.P., Teller, J.T., Trumbore, S., Bonani, G., Wolfli, W., 1989. Routing of meltwater from the Laurentide Ice Sheet during the Younger Dryas cold episode. *Nature* 341, 318–321.
- Buckley, M.W., Marshall, J., 2016. Observations, inferences, and mechanisms of the Atlantic Meridional Overturning Circulation: A review. *Reviews of Geophysics* 54, 5–63.

- Bugden, G.L., 1991. Changes in the temperature-salinity characteristics of the deeper waters of the Gulf of St. Lawrence over the past several decades. *The Gulf of St. Lawrence: small ocean or big estuary* 113, 139–147.
- Carlson, A.E., LeGrande, A.N., Oppo, D.W., Came, R.E., Schmidt, G.A., Anslow, F.S., Licciardi, J.M., Obbink, E.A., 2008. Rapid early Holocene deglaciation of the Laurentide Ice Sheet. *Nature Geoscience* 1, 620–624.
- Casse, M., Montero-Serrano, J.C., St-Onge, G., 2017. Influence of the Laurentide Ice Sheet and relative sea-level changes on sediment dynamics in the Estuary and Gulf of St. Lawrence since the last deglaciation. *Boreas* 46, 541–561.
- Chivall, D., M'Boule, D., Sinke-Schoen, D., Damsté, J.S.S., Schouten, S., van der Meer, M.T., 2014. Impact of salinity and growth phase on alkenone distributions in coastal haptophytes. *Organic Geochemistry* 67, 31–34.
- Claret, M., Galbraith, E.D., Palter, J.B., Bianchi, D., Fennel, K., Gilbert, D., Dunne, J.P., 2018. Rapid coastal deoxygenation due to ocean circulation shift in the northwest Atlantic. *Nature Climate Change* 8, 868–872.
- Clark, J.A., Farrell, W.E., Peltier, W.R., 1978. Global changes in postglacial sea level: A numerical calculation. *Quaternary Research* 9, 265–287.
- Clark, P.U., Dyke, A.S., Shakun, J.D., Carlson, A.E., Clark, J., Wohlfarth, B., Mitrovica, J.X., Hostetler, S.W., McCabe, A.M., 2009. The last glacial maximum. *Science* 325, 710–714.
- Clarke, G.K., Leverington, D.W., Teller, J.T., Dyke, A.S., 2004. Paleohydraulics of the last outburst flood from glacial Lake Agassiz and the 8200BP cold event. *Quaternary Science Reviews* 23, 389–407.
- Cohmap Members, 1988. Climatic changes of the last 18,000 years: observations and model simulations. *Science* 241, 1043–1052.
- Conte, M.H., Sicre, M.A., Rühlemann, C., Weber, J.C., Schulte, S., Schulz-Bull, D., Blanz, T., 2006. Global temperature calibration of the alkenone unsaturation index ($U_{37}^{K'}$) in surface waters and comparison with surface sediments. *Geochemistry, Geophysics, Geosystems* 7.
- Coolen, M.J., Muyzer, G., Rijpstra, W.I.C., Schouten, S., Volkman, J.K., Damsté, J.S.S., 2004. Combined DNA and lipid analyses of sediments reveal changes in Holocene haptophyte and diatom populations in an Antarctic lake. *Earth and Planetary Science Letters* 223, 225–239.
- Coolen, M.J., Saenz, J.P., Giosan, L., Trowbridge, N.Y., Dimitrov, P., Dimitrov, D., Eglinton, T.I., 2009. DNA and lipid molecular stratigraphic records of haptophyte succession in the Black Sea during the Holocene. *Earth and Planetary Science Letters* 284, 610–621.

- Cranwell, P., 1985. Long-chain unsaturated ketones in recent lacustrine sediments. *Geochimica et Cosmochimica Acta* 49, 1545–1551.
- Dalton, A.S., Margold, M., Stokes, C.R., Tarasov, L., Dyke, A.S., Adams, R.S., Allard, S., Arends, H.E., Atkinson, N., Attig, J.W., et al., 2020. An updated radiocarbon-based ice margin chronology for the last deglaciation of the North American Ice Sheet Complex. *Quaternary Science Reviews* 234, 106223.
- D’Andrea, W.J., Lage, M., Martiny, J.B.H., Laatsch, A.D., Amaral-Zettler, L.A., Sogin, M.L., Huang, Y., 2006. Alkenone producers inferred from well-preserved 18s rDNA in greenland lake sediments. *Journal of Geophysical Research: Biogeosciences* 111, G03013.
- De Leeuw, J.W., vd Meer, F., Rijpstra, W., Schenck, P., 1980. On the occurrence and structural identification of long chain unsaturated ketones and hydrocarbons in sediments. *Physics and Chemistry of the Earth* 12, 211–217.
- De Rosa, M., Gambacorta, A., 1988. The lipids of archaebacteria. *Progress in Lipid Research* 27, 153–175.
- de Vernal, A., Guiot, J., Turon, J.L., 1993. Late and postglacial paleoenvironments of the Gulf of St. Lawrence: marine and terrestrial palynological evidence. *Géographie physique et Quaternaire* 47, 167–180.
- de Vernal, A., Hillaire-Marcel, C., 2006. Provincialism in trends and high frequency changes in the northwest North Atlantic during the Holocene. *Global and Planetary Change* 54, 263–290.
- Diaz, R.J., Rosenberg, R., et al., 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna. *Oceanography and marine biology. An Annual Review* 33, 245–303.
- Dyke, A.S., 2004. An outline of North American deglaciation with emphasis on central and northern Canada. *Developments in Quaternary Sciences* 2, 373–424.
- Eglinton, T.I., Eglinton, G., 2008. Molecular proxies for paleoclimatology. *Earth and Planetary Science Letters* 275, 1–16.
- El-Sabh, M.I., Silverberg, N., 1990. The St. Lawrence Estuary: Introduction, in: *Oceanography of a large-scale estuarine system: The St. Lawrence*. Springer, pp. 1–9.
- Epstein, B.L., D’Hondt, S., Quinn, J.G., Zhang, J., Hargraves, P.E., 1998. An effect of dissolved nutrient concentrations on alkenone-based temperature estimates. *Paleoceanography* 13, 122–126.
- Farrimond, P., Eglinton, G., Brassell, S., 1986. Alkenones in Cretaceous black shales, Blake-Bahama Basin, western North Atlantic. *Organic Geochemistry* 10, 897–903.

- Fillon, R.H., 1976. Hamilton Bank, Labrador Shelf: Postglacial sediment dynamics and paleo-oceanography. *Marine Geology* 20, 7–25.
- Fisher, T.G., 2020. Megaflooding associated with glacial Lake Agassiz. *Earth-Science Reviews* 201, 102974.
- Francis, C.A., Roberts, K.J., Beman, J.M., Santoro, A.E., Oakley, B.B., 2005. Ubiquity and diversity of ammonia-oxidizing archaea in water columns and sediments of the ocean. *Proceedings of the National Academy of Sciences* 102, 14683–14688.
- Freitas, F.S., Pancost, R.D., Arndt, S., 2017. The impact of alkenone degradation on paleothermometry: A model-derived assessment. *Paleoceanography* 32, 648–672.
- Frölicher, T.L., Ashwanden, M., Gruber, N., Jaccard, S.L., Dunne, J.P., Paynter, D., 2020. Contrasting upper and deep ocean oxygen response to protracted global warming. *Global Biogeochemical Cycles* 34, e2020GB006601.
- Galbraith, P.S., 2006. Winter water masses in the Gulf of St. Lawrence. *Journal of Geophysical Research: Oceans* 111, C06022.
- Galbraith, P.S., Chassé, J., Shaw, J.L., Dumas, J., Bourassa, M.N., 2024. Physical Oceanographic Conditions in the Gulf of St. Lawrence during 2023. *Canadian Technical Report of Hydrography and Ocean Sciences* 378: v. + 91 p. .
- Ganachaud, A., Wunsch, C., 2000. Improved estimates of global ocean circulation, heat transport and mixing from hydrographic data. *Nature* 408, 453–457.
- Gatien, M.G., 1976. A study in the slope water region south of Halifax. *Journal of the Fisheries Board of Canada* 33, 2213–2217.
- Genovesi, L., De Vernal, A., Thibodeau, B., Hillaire-Marcel, C., Mucci, A., Gilbert, D., 2011. Recent changes in bottom water oxygenation and temperature in the Gulf of St. Lawrence: Micropaleontological and geochemical evidence. *Limnology and Oceanography* 56, 1319–1329.
- Gilbert, D., 2004. Propagation of temperature signals along the northwest Atlantic continental shelf edge and into the Laurentian Channel. Abstract, ICES CM Annual Science Conference, Vigo, Spain. pp. 22–25.
- Gilbert, D., Sundby, B., Gobeil, C., Mucci, A., Tremblay, G.H., 2005. A seventy-two-year record of diminishing deep-water oxygen in the St. Lawrence Estuary: The northwest Atlantic connection. *Limnology and Oceanography* 50, 1654–1666.
- Gonçalves Neto, A., Palter, J.B., Xu, X., Fratantoni, P., 2023. Temporal variability of the Labrador Current pathways around the Tail of the Grand Banks at intermediate depths in a high-resolution ocean circulation model. *Journal of Geophysical Research: Oceans* 128, e2022JC018756.

- Guo, J., Yuan, H., Song, J., Qu, B., Xing, J., Wang, Q., Li, X., Duan, L., Li, N., Wang, Y., 2021. Variation of isoprenoid GDGTs in the stratified marine water column: Implications for GDGT-based TEX₈₆ paleothermometry. *Frontiers in Marine Science* 8, 715708.
- Han, G., Chen, N., Ma, Z., 2014. Is there a north-south phase shift in the surface Labrador Current transport on the interannual-to-decadal scale? *Journal of Geophysical Research: Oceans* 119, 276–287.
- He, F., Clark, P.U., 2022. Freshwater forcing of the Atlantic meridional overturning circulation revisited. *Nature Climate Change* 12, 449–454.
- Heath, S.L., Loope, H.M., Curry, B.B., Lowell, T.V., 2018. Pattern of southern Laurentide Ice Sheet margin position changes during Heinrich Stadials 2 and 1. *Quaternary Science Reviews* 201, 362–379.
- Heaton, T.J., Köhler, P., Butzin, M., Bard, E., Reimer, R.W., Austin, W.E., Ramsey, C.B., Grootes, P.M., Hughen, K.A., Kromer, B., et al., 2020. Marine20—the marine radiocarbon age calibration curve (0–55,000 cal BP). *Radiocarbon* 62, 779–820.
- Hemming, S.R., 2004. Heinrich events: Massive late Pleistocene detritus layers of the North Atlantic and their global climate imprint. *Reviews of Geophysics* 42.
- Herbert, T., 2006. Alkenone paleotemperature. *The Oceans and Marine Geochemistry* 6, 391.
- Hillaire-Marcel, C., De Vernal, A., Candon, L., Bilodeau, G., Stoner, J., 2001a. Changes of potential density gradients in the northwestern North Atlantic during the last climatic cycle based on a multiproxy approach. *Geophysical Monograph Series* 126, 83–100.
- Hillaire-Marcel, C., de Vernal, A., Bilodeau, G., Weaver, A.J., 2001b. Absence of deep-water formation in the Labrador Sea during the last interglacial period. *Nature* 410, 1073–1077.
- Ho, S.L., Laepple, T., 2016. Flat meridional temperature gradient in the early Eocene in the subsurface rather than surface ocean. *Nature Geoscience* 9, 606–610.
- Ho, S.L., Mollenhauer, G., Fietz, S., Martínez-García, A., Lamy, F., Rueda, G., Schipper, K., Méheust, M., Rosell-Melé, A., Stein, R., et al., 2014. Appraisal of TEX₈₆ and TEX₈₆^L thermometries in subpolar and polar regions. *Geochimica et Cosmochimica Acta* 131, 213–226.
- Hoogakker, B.A., McCave, I.N., Elderfield, H., Hillaire-Marcel, C., Simstich, J., 2015. Holocene climate variability in the Labrador Sea. *Journal of the Geological Society* 172, 272–277.
- Hopmans, E.C., Schouten, S., Damsté, J.S.S., 2016. The effect of improved chromatography on GDGT-based palaeoproxies. *Organic Geochemistry* 93, 1–6.

- Hopmans, E.C., Weijers, J.W., Schefuß, E., Herfort, L., Damsté, J.S.S., Schouten, S., 2004. A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids. *Earth and Planetary Science Letters* 224, 107–116.
- Huguet, C., Hopmans, E.C., Febo-Ayala, W., Thompson, D.H., Damsté, J.S.S., Schouten, S., 2006. An improved method to determine the absolute abundance of glycerol dibiphytanyl glycerol tetraether lipids. *Organic Geochemistry* 37, 1036–1041.
- Hurley, S.J., Lipp, J.S., Close, H.G., Hinrichs, K.U., Pearson, A., 2018. Distribution and export of isoprenoid tetraether lipids in suspended particulate matter from the water column of the Western Atlantic Ocean. *Organic Geochemistry* 116, 90–102.
- Jenkyns, H., Schouten-Huibers, L., Schouten, S., Sinninghe Damsté, J., 2012. Warm Middle Jurassic–Early Cretaceous high-latitude sea-surface temperatures from the Southern Ocean. *Climate of the Past* 8, 215–226.
- Jutras, M., Dufour, C., Mucci, A., Cyr, F., Gilbert, D., 2020. Temporal changes in the causes of the observed oxygen decline in the St. Lawrence Estuary. *Journal of Geophysical Research: Oceans* 125, e2020JC016577.
- Jutras, M., Dufour, C.O., Mucci, A., Talbot, L.C., 2023a. Large-scale control of the retroflexion of the Labrador Current. *nature communications* 14, 2623.
- Jutras, M., Mucci, A., Chaillou, G., Nesbitt, W.A., Wallace, D.W., 2023b. Temporal and spatial evolution of bottom-water hypoxia in the St. Lawrence estuarine system. *Biogeosciences* 20, 839–849.
- Kaiser, J., Wang, K.J., Rott, D., Li, G., Zheng, Y., Amaral-Zettler, L., Arz, H.W., Huang, Y., 2019. Changes in long chain alkenone distributions and Isochrysidales groups along the Baltic Sea salinity gradient. *Organic Geochemistry* 127, 92–103.
- Karner, M.B., DeLong, E.F., Karl, D.M., 2001. Archaeal dominance in the mesopelagic zone of the Pacific Ocean. *Nature* 409, 507–510.
- Kaufman, D., McKay, N., Routson, C., Erb, M., Dätwyler, C., Sommer, P.S., Heiri, O., Davis, B., 2020. Holocene global mean surface temperature, a multi-method reconstruction approach. *Scientific data* 7, 201.
- Kaufman, D.S., Ager, T.A., Anderson, N.J., Anderson, P.M., Andrews, J.T., Bartlein, P.J., Brubaker, L.B., Coats, L.L., Cwynar, L.C., Duvall, M.L., et al., 2004. Holocene thermal maximum in the western Arctic (0–180°W). *Quaternary Science Reviews* 23, 529–560.
- Keeling, R.F., Körtzinger, A., Gruber, N., 2010. Ocean deoxygenation in a warming world. *Annual Review of Marine Science* 2, 199–229.
- Keigwin, L., Sachs, J., Rosenthal, Y., Boyle, E., 2005. The 8200 year BP event in the slope water system, western subpolar North Atlantic. *Paleoceanography* 20.

- Kelson, R., Straub, D., Dufour, C., 2022. Using CMIP6 models to assess the significance of the observed trend in the Atlantic Meridional Overturning Circulation. *Geophysical Research Letters* 49, e2022GL100202.
- Kim, B., Zhang, Y.G., 2023. Methane index: towards a quantitative archaeal lipid biomarker proxy for reconstructing marine sedimentary methane fluxes. *Geochimica et Cosmochimica Acta* 354, 74–87.
- Kim, J.H., Van der Meer, J., Schouten, S., Helmke, P., Willmott, V., Sangiorgi, F., Koç, N., Hopmans, E.C., Damsté, J.S.S., 2010. New indices and calibrations derived from the distribution of crenarchaeal isoprenoid tetraether lipids: Implications for past sea surface temperature reconstructions. *Geochimica et Cosmochimica Acta* 74, 4639–4654.
- Kim, J.H., Schouten, S., Hopmans, E.C., Donner, B., Damsté, J.S.S., 2008. Global sediment core-top calibration of the TEX₈₆ paleothermometer in the ocean. *Geochimica et Cosmochimica Acta* 72, 1154–1173.
- Kim, J.H., Schouten, S., Rodrigo-Gámiz, M., Rampen, S., Marino, G., Huguet, C., Helmke, P., Buscail, R., Hopmans, E.C., Pross, J., et al., 2015. Influence of deep-water derived isoprenoid tetraether lipids on the TEX₈₆^H paleothermometer in the Mediterranean Sea. *Geochimica et Cosmochimica Acta* 150, 125–141.
- Könneke, M., Bernhard, A.E., de La Torre, J.R., Walker, C.B., Waterbury, J.B., Stahl, D.A., 2005. Isolation of an autotrophic ammonia-oxidizing marine archaeon. *Nature* 437, 543–546.
- Koutitonsky, V.G., Bugden, G.L., 1991. The physical oceanography of the Gulf of St. Lawrence: a review with emphasis on the synoptic variability of the motion, in: Therriault, J.C. (Ed.), *The Gulf of St. Lawrence: Small Ocean or Big Estuary?*. Canadian Special Publication of Fisheries and Aquatic Sciences 113, pp. 57–90.
- Kusch, S., Rethemeyer, J., Schefuß, E., Mollenhauer, G., 2010. Controls on the age of vascular plant biomarkers in Black Sea sediments. *Geochimica et Cosmochimica Acta* 74, 7031–7047.
- Kusch, S., Walter, S.R.S., Hemingway, J.D., Pearson, A., 2018. Improved chromatography reveals multiple new bacteriohopanepolyol isomers in marine sediments. *Organic Geochemistry* 124, 12–21.
- Lambeck, K., Rouby, H., Purcell, A., Sun, Y., Sambridge, M., 2014. Sea level and global ice volumes from the Last Glacial Maximum to the Holocene. *Proceedings of the National Academy of Sciences* 111, 15296–15303.
- Latif, M., Sun, J., Visbeck, M., Hadi Bordbar, M., 2022. Natural variability has dominated Atlantic meridional overturning circulation since 1900. *Nature Climate Change* 12, 455–460.

- Lemay-Tougas, M., 2014. Changements climatiques le long de la Côte Nord de l'Estuaire et du Golfe du Saint-Laurent durant l'Holocène: relation entre les conditions hydrographiques et le développement des tourbières ombrotrophes côtières. Ph.D. thesis. Université du Québec à Montréal.
- Levac, E., 2001. High resolution Holocene palynological record from the Scotian Shelf. *Marine Micropaleontology* 43, 179–197.
- Levac, E., 2003. Palynological records from Bay of Islands, Newfoundland: Direct correlation of Holocene paleoceanographic and climatic changes. *Palynology* 27, 135–154.
- Leverington, D.W., Teller, J.T., 2003. Paleotopographic reconstructions of the eastern outlets of glacial Lake Agassiz. *Canadian Journal of Earth Sciences* 40, 1259–1278.
- Levin, L., Ekau, W., Gooday, A., Jorissen, F., Middelburg, J., Naqvi, S., Neira, C., Rabalais, N., Zhang, J., 2009. Effects of natural and human-induced hypoxia on coastal benthos. *Biogeosciences* 6, 2063–2098.
- Levin, L.A., 2018. Manifestation, drivers, and emergence of open ocean deoxygenation. *Annual Review of Marine Science* 10, 229–260.
- Leydet, D.J., Carlson, A.E., Teller, J.T., Breckenridge, A., Barth, A.M., Ullman, D.J., Sinclair, G., Milne, G.A., Cuzzone, J.K., Caffee, M.W., 2018. Opening of glacial Lake Agassiz's eastern outlets by the start of the Younger Dryas cold period. *Geology* 46, 155–158.
- Liao, S., Huang, Y., 2022. Group 2i Isochrysidales flourishes at exceedingly low growth temperatures (0 to 6°C). *Organic Geochemistry* 174, 104512.
- Liao, S., Wang, K.J., Huang, Y., 2023. Unusually high production of C_{37:4} alkenone by an Arctic *Gephyrocapsa huxleyi* strain grown under nutrient-replete conditions. *Organic Geochemistry* 177, 104539.
- Liao, S., Yao, Y., Wang, L., Wang, K.J., Amaral-Zettler, L., Longo, W.M., Huang, Y., 2020. C₄₁ methyl and C₄₂ ethyl alkenones are biomarkers for Group II Isochrysidales. *Organic Geochemistry* 147, 104081.
- Lochte, A.A., Repschläger, J., Seidenkrantz, M.S., Kienast, M., Blanz, T., Schneider, R.R., 2019. Holocene water mass changes in the Labrador Current. *The Holocene* 29, 676–690.
- Lochte, A.A., Schneider, R., Kienast, M., Repschläger, J., Blanz, T., Garbe-Schönberg, D., Andersen, N., 2020. Surface and subsurface Labrador Shelf water mass conditions during the last 6000 years. *Climate of the Past* 16, 1127–1143.
- Longo, W.M., Theroux, S., Giblin, A.E., Zheng, Y., Dillon, J.T., Huang, Y., 2016. Temperature calibration and phylogenetically distinct distributions for freshwater alkenones: Evidence from northern Alaskan lakes. *Geochimica et Cosmochimica Acta* 180, 177–196.

- Lund, D.C., Curry, W., 2006. Florida Current surface temperature and salinity variability during the last millennium. *Paleoceanography* 21.
- Lund, D.C., Lynch-Stieglitz, J., Curry, W.B., 2006. Gulf Stream density structure and transport during the past millennium. *Nature* 444, 601–604.
- Lynch-Stieglitz, J., Vollmer, T.D., Valley, S.G., Blackmon, E., Gu, S., Marchitto, T.M., 2024. A diminished North Atlantic nutrient stream during Younger Dryas climate reversal. *Science* 384, 693–696.
- Marlowe, I., Brassell, S., Eglinton, G., Green, J., 1984. Long chain unsaturated ketones and esters in living algae and marine sediments. *Organic Geochemistry* 6, 135–141.
- Marlowe, I., Brassell, S., Eglinton, G., Green, J., 1990. Long-chain alkenones and alkyl alkenoates and the fossil coccolith record of marine sediments. *Chemical Geology* 88, 349–375.
- Marret, F., de Vernal, A., 2024. Dinoflagellate cysts as proxies of environmental, ocean and climate changes in the Atlantic realm during the quaternary. *Frontiers in Ecology and Evolution* 12, 1378931.
- Marshall, N.R., de Vernal, A., Mucci, A., Filippova, A., Kienast, M., Gibb, O., Hillaire-Marcel, C., 2021a. Biogenic carbonate fluxes and preservation in the northwestern Labrador Sea since the Last Glacial Maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 576, 110498.
- Marshall, N.R., de Vernal, A., Mucci, A., Kienast, M., Filippova, A., Hillaire-Marcel, C., 2021b. Carbonate dissolution and environmental parameters govern coccolith vs. alkenone abundances in surface sediments from the northwest North Atlantic. *Marine Micropaleontology* 169, 102032.
- McManus, J.F., Francois, R., Gherardi, J.M., Keigwin, L.D., Brown-Leger, S., 2004. Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes. *Nature* 428, 834–837.
- Mollenhauer, G., Eglinton, T.I., Ohkouchi, N., Schneider, R.R., Müller, P.J., Grootes, P.M., Rullkötter, J., 2003. Asynchronous alkenone and foraminifera records from the Benguela Upwelling System. *Geochimica et Cosmochimica Acta* 67, 2157–2171.
- Mucci, A., Starr, M., Gilbert, D., Sundby, B., 2011. Acidification of lower St. Lawrence Estuary bottom waters. *Atmosphere-Ocean* 49, 206–218.
- Müller, P.J., Kirst, G., Ruhland, G., Von Storch, I., Rosell-Melé, A., 1998. Calibration of the alkenone paleotemperature index $U_{37}^{K'}$ based on core-tops from the eastern South Atlantic and the global ocean (60°N–60°S). *Geochimica et Cosmochimica Acta* 62, 1757–1772.

- Naughton, F., Sánchez-Goñi, M.F., Landais, A., Rodrigues, T., Riveiros, N.V., Toucanne, S., 2023. The Bølling–Allerød Interstadial, in: *European glacial landscapes*. Elsevier, pp. 45–50.
- Orme, L.C., Miettinen, A., Seidenkrantz, M.S., Tuominen, K., Pearce, C., Divine, D.V., Oksman, M., Kuijpers, A., 2021. Mid to late-Holocene sea-surface temperature variability off north-eastern Newfoundland and its linkage to the North Atlantic Oscillation. *The Holocene* 31, 3–15.
- Oschlies, A., Brandt, P., Stramma, L., Schmidtko, S., 2018. Drivers and mechanisms of ocean deoxygenation. *Nature Geoscience* 11, 467–473.
- Palter, J.B., Trossman, D.S., 2018. The sensitivity of future ocean oxygen to changes in ocean circulation. *Global Biogeochemical Cycles* 32, 738–751.
- Polik, C.A., Elling, F.J., Pearson, A., 2018. Impacts of paleoecology on the TEX₈₆ sea surface temperature proxy in the Pliocene-Pleistocene Mediterranean Sea. *Paleoceanography and Paleoclimatology* 33, 1472–1489.
- Portela, E., Kolodziejczyk, N., Gorgues, T., Zika, J., Perruche, C., Mignot, A., 2024. The ocean's meridional oxygen transport. *Journal of Geophysical Research: Oceans* 129, e2023JC020259.
- Prahl, F., Sparrow, M., Wolfe, G., 2003. Physiological impacts on alkenone paleothermometry. *Paleoceanography* 18, 1025.
- Prahl, F.G., Wakeham, S.G., 1987. Calibration of unsaturation patterns in long-chain ketone compositions for palaeotemperature assessment. *Nature* 330, 367–369.
- Qin, W., Amin, S.A., Lundeen, R.A., Heal, K.R., Martens-Habbena, W., Turkarslan, S., Urakawa, H., Costa, K.C., Hendrickson, E.L., Wang, T., et al., 2018. Stress response of a marine ammonia-oxidizing archaeon informs physiological status of environmental populations. *The ISME Journal* 12, 508–519.
- Qin, W., Carlson, L.T., Armbrust, E.V., Devol, A.H., Moffett, J.W., Stahl, D.A., Ingalls, A.E., 2015. Confounding effects of oxygen and temperature on the TEX₈₆ signature of marine Thaumarchaeota. *Proceedings of the National Academy of Sciences* 112, 10979–10984.
- Qin, W., Meinhardt, K.A., Moffett, J.W., Devol, A.H., Virginia Armbrust, E., Ingalls, A.E., Stahl, D.A., 2017. Influence of oxygen availability on the activities of ammonia-oxidizing archaea. *Environmental Microbiology Reports* 9, 250–256.
- Rabalais, N.N., Turner, R.E., Wiseman Jr, W.J., 2001. Hypoxia in the Gulf of Mexico. *Journal of Environmental Quality* 30, 320–329.
- Rahman, A., de Vernal, A., 1994. Surface oceanographic changes in the eastern Labrador Sea: Nannofossil record of the last 31,000 years. *Marine Geology* 121, 247–263.

- Rahmstorf, S., Box, J.E., Feulner, G., Mann, M.E., Robinson, A., Rutherford, S., Schaffernicht, E.J., 2015. Exceptional twentieth-century slowdown in Atlantic Ocean overturning circulation. *Nature Climate Change* 5, 475–480.
- Rashid, H., Piper, D.J., Lazar, K.B., McDonald, K., Saint-Ange, F., 2017. The Holocene Labrador Current: Changing linkages to atmospheric and oceanographic forcing factors. *Paleoceanography* 32, 498–510.
- Rattanasriampaipong, R., Tierney, J.E., Abell, J.T., Gilmore, L.D., 2025. A nutrient effect on the TEX₈₆ paleotemperature proxy. *Geophysical Research Letters* 52, e2025GL115237.
- Ritz, S.P., Stocker, T.F., Grimalt, J.O., Menviel, L., Timmermann, A., 2013. Estimated strength of the Atlantic overturning circulation during the last deglaciation. *Nature Geoscience* 6, 208–212.
- Rontani, J.F., Harji, R., Guasco, S., Prahl, F.G., Volkman, J.K., Bhosle, N.B., Bonin, P., 2008. Degradation of alkenones by aerobic heterotrophic bacteria: selective or not? *Organic Geochemistry* 39, 34–51.
- Rosell-Melé, A., 1998. Interhemispheric appraisal of the value of alkenone indices as temperature and salinity proxies in high-latitude locations. *Paleoceanography* 13, 694–703.
- Rousseau, S., Lavoie, D., Jutras, M., Chassé, J., 2025. Transit time of deep and intermediate waters in the Gulf of St. Lawrence. *Ocean Modelling* 195, 102526.
- Sachs, J.P., 2007. Cooling of Northwest Atlantic slope waters during the Holocene. *Geophysical Research Letters* 34, L03609.
- Saucier, F.J., Roy, F., Gilbert, D., Pellerin, P., Ritchie, H., 2003. Modeling the formation and circulation processes of water masses and sea ice in the Gulf of St. Lawrence, Canada. *Journal of Geophysical Research: Oceans* 108.
- Schmidt, M.W., Lynch-Stieglitz, J., 2011. Florida Straits deglacial temperature and salinity change: Implications for tropical hydrologic cycle variability during the Younger Dryas. *Paleoceanography* 26.
- Schmidt, M.W., Weinlein, W.A., Marcantonio, F., Lynch-Stieglitz, J., 2012. Solar forcing of Florida Straits surface salinity during the early Holocene. *Paleoceanography* 27.
- Schmidtko, S., Stramma, L., Visbeck, M., 2017. Decline in global oceanic oxygen content during the past five decades. *Nature* 542, 335–339.
- Schouten, S., Hopmans, E.C., Damsté, J.S.S., 2013. The organic geochemistry of glycerol dialkyl glycerol tetraether lipids: A review. *Organic Geochemistry* 54, 19–61.

- Schouten, S., Hopmans, E.C., Schefuß, E., Damste, J.S.S., 2002. Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures? *Earth and Planetary Science Letters* 204, 265–274.
- Shaw, J., Gareau, P., Courtney, R., 2002. Palaeogeography of Atlantic Canada 13–0 kyr. *Quaternary Science Reviews* 21, 1861–1878.
- Shaw, J., Piper, D., Fader, G., King, E., Todd, B., Bell, T., Batterson, M., Liverman, D., 2006. A conceptual model of the deglaciation of Atlantic Canada. *Quaternary Science Reviews* 25, 2059–2081.
- Sherwood, O.A., Lehmann, M.F., Schubert, C.J., Scott, D.B., McCarthy, M.D., 2011. Nutrient regime shift in the western North Atlantic indicated by compound-specific $\delta^{15}\text{N}$ of deep-sea gorgonian corals. *Proceedings of the National Academy of Sciences* 108, 1011–1015.
- Sicre, M.A., Bard, E., Ezat, U., Rostek, F., 2002. Alkenone distributions in the North Atlantic and Nordic sea surface waters. *Geochemistry, Geophysics, Geosystems* 3, 1–13.
- Sikes, E.L., Sicre, M.A., 2002. Relationship of the tetra-unsaturated C_{37} alkenone to salinity and temperature: Implications for paleoproxy applications. *Geochemistry, Geophysics, Geosystems* 3, 1–11.
- Sinninghe Damsté, J.S., 2016. Spatial heterogeneity of sources of branched tetraethers in shelf systems: The geochemistry of tetraethers in the Berau River delta (Kalimantan, Indonesia). *Geochimica et Cosmochimica Acta* 186, 13–31.
- Smith, P.C., Schwing, F.B., 1991. Mean circulation and variability on the eastern Canadian continental shelf. *Continental Shelf Research* 11, 977–1012.
- Solignac, S., Seidenkrantz, M.S., Jessen, C., Kuijpers, A., Gunvald, A.K., Olsen, J., 2011. Late-Holocene sea-surface conditions offshore Newfoundland based on dinoflagellate cysts. *The Holocene* 21, 539–552.
- Solignac, S., de Vernal, A., Hillaire-Marcel, C., 2004. Holocene sea-surface conditions in the North Atlantic—contrasted trends and regimes in the western and eastern sectors (Labrador Sea vs. Iceland Basin). *Quaternary Science Reviews* 23, 319–334.
- Srokosz, M., Bryden, H., 2015. Observing the Atlantic Meridional Overturning Circulation yields a decade of inevitable surprises. *Science* 348, 1255–1257.
- Stevens, S.W., Pawlowicz, R., Tanhua, T., Gerke, L., Nesbitt, W.A., Drozdowski, A., Chassé, J., Wallace, D.W., 2024. Deep inflow transport and dispersion in the Gulf of St. Lawrence revealed by a tracer release experiment. *Communications Earth & Environment* 5, 338.
- Stokes, C.R., 2017. Deglaciation of the Laurentide ice sheet from the last glacial maximum. *Cuadernos de investigación geográfica: Geographical Research Letters* 43, 377–428.

- Summons, R.E., Welander, P.V., Gold, D.A., 2022. Lipid biomarkers: molecular tools for illuminating the history of microbial life. *Nature Reviews Microbiology* 20, 174–185.
- Teller, J.T., 2013. Lake Agassiz during the Younger Dryas. *Quaternary Research* 80, 361–369.
- Teller, J.T., Leverington, D.W., 2004. Glacial Lake Agassiz: A 5000 yr history of change and its relationship to the $\delta^{18}\text{O}$ record of Greenland. *Geological Society of America Bulletin* 116, 729–742.
- Teller, J.T., Leverington, D.W., Mann, J.D., 2002. Freshwater outbursts to the oceans from glacial Lake Agassiz and their role in climate change during the last deglaciation. *Quaternary Science Reviews* 21, 879–887.
- Theroux, S., D'Andrea, W.J., Toney, J., Amaral-Zettler, L., Huang, Y., 2010. Phylogenetic diversity and evolutionary relatedness of alkenone-producing haptophyte algae in lakes: implications for continental paleotemperature reconstructions. *Earth and Planetary Science Letters* 300, 311–320.
- Thibodeau, B., De Vernal, A., Hillaire-Marcel, C., Mucci, A., 2010. Twentieth century warming in deep waters of the Gulf of St. Lawrence: A unique feature of the last millennium. *Geophysical Research Letters* 37.
- Thibodeau, B., Not, C., Zhu, J., Schmittner, A., Noone, D., Tabor, C., Zhang, J., Liu, Z., 2018. Last century warming over the Canadian Atlantic shelves linked to weak Atlantic meridional overturning circulation. *Geophysical Research Letters* 45, 12–376.
- Thibodeau, B., de Vernal, A., Limoges, A., 2013. Low oxygen events in the Laurentian Channel during the Holocene. *Marine Geology* 346, 183–191.
- Thibodeau, B., de Vernal, A., Mucci, A., 2006. Recent eutrophication and consequent hypoxia in the bottom waters of the Lower St. Lawrence Estuary: Micropaleontological and geochemical evidence. *Marine Geology* 231, 37–50.
- Thornalley, D.J., Oppo, D.W., Ortega, P., Robson, J.I., Brierley, C.M., Davis, R., Hall, I.R., Moffa-Sanchez, P., Rose, N.L., Spooner, P.T., et al., 2018. Anomalously weak Labrador Sea convection and Atlantic overturning during the past 150 years. *Nature* 556, 227–230.
- Tierney, J.E., Tingley, M.P., 2015. A TEX₈₆ surface sediment database and extended Bayesian calibration. *Scientific Data* 2, 1–10.
- Vilks, G., Rashid, M., 1976. Post-glacial paleo-oceanography of Emerald Basin, Scotian Shelf. *Canadian Journal of Earth Sciences* 13, 1256–1267.
- Volkman, J., Eglinton, G., Corner, E., Sargent, J., 1980. Novel unsaturated straight-chain C₃₇-C₃₉ methyl and ethyl ketones in marine sediments and a coccolithophore *Emiliania huxleyi*. *Physics and Chemistry of the Earth* 12, 219–227.

- Wang, K.J., Huang, Y., Kartzinel, T., Majaneva, M., Richter, N., Liao, S., Andresen, C.S., Vermassen, F., 2024. Group 2i Isochrysidales thrive in marine and lacustrine systems with ice cover. *Scientific Reports* 14, 11449.
- Wang, K.J., Huang, Y., Majaneva, M., Belt, S.T., Liao, S., Novak, J., Kartzinel, T.R., Herbert, T.D., Richter, N., Cabedo-Sanz, P., 2021. Group 2i Isochrysidales produce characteristic alkenones reflecting sea ice distribution. *Nature Communications* 12, 15.
- Warden, L., van der Meer, M.T., Moros, M., Damsté, J.S.S., 2016. Sedimentary alkenone distributions reflect salinity changes in the Baltic Sea over the Holocene. *Organic Geochemistry* 102, 30–44.
- Weijers, J.W., Lim, K.L., Aquilina, A., Sinninghe Damsté, J.S., Pancost, R.D., 2011. Biogeochemical controls on glycerol dialkyl glycerol tetraether lipid distributions in sediments characterized by diffusive methane flux. *Geochemistry, Geophysics, Geosystems* 12.
- Wu, X., Lemay-Tougas, M., de Vernal, A., Garneau, M., Fréchette, B., Audet, T., Hillaire-Marcel, C., 2023. Multi-proxy reconstruction of climate changes in the Lower St. Lawrence Estuary, Canada, during the Middle and Late-Holocene. *The Holocene* 33, 1346–1361.
- Wu, X., de Vernal, A., Fréchette, B., Moros, M., Perner, K., 2022. The signal of climate changes over the last two millennia in the Gulf of St. Lawrence, eastern Canada. *Quaternary Research* 106, 28–43.
- Yamamoto, A., Abe-Ouchi, A., Shigemitsu, M., Oka, A., Takahashi, K., Ohgaito, R., Yamanaka, Y., 2015. Global deep ocean oxygenation by enhanced ventilation in the Southern Ocean under long-term global warming. *Global Biogeochemical Cycles* 29, 1801–1815.
- Zhang, Y.G., Liu, X., 2018. Export depth of the TEX₈₆ signal. *Paleoceanography and Paleoclimatology* 33, 666–671.
- Zhang, Y.G., Zhang, C.L., Liu, X.L., Li, L., Hinrichs, K.U., Noakes, J.E., 2011. Methane Index: A tetraether archaeal lipid biomarker indicator for detecting the instability of marine gas hydrates. *Earth and Planetary Science Letters* 307, 525–534.
- Zhao, J., An, C., Longo, W.M., Dillon, J.T., Zhao, Y., Shi, C., Chen, Y., Huang, Y., 2014. Occurrence of extended chain length C₄₁ and C₄₂ alkenones in hypersaline lakes. *Organic Geochemistry* 75, 48–53.
- Zheng, Y., Heng, P., Conte, M.H., Vachula, R.S., Huang, Y., 2019. Systematic chemotaxonomic profiling and novel paleotemperature indices based on alkenones and alkenoates: Potential for disentangling mixed species input. *Organic Geochemistry* 128, 26–41.

Zheng, Y., Huang, Y., Andersen, R.A., Amaral-Zettler, L.A., 2016. Excluding the di-unsaturated alkenone in the U_{37}^K index strengthens temperature correlation for the common lacustrine and brackish-water haptophytes. *Geochimica et Cosmochimica Acta* 175, 36–46.