# Paleoceanographic reconstructions across the Plio-Pleistocene from clumped isotope thermometry

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Til Øyvind og Olav,

min lille familie

# Scientific environment

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We did it!

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# Abstract

The application of clumped isotope thermometry ($\Delta_{47}$) to foraminifera offers a novel approach for estimating past ocean temperatures. Unlike many other paleothermometers, this method provides temperature estimates that are unaffected by changes in the chemical composition of seawater, making it a particularly powerful tool for reconstructing past temperatures on million-year timescales. In this PhD thesis, clumped isotope thermometry is utilized to constrain deep sea and surface ocean temperatures during several intervals over the past 5 million years, which includes the warm Pliocene and the onset of major Northern Hemisphere glaciations. The $\Delta_{47}$-based temperature reconstructions are combined with foraminiferal Mg/Ca-based estimates measured on the same samples to validate both absolute values and assess relative changes in temperature across the Plio-Pleistocene.

In the first paper, paired benthic foraminiferal $\Delta_{47}$ and Mg/Ca measurements from two sites in the deep Pacific and North Atlantic were used to investigate bottom water temperatures (BWTs) during Marine Isotope Stage (MIS) M2 (3.312–3.264 million years ago, Ma) and the first half of the mid-Piacenzian Warm Period (mPWP, 3.264–3.025 Ma). The results show that a large BWT gradient of up to ~4°C between the deep Atlantic and Pacific oceans existed throughout the study interval, with the deep North Atlantic significantly warmer, and likely saltier, than at present. These data demonstrate that the physical properties of the Late Pliocene deep ocean were less spatially homogeneous than at present and suggest a fundamentally different mode of deep ocean circulation and/or mixing compared to the modern ocean. Furthermore, we resolve a bottom water cooling in both basins during MIS M2 with an amplitude strongly suggesting that the large changes in benthic foraminiferal $\delta^{18}O$ associated with this event reflect a change the deep ocean temperature rather than ice volume as has previously been suggested.

In the second paper, MIS M2 surface cooling was reassessed with clumped isotope thermometry at two sites in the North Atlantic (IODP Site U1308 and U1313). Planktic foraminiferal $\Delta_{47}$-based temperatures was compared to existing alkenone- and Mg/Ca-based estimates from the same sites to better constrain both absolute temperatures and

the relative changes associated with MIS M2. To further investigate the spatiotemporal cooling patterns during this event, a globally distributed set of new and existing sea surface temperature (SST) records was compiled. The results show that the mid-to-high latitudes of both hemispheres cooled by 2–4°C during MIS M2. These results contrast with previous suggestions of a distinct change in Atlantic northward heat transport as the key driver behind MIS M2 cooling — as this should have also provided a concurrent pattern of Southern Hemisphere warming — but they are in good agreement with the observations in the first paper that deep water sourced from both hemispheres cooled during MIS M2. Nevertheless, we find that relatively warm conditions still prevailed during MIS M2, with global SSTs as warm or warmer than in the Late Holocene. North Atlantic SSTs were up to ~5°C warmer than the Late Holocene, arguing against a large Northern Hemisphere glacial advance during MIS M2.

The third paper combines new and published benthic foraminiferal $\Delta_{47}$- and Mg/Ca-based BWT records from Pacific Site 849 to investigate the long-term thermal evolution of the deep Pacific over the last 5 million years. A key finding of this study is that the mPWP may have been the coldest interval of the Pliocene in the deep Pacific, challenging the characterization of this interval as globally warm. Furthermore, comparison of the Site 849 record to available constraints from the deep North Atlantic shows that a large deep ocean temperature gradient between the two basins existed for most of the Late Pliocene, before temperatures converged between 2.7–2.6 Ma — in agreement with previous findings. However, our records also show that a large gradient (~3°C) immediately reemerged between 2.6–2.5 Ma and intermittently up until at least 2.0 Ma. This suggests that that the reorganization of heat between the two basins at the Plio-Pleistocene transition represented a short-lived event rather than a permanent state change, and that a modern-like thermal structure in the Pacific and Atlantic was only established in the last ~2.0 Ma.

To summarize, the three thesis papers provide new insights on evolution and variability of Plio-Pleistocene climate and highlight the usefulness of the multi-proxy approach of combining foraminiferal $\Delta_{47}$ and Mg/Ca to reconstruct past ocean temperatures. While

Mg/Ca provides the possibility of resolving relative temperatures changes at high resolution, $\Delta_{47}$ provides a critical cross-check on the absolute values.

# Sammendrag

Bruk av isotopklyngetermometri ($\Delta_{47}$) på foraminiferer er en relativt ny tilnærming for å estimere havtemperaturer tilbake i tid. I motsetning til mange andre paleotermometre gir denne metoden temperaturer som er upåvirket av endringer i den kjemiske sammensetningen av sjøvann, noe som gjør den til et særlig egnet verktøy for å rekonstruere havtemperaturer over lange, geologiske tidsskalaer. I denne doktorgradsavhandlingen brukes isotopklyngetermometri for å gjenskape dyphavs- og havoverflatetemperaturer i flere intervaller over de siste 5 millioner årene. I tillegg ble $\Delta_{47}$-baserte estimater kombinert med Mg/Ca målt på de samme prøvene for å validere både absolutte temperaturer og vurdere relative temperaturendringer over studieintervallet.

I den første artikkelen kombineres $\Delta_{47}$ og Mg/Ca målt på bentiske foraminiferer fra to dyphavslokaliteter i Nord-Atlanteren og Stillehavet for å undersøke bunnvannstemperaturer i isotoptrinn (MIS) M2 (3.312–3.264 millioner år siden, Ma) og første halvdel av mPWP (3.264–3.025 Ma). Resultatene viser at en stor temperaturgradient eksisterte mellom dypvannsmassene i Stillehavet og Atlanterhavet gjennom studieintervallet, der det dype Atlanterhavet var betraktelig varmere og sannsynligvis saltere enn i dag. Dataene viser at dypvannsmassene i de ulike havbassengene hadde betraktelig mer ulike fysiske egenskaper i sen-Pliocen enn i dag, og antyder en fundamentalt annerledes dyphavssirkulasjon eller vannmassemiksing enn i det moderne havet. Videre viser vi at en nedkjøling observert i begge dyphavsbassengene under isotoptrinn M2 tyder på at de store endringene i bentisk $\delta^{18}O$ som karakteriserer dette intervallet reflekterer temperaturendringer i dyphavet i stedet for kraftig isvekst på land.

I den andre artikkelen ble overflatenedkjølingen i isotoptrinn M2 på to lokaliteter i Nord-Atlanteren (IODP Site U1308 og U1313) revurdert med $\Delta_{47}$ utført på planktiske foraminiferer. Disse temperaturene sammenlignes med eksisterende Mg/Ca- og alkenone-baserte overflatetemperaturdata fra de samme lokalitetene. I tillegg ble det globale nedkjølingsmønsteret i forbindelse med denne hendelsen undersøkt ved å samle nye og eksisterende temperaturdata. Resultatene viser 2–4°C med nedkjøling på

middels høye og høye breddegrader på både den nordlige og sørlige halvkule. Disse resultatene står i kontrast til tidligere forslag om en kraftig endring i varmetransport til høye nordlige breddegrader som nøkkeldriveren bak nedkjølingen i isotoptrinn M2 — da dette burde gitt en oppvarming på den sørlige halvkule. Derimot støtter disse resultatene opp under funnene fra artikkel en, som viser at dypvann produsert på høye breddegrader i både nord og sør ble nedkjølt samtidig. Til tross for denne nedkjølingen var forholdene under isotoptrinn M2 relativt varme. Globale havoverflatetemperaturer forble like varme eller varmere enn i sen-holocen. Særlig var Nord-Atlanteren karakterisert av varme forhold, med havoverflatetemperaturer opp til 5°C varmere enn i holocen, noe som også argumenterer mot stor isutbredelse på den nordlige halvkule på dette tidspunktet.

Den tredje artikkelen kombinerer nye og publiserte $\Delta_{47}$- og Mg/Ca-baserte bunnvannstemperaturer fra en lokalitet i Stillehavet for å undersøke temperaturutviklingen av det dype Stillehavet over de siste 5 millioner årene. Et sentralt funn fra denne studien er at mPWP kan ha vært det kaldeste intervallet i pliocen i det dype Stillehavet, noe som utfordrer den klassiske tolkningen av klimaet i dette intervallet som globalt varmt og stabilt. Sammenligning med rekonstruerte dypvannstemperaturer fra Nord-Atlanteren viser at den store temperaturgradienten mellom de to dyphavsbassengene forsvant mellom 2.7 og 2.6 million år siden, i samsvar med tidligere funn. I motsetning til tidligere studier viser derimot vår sammenligning at en stor temperaturgradient (~3°C) gjenoppsto umiddelbart etterpå mellom 2.6 og 2.5 millioner år siden, og også periodevis frem til for 2 millioner år siden. Dette antyder at omorganiseringen av varme mellom de to havbassengene for 2.7 millioner år siden var en kortvarig hendelse snarere enn en permanent endring, og at en permanent, moderne temperaturstruktur i Stillehavet og Atlanterhavet først ble etablert i løpet av de siste 2 millioner år. For å oppsummere gir alle de tre artiklene ny innsikt i utviklingen og variabiliteten til klima i plio-pleistocen, og fremhever hvordan kombinasjonen av $\Delta_{47}$- og Mg/Ca målt på foraminiferer gir robuste estimater av havtemperaturer. Mens Mg/Ca gir mulighet for å undersøke relative temperaturendringer med høy oppløsning, gir $\Delta_{47}$ en kritisk kryssjekk av de absolutte verdiene.

## List of Publications

**Paper I**

**Braaten, A. H**., Jakob, K. A., Ho, S. L., Friedrich, O., Galaasen, E. V., De Schepper, S., Wilson, P. A. and Meckler, A. N.: Limited exchange between the deep Pacific and Atlantic oceans during the warm mid-Pliocene and MIS M2 “glaciation”, *Clim. Past*, accepted, 2023. [Enclosed within this thesis is the accepted version of the manuscript]

**Paper II**

**Braaten, A. H**., Galaasen, E. V., Ho, S. L., Meinicke, N., Jakob, K. A., Friedrich, O., De Schepper, S., Wilson, P. A. and Meckler, A. N.: Global response to the hypothesized ´failed initiation´ of Northern Hemisphere glaciation during Marine Isotope Stage M2 (~3.3 Ma). *Manuscript in preparation for Paleoceanography and Paleoclimatology.*

**Paper III**

**Braaten, A. H**., Friedrich, O., Galaasen, E. V., Jakob, K. A., Ho, S. L. and Meckler, A. N.: Pacific deep-sea temperature evolution across the Plio-Pleistocene. *Manuscript in preparation.*

**Appendix I**

Friedrich, O., Jakob, K. A., Ho, S. L., **Braaten, A. H**., Bahr, A., Wilson, P. A., Pross, J., Scholz, C., Rheinberger, S., and Meckler, A. N. Significant Northern Hemisphere glaciation before 2.6 Ma as evidenced by Pacific temperature records. *Manuscript in preparation.*

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# 1. Introduction

## 1.1 Rationale

Global climate is currently warming at an alarming rate, and temperatures are projected to continue to increase in the future. The Intergovernmental Panel on Climate Change (IPCC) documents overwhelming evidence that human activities have changed the climate, and that limiting global warming to 1.5°C will be impossible unless there are large, rapid, and sustained reductions in anthropogenic greenhouse emissions (IPCC, 2023). Continued global warming is projected to lead to reductions in global ice sheet and sea-ice extent, rising sea levels, and an increase in the frequency and intensity of extreme weather events (IPCC, 2023). Understanding how the climate system has operated under similarly warm conditions in the past is key for our ability to accurately predict the global effects of this warming in the future. Under moderate greenhouse gas emission scenarios (e.g. Representative Concentration Pathway 4.5; RCP4.5), future climate is estimated to reach conditions similar to those of the Pliocene epoch (5.33–2.58 million years ago; Ma) by the middle of the 21$^{st}$ century (Burke et al., 2018). Past periods of warmth such as the Pliocene thus represent useful case studies for understanding climate states similar to those we may soon face.

To characterize past climate states, we rely on reconstructing environmental variables from proxies preserved in the geological record. Deep-sea sediments, for example, are rich in information about the state of the overlying ocean. The ocean, in turn, plays an integral role in modulating Earth's climate by absorbing and distributing heat, carbon and water vapor around the globe, while its temperature mirrors that of the global mean on geological timescales (e.g. Goudsmit-Harzevoort et al., 2023). This allows us to use deep-sea sediments to reconstruct key variables of past climate states and understand the mechanisms and feedbacks that drive global climate change on various timescales.

Climate system information preserved in deep-sea sediments is mainly available in the form of (organic and inorganic) biological remains that were affected by and can now serve as a proxy for the environmental conditions in which they were formed. A number of different proxies can be used to reconstruct past ocean temperatures, each with their own set of strengths and limitations. Some proxy systems are limited to settings and/or intervals where the chemical composition can be well constrained, while others are complicated by vital effects and poorly understood biological controls. An example of an organic proxy is the alkenone unsaturation index ($U^{k'}_{37}$) (Prahl et al., 1988), which utilizes lipids produced by microalgae that can be preserved within sediments for millions of years, and is one of the most widely used methods for estimating past sea surface temperatures (SSTs). Uncertainties regarding the alkenone paleothermometer include the possible nonlinear $U^{k'}_{37}$-SST sensitivity at low and high ends of the calibration range (Conte et al., 1998; Sikes & Volkman, 1993), as well as the seasonality of production in many areas of the global ocean (Müller et al., 1998; Tierney & Tingley, 2018).

Calcium carbonate-based ($CaCO_3$) proxies such as the extent of Mg substitution in the carbonate (Mg/Ca; Nürnberg et al., 1996) and its oxygen isotopic composition ($\delta^{18}O$; e.g. Emiliani, 1954; Urey, 1947) hold the advantage that they can be applied to both benthic and planktic organisms (e.g., foraminifera) and can therefore be used to reconstruct conditions in both the surface and deep ocean. However, most of these temperature proxies suffer additional non-thermal influences, such as the chemical composition of the seawater that the $CaCO_3$ was precipitated in. The $\delta^{18}O$ of foraminiferal calcite is influenced by both temperature and the $\delta^{18}O$ of the seawater ($\delta^{18}O_{sw}$), the latter in turn strongly influenced locally by evaporation or input of freshwater, and globally by changes in ice volume (e.g. Pearson, 2012). Similarly, the ratio of Mg/Ca in foraminifera is influenced by the Mg/Ca of seawater ($Mg/Ca_{sw}$). While globally uniform at any given time, $Mg/Ca_{sw}$ is known to have changed on geological timescales. However, estimates of the magnitude of these changes across the Plio-Pleistocene, and therefore their influence on reconstructed temperature, varies considerably between studies (Coggon et al., 2010; Evans et al., 2016; Tierney et al., 2019). Additionally, this proxy can also be sensitive to the influence of secondary environmental factors such as pH and salinity (Evans et al., 2016; Gray & Evans, 2019; Hönisch et al., 2013; Lea et al., 1999).

Carbonate clumped isotope thermometry ($\Delta_{47}$) offers an alternative approach for estimating past ocean temperatures. This paleothermometer is based in the distribution of isotopes within the carbonate ions, and does not require knowledge of the composition of seawater (e.g. Eiler, 2011). The proxy therefore bypasses many of the systematic uncertainties limiting other proxies. However, the analytical uncertainty of this approach is large, and achieving a meaningful level of confidence requires a large extent of replication. For this reason, the application of this proxy in paleoceanographical studies has only relatively recently become viable, as methodological advances have substantially decreased sample amount requirements allowing for the applicability to small carbonate samples (Hu et al., 2014; Meckler et al., 2014; Müller et al., 2017; Petersen & Schrag, 2014; Schmid & Bernasconi, 2010). In this thesis, the clumped isotope paleothermometer is utilized to constrain deep sea and surface ocean temperatures during intervals select intervals over the last 5 million years, including the warm Pliocene and the major intensification of Northern Hemisphere glaciations. All the studies herein combine $\Delta_{47}$-based temperatures with Mg/Ca analyses conducted at higher resolution, allowing us to reliably constrain both absolute temperatures ($\Delta_{47}$) and relative changes at higher resolution (Mg/Ca).

## 1.2 Carbonate clumped isotope thermometry

The carbonate clumped isotope thermometer is based on the quantification of bonds between rare, heavy isotopes of carbon ($^{13}C$) and oxygen ($^{18}O$) within the crystal lattice of carbonate minerals (Eiler, 2007, 2011; Ghosh et al., 2006; Schauble et al., 2006). Because bonds between heavy isotopes have lower zero-point energies, the isotopic substitution of a lighter isotope for a heavier isotope increases the thermodynamic stability of a molecule (Urey, 1947). A small non-linearity in the stability of consecutive heavy isotope substitutions promotes the formation of multiply-substituted isotopologues at the expense of singly-substituted species (Eiler, 2007; Schauble et al., 2006). This thermodynamic preference for rare, heavy isotopes to bond within the same carbonate ion ($CO_3^{2-}$) increases with decreasing temperatures (Schauble et al., 2006; Urey, 1947). Therefore, the excess abundance of $^{13}C$-$^{18}O$ bonds relative to a stochastic (i.e. random) distribution can be utilized to determine the ambient temperature at the time of carbonate precipitation (Eiler, 2007; Ghosh et al., 2006; Schauble et al., 2006).

To quantify the relative abundance of $^{13}C$-$^{18}O$ bonds, the abundance of isotopologues with mass 47 (mostly $^{13}C^{18}O^{16}O$) is measured on $CO_2$ gas extracted through temperature-controlled phosphoric acid digestion of the carbonate material (Ghosh et al., 2006; Huntington et al., 2009). Results are reported as $\Delta_{47}$ (Eq. 1), a parameter defined as the temperature-dependent excess ratio (in ‰) between the measured mass 47 isotopologues relative to the stochastic distribution expected from the bulk composition (Eiler, 2007):

$$\Delta_{47} = \left[\left(\frac{R^{47}}{R^{47*}} - 1\right) - \left(\frac{R^{46}}{R^{46*}} - 1\right) - \left(\frac{R^{45}}{R^{45*}} - 1\right)\right] \times 1000 \qquad \text{(Eq.1)}$$

Where $R^{47}$, $R^{46}$, and $R^{45}$ are the measured ratios (relative to mass 44) of mass 47, 46 and 45, respectively, and $R^{47*}$, $R^{46*}$, and $R^{45*}$ are the expected ratios for a random distribution.

The analysis of clumped isotopes is technically demanding. The target isotopologue for clumped isotope analysis occurs in natural materials in extremely low abundances, and the temperature-dependent excess abundances relative to the stochastic distribution are subtle (Eiler, 2007, 2011). Extremely high precision is thus required to meaningfully analyze the $\Delta_{47}$ signal, typically requiring long measurement time and extensive replication. Furthermore, $\Delta_{47}$ is susceptible to interference from contaminants such as organics or sulfides and the method therefore requires rigorous purification of the analyte gas (e.g. Eiler, 2007, 2011). Clumped isotope measurements also require correction for two mass-spectrometer specific effects. Firstly, most mass spectrometers exhibit a small offset between the actual and measured $\Delta_{47}$, where the measured value is dependent on the bulk composition of the $CO_2$ gas. This non-linearity is caused by negative background effects on the Faraday collectors of the mass spectrometer, and can be corrected for through pressure baseline determination (Bernasconi et al., 2013; Fiebig et al., 2016; He et al., 2012). Secondly, composition-independent scale compression occurs as a result of some extent of reordering in the mass spectrometer source (Dennis et al., 2011; Huntington et al., 2009), and needs to be corrected for based on abundant measurements of standards with different $\Delta_{47}$ compositions.

Recent advances in methodological procedures have helped to further reduce inter-laboratory differences. These include the monitoring of backgrounds for pressure baseline corrections (Meckler et al., 2014), widespread use and interlaboratory standardization of carbonate standards (Bernasconi et al., 2018, 2021; Daëron et al., 2016) and use of updated IUPAC-recommended $^{17}O$ abundance correction parameters (Brand et al., 2010). The development of micro-volume analysis (Schmid & Bernasconi, 2010) and the long-integration duel inlet (LIDI) approach of Hu et al. (2014) has helped reduce sample size requirements, leading to increased applicability in many areas of paleoclimate research.

The strength of the carbonate clumped isotope thermometer lies in the purely temperature dependent nature of isotopic clumping. Because $\Delta_{47}$ is independent of the chemical composition of its parent water (Ghosh et al., 2006) it is a particularly powerful tool for reconstructing ocean temperatures in environments where seawater chemistry cannot be well constrained. Furthermore, the combination of $\Delta_{47}$-derived temperatures and oxygen isotopic composition of the carbonate — which is measured simultaneously — can be used to reconstruct seawater $\delta^{18}O$. This information, in turn, can be used to infer changes in global ice volume or local salinity. Additionally, the clumped isotope signature of both planktic and benthic foraminifera appear unaffected by biologically-controlled secondary ("vital") effects (Meinicke et al., 2020; Peral et al., 2018; Piasecki et al., 2019; Tripati et al., 2010). This represents a major advantage over the Mg/Ca and $\delta^{18}O$ paleothermometers, especially for the application in deep time intervals characterized by species that are now extinct. Finally, the primary clumped isotope signal in carbonates appears unaffected by solid-state reordering on timescales of $10^6$–$10^8$ years when subjected to temperatures less than ~100°C (Dennis & Schrag, 2010; Henkes et al., 2014), enhancing the confidence in the application of the $\Delta_{47}$ paleothermometer on million-year time scales. The main risk for paleoceanographic applications is thus likely diagenetic alteration of the primary $\Delta_{47}$ signal through processes that add secondary inorganic calcite or replace the original biogenic calcite (Leutert et al., 2019).

While clumped isotope thermometry is a highly powerful tool for paleoceanographic research, this method also has its own set of drawbacks. Due to the large analytical uncertainties associated with clumped isotope measurements, the amount of carbonate material needed to produce reliable temperature estimates is at least one order of magnitude larger than what is required for other carbonate-based proxies such as Mg/Ca. This limits the use of this method in certain settings where foraminiferal abundances are low, for instance at many high latitude locations. The highly time-intensive nature of the measurements and the relatively large analytical uncertainties makes the proxy less suited for resolving small and/or rapid changes in temperature. On Plio-Pleistocene timescales, the $\Delta_{47}$ paleothermometer offers a possibility to constrain absolute temperatures void of many of the uncertainties plaguing other proxies, and a particularly useful tool when complemented with other methods that are also able to resolve changes at higher resolution.

## 1.3 Evolution of Plio-Pleistocene climate

The past ~5.33 million years represents an interval of substantial changes in the global climate system. Over that interval, Earth has transitioned from the relatively warm Pliocene epoch (5.33–2.58 million years ago, Ma) to the cooler Pleistocene (2.58–0.011 Ma) characterized by Northern Hemisphere glacial-interglacial cycles (e.g. Lisiecki & Raymo, 2005; Mudelsee & Raymo, 2005; Fig. 1). The Early Pliocene (Zanclean; 5.33–3.6 Ma) is suggested to have been globally warm and stable, with global temperatures (Fedorov et al., 2013) and sea level (Dumitru et al., 2019; Grant et al., 2019; Rohling et al., 2014) greatly elevated compared to the present. During the Pliocene climatic optimum (4.4–4.0 Ma) — likely the warmest interval of the past ~5.33 Ma — reconstructed sea surface temperatures (SSTs) average ~4°C above pre-industrial (Fedorov et al., 2013). Compared to today, the Early Pliocene ocean appears to have been characterized by similar maximum temperatures in the topical warm

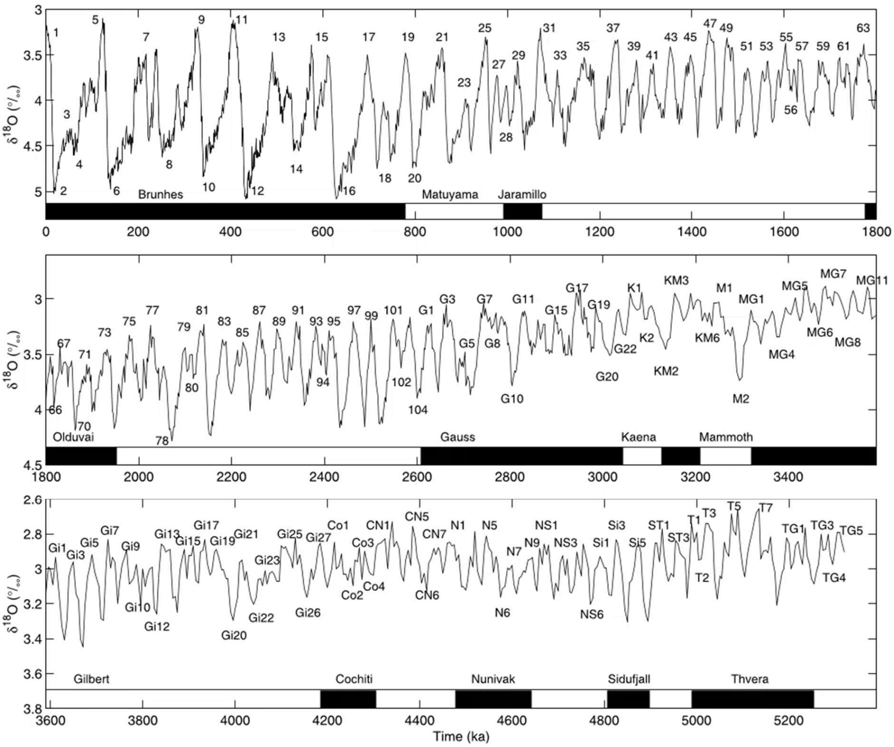


*Fig. 1: The global benthic foraminiferal $\delta^{18}O$ stack (LR04) showing changes in global ice volume and deep sea temperatures across the past 5.3 Ma. (Figure from Lisiecki & Raymo, 2005). Numbers and number-letter combinations refer to Marine Isotope Stages.*

pools, but substantially reduced zonal and meridional temperature gradients (Fedorov et al., 2013; Meinicke et al., 2021; Wara et al., 2005).

A long term transition towards bipolar glaciation started in the Late Pliocene (Piacenzian; 3.6–2.58 Ma), with increases in global ice volume (Lisiecki & Raymo, 2005; Mudelsee & Raymo, 2005) accompanied by a gradual decrease in atmospheric $CO_2$ (de la Vega et al., 2020; Martínez-Botí et al., 2015) and cooling surface temperatures (e.g., Herbert et al., 2010, 2016; Fig. 2). Superimposed on this cooling trend was the mid-Piacenzian Warm Period (mWPW, previously the mid-Pliocene Warm Period), a ~200 kyr interval of global warmth. At this time, globally averaged surface temperatures were elevated by 2–3°C compared to the pre-industrial (Haywood et al., 2020; McClymont et al., 2020), while sea-level estimates around ~20 meters above present suggests greatly reduced ice sheet extent in both hemispheres (Dumitru et al., 2019; Dwyer & Chandler, 2009; Grant et al., 2019; Rohling et al., 2014). Atmospheric $CO_2$ concentrations were broadly comparable to today (350–450 ppm; de la Vega et al., 2020 and references therein). The mPWP thus offers an opportunity to study a climate system in long-term equilibrium with modern or near-future atmospheric $CO_2$.

Compared to the rest of the Cenozoic, the paleogeography of the Late Pliocene was quite similar to today, with only a few ocean gateways not having fully reached their modern configurations (e.g., Cane & Molnar, 2001; Groeneveld et al., 2014; Otto-Bliesner et al., 2013). Yet, ocean circulation appears to have been notably different from that of the modern ocean. Today, deep water formation is inhibited in the subarctic North Pacific due to relatively fresh surface conditions (reviewed in Ferreira et al., 2018). In contrast, North Pacific Deep Water (NPDW) formation and Pacific Meridional Overturning Circulation (PMOC) have been proposed to have been active in the warm Pliocene (Burls et al., 2017; Ford et al., 2022; Shankle et al., 2021), with potentially important implications for heat and moisture transport and $CO_2$ sequestration in the deep ocean (Burls et al., 2017; Thomas et al., 2021). Thermohaline circulation in the Atlantic (Atlantic Meridional Overturning Circulation, AMOC) may have been more vigorous than at present in the Pliocene leading to enhanced northward heat transport in the Atlantic (e.g., Zhang et al., 2021).

Climatic conditions during much of the Late Pliocene were generally warmer than the present, but this interval also contains episodes of distinct climate variability, most notably, a short-lived and enigmatic cooling event during Marine Isotope Stage (MIS) M2 (3.312–3.264 Ma). Occurring immediately prior to the mPWP, this event represents the largest benthic foraminiferal oxygen isotope excursion of the Pliocene prior to the intensification of Northern Hemisphere Glaciation (Lisiecki & Raymo, 2005) and is marked by the appearance of ice-rafted debris (IRD) in the northern North Atlantic (Kleiven et al., 2002) and Arctic Ocean (Knies et al., 2014; Moran et al., 2006). While MIS M2 has been suggested to represent a large-scale Northern Hemisphere glaciation

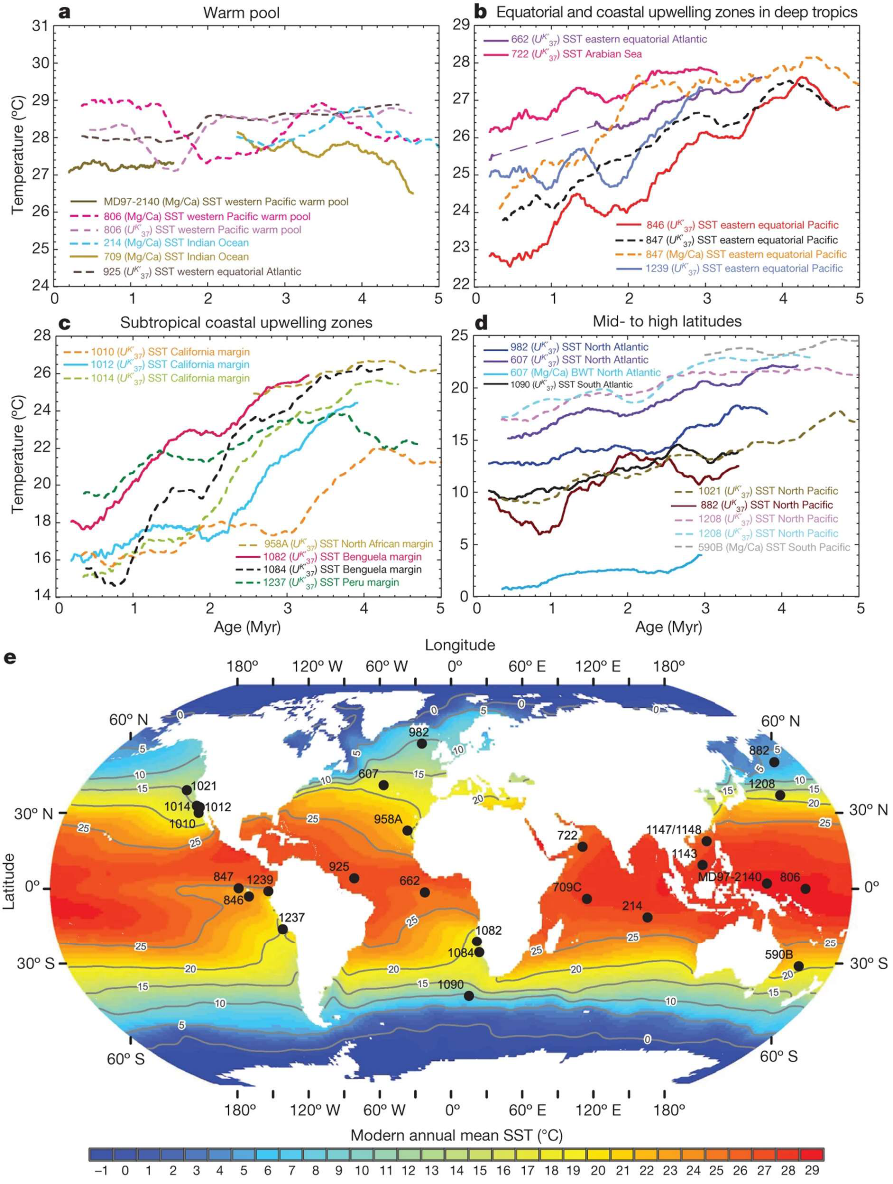


***Fig. 2****: (a-d) Temperature evolution in different regions of the ocean over the past 5 million years (e) map of site locations in a-d. Figure from Fedorov et al. (2013).*

(e.g. De Schepper et al., 2013), this contrasts with reconstructions of Holocene-like conditions at Lake El'gygytgyn (NE Russia; Brigham-Grette et al., 2013). Southern Ocean IRD records (McKay et al., 2012; Passchier, 2011) also record growth of the Antarctic ice sheet during MIS M2, opening for the possibility that most of the ice sheet expansion (corresponding to ~10–60 meter sea-level drop; Dwyer & Chandler, 2009; Naish & Wilson, 2009; Rohling et al., 2014) associated with this event may have instead occurred in the Southern Hemisphere (Brigham-Grette et al., 2013; Kirby et al., 2020; McClymont et al., 2023). While model scenarios suggest the possibility of large ice growth in both hemispheres (Dolan et al., 2015), more proxy data is needed to further constrain plausible scenarios for ice sheet growth during MIS M2 and deconvolve the signals embedded in the associated oxygen isotope excursion

# 2. Objectives

The overarching objective of this PhD project was to harness the potential of the clumped isotope ($\Delta_{47}$) thermometer to investigate long-standing questions about Plio-Pleistocene climate. The technique was applied to planktic and benthic foraminifera to reconstruct ocean temperatures during several intervals over the past 5 million years, with a particular focus on the mid-Piacenzian warm period (~3.3–3.0 Ma) and the Marine Isotope Stage (MIS) M2 cooling event (3.312–3.264 Ma). The $\Delta_{47}$-based estimates were combined with Mg/Ca data to validate both absolute values and assess relative changes in temperature across the Plio-Pleistocene.

The specific objectives were to:

i) Use paired measurements of benthic foraminiferal Mg/Ca and $\Delta_{47}$ to provide robust constraints on mid-Piacenzian bottom water temperatures in the deep Pacific and Atlantic oceans and investigate the proposed existence of a large deep-sea temperature and salinity gradient between the two basins at that time (Paper I).

ii) Constrain the sea surface and bottom water temperature change associated with MIS M2 and assess the climate response and drivers for this cooling event (Papers I and II).

iii) Reconstruct the long-term thermal evolution of the deep Pacific across the Plio-Pleistocene using paired measurements of benthic foraminiferal Mg/Ca and $\Delta_{47}$ (Paper III).

# 3. Materials and Methods

## 3.1 Materials

Sediment samples were obtained from the core repositories of the Ocean Drilling Program (ODP) and Integrated Ocean Drilling program (IODP) from two different study sites; ODP Site 849 in the East Pacific and IODP Site U1308 in the North Atlantic (Fig. 3). Additional samples from IODP Sites U1308 and U1313 (Fig. 3) covering Marine Isotope Stage M2 were provided by collaborators. Coordinates and water depths for each study site are provided in Table 1.

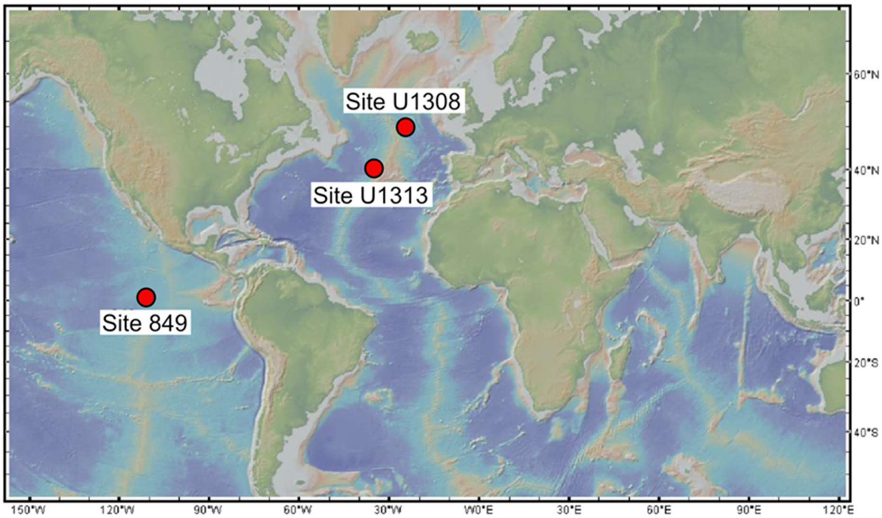


***Fig. 3:*** *Locations of ODP/IODP sites investigated as part of this PhD project. The bathymetric map was generated using GeoMapApp (Ryan et al., 2009).*

ODP Site 849 in the deep (~3800 m) Equatorial East Pacific (EEP) was chosen for bottom water temperature reconstructions for Papers I (3.33–3.16 Ma) and III (5–0 Ma) as it has been suggested to approximate mean deep Pacific conditions (Kwiek & Ravelo, 1999; Mix et al., 1995). Given the size of this basin, the deep Pacific in turn is likely the best approximation of the global deep ocean. Furthermore, given the water depth of Site 849, it is unlikely to have been affected by North Pacific Deep Water (NPDW) which is suggested to have formed throughout much of the Pliocene but existed as a mid-depth water mass with a core at ~1500 meters (e.g., Burls et al., 2017; Ford et al., 2022). Site 849 also benefits from excellent age control, high sedimentation rates and good foraminiferal test preservation in the Plio-Pleistocene (Jakob, Ho, et al., 2021; Jakob, Pross, et al., 2021). For the Pacific-Atlantic BWT comparison in Paper I, we chose deep North Atlantic Site U1308 as complement to the data from the Pacific. This site was selected as it is one of very few North Atlantic sites of comparable depth that i) extends through to the Pliocene, ii) had available and reliable age constraints for much of the study interval and iii) contained abundant and well-preserved foraminiferal tests.

*Table 1: Locations, water depths and paper references for the sites investigated as part of this PhD project.*

| **Site** | **Latitude** | **Longitude** | **Depth (m)** | **Paper ref.** |
|---|---|---|---|---|
| ODP 849 | 0°11’N | 110°31’W | 3851 | Papers I and III |
| IODP U1308 | 49°52’N | 24°14’W | 3871 | Papers I and II |
| IODP U1313 | 40°00’N | 32°52’W | 3412 | Paper II |

For Paper II, we reconstructed MIS M2 $\Delta_{47}$-based SSTs from Site U1308 and U1313, both situated in the North Atlantic. High-resolution $U^{k'}_{37}$ and planktic foraminiferal Mg/Ca records were already available from these sites (De Schepper et al., 2013; Naafs et al., 2010, 2012), making these sites ideal locations to compare temperature estimates from different proxies and try to resolve existing discrepancies. For example, the Site U1313 Mg/Ca and $U^{k'}_{37}$ records are in very good agreement in the intervals before and after MIS M2 but diverge by as much as ~5°C during the height of the cooling event. It has previously been suggested that this proxy offset may represent transient shifts in seasonality or depth habitat of the foraminifera (De Schepper et al., 2013). By measuring $\Delta_{47}$ on the same species of planktic foraminifera used for Mg/Ca analysis, we can constrain absolute temperatures during MIS M2, and test whether the observed offset with $U^{k'}_{37}$ represents differences in habitat and/or seasonality, or the effect of non-thermal influences on one of the other records.

## 3.2 Sample preparation and clumped isotope analysis

All newly obtained samples were dried, weighed and wet-sieved to remove the <63 μm size fraction, and then dry-sieved to isolate the size fractions used for analyses (150–250 and 250–355 μm). Specimens of benthic (Papers I and III) and planktic (Paper II) foraminifera were picked from the dried sediment fractions under a light microscope. Prior to clumped isotope analyses, foraminiferal tests were cleaned to remove any potential contaminants. To achieve this, tests were carefully cracked open between two glass plates to expose individual chambers. The crushed tests were subsequently cleaned through several ultrasonication-steps in deionized (DI) water and methanol. After each ultrasonication step, samples were rinsed with DI water. The cleaned samples were removed of excess water and oven dried at 50°C over night.

Clumped isotope measurements were performed at the Facility for advanced isotopic research and monitoring of weather, climate and biogeochemical cycling (FARLAB), at the Department of Earth Science, University of Bergen, using two different Thermo Scientific MAT 253Plus dual inlet mass spectrometers coupled to Kiel IV carbonate devices. The Kiel devices were fitted with PoraPak traps in order to capture potential organic contaminants (see Schmid & Bernasconi, 2010). The traps were heated to 150°C for at least one hour between runs for cleaning. Four carbonate standards (ETH 1–4, Bernasconi et al., 2018) were used for correction (ETH 1–3) and to monitor instrument performance and accuracy of the corrections (ETH 4). Each analytical run consisted of a roughly 1:1 ratio of carbonate standards and samples. A micro-volume measurement approach (Hu et al., 2014; Meckler et al., 2014; Müller et al., 2017; Schmid & Bernasconi, 2010) was utilized, where many replicate measurements (typically 25–30) of small subsamples (~ 100 μg) were pooled together to produce final

$\Delta_{47}$ values. Depending on foraminiferal abundances, measurements from one or more individual samples were grouped together for each temperature. All temperatures were calculated from averaged $\Delta_{47}$ using the combined foraminifera-based calibration of Meinicke et al. (2020) updated by Meinicke et al. (2021). Further details regarding study sites, age models, geochemical analyses and data correction are provided in the individual manuscripts in this thesis (Papers I–III).

# 4. Summary of Papers

**Paper I**: *Limited exchange between the deep Pacific and Atlantic oceans during the warm mid-Pliocene and MIS M2 "glaciation".*

In Paper I, we present benthic foraminiferal Mg/Ca- and $\Delta_{47}$- based bottom water temperature estimates from North Atlantic IODP Site U1308 and Equatorial East Pacific ODP Site 849. These new records cover Marine Isotope Stage (MIS) M2 and the first half of the mid-Piacenzian Warm Period. We demonstrate that a large temperature gradient (up to 4°C) existed between the two basins throughout the study interval, and that the deep North Atlantic was considerably warmer and likely saltier than today. Our results thus indicate that the deep Pacific and Atlantic oceans were bathed by water masses with distinctly different physical properties during the mid-Piacenzian. This pattern contrasts with the modern deep ocean, which is characterized by deep waters that are much more spatially uniform in temperature and salinity. The mid-Piacenzian appears to have been characterized by a fundamentally different mode of ocean circulation and/or mixing in the mid-Piacenzian compared to the modern ocean, where salt and heat is efficiently distributed from the Atlantic into the deep Pacific. Our records also provide compelling new insights into the MIS M2 cooling event. We demonstrate that BWTs in both basins cooled by 3–4°C during this event, accounting for most of the benthic foraminiferal $\delta^{18}O$ ($\delta^{18}O_b$) signal associated with MIS M2. The highly resolved Mg/Ca record from Site 849 shows that this severe cooling of the deep Pacific lagged $\delta^{18}O_b$ by up to 20 kyr but was in-phase with a relatively large (~100 ppm) decrease in atmospheric $CO_2$. We speculate that the early increase in $\delta^{18}O_b$, lacking a synchronous drop in temperature, represents an increase in global ice volume — likely of a magnitude at the lower end of estimates of sea level drop associated with MIS M2 — and that the subsequent increase in $\delta^{18}O_b$ reflects cooling of the deep ocean. Furthermore, we suggest that the concurrent decrease in $CO_2$ was the main driver of the observed deep-sea cooling.

**Paper II**: *Global Response to the Hypothesized 'Failed Initiation' of Northern Hemisphere Glaciation During Marine Isotope Stage M2 (~3.3 Ma).*

In paper II, we use planktic foraminiferal $\Delta_{47}$ to reassess MIS M2 surface cooling at two sites in the North Atlantic (IODP Sites U1308 and U1313). We compare the new data with existing alkenone and Mg/Ca records from the same sites to better constrain both absolute temperatures and the relative change associated with MIS M2. The good agreement between $\Delta_{47}$ and $U^{k'}_{37}$-based estimates in the intervals where both diverge from Mg/Ca argues against habitat or seasonal differences as the reason for these discrepancies, and suggest that secondary factors (e.g. salinity/pH) may have influenced the Mg/Ca records. To further investigate the spatiotemporal cooling pattern during MIS M2, we compiled a global set of new and existing proxy records. Relative to the preceding interglacial (MIS MG1), we find that the mid-to-high latitude surface ocean of both hemispheres cooled by 2–4°C. Further, we find that there was little temperature change in the tropics and subtropics, despite a large (~100 ppm) decline in atmospheric $CO_2$. Despite the widespread cooling, temperatures remained as warm or warmer than during the late Holocene. Conditions were particularly warm in the North Atlantic, where MIS M2 temperatures remained up to ~5°C warmer than the late Holocene, which is difficult to reconcile with suggestions of a large Northern Hemisphere glacial advance at that time. This may indicate that ice-growth during MIS M2 was largely constrained to the Antarctic ice-sheet.

Comparison between the compiled SST records and the sub-millennial resolution BWT record from Site 849 (Paper I), reveals an apparent lag of up to 20 kyr between the onset of North Atlantic surface cooling and the subsequent cooling of Pacific deep waters sourced from the high southern latitudes. We suggest that the North Atlantic cooled first — in response to changes in North Atlantic circulation and frontal positions, and further amplified by orbital forcing — but that the later drawdown of $CO_2$ and resulting global-scale cooling was key for the full climate response and its expression in global benthic $\delta^{18}O$ records.

**Paper III**: *Pacific deep-sea temperature evolution across the Plio-Pleistocene.*

In paper III, we present deep Pacific bottom water temperatures from ODP Site 849 for five times-slices across the Pliocene and Pleistocene from benthic foraminiferal Mg/Ca and $\Delta_{47}$. These new data are combined with — and provide a long-term perspective for — higher resolution records from the same site reported in Paper I and a co-authored manuscript in preparation (Appendix I) covering the interval 3.3–2.0 Ma. The study furthermore compares the long-term evolution of deep Pacific temperatures with available constraints from the deep North Atlantic. Our records indicate that average temperatures in the deep Pacific have cooled by ~3°C since the Early Pliocene, with much of that cooling occurring in the interval immediately following the Plio-Pleistocene transition. A key finding of this study is that the Late Pliocene may represent a period of more variable deep ocean temperatures, and thus climate, than has traditionally been suggested. Intriguingly, the combined records from Site 849 show that the mPWP, often used as a prime example for a warm climate state, may represent the coldest interval of the Pliocene in the deep Pacific. This finding is consistent with observations of cool mPWP temperatures in the deep North Pacific and in the Ross Sea, suggesting that it likely reflects advection of a Southern Ocean cooling. Comparison of the Site 849 records to constraints from the North Atlantic reveals inverse BWT trends between the two basins during the interval 3.3–2.7 Ma, with large (up to 4°C) temperature gradients persisting for most of that time. We find that deep sea temperatures in the Pacific and North Atlantic converged between 2.7–2.6 Ma, a feature first noted by Woodard et al. (2014) and interpreted by those authors to indicate a redistribution of heat between the two basins that contributed to the intensification of Northern Hemisphere Glaciation. However, we find that a large gradient of up to 3°C immediately reemerged between 2.6–2.5 Ma and existed intermittently until at least 2.0 Ma, suggesting that the reorganization of heat between the two basins just prior to the Plio-Pleistocene boundary represented a short-lived event rather than a permanent state change.

# 5. Synthesis and Outlook

Advances in clumped isotope ($\Delta_{47}$) thermometry over the past decade — particularly related to reduction of sample size requirements — have opened for the application of this method to foraminifera and many new avenues of paleoceanographic research. In this thesis, the clumped isotope paleothermometer was applied to benthic and planktic foraminifera to reconstruct ocean temperatures across intervals spanning the Pliocene and Pleistocene, with a particular focus on the mid-Piacenzian warm period (~3.264–3.025 Ma) and the Marine Isotope Stage (MIS) M2 cooling event (3.312–3.264 Ma). A general theme echoed in all three papers is the robustness and synergies provided by the multi-proxy approach of combining foraminiferal Mg/Ca and $\Delta_{47}$ in temperature reconstructions. While Mg/Ca allows resolving relative temperatures changes at high resolution, $\Delta_{47}$ provides a critical cross-check on the absolute values that also helps eliminate (or, as exemplified in the SST comparison in Paper II, reveal) lingering uncertainties.

In Paper I, we pair benthic foraminiferal $\Delta_{47}$ and Mg/Ca temperatures from two sites in the Pacific and North Atlantic to investigate deep sea temperatures during MIS M2 and the first half of the mid-Piacenzian Warm Period. Earlier BWT reconstructions for this interval have provided ambiguous results, with different studies suggesting North Atlantic temperatures were either similar to today (Cronin et al., 2005; Dwyer et al., 1995; Dwyer & Chandler, 2009) or significantly warmer (Bartoli et al., 2005; Sosdian & Rosenthal, 2009), while the deep North Pacific was suggested to have been colder than at present (Woodard et al., 2014). One challenge has been, however, that the Mg/Ca data presented in the different studies were based on different species, calibrations and correction choices, leaving open questions regarding the comparability of the records. Our Mg/Ca records at both sites were generated on the same species and the data were treated identically, making the records more directly comparable than those in previous studies. In addition, $\Delta_{47}$ measured on the same samples provide a critical independent check on absolute temperatures. The data confirm that a large temperature gradient of up to ~4°C between the deep Atlantic and Pacific oceans existed in the mid-Piacenzian, with the North Atlantic significantly warmer than at present, and thus suggest that the

Pliocene deep ocean was less homogeneous in temperature than it is today. These results underline the importance for well constrained and directly comparable data (in terms of methodology, calibrations, and various adjustments such as for $Mg/Ca_{sw}$) when assessing records from different sites and basins. They also highlight that care should be exercised when interpreting data from individual sites in a global context — at least for the Pliocene. Reconstructed deep-sea temperatures in the geological past are typically interpreted to representative of the mean ocean, and thus in turn for global mean surface temperatures (e.g. Goudsmit-Harzevoort et al., 2023; Hansen et al., 2013). In Papers I and III, we demonstrate that this was not the case for the Late Pliocene.

In Paper III, we demonstrate that a large temperature gradient existed between the deep North Atlantic and Pacific basins throughout the interval 3.3–2.7 Ma. Woodard et al. (2014) previously showed that this Pliocene Atlantic-Pacific BWT gradient was abruptly reduced to <1°C at 2.73 Ma and proposed a change in interhemispheric heat transport as a driver of iNHG. Our results agree that deep sea temperatures converged between 2.7–2.6 Ma, indicating a redistribution of heat from the Atlantic into the Pacific, but also show that a large gradient (~3°C) immediately reemerged between 2.6–2.5 Ma and existed intermittently up until at least 2.0 Ma. This suggests that that the reorganization of heat between the two basins represented a short-lived event rather than a permanent state change. As the high-resolution, deep Pacific Mg/Ca-based BTW record ends at 2.0 Ma, more work is needed to determine exactly when a modern-like thermal structure was fully established in the Pacific and Atlantic oceans. Similarly, more work is needed to constrain the timing of cessation of North Pacific Deep Water formation, as well as its influence on deep Pacific temperatures and potential significance on global circulation patterns throughout the Pliocene. Due to the dearth of Pliocene BWT data from either basin before 3.3 Ma it also remains highly uncertain when the large Atlantic-Pacific deep sea temperature gradient first appeared — and whether it was a strictly Late Pliocene phenomenon or a long-lasting feature of the Cenozoic climate system. Determining this could improve our mechanistic understanding of how this gradient was established, and further help identify how it affected global climate. Although not all ocean gateways had fully reached their modern configurations, many important boundary conditions including continental positions, major ocean currents and atmospheric $CO_2$ concentrations in the Pliocene were broadly similar to today (de la Vega et al., 2020; Haywood et al., 2013, 2020) — and almost certainly more similar than more distant intervals in the geological past. Extension of the currently available BWT records in both basins — with directly comparable, preferably multi-proxy records — through the Early Pliocene and beyond is needed to further investigate the climate conditions associated with large deep ocean temperature gradients and how they, in turn, impacted Earth System interactions.

Papers I and II provide new insights into the enigmatic MIS M2 cooling event. This event is associated with the largest benthic foraminiferal $\delta^{18}O$ excursion of the Pliocene prior to the onset of large-scale Northern Hemisphere glaciation, and it has been suggested that MIS M2 may mark an early onset of extensive bipolar glaciation. In Paper I, BWT records show that the deep Pacific and North Atlantic basins both cooled by up to 3–4°C during MIS M2. The amplitude of this cooling suggests that the changes in benthic foraminiferal $\delta^{18}O$ were mostly driven by temperature change in the deep ocean rather than ice volume.

In Paper II, we provide further constraints on the MIS M2 cooling event by presenting new planktic foraminiferal $\Delta_{47}$ temperatures from two North Atlantic sites and studying the global, spatiotemporal surface cooling patterns. We find that surface conditions during MIS M2 were as warm or warmer-than-present, and that conditions in the North Atlantic were particularly warm (up to 5°C warmer than the late Holocene). These findings are difficult to reconcile with a large proximal glacial advance and support the conclusion from Paper I that MIS M2 likely does not reflect a significant Northern Hemisphere glaciation.

We also observe a large temporal offset (~20 kyr) between the onset of North Atlantic surface cooling and substantial cooling of deep waters sourced from the high southern latitudes (from Paper I), the latter concurrent with a relative large drawdown of atmospheric $CO_2$ (de la Vega et al., 2020). Unfortunately, due the comparatively low resolution of most SST records from outside of the North Atlantic region, the timing of surface cooling at other locations is more ambiguous. Additional high-resolution SST records, particularly from the high southern latitudes would be helpful to further constrain the timing and sequence of events surrounding MIS M2. SST compilations akin to that provided in Paper II covering some of the early Pleistocene glacial-interglacial cycles (e.g., MIS 101-100) would also be useful to further constrain how climate perturbations evolved through the Plio-Pleistocene and to assess whether there was a common or changing sets of drivers and feedbacks involved.

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# Paper I

## Limited exchange between the deep Pacific and Atlantic oceans during the warm mid-Pliocene and MIS M2 "glaciation"

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## Abstract

The Piacenzian stage (3.6–2.6 Ma) of the Pliocene is the most recent period where Earth experienced sustained intervals of global warmth analogous to predicted near-future climates. Despite considerable efforts to characterize and understand the climate dynamics of the Piacenzian, the deep ocean and its response to this warming remains poorly understood. Here we present new mid-Piacenzian Mg/Ca and $\Delta_{47}$ ("clumped isotope") temperatures from the deep Pacific and North Atlantic oceans. These records cover the transition from Marine Isotope Stage (MIS) M2 — considered the most pronounced "glacial" stage of the Pliocene prior to the intensification of Northern Hemisphere glaciaion — to the warm KM5 interglacial. We find that a large (>4°C) temperature gradient existed between these two basins throughout that interval, with the deep North Atlantic considerably warmer and likely saltier than at present. We interpret our results to indicate that the deep Pacific and North Atlantic oceans were bathed by water masses with very different physical properties during the mid-Piacenzian, and that only limited deep oceanic exchange occurred between the two basins. Our results point to a fundamentally different mode of ocean circulation or mixing compared to the present, where heat and salt is distributed from the North Atlantic into the Pacific. The amplitude of cooling observed at both sites during MIS M2 suggests that changes in benthic $\delta^{18}O$ associated with this cold stage were mostly driven by temperature change in the deep ocean rather than ice volume.

## 1 Introduction

Our ability to predict future climate change in response to anthropogenic $CO_2$ emissions partially rests on our understanding of how the climate system has operated under similar conditions in the past. The Piacenzian stage of the Pliocene (3.6–2.6 million years ago, Ma) is the most recent interval in the geological past with sustained intervals of global warmth. The mid-Piacenzian warm period (mPWP, 3.264–3.025 Ma) in particular, has received considerable attention as a useful point of comparison for near-future climates (e.g. Burke et al., 2018). At this time, atmospheric $CO_2$ concentrations were comparable to the present (~350–450 ppm, de la Vega et al., 2020 and references therein) and many important tectonic and geographical boundary conditions were similar to today.

Considerable efforts have been made to characterize and understand the climate dynamics of the mPWP. Globally averaged surface temperatures were elevated by ~2–3 °C relative to the pre-industrial (McClymont et al., 2020; Haywood et al., 2020), with much of that warming concentrated in the high latitudes. Meanwhile, maximum temperatures in the tropical warm pools appear to have been comparable to today (~29 °C) (Wara et al., 2005; Meinicke et al., 2021), resulting in significantly reduced meridional temperature gradients. Sea-level rise of the magnitude proposed for the mPWP (~20 meters above present) (Dwyer and Chandler, 2009; Rohling et al., 2014; Grant et al., 2019; Dumitru et al., 2019) would require reduced ice sheet extent in both hemispheres. In equilibrium with $CO_2$ concentrations comparable to the early 21$^{th}$ Century, it appears that the climate of the mid-Piacenzian was warm enough to prevent growth of significant continental ice in the Northern Hemisphere (Dumitru et al., 2019).

Earth system models have largely been unable to simulate the full magnitude of Arctic amplification and reduced meridional temperature gradients implied by proxy reconstructions (Dowsett et al., 2012; Salzmann et al., 2013; de Nooijer et al., 2020), suggesting that key feedback mechanisms for the mPWP may be underestimated or missing in these models. Increased poleward heat transport, decreased ice-albedo and feedbacks related to cloud-cover are some of the mechanisms proposed to have contributed to Pliocene warmth (Fedorov et al., 2006), but a full understanding of the processes that caused and maintained these conditions is still missing.

While climatic conditions of the Piacenzian were typically warm, this stage also contains distinct climate variability. Most notably, it includes a short-lived but pronounced "glacial" event during Marine Isotope Stage (MIS) M2 (3.312–3.264 Ma) immediately prior to the mPWP. MIS M2 is the largest positive benthic oxygen isotope excursion (~0.6 ‰) in the Pliocene prior to the intensification of Northern Hemisphere glaciation (iNHG) (Lisiecki and Raymo, 2005), and has been suggested to represent an early, “failed attempt” at establishing a pattern of Northern Hemisphere glacial-interglacial cycles (Haug and Tiedemann, 1998). Estimates of sea-level fall associated with this event vary greatly, ranging from ~10 to 65 meters below present level (Dwyer and Chandler, 2009; Naish and Wilson, 2009; Miller et al., 2012). To what extent the oxygen isotope event reflects ice growth on land versus cooling of the deep ocean, however, remains a topic of debate.

The deep ocean plays an integral role in modulating climate on long and short timescales, acting as a major reservoir for heat and $CO_2$ that responds to and affects surface conditions. Although the Pliocene deep ocean remains poorly characterized, with available temperature records sparse and occasionally contradictory, existing reconstructions suggest the deep ocean could have operated differently than today. In the North Atlantic, available data suggest average mPWP bottom water temperatures (BWTs) were either similar to today (Dwyer et al., 1995; Cronin et al., 2005; Dwyer and Chandler, 2009) or significantly warmer (Bartoli et al., 2005; Sosdian and Rosenthal, 2009). The deep North Pacific, however, may have been — on average — colder than today during the mPWP (Woodard et al., 2014). Based on comparison of this North Pacific record (Site 1208, 3346 meters water depth) with North Atlantic BWTs from Site 607 (3426 meters water depth, Sosdian and Rosenthal, 2009), Woodard et al. (2014) conclude that a large bottom water temperature gradient of up to 4 °C existed between the two basins in the Pliocene prior to the iNHG at ~2.7 Ma. In comparison, the modern deep ocean is relatively isothermal across the various basins, with only a ~1°C difference between the deep (>3000 meters) Atlantic, Pacific and Indian Oceans (Locarnini et al., 2013) (Fig. 1). The existence of a strong temperature gradient in the Pliocene would have important implications for characterising ocean circulation and global climate, determining for example where heat resided in the climate system and the route and efficiency of heat transport. A growing number of studies have suggested that the North Pacific Ocean was a site of deep convection and deep water formation (North Pacific Deep Water, NPDW) (Burls et al., 2017; Shankle et al., 2021; Ford et al., 2022) in the warm Pliocene. If true, this would leave open the possibility that the records of Woodard et al. (2014) from Shatsky Rise, which suggest colder-than-present temperatures during the mPWP, are recording a local North Pacific signal rather than representing the deep Pacific as a whole.

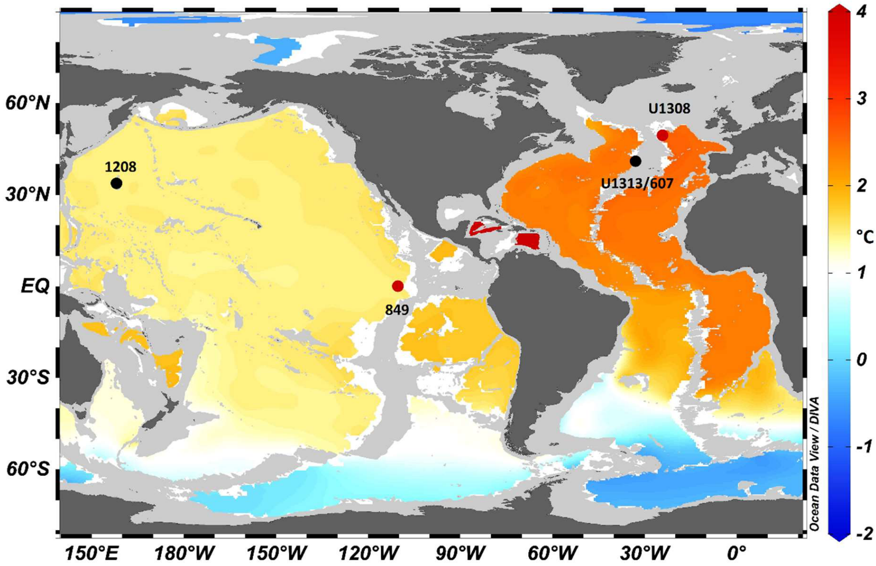



***Figure 1.*** *Modern water temperatures at 3800 meters water depth with locations of sites used (in red) and referenced (in black). Temperature data from the World Ocean Atlas 2013 (Locarnini et al., 2013). Map generated in Ocean Data View (ODV 5.6.3, Schlitzer, 2023).*

Available BWT records from the mid-Piacenzian have exclusively been based on Mg/Ca thermometry. The Mg/Ca paleothermometer is influenced by a number of non-thermal effects that complicate the application of this proxy, which could explain some of the discrepancies observed between various Pliocene BWT records. Mg/Ca ratios of epifaunal benthic foraminifera can be affected by changes in carbonate ion saturation state (Elderfield et al., 2006; Lear et al., 2010), and it has been suggested that the North Atlantic Mg/Ca-based temperature record by Sosdian and Rosenthal (2009) was compromised by such effects (Yu and Broecker, 2010). Additionally, strong vital effects have been documented in foraminifera — making species-specific calibrations necessary (i.e. Lear et al., 2002), and some of the Mg/Ca-based estimates are from ostracods, possibly explaining discrepancies from foraminiferal records. Furthermore, seawater Mg/Ca ($Mg/Ca_{sw}$), while globally uniform at any given time, changes on geological timescales (e.g. Wilkinson and Algeo, 1989; Dickson, 2004; Coggon et al., 2010). Adjustments for this change on long time scales have been applied since the first applications of the Mg/Ca BWT proxy (Lear et al., 2000), but estimates of the magnitude of change — and thus its effect on reconstructed temperatures — varies between studies (Evans et al., 2016; Tierney et al., 2019).

A novel approach for estimating BWTs in the Pliocene is carbonate clumped isotope ($\Delta_{47}$) thermometry of benthic foraminifera. This paleothermometer is based on the thermodynamic preference for rare, heavy isotopes to bond within the same carbonate ion with decreasing temperatures, and involves measuring the excess abundance of $^{13}C$-$^{18}O$ bonds relative to their stochastic abundance (Ghosh et al., 2006; Schauble et al., 2006). This proxy produces temperature estimates that are independent of the chemical composition of the parent water (e.g. Eiler, 2011), making it a particularly powerful tool for reconstructing ocean temperatures in environments where the composition of seawater cannot be well constrained. Furthermore, no detectable species-specific vital effects have been found for benthic foraminifera (Tripati et al., 2010; Peral et al., 2018; Piasecki et al., 2019). While $\Delta_{47}$ is a highly useful proxy for reconstructing absolute temperatures, the large quantities of carbonate sample material required for reliable temperatures coupled with the large analytical uncertainties and time-intensive nature of the measurements, makes it less suited for high-resolution work.

To address the discrepancies between currently available deep-sea temperature records for the mid-Piacenzian and assess the existence of a large temperature gradient between the Pacific and Atlantic basins we present new paired benthic foraminiferal Mg/Ca and $\Delta_{47}$ temperatures from Ocean Drilling Program (ODP) Site 849 in the deep Equatorial East Pacific and Integrated Ocean Drilling Program (IODP) Site U1308 in the deep North Atlantic. The records cover the interval from Marine Isotope Stage (MIS) M2 — considered the most pronounced "glacial" stage of the Pliocene prior to iNHG — to the warm interglacial MIS KM5c, which has a near identical orbital configuration to the present and thus possibly offers the best analogue for our current climate (i.e. Haywood et al., 2013). This allows us to not only compare mean deep-sea temperatures in the

Pacific and Atlantic basins, but also to investigate the variability over key warming and cooling stages of the Piacenzian. Because Mg/Ca records at both sites were generated on the same shallow-infaunal benthic foraminiferal species (*Oridorsalis umbonatus*), and samples and data were treated identically, the records are more directly comparable than those of previous studies. $\Delta_{47}$ temperatures measured on the same samples provide an independent check on absolute Mg/Ca temperatures, bypassing uncertainties related to seawater chemistry or species effects. In combination, the two proxies provide robust constraints on bottom-water temperatures in the deep Pacific and North Atlantic for the mid-Piacenzian and allows us to examine if changes in benthic $\delta^{18}O$ associated with MIS M2 are caused by temperature or ice volume.

# 2 Materials and Methods

## 2.1 Materials, site locations and sample processing

### 2.1.1 ODP Site 849

ODP Site 849 is situated on the western flank of the East Pacific Rise (Fig. 1) (0°11’N, 110°31’W) at a water depth of 3851 meters (Mayer et al., 1992). It is today bathed by Pacific Deep Water (PDW), a water mass largely consisting of Antarctic Bottom Water (AABW), with smaller contributions from Antarctic Intermediate Water (AAIW) and recirculated North Atlantic Deep Water (NADW) (Mix et al., 1995; Kwiek and Ravelo, 1999). This study site was chosen as it is considered to approximate mean deep Pacific conditions, and is suggested to have been permanently bathed by Southern Component Waters (SCW) throughout the Plio-Pleistocene (Mix et al., 1995). Although the present day water depth at Site 849 sits below the modern eastern equatorial lysocline at ~3400 (Berger et al., 1982) the site has remained above the carbonate compensation depth for the past 34 Ma (Pälike et al., 2012). Previous studies have concluded that this site exhibits good foraminiferal test preservation, excellent age control and high sedimentation rates across our study interval (Jakob et al., 2021a, Jakob et al., 2021b, see also Fig. S1). We investigated samples along the primary shipboard splice, from cores 849D-8H-5-6 cm to 849D-8H-6-96 cm and 849C-9H-1-46 cm to 849C-9H-3-18 cm (87.67–92.77 meters composite depth, mcd), corresponding to 3.160–3.334 Ma on the updated age model of Jakob et al. (2021b). A total of 248 (20 $cm^3$) samples were collected at 2-cm intervals, and the material was dried, weighed and washed over a 63 µm sieve. Tests of the benthic foraminifer *O. umbonatus* were picked from the >150 µm dried sediment fraction for Mg/Ca analysis. In addition, remaining benthic foraminifera were picked from selected samples (n=44, >150 µm fraction) for clumped isotope analysis.

### 2.1.2 IODP Site U1308

IODP Site U1308 constitutes a reoccupation of Deep Sea Drilling Project (DSDP) Site 609, a benchmark location for late Pleistocene North Atlantic climate records. Site U1308 is situated on the eastern flank of the Mid-Atlantic Ridge (Fig. 1) (49°52'N, 24°14'W) at a water depth of 3871 meters (Expedition 303 Scientists, 2006). Today, this site is bathed by Lower North Atlantic Deep Water (LNADW) and Lower Deep Water (LDW), with LDW consisting of a mixture of 70–80 % NADW and 20–30% AABW (Arhan et al., 2003). Site U1308 was chosen as it is situated at the same depth as our Pacific site and exhibits good foraminiferal test preservation for our target interval (see suppl. information and Fig. S2).

We investigated samples from cores U1308C-25H-5-80 cm to U1308C-26H-6-71.5 cm (253.81–264.71 mcd). Very little work has been done on this portion of the sequence because it falls below the primary shipboard splice (0–248 mcd, ~0–3.1 Ma). However, an age model and benthic foraminiferal (*Cibicidoides wuellerstorfi* and *Uvigerina peregrina*) stable isotope data are available for a short interval from 258.95–264.71 mcd, corresponding to MIS M2 (De Schepper et al., 2013). To extend this record, 53 (20 $cm^3$) samples were collected at 10 cm spacing from 253.81–259.01 mcd. The new samples were dried, weighed and washed over a 63 µm sieve. The >150 µm sediment fraction of each of these samples was picked for *O. umbonatus* and *C. wuellerstorfi*/*Cibicidoides mundulus* for Mg/Ca and stable isotope analysis, respectively. The interval from 258.95–264.71 mcd was sampled by De Schepper et al. (2013) at a higher resolution, on average every 5 cm (n=113). These samples were picked for *O. umbonatus* for Mg/Ca analysis. Furthermore, remaining benthic foraminifera were picked from 34 samples (>150 μm) across the full study interval for clumped isotope analysis.

## 2.2 Methods

### 2.2.1 Stable isotope analysis and age model for Site U1308

Stable isotope ($\delta^{18}O$ and $\delta^{13}C$) analyses were performed on both *C. wuellerstorfi* and *C. mundulus*, as neither species was present continuously throughout the entire study interval. Prior to analysis, foraminiferal tests were ultrasonicated in methanol for 15 seconds to remove fine-grained particles. Analyses were carried out at the Facility for Advanced Isotopic Research and Monitoring of Weather, Climate and Biogeochemical Cycling (FARLAB), Department of Earth Science, University of Bergen, using a Finnigan MAT 253 mass spectrometer coupled to a Kiel IV carbonate device. Measurements were performed on 1–3 tests and replicated two or more times when abundances allowed (~76% of the 47 samples measured). Six samples did not contain enough material for analysis. The long-term reproducibility (1σ) of the in-house working standard (CM12, Carrara marble) during the analysis window was 0.03‰ and 0.06‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively. Results are reported relative to Vienna Pee Dee Belemnite (VPDB), calibrated using National Bureau of Standards (NBS)-19 and crosschecked with NBS-18. We detect no systematic variations in oxygen isotopic offsets between the two species and present the data as an averaged composite record. An apparent inter-lab offset between previously the published benthic foraminiferal $\delta^{18}O$ ($\delta^{18}O_b$) of De Schepper et al. (2013) and our new record was observed. We adjust for this offset by adding 0.29‰ to the values reported in De Schepper et al. (2013) (see supplementary information and Fig. S3 for details).

For Site U1308, a continuation of the existing age model by De Schepper et al. (2013) was established for the interval from 253.81–258.95 mcd by tuning our new $\delta^{18}O_b$ record to the LR04 benthic foraminiferal oxygen isotope stack (Lisiecki and Raymo, 2005) using the software program QAnalySeries 1.5.0.(Kotov and Pälike, 2018). Minor adjustments were also made to the existing age model between 258.95–264.71 mcd. The updated tie-points used for the age model are presented in Table 1.

***Table 1. Tie-points used for the updated age model of IODP U1308***

| Depth (mcd) | Age (Ma) |
|---|---|
| 254.66 | 3.207 |
| 256.77 | 3.240 |
| 261.11 | 3.284 |
| 262.35 | 3.302 |
| 263.25 | 3.320 |
| 263.38 | 3.327 |
| 264.70 | 3.340 |

## 2.2.2 Mg/Ca temperatures

The benthic foraminiferal species *O. umbonatus* was used for Mg/Ca analysis at both sites. This species was selected because i) it is well buffered against the influence of changes in deep ocean carbonate ion/pH due to its shallow-infaunal habitat (Rathmann and Kuhnert, 2008; Lear et al., 2015), ii) it contains large chambers that can be thoroughly cleaned for Mg/Ca analysis, and iii) it exhibits low sensitivity to temporal variations in the Mg/Ca of seawater (Lear et al., 2015). Furthermore, core top measurements of this species from Site 849 (Jakob et al., 2021a) and North Atlantic Site U1313 (Jakob et al., 2020 suppl. information), have produced Mg/Ca temperatures that are indistinguishable from modern BWTs at the respective sites. These core top studies treated materials identically to our Pliocene samples.

Foraminiferal tests were cracked, homogenized and cleaned following the cleaning protocol of Barker et al. (2003) with the reductive cleaning step omitted to avoid decreasing their Mg/Ca ratios (Barker et al., 2003; Rosenthal et al., 2004). Samples were measured using an Agilent Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) 720 at the Institute of Earth Sciences, Heidelberg University. Reported Mg/Ca values have been normalized relative to the ECRM 751-1 standard (Greaves et al., 2008). Fe/Ca and Mn/Ca ratios were screened to identify potential contamination from clays or coatings that were not removed in the cleaning process (see suppl. information and Fig. S4–S5 for details). Fe/Ca and Mn/Ca ratios were not normalized as the Fe and Mn concentrations of the ECRM standard typically were below the detection limit of the ICP-OES. The ECRM standard was measured at least every 20$^{th}$ sample to monitor instrumental precision. Based on these replicate measurements, the standard deviation for Mg/Ca is ± 0.02 mmol/mol and ± 0.03 mmol/mol for Site 849 and Site U1308 samples, respectively.

Bottom water temperatures were calculated using the *O. umbonatus*-specific calibration by Lear et al. (2002):

$$T = \left[\ln \frac{Mg/Ca}{1.008}\right] \times \left[\frac{1}{0.114}\right] \qquad (1)$$

This calibration is based on multiple, globally distributed core tops, making it applicable to both study sites. Furthermore, the calibration temperature range of 0.8–9.9 °C covers the temperature range we expect to find in the mid-Pliocene deep ocean. Because this calibration was based on data from materials cleaned following a procedure that includes a reductive step, measured Mg/Ca was adjusted downwards by 10% to account for this difference (Barker et al., 2003; Ford et al., 2016). Values were also adjusted to account for past variation in Mg/Ca$_{sw}$ following Lear et al. (2002) using estimates of past Mg/Ca$_{sw}$ from Evans et al. (2016). Uncertainties associated with our Mg/Ca-based BWT record were calculated using the Paleo-Seawater Uncertainty Solver (PSU Solver) MATLAB script of Thirumalai et al. (2016).

### 2.2.3 $\Delta_{47}$ temperatures

Before clumped isotope ($\Delta_{47}$) analysis, foraminiferal tests were carefully cracked open to expose the inside of individual chambers. The broken open tests were ultrasonicated for 10 s in DI water, then 10 s in methanol, followed by another two ultrasonication steps with DI water. Samples were rinsed with DI water after each ultrasonication. Cleaned samples were oven-dried at 50°C until any remaining water was fully evaporated. Scanning electron microscope (SEM) images (Fig. S1 and S2) were taken from a random selection of cleaned samples to verify i) that cleaning had fully removed potential contaminants and ii) that tests were well-preserved (see suppl. information).

Clumped isotope measurements were performed using two different Thermo Scientific MAT 253Plus mass spectrometers coupled to Kiel IV carbonate devices, located at FARLAB, Department of Earth Science, University of Bergen. The analytical approach is described in detail by Meckler et al. (2014), Piasecki et al. (2019) and Meinicke et al. (2020). To remove potential organic contaminants, the Kiel devices were equipped with PoraPak traps which were held at -20°C during runs. The traps were baked at 150°C for at least one hour between runs for cleaning. A mix of samples and carbonate standards in a roughly 1:1 ratio was measured in each analytical run. Micro-volume aliquots (70-100 µg) were individually reacted with phosphoric acid (at 70°C) in the Kiel device, and the resulting gas was subsequently measured using the long-integration dual-inlet method (LIDI, Hu et al. 2014) for a total of 400 s. Raw data were corrected for pressure baseline effects based on five daily peak scans (5–25 V, Meckler et al. 2014). Using carbonate standards ETH 1–3, the data were further corrected for scale compression and transferred to the I-CDES scale (Bernasconi et al., 2021). Standard data from the same and adjacent days were used for data correction, using a moving window approach. All data correction was done using the Easotope software package (John and Bowen, 2016).

Due to the large analytical uncertainty associated with individual $\Delta_{47}$ measurements, extensive replication (preferably a minimum of 25–30 measurements) is required to produce reliable temperatures. A large number of benthic foraminiferal species were used to obtain sufficient amounts of sample material (2–4 mg) needed per $\Delta_{47}$ temperature. Whenever possible, measurements were performed on aliquots of species- or genus-specific materials. Replicate measurements (n=23–40) from 2–9 adjacent samples were combined to produce each data point. Temperatures were calculated from these averaged $\Delta_{47}$ values using the combined foraminifera-based calibration by Meinicke et al. (2020), updated to the I-CDES scale by Meinicke et al. (2021):

$$T = \sqrt{\frac{0.0397 \times 10^6}{\Delta^{47} - 0.1518}} - 273.15 \qquad (2)$$

With temperatures given in °C.

The combined analytical and calibration uncertainty was calculated using a Monte Carlo approach (5000 iterations) that samples a random slope-intercept pair for the calibration and a random $\Delta_{47}$ value generated from the analytical error and is expressed as 95% confidence intervals on the average temperatures.

### 2.2.4 Seawater $\delta^{18}O$

Seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$) was calculated from $\delta^{18}O_b$ in combination with the BWT from Mg/Ca using the *Cibicidoides* and *Planulina* compilation (Eq. 9) from Marchitto et al. (2014):

$$\delta^{18}O_{sw} = [0.245 \times T] - [0.0011 \times T^2] + \delta^{18}O_b - 3.31 \qquad (3)$$

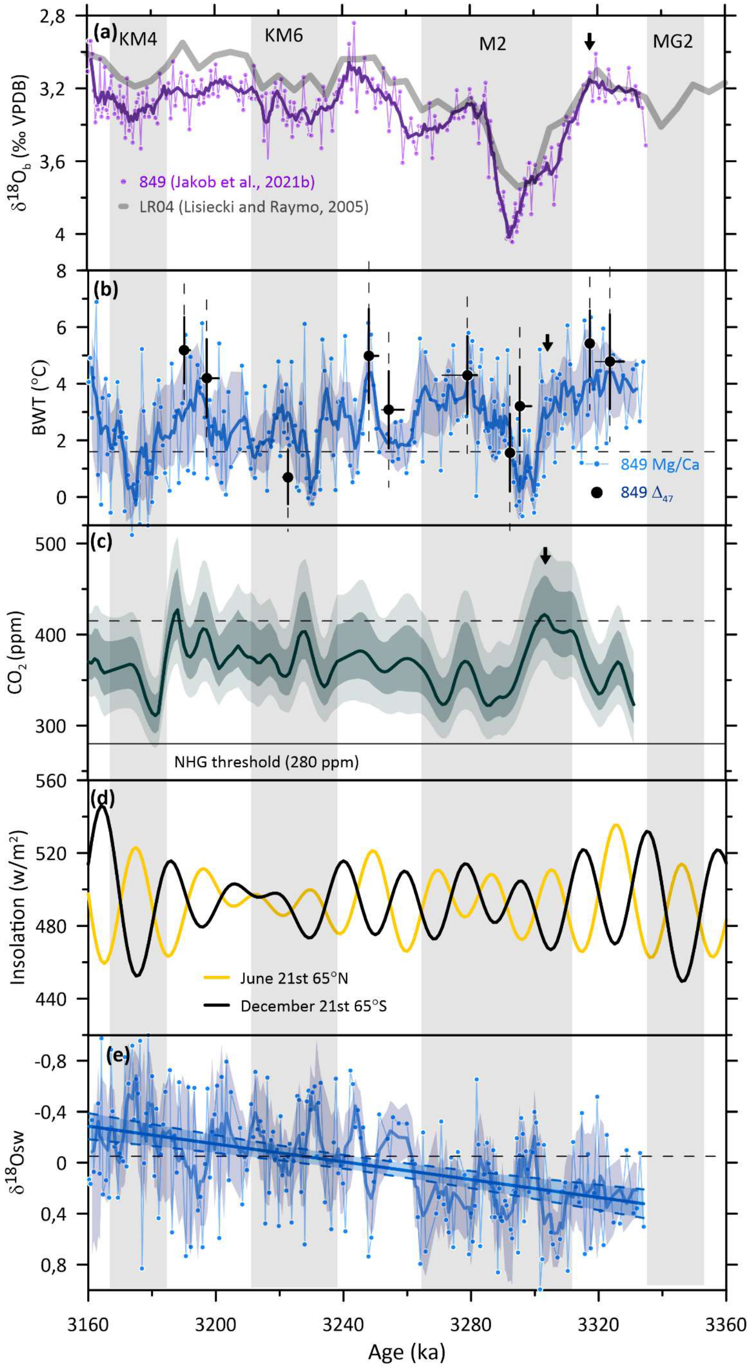
Due to the good agreement between the absolute temperatures suggested by the two proxies at both sites (see results), we calculate $\delta^{18}O_{sw}$ from BWT estimates from Mg/Ca, not $\Delta_{47}$, as i) the Mg/Ca records are of significantly higher resolution and ii) the propagated (2σ) uncertainties associated with individual Mg/Ca measurements (±1.2°C and ±1.5°C for 849 and U1308 samples respectively) are smaller than those for the $\Delta_{47}$-based temperature estimates (average of ±2.7°C at both sites). For $\delta^{18}O_{sw}$ calculation we use the published $\delta^{18}O_b$ from Jakob et al. (2021b, generated on *O. umbonatus*) for Site 849 and for Site U1308 the combined record from this study (*C. wuellerstorfi* and *C. mundulus)* and De Schepper et al. (2013) (*C. wuellerstorfi* and *Uvigerina peregrina*), with a +0.29‰ correction of values from the latter (see suppl. Information). To account for species-specific offsets, we normalize measured $\delta^{18}O_b$ of *O. umbonatus* and *Uvigerina spp*. to *Cibicidoides* by subtracting 0.64‰ (Shackleton et al., 1984), allowing us to apply Eq. 3 to all samples.

# 3 Results

## 3.1 Pacific Site 849

A total of 233 Mg/Ca measurements were carried out for the interval 3.334–3.160 Ma, yielding a mean temporal resolution of 800 yr. The five-point moving average of Mg/Ca-based BWTs ranges between -0.3°C and 4.6°C (Fig. 2b) while individual values vary from -1.3°C to 6.9°C. The average uncertainty (2σ) associated with the Mg/Ca-based temperatures is ±1.2°C. The equation used to calculate these temperatures has a calibration range of 0.8–9.9 °C (Lear et al., 2002). In total, 42 (~5%) of our measurements fall below this range (-1.3–0.8°C) and are therefore associated with greater uncertainty than the remainder of the record. However, the same would also be true for all other currently available *O. umbonatus*-specific Mg/Ca calibrations (see Jakob et al., 2021a and references therein for a review).

The average Mg/Ca-based temperature over the study interval is ~2.5±1.2°, ~1°C warmer than present BWT at this site (1.6°C, Locarnini et al., 2013) but large changes in BWT are observed throughout the record. Peak temperatures (>4°C) are recorded during all the studied interglacial (as defined from $\delta^{18}O_b$) Marine Isotope Stages (MG1, M1, KM5 and KM3). We observe strong cooling (by ~4°C) associated with the large positive $\delta^{18}O_b$ excursion during MIS M2, although the cooling appears significantly delayed relative to the signal in $\delta^{18}O_b$. Cooling of similar amplitude is also recorded for KM6 and KM4, Marine Isotope Stages not appearing as pronounced glacial stages in benthic oxygen isotope records (Fig. 2a and b).



(a)
KM4
KM6
M2
MG2
δ18Ob (‰ VPDB)
849 (Jakob et al., 2021b)
LR04 (Lisiecki and Raymo, 2005)
(b)
BWT (°C)
849 Mg/Ca
849 Δ47
(c)
CO2 (ppm)
NHG threshold (280 ppm)
(d)
Insolation (w/m2)
June 21st 65°N
December 21st 65°S
(e)
δ18Osw
Age (ka)

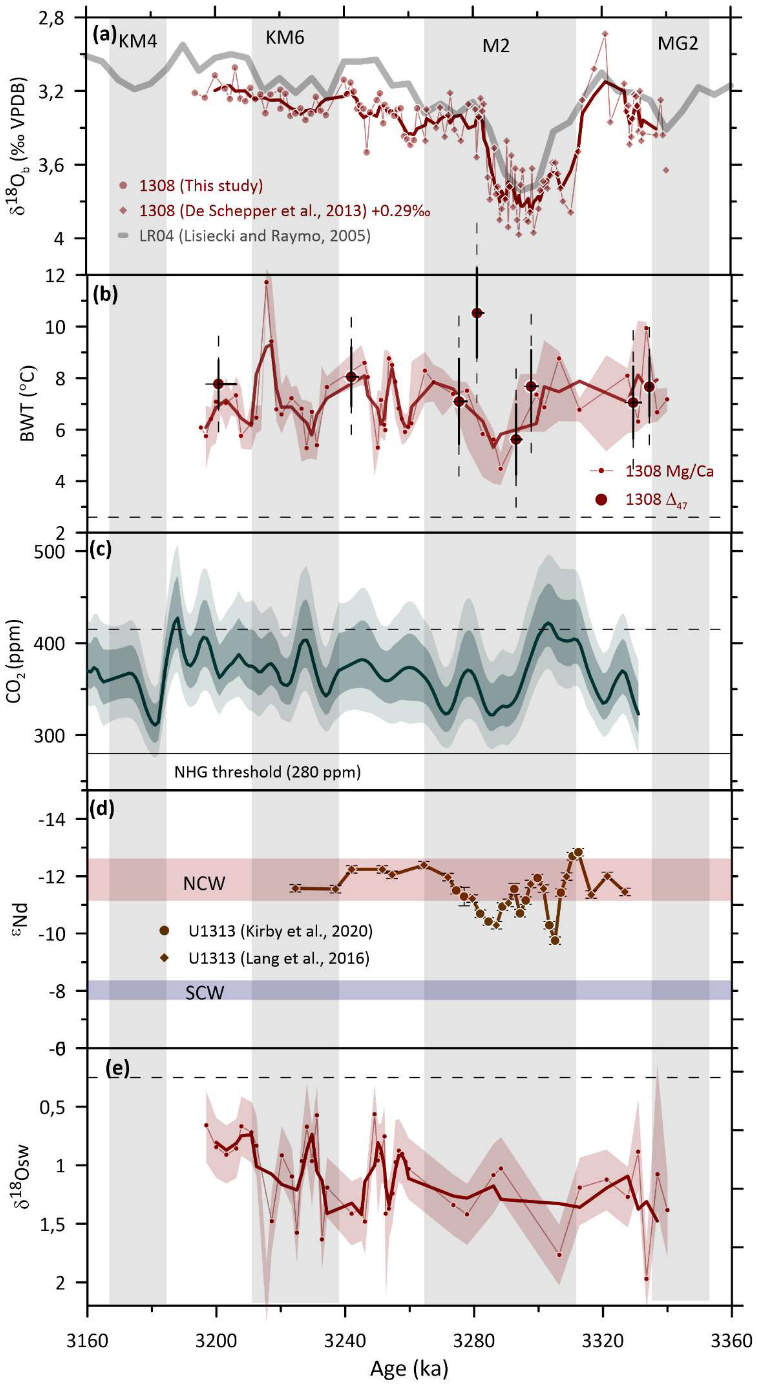
***Figure 2.*** *Climate indicators and results from Pacific ODP Site 849. All horizontal stippled lines indicate modern values ($CO_2$ = 2022). (a) Benthic foraminiferal $\delta^{18}O$ from Site 849 (Jakob et al. 2021b, shown with 5pt running mean) and global benthic foraminiferal $\delta^{18}O$ stack (Lisiecki and Raymo, 2005). (b) 849 temperature records. Mg/Ca temperatures shown with 5pt running mean. Horizontal error bars on $\Delta_{47}$ temperatures indicate the age range of all individual samples used for each data point. Temperature uncertainties are expressed as solid (68% CI) and stippled (95% CI) bars. (c) Interpolated 1 ka resolution $\delta^{11}B$-derived $CO_2$ estimates from de la Vega et al. (2020). Confidence intervals expressed as dark (68%) and light (95%) shading. (d) Summer insolation forcing at 65°N and 65°S (Laskar et al., 2004). (e) calculated $\delta^{18}O_{sw}$, shown with a linear regression to highlight the overall trend (shading = 95% CI). Note arrows indicating the temporal offsets in the increase in $\delta^{18}O_b$ and decrease in temperature and $CO_2$. Shaded envelopes on Mg/Ca temperatures and $\delta^{18}O_{sw}$represent 2σ uncertainties modelled with PSU solver (Thirumalai et al., 2016)*

Ten clumped isotope temperatures were generated over the interval from 3.328–3.189 Ma (Fig. 2b), with each data point representing an average over 23–40 replicate measurements from 2–9 adjacent samples (time interval spanned indicated by horizontal bars in Fig. 2b). $\Delta_{47}$-based BWTs range from 0.7±1.9°C to 5.4±2.3°C (95% CI). The average $\Delta_{47}$-based BWT over the studied interval is 3.5±0.8°C.

Our calculated $\delta^{18}O_{sw}$ record (Fig. 2e) indicates an average value of ~0.0±0.3‰ (2σ) (present bottom water $\delta^{18}O_{sw}$ at Site 849: -0.05‰, LeGrande and Schmidt, 2006) over the study interval. Although $\delta^{18}O_{sw}$ is variable, there is a clear trend of decreasing values over the record — values are higher before and during MIS M2 than afterwards. Average $\delta^{18}O_{sw}$ from 3.334–3.264 Ma (MIS M2 and MG1) is ~+0.3‰. Between 3.263 and 3.160 Ma (MIS M1–KM3), the average $\delta^{18}O_{sw}$ is ~-0.1‰.

## 3.2 North Atlantic Site U1308

A total of 49 Mg/Ca measurements were performed for the interval ~3.334–3.196 Ma, yielding a mean temporal resolution of ~3 kyr. The three-point smoothed average of Mg/Ca-based bottom-water temperatures ranges from 5.3–9.3°C, with individual values between 4.5–11.7°C (Fig. 3b). The average uncertainty (2σ) associated with the Mg/Ca-based temperatures is ±1.5°C. A single measurement (11.7°C) falls outside the calibration temperature range of 0.8–9.9°C. The average BWT across the study interval is ~7.2±1.5°C, approximately 4.5°C warmer than the present BWT at this site



(a)
KM4
KM6
M2
MG2
2,8
3,2
3,6
4
δ18Ob (‰ VPDB)
1308 (This study)
1308 (De Schepper et al., 2013) +0.29‰
LR04 (Lisiecki and Raymo, 2005)
(b)
12
10
8
6
4
2
BWT (°C)
1308 Mg/Ca
1308 Δ47
(c)
500
400
300
CO2 (ppm)
NHG threshold (280 ppm)
(d)
-14
-12
-10
-8
-6
εNd
NCW
U1313 (Kirby et al., 2020)
U1313 (Lang et al., 2016)
SCW
(e)
0,5
1
1,5
2
δ18Osw
3160
3200
3240
3280
3320
3360
Age (ka)

***Figure 3.*** *Climate indicators and results from North Atlantic IODP Site U1308. All horizontal stippled lines indicate modern values ($CO_2$ = 2022). (a) Benthic foraminiferal $\delta^{18}O$ from Site U1308 (shown with 3pt running mean and global benthic foraminiferal $\delta^{18}O$ stack. (b) U1308 temperature records Mg/Ca temperatures shown with 3pt running mean. Horizontal error bars on $\Delta_{47}$ temperatures indicate the age range of all individual samples used for each data point. Temperature uncertainties are expressed as solid (68% CI) and stippled (95% CI) bars. (c) Interpolated 1 ka resolution $\delta^{11}B$-derived $CO_2$ estimates from de la Vega et al. (2020). Confidence intervals expressed as dark (68%) and light (95%) shading. (d) fish debris Nd isotope data from North Atlantic IODP Site U1313 (Lang et al., 2016; Kirby et al., 2020). Estimates of SCW and NCW end-member $\varepsilon_{Nd}$ composition following Lang et al., (2016). (e) calculated $\delta^{18}O_{sw}$ shown with a linear regression to highlight the overall trend (shading = 95% CI ). Shaded envelopes on Mg/Ca temperatures and $\delta^{18}O_{sw}$ represent 2σ uncertainties modelled with PSU solver (Thirumalai et al., 2016).*

(2.6°C, Locarnini et al., 2013). The coldest temperatures of the record are reached during MIS M2, but similar temperatures are also reconstructed for MIS KM6. However, the temporal resolution across the most intense $\delta^{18}O_b$ excursion of MIS M2 is low, and our record may underestimate the temperature change associated with this event.

Eight clumped isotope temperatures were generated for the interval from 3.335–3.199 Ma (Fig. 3b), each calculated from an average of 27–34 replicate measurements from 2–7 neighboring samples. $\Delta_{47}$-based BWTs range from 5.6±2.7°C to 10.5±3.4°C (95% CI), with both the warmest and coldest data points falling within different stages of MIS M2. The average $\Delta_{47}$-based BWT across the full study interval is 7.7±1.0°C (95% CI).

Our calculated record of $\delta^{18}O_{sw}$ (Fig. 3e) indicates an average of 1.1±0.3‰ (2σ) over the study interval, considerably higher than the present bottom water $\delta^{18}O_{sw}$ at Site U1308 of 0.25‰ (LeGrande and Schmidt, 2006). Similarly to Site 849, there is an apparent trend of decreasing values over the record — with somewhat higher $\delta^{18}O_{sw}$ before and during MIS M2 than afterwards. However, the significantly lower temporal resolution of the Site U1308 $\delta^{18}O_{sw}$ record makes this finding more uncertain than is the case for the Pacific.

# 4 Discussion

## 4.1 Comparison between Mg/Ca and $\Delta_{47}$ temperatures

Comparison of our Mg/Ca- and $\Delta_{47}$-based BWT records reveal good proxy agreement at both our Pacific and North Atlantic sites. At Pacific Site 849, all $\Delta_{47}$ temperatures are within error (95% CI) of the Mg/Ca-based record (Fig. 2b). The two proxies suggest similar average temperatures (Mg/Ca=~2.5±1.2°C, $\Delta_{47}$=3.5±0.8°C), 1–2°C warmer than modern BWT at this site. At North Atlantic Site U1308, both proxies record similar average temperatures (Mg/Ca=7.2±1.5°C, $\Delta_{47}$=7.7±1.0°C) approximately 4.5°C warmer than modern BWTs at this location (Fig. 3b). The $\Delta_{47}$-based temperature at 3.280 Ma (10.5±3.4°C) is considerably warmer than three Mg/Ca-derived temperatures generated on some of the same samples (6.2–7.4°C). We find no obvious explanation for this discrepancy. None of the individual $\Delta_{47}$ replicates (n=32) are classified as outliers according to our criteria (4x SD), and the $\delta^{18}O_b$ values measured alongside the $\Delta_{47}$ are in excellent agreement with $\delta^{18}O_b$ measured separately (Fig. 4). It is possible that our Mg/Ca is underestimating BWT warming at the termination of M2, although we find this explanation to be unlikely. Extreme bottom-water warming at this time is not supported by either of the proxy records from the Pacific (Fig. 2b), or by the $\delta^{18}O_b$ records from either site (Fig. 2a and Fig. 3a). Furthermore, no available SST records from the high-latitude North Atlantic indicate such warming (e.g. Lawrence et al., 2009; Bachem et al., 2017; Clotten et al., 2018). We therefore conclude that this single $\Delta_{47}$-based temperature likely overestimates BWTs at the termination of MIS M2. The otherwise good agreement between the proxies at both study sites adds confidence to our approach and supports the choice of the Mg/Ca calibration and other input parameters for Mg/Ca temperatures.

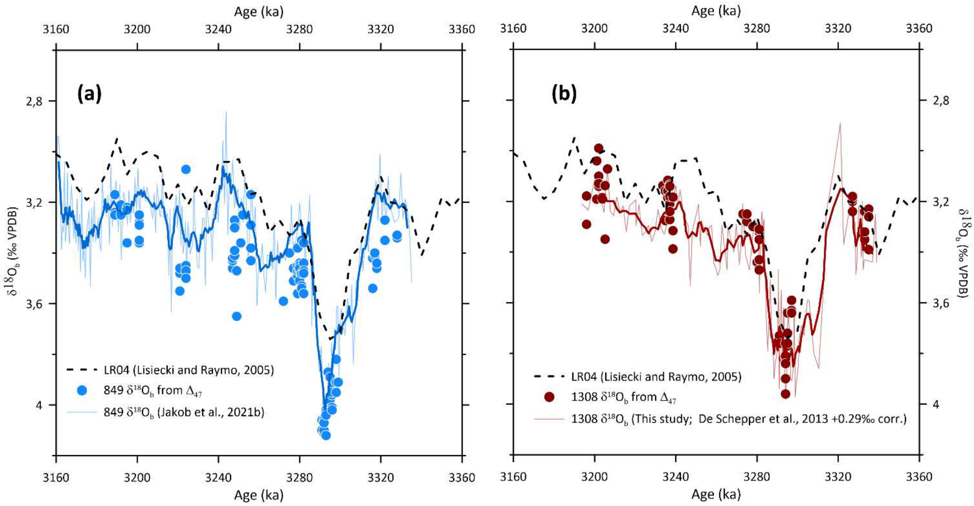



***Figure 4**. $\delta^{18}O_b$ from individual $\Delta_{47}$ measurements of Uvigerina spp. and Cibicidoides spp. (normalized to equilibrium following Shackleton et al., 1984)) from (a) Pacific ODP Site 849 and (b) North Atlantic Site U1308*

## 4.2 Warm and salty deep North Atlantic

Previously published North Atlantic BWT reconstructions from the Pliocene have produced contradictory results. While ostracod-based Mg/Ca records from numerous sites in the deep North and South Atlantic suggest mid-Piacenzian temperatures were broadly similar to today, at around 2–3°C (Dwyer et al., 1995; Cronin et al., 2005; Dwyer and Chandler, 2009), studies based on Mg/Ca from benthic foraminifera indicate average temperatures of up to ~6°C — more than 3°C warmer than present (Bartoli et al., 2005; Sosdian and Rosenthal, 2009). Our paired benthic foraminiferal Mg/Ca and $\Delta_{47}$ records suggest even warmer temperatures than previously estimated, with both proxies recording average BWTs above 7°C. We note that none of these previously published Mg/Ca-derived BWT records for the Pliocene were adjusted for estimated changes in $Mg/Ca_{sw}$. While the record of Sosdian and Rosenthal (2009) (3.150–0 Ma) does not overlap with our new Site U1308 record, recalculating (see Suppl. information and Fig. S6) their data produces average temperatures for their mid–Piacenzian interval closest to our records (3.150–3.0 Ma, ~7.7°C) that are in excellent agreement with our

Mg/Ca and $\Delta_{47}$ records. The records of Bartoli et al. (2005) cannot be recalculated in their published format.

Our new records indicate that BWTs in the deep North Atlantic Ocean were elevated by ~4.5–5.0°C relative to modern, considerably more than the estimated global average surface warming of 2–3°C relative to the pre-industrial during the MIS KM5c time slice (McClymont et al., 2020; Haywood et al., 2020). Sea surface temperature reconstructions from the mPWP suggest that warming was particularly pronounced in the high northern latitudes, and possibly more so in the North Atlantic than at comparable latitudes in the Pacific (McClymont et al. 2020). Our records are in fact in good agreement with the PRISM (Pliocene Research, Interpretation and Synoptic Mapping) dataset, which reconstructs SSTs 4–5°C warmer than today in the source region of NADW (Dowsett et al., 2009a,b).

The deep water filling the North Atlantic was not just warmer, but likely also more saline than today. Our average calculated deep North Atlantic $\delta^{18}O_{sw}$ of 1.1‰ for the mid-Piacenzian is considerably higher than its present value of 0.25‰ and similar to values observed in surface water in the Mediterranean Sea and North Atlantic Subtropical gyre today. Given the paucity of information about $\delta^{18}O_{sw}$-salinity relationships for the Pliocene, an exact quantification is difficult. However, we find it likely than this greatly elevated $\delta^{18}O_{sw}$ is reflective of a considerable increase in salinity compared to today. This would have aided the formation of warm Northern-sourced deep water by offsetting the buoyancy effect of the elevated temperature and may help explain how this water mass was sufficiently dense to fill the abyssal Atlantic despite potential competition from other, colder deep water masses sourced elsewhere. This salinification of the deep North Atlantic is supported by recent modelling efforts. Weiffenbach et al. (2023) show that an increase in salinity in the high latitude North Atlantic is a consistent feature in the PlioMIP2 (Pliocene Model Intercomparison Project Phase 2) ensemble. In these models, a closed Bering Strait and Canadian Archipelago (Haywood et al., 2020) results in dramatically lower freshwater transport from the Arctic Ocean into the North Atlantic, which in turn contributes to elevated salinity (~2 PSU) in the Labrador Sea and the subpolar (40–60°C) North Atlantic. The

PlioMIP2 ensemble also simulates lower precipitation-evaporation (P-E) over the Labrador Sea and subtropical Atlantic (Feng et al., 2022), further contributing to elevated surface salinity in these regions.

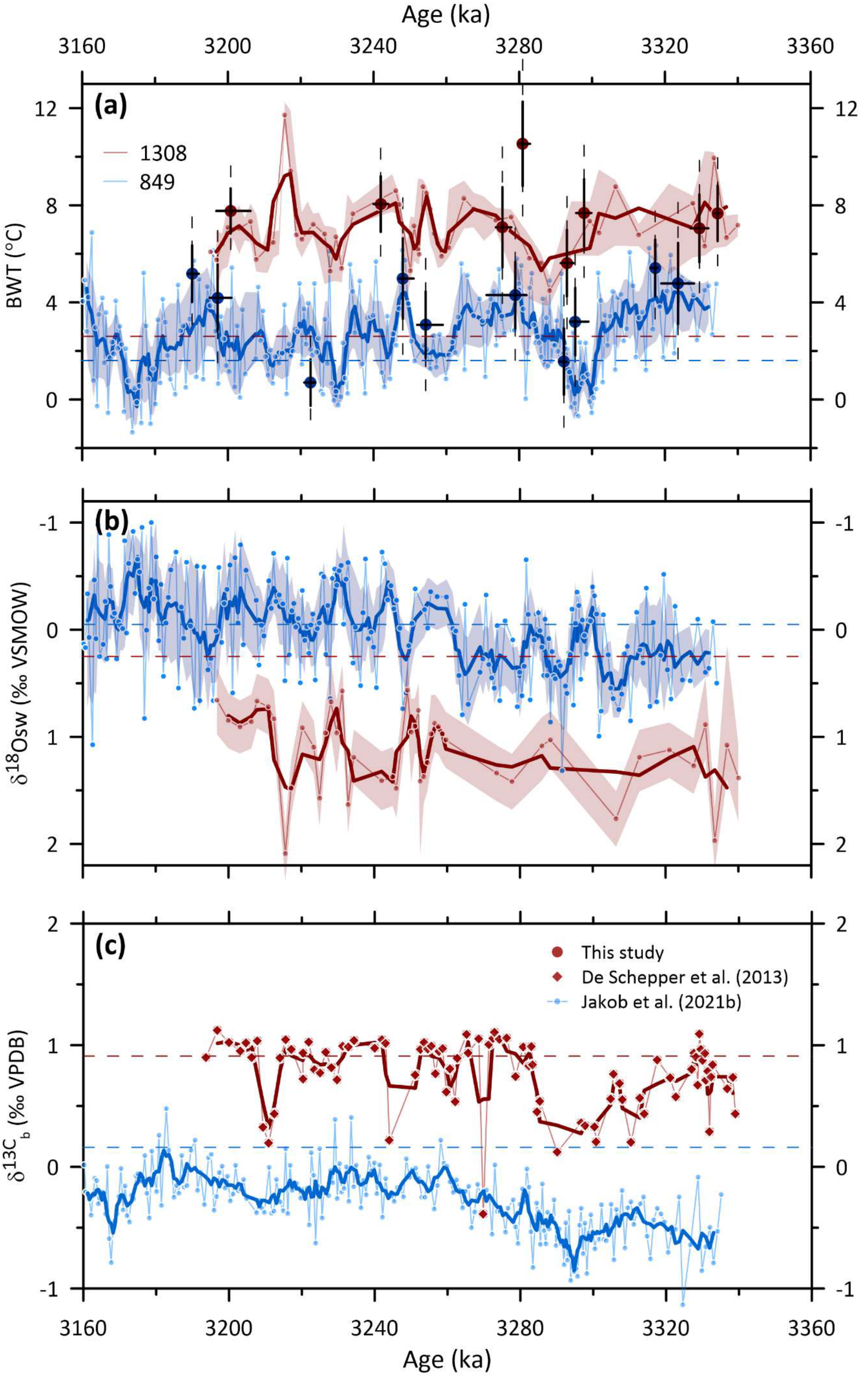
## 4.3 Pacific–Atlantic temperature gradient

The deep Atlantic and Pacific Mg/Ca and $\Delta_{47}$ records confirm a large temperature gradient between these basins during the mid-Piacenzian (Fig. 5a). At the depth of our study sites (~3800 m), bottom water masses bathing the deep North Atlantic today are slightly warmer (2.6°C vs. 1.6°C) and saltier (34.9 vs 34.7 PSU) than in the Pacific (Locarnini et al., 2013). The existence of a large temperature gradient of up to 4°C between these two basins in the Pliocene was first suggested by Woodard et al. (2014). Their foraminiferal Mg/Ca-based BWTs from ODP 1208 suggest temperatures in the North Pacific were possibly somewhat colder than today (when adjusted for $Mg/Ca_{sw}$ — see suppl. information and Fig. S6) during the mid-Piacenzian. In contrast, at Site 849 we observe warmer BWTs during the mid-Piacenzian compared to today. At face value, this discrepancy would suggest that different water masses influenced the North Pacific and the central Pacific. As deep-water formation in the North Pacific has been suggested for the Pliocene (Burls et al., 2017; Shankle et al., 2021; Ford et al., 2022), it is possible that temperatures at Site 1208 were more directly influenced by this water mass and are thus more representative of the Pacific Ocean as a whole than those at Site 849. It is however important to keep in mind that the absolute Mg/Ca-based temperatures are highly calibration dependent and are currently only cross-validated with $\Delta_{47}$ at our study sites.

Nevertheless, our new records substantiate the main interpretation of Woodard et al. (2014) that the deep North Atlantic Ocean was significantly warmer than the deep Pacific Ocean during the mid-Piacenzian (Fig 5a). We also document a large offset in $\delta^{18}O_{sw}$ between the deep Pacific (0.0‰) and deep North Atlantic Ocean (1.1‰, Fig 5b), likely reflecting a marked salinity gradient between the saltier Atlantic and fresher Pacific oceans. With respect to the ocean-wide salinity budget, a slight freshening of the deep Pacific is likely considering the strong salinification of the much narrower deep

North Atlantic inferred from our records. We interpret our results to indicate that the deep Pacific and North Atlantic oceans were bathed by water masses with distinctly different physical properties during the mid-Pliocene. Hypothetically, one possible explanation for the observed temperature gradient, if water mass mixing was identical to today, could be that the Southern Ocean end member cooled enough to compensate for the warm Atlantic waters to produce a cold Pacific end result. Given the globally warm surface conditions of the mid-Pliocene, this scenario is, however, rather unlikely. Another possibility is that the deep central Pacific was bathed by a water mass sourced from the North Pacific rather than from the Southern Ocean. While formation of NPDW has been suggested for the Pliocene (Burls et al., 2017; Shankle et al., 2021; Ford et al., 2022), the modelled spatial extent of NPDW during the mPWP does not support a large influence of this water mass on the abyssal central Pacific (Ford et al., 2022). Instead, we consider it more likely that limited oceanic exchange occurred between the two basins at this time. This suggests a fundamentally different mode of ocean circulation or mixing compared to the present, where heat and salt is distributed from the North Atlantic into the Pacific. Although some surface exchange between the Pacific and Atlantic Oceans through the Central American Seaway (CAS) may have still occurred in the mid-Piacenzian, the seaway was too shallow as this point to significantly influence deep ocean circulation (e.g. Straume et al., 2020).

Due to the lack of comparable BWT records from the Pacific and Atlantic before 3.3 Ma, it is unclear when the mid-Piacenzian circulation state commenced. Determining this would likely provide further clues of the effects it had on the warm climates of the Pliocene. Woodard et al. (2014) suggest that this mode of circulation was abruptly terminated at 2.7 Ma, when the temperature gradient between the North Atlantic and North Pacific was reduced from ~4C° to ~1C°. They therefore suggest this as a potential contributing factor for iNHG. However, it is unclear if the large gradient between the central Pacific and North Atlantic also ceased at 2.7 Ma. Furthermore, as the North Pacific BWT record ends at 2.5 Ma, it remains unclear if the gradient between this site and the North Atlantic was permanently reduced after iNHG or reemerged at points during the Pleistocene.



Age (ka)
3160
3200
3240
3280
3320
3360
(a)
1308
849
BWT (°C)
12
8
4
0
(b)
δ18Osw (‰ VSMOW)
-1
0
1
2
(c)
This study
De Schepper et al. (2013)
Jakob et al. (2021b)
δ13Cb (‰ VPDB)
2
1
0
-1
Age (ka)

***Figure 5.*** *Comparison of water-mass characteristics at Site U1308 (in red) and Site 849 (in blue). Horizontal stippled lines reflect modern values at the respective locations (a) Reconstructed bottom water temperatures from Mg/Ca and $\Delta_{47}$. Mg/Ca temperatures shown with 5pt and 3pt running means for Site 849 and U1308, respectively. Horizontal error bars on $\Delta_{47}$ temperatures indicate the age range of all individual samples used for each data point. Temperature uncertainties are expressed as solid (68% CI) and stippled (95% CI) bars. (b) calculated $\delta^{18}O_{sw}$ and linear fit (shading = 95% CI ), c) $\delta^{13}C_b$ from 849 (Jakob et al., 2021b) and 1308 (This study; De Schepper et al., 2013). Current δ13Cb values reflect the Holocene averages at sites 849 (Mix et al., 1995) and U1308 (Hodell et al., 2008). Shaded envelopes on Mg/Ca temperatures and δ18Osw represent 2σ uncertainties modelled with PSU Solver (Thirumalai et al., 2016).*

## 4.4 Marine Isotope stage M2

Interrupting the warm and mostly stable, high $CO_2$ climate of the mid-Piacenzian is Marine Isotope Stage M2 (3.312–3.264 Ma), representing the largest positive benthic oxygen isotope excursion in the Pliocene prior to iNHG (Lisiecki and Raymo, 2005). The ~0.64% increase in the global $\delta^{18}O_b$ stack suggests either a major increase in land ice-volume, strong cooling of the deep ocean, or some combination thereof. Estimates of sea-level fall associated with this event range from relatively minor (Naish and Wilson, 2009; Rohling et al., 2014) to more than 60 meters below modern (Dwyer and Chandler, 2009), consistent with a very large build-up of ice on land. While the most conservative of these estimates could be explained by an expansion of the Antarctic ice sheet at that time — as is documented in Southern Ocean IRD records (e.g. Passchier, 2011; McKay et al., 2012) — the largest estimate would also require substantial glaciation of the Northern Hemisphere. Although sedimentological evidence suggests at least some ice-growth in the circum-Arctic during M2 (i.e. De Schepper et al., 2014 and references therein), there is no conclusive evidence for the existence of large Northern Hemisphere ice sheets at that time. Deconvolving the ice-volume signal from the benthic $\delta^{18}O$ record, which would help constrain the extent of glacial expansion and plausible scenarios for ice-sheet growth, has thus far been hampered by a lack of high-resolution BWT reconstructions from this time interval.

Our Pacific Mg/Ca record represents the highest-resolution BWT record for MIS M2 to date and it is the first record of sufficient temporal resolution to investigate potential leads and lags in the climate system. Our data suggest abrupt MIS M2 cooling of 3–4°C in the deep Central Pacific starting at ~3.30 Ma. This cooling appears to lag changes in benthic $\delta^{18}O$ (Jakob et al., 2021b, Fig. 2a, measured on the same samples) by approximately 20 kyr, but it is in phase with a decrease in $CO_2$ of approximately 100 ppm (de la Vega et al., 2020, Fig.2c, Fig. S7). We speculate that the early increase in $\delta^{18}O_b$ prior to the onset of M2, which is lacking a synchronous drop in BWT, represents an increase in global ice volume, and that the subsequent $\delta^{18}O_b$ increase reflects cooling of the deep ocean. Interpreting calculated bottom water $\delta^{18}O_{sw}$ entirely as a measure of ice volume suggests elevated ice volume (relative to present) during the entire early half of our 849 record (3.334–3.264), i.e., not only during the MIS M2 cooling event, but also during the preceding interglacial (MIS MG1) (Fig. 2e). Following the termination of MIS M2, a gradual change in $\delta^{18}O_{sw}$ implies a decrease in ice-volume relative to present. However, the large spatial differences between North Atlantic and Pacific bottom water $\delta^{18}O_{sw}$ inferred from our records (Fig. 5b) complicates the interpretation of $\delta^{18}O_{sw}$ as entirely reflective of ice-volume — unless the variations are seen globally.

Our North Atlantic Site U1308 Mg/Ca record is of significantly lower temporal resolution than at Site 849. However, we observe MIS M2 BWT cooling of a similar amplitude as seen in the Central Pacific. While a lag in cooling relative to $\delta^{18}O_b$ also appears to exist in the North Atlantic (Fig. 3b), this finding is not as robust as in the Pacific. Despite the cooling observed during MIS M2, North Atlantic BWTs remain warmer than present throughout the event. This is in line with SST reconstructions from the North Atlantic and Nordic Seas showing that temperatures remained as warm or warmer than the Holocene average during MIS M2 (Lawrence et al., 2009; Bachem et al., 2017; De Schepper et al., 2013; Naafs et al., 2010). The sustained high-latitude warmth in the source region of NCW throughout MIS M2 inferred from our records add further evidence that ice-sheet advance in the Northern Hemisphere was possibly limited to the circum-Arctic.

Based on benthic $\delta^{13}C$ and Nd-isotope records, Kirby et al. (2020) conclude that — unlike during early and late Pleistocene glacials such as MIS 100 and 2 — NCW largely prevailed in the deep North Atlantic Ocean during M2. This interpretation is supported by our BWT records showing that the large temperature gradient between the Pacific and North Atlantic was maintained over M2 (Fig. 4a). Furthermore, fish debris Nd-isotope ratios from North Atlantic Site U1313 (Kirby et al., 2020, Fig. 3d) suggest that the smaller incursions of Southern Component Waters (SCW) peaked well before $\delta^{18}O_b$ and minima in BWT and atmospheric $CO_2$, further supporting that an influx of southern waters is not responsible for the observed cooling at Site U1308. This suggests global-scale cooling during MIS M2, with the source regions for both Southern- and Northern-sourced deep waters cooling concurrently.

Given the lack of major SCW incursions into the deep North Atlantic, and that cooling in the Pacific appears to be in-phase with $CO_2$ (de la Vega et al., 2020, Fig. 2c), we interpret our data to indicate that the deep Pacific, and not the Atlantic, was the ultimate sink for $CO_2$ sequestered from the atmosphere over this event, as was speculated by Kirby et al. (2020). We furthermore suggest the decrease in atmospheric $CO_2$ concentrations as the main driver behind the observed MIS M2 deep sea cooling.

At Site 849, our Mg/Ca record reveals additional large changes in deep Pacific temperatures during the mPWP that have not previously been fully documented. Cooling events of similar amplitude to that of MIS M2 also occur during MIS KM4 and KM6, but these stages are not reflected as significant glacial events in the $\delta^{18}O_b$ record. This suggests that increases in $\delta^{18}O_{sw}$ compensated for the decreases in temperature, leaving $\delta^{18}O_b$ largely unaffected. Cooling during KM4 is associated with a $CO_2$ decrease of similar magnitude to that documented for MIS M2 (~100 ppm). Thus, despite the anomalous $\delta^{18}O_b$ excursion associated with MIS M2, this event does not appear to not be unique in terms of BWT cooling and atmospheric $CO_2$ decrease in the mid-Piacenzian. The amplitude of cooling observed at both sites during MIS M2 suggests that changes in benthic $\delta^{18}O$ associated with this cold stage were mostly driven by temperature change in the deep ocean rather than ice volume.

# 5. Conclusions

We present new benthic foraminiferal Mg/Ca and $\Delta_{47}$ records from Equatorial East Pacific Site 849 and North Atlantic Site U1308, spanning MIS M2 and the first half of the mid-Piacenzian Warm Period. We demonstrate that a large bottom water temperature gradient of >4°C existed between the deep Pacific and Atlantic basins at this time, in line with previous findings, and that the mid-Piacenzian deep ocean was less homogenous than at present not just in temperature, but also in $\delta^{18}O_{sw}$ and thus likely salinity. We propose that this was caused by limited oceanic exchange between the deep Atlantic and Pacific oceans, suggesting a fundamentally different mode of ocean circulation and/or mixing than at present. We furthermore find that both basins cooled by 3–4°C during MIS M2, suggesting that the large positive oxygen isotope excursion associated with this event largely reflects global-scale cooling in the deep ocean—likely driven by decreasing $CO_2$ concentrations — rather than a substantial increase in ice volume on land. Our observation that cooling events of a similar amplitude also occurred in the following two "glacial" Marine Isotope Stages (KM4 and KM6) suggests that that the climatic impact of the M2 event was not as unique as suggested by the benthic $\delta^{18}O$ record alone, and that deep ocean temperatures in the mid-Piacenzian were more variable than has previously been documented.

## Data availability

The data from this paper are archived in the supplement (Table S1-6). In addition, all trace metal data, calculated Mg/Ca and $\Delta_{47}$ temperatures, and new stable isotope data are available at PANGAEA (https://**doi.org**/10.1594/PANGAEA.960832)

## Author contribution

AHB, SLH, KAJ, OF and ANM initiated and designed the study. AHB generated and analyzed clumped isotope data under the supervision of EVG and ANM. SLH generated and analyzed clumped isotope data under the supervision of ANM. KAJ generated and analyzed Mg/Ca data under the supervision of OF. All the authors contributed to the palaeoceanographic interpretation. AHB wrote the paper with contributions from all co-authors.

## Competing interests

The authors declare that they have no conflict of interest.

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# Supplementary information

## S1 Correction of $\delta^{18}O_b$ inter-lab offset

In our Site U1308 records from 258.95–264.71 mcd we observe a significant inter-lab offset (Fig. S3, average: +0.29‰) between the $\delta^{18}O_b$ measured alongside $\Delta_{47}$ and the previously published $\delta^{18}O_b$ of De Schepper et al. (2013). In the adjacent interval from 253.95–259.01 mcd we find that the $\delta^{18}O_b$ (corrected for species-specific offsets) measured alongside $\Delta_{47}$ is in good agreement with our new stable isotope data from *C. wuellerstorfi* and *C. mundulus* measured on a different instrument. Due to the good agreement between our two new sets of stable isotope data, we have adjusted the published $\delta^{18}O_b$-data of De Schepper et al. (2013) by 0.29‰. This adjustment also brings the published data in better agreement with the global benthic oxygen isotope stack (Lisiecki and Raymo, 2005).

## S2 Evaluation of contamination on Mg/Ca ratios of O. umbonatus

Clay, Fe-Mn oxyhydroxides or Fe-Mn carbonate coatings that are not removed during cleaning can bias reconstructed Mg/Ca temperatures (Barker et al., 2003). Typically, Al/Ca, Fe/Ca and Mn/Ca ratios above 0.1 mmol/mol are considered to indicate the presence of such contamination. In our samples, Al concentrations are near or below the detection limit of the ICP-OES, arguing against clay contamination. Fe/Ca ratios (Fig. S4 and S4) remain consistently above 0.1 mmol/mol for all Site U1308 samples (average 0.67 mmol/mol) and for a large portion of Site 849 samples (average 0.2 mmol/mol) suggesting Fe-bearing coatings might have been present on the surface of *O. umbonatus* tests. However, we find no correlation between Fe/Ca and Mg/Ca values ($R^2$ =0.25 for Site 849, $R^2$ =0.01 for Site U1308) showing that high Fe/Ca ratios are not associated with high Mg/Ca values. This indicates that Fe-bearing coatings have not influenced Mg/Ca towards higher (i.e., warmer) values.

Mn/Ca values are also consistently above the 0.1 mmol/mol threshold indicative of Mn-bearing coatings at both sites (Fig. S4 and S4). However, again we find no correlation between Mg/Ca and Mn/Ca ($R^2$ =0.06 for Site 849, $R^2$ =0.0009 for Site U1308), which would be expected if our samples were overgrown with Mn-rich coatings. Furthermore, the highest Mg/Ca ratios measured at both sites are associated with Mn/Ca values that are below the average Mn/Ca ratios for our records (1.0 mmol/mol at Site 849, 1.1 mmol/mol at Site U1308) further indicating that overgrowths did not bias the original Mg/Ca towards higher values. Additionally, SEM images do not show microcrystalline overgrowths on benthic foraminiferal test surfaces (Fig. S1 and S2).

# S3 Recalculation of published mid-Pliocene Mg/Ca records

To make previously published Mg/Ca records from Site 1208 (North Pacific, Woodard et al., 2014) and Site 607 (North Atlantic, Sosdian and Rosenthal, 2009) more comparable to our new records, we recalculated these data to adjust for changes in $Mg/Ca_{sw}$ following Lear et al. (2002) and using estimates of past $Mg/Ca_{sw}$ of Evans et al. (2016). The record of Sosdian and Rosenthal (2009) was generated on *C. wuellerstorfi* and *O. umbonatus*. From their full dataset, they calculate an interspecies Mg/Ca offset of 0.16 mmol/mol. After normalizing *O. umbonatus* to *C. wuellerstorfi*, their published temperatures were calculated by applying a regional *Cibicidoides* Mg/Ca-temperature calibration to the composite Mg/Ca record. Here, we instead normalize values to *O. umbonatus* and apply the *O. umbonatus*-specific calibration of Lear et al. (2002) — also used for our Site U1308 record — following Jakob et al. (2020). The adjusted temperature record of Sosdian and Rosenthal (2009) and Woodard et al. (2014) are presented in Fig. S6. We find that the recalculated North Atlantic record of Sosdian and Rosenthal (2009) is in very good agreement with our Site U1308 data, with both records indicating average temperatures of 7-8°C.

The adjusted North Pacific record of Woodard et al. (2014) is in better agreement with our Site 849 temperatures than the original record, but still suggests colder-than-present average temperatures. While applying a different calibration to these data could bring the absolute temperatures of this record more in line with our Site 849 data, we also note that temperatures at these two sites occasionally appear to record opposite trends (e.g. during KM5 and KM6), supporting a difference in the evolution on BWT and sourcing of deep water masses at these sites.

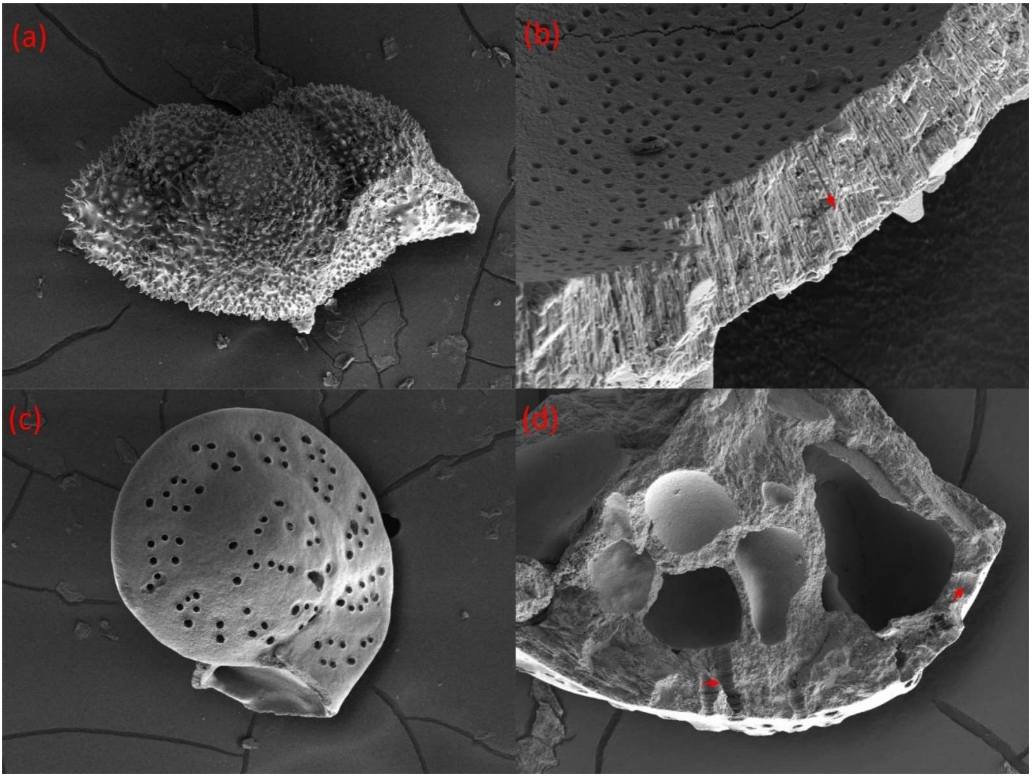


***Fig. S1:*** *Scanning Electron Microscope images of benthic foraminifera from Site 849. (a) Uvigerina spp. from sample 9H-1,140-142 cm (b) Inside view of Uvigerina spp. fragment from sample 9H-1,140-142 cm (c) Cibicidoides spp. from sample 8H-5,112-114 cm (d) Inside view of Cibicidoides spp. fragment from sample 8H-5,112-114 cm. Tests are well preserved — note the preservation of delicate pore channels and layered wall structure in close-up views (arrows).*

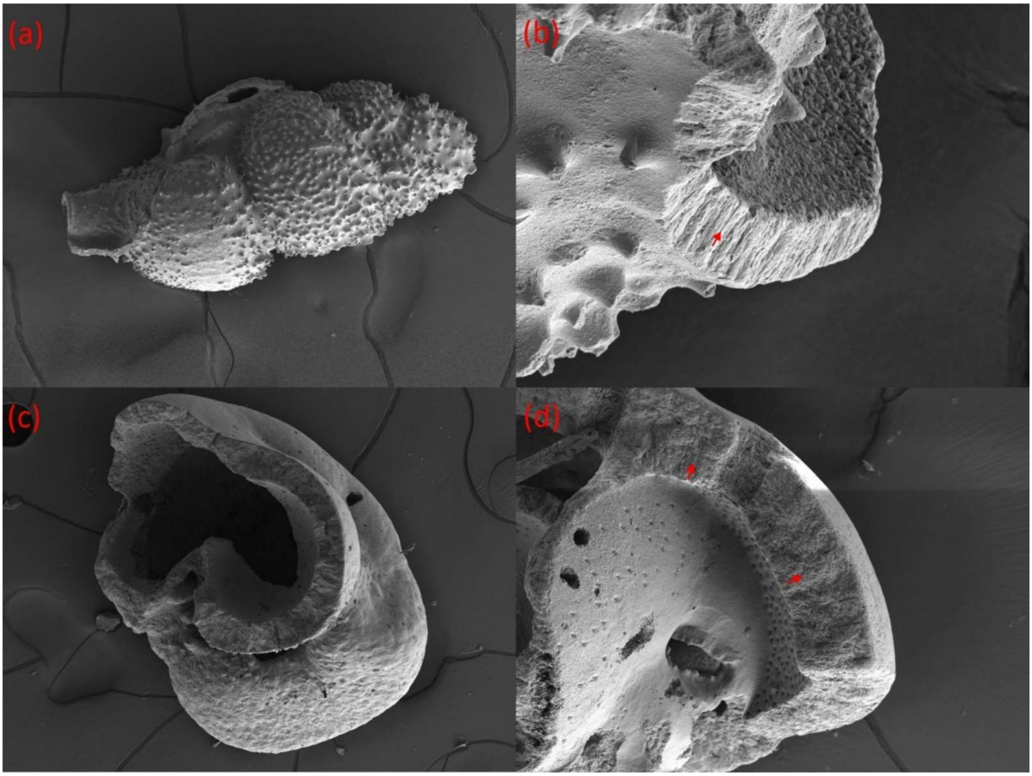


***Fig. S2:*** *Scanning Electron Microscope images of benthic foraminifera from Site U1308. (a) Uvigerina spp. from sample 26H-4,101-103 cm (b) Inside view of Uvigerina spp. fragment from sample 26H-4,101-103 cm (c) Globocassidulina spp. from sample 25H-5,130-132 cm (d) Inside view of Globocassidulina spp. fragment from sample 25H-5,130-132 cm. Tests are well preserved — note the preservation of delicate pore channels in close-up views (arrows).*

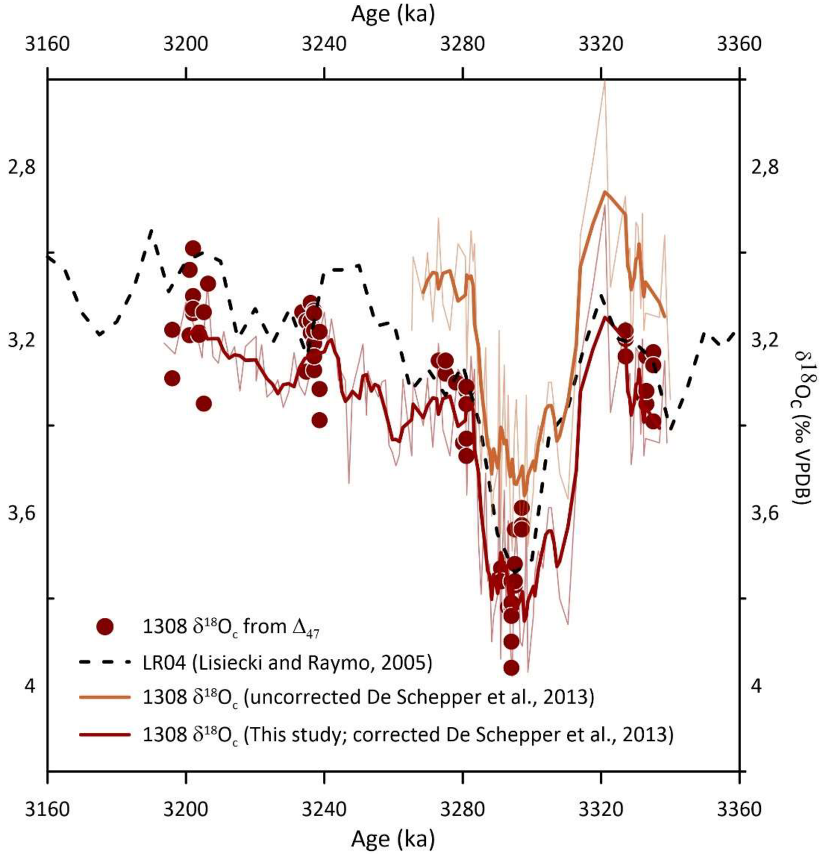


***Fig. S3:*** *Foraminiferal $\delta^{18}O_b$ data from North Atlantic Site U1308 alongside the global benthic oxygen isotope stack of Lisiecki and Raymo (2005). Orange line: De Schepper et al. (2013) Cibicidoides wuellerstorfi and Uvigerina peregrina data. Red line: This study (C. wuellerstorfi and Cibicidoides mundulus) and adjusted (+0.29‰) data of De Schepper et al. (2013). Red circles: This study from individual $\Delta_{47}$ measurements of Uvigerina spp. and Cibicidoides spp. All C. mundulus, C. wuellerstorfi and Cibicidoides spp. data normalized to equilibrium (+0.64‰) following Shackleton et al. (1984).*

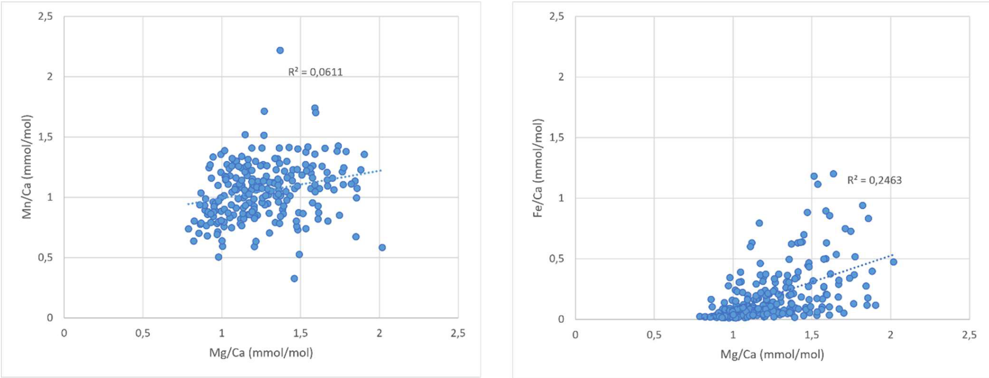


***Fig. S4:*** *Cross plot between Site 849 O.umbonatus Mg/Ca and Mn/Ca ratios (left) and Mg/Ca and Fe/Ca ratios (right)*

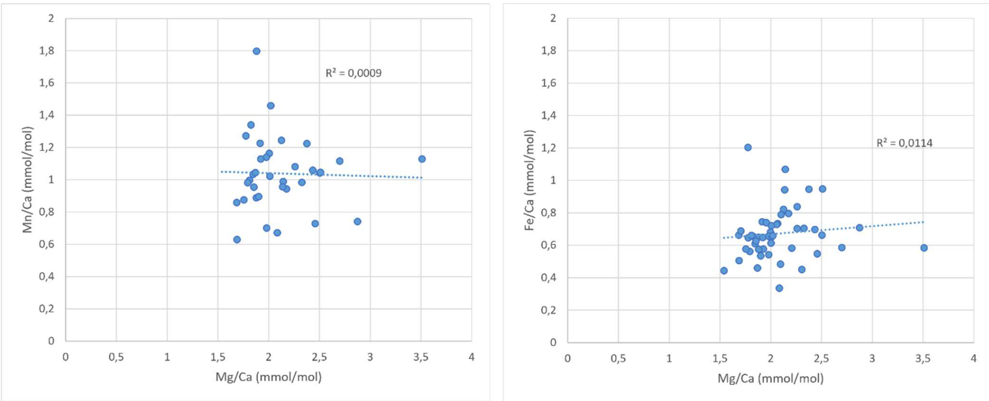


***Fig. S5:*** *Cross plot between Site U1308 O.umbonatus Mg/Ca and Mn/Ca ratios (left) and Mg/Ca and Fe/Ca ratios (right)*

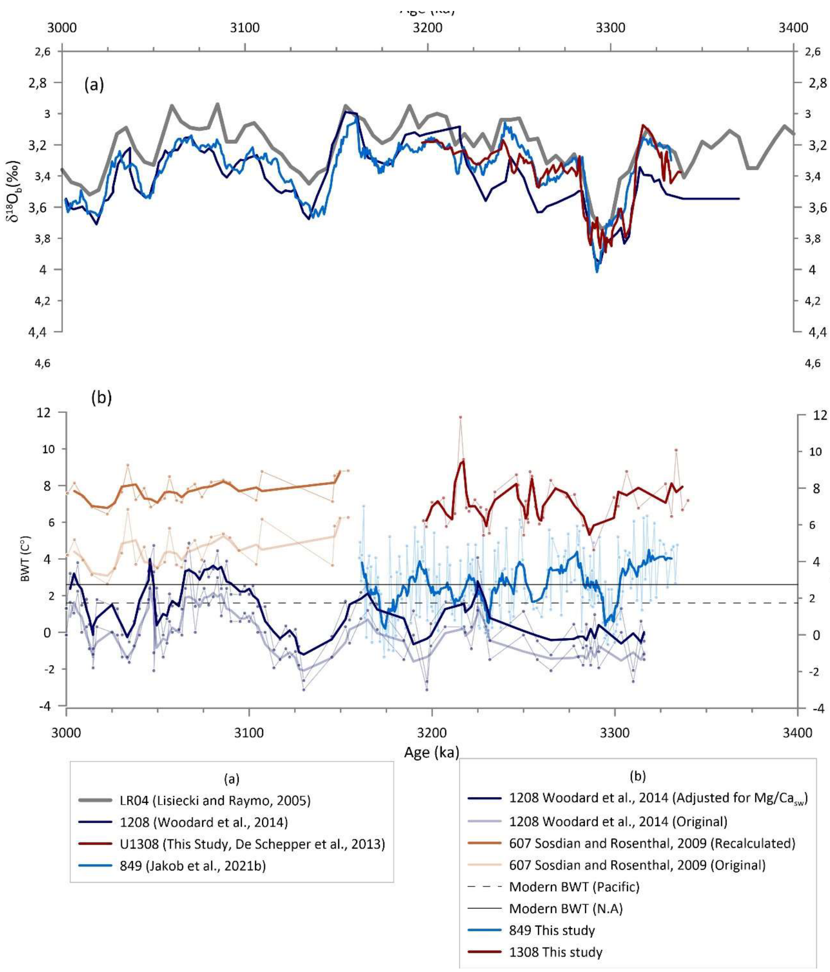


***Fig. S6:*** *a) Benthic foraminiferal $\delta^{18}O$ ($\delta^{18}O_b$) from Site 849 (light blue, 5 pt. running mean, Jakob et al., 2021), Site 1208 (dark blue, 3 pt. running mean, Woodard et al., 2014), and Site U1308 (red, 3 pt. running mean: this study and De Schepper et al., 2013) and the global δ18O$_b$ stack of Lisiecki and Raymo (2005) (grey). Note the good stratigraphic agreement between sites for our study interval. b) Mg/Ca-based temperature records covering the mid-Pliocene. Site U1308 (red, 3 pt. running mean, this study), Site 849 (blue, 5 pt. running mean, this study), Site 607 (light and dark orange representing original and adjusted values, respectively. 3 pt. running mean, Sosdian and Rosenthal, 2009) and Site 1208 (light and dark blue representing original and adjusted values, respectively. 3 pt. running mean, Woodard et al., 2014).*

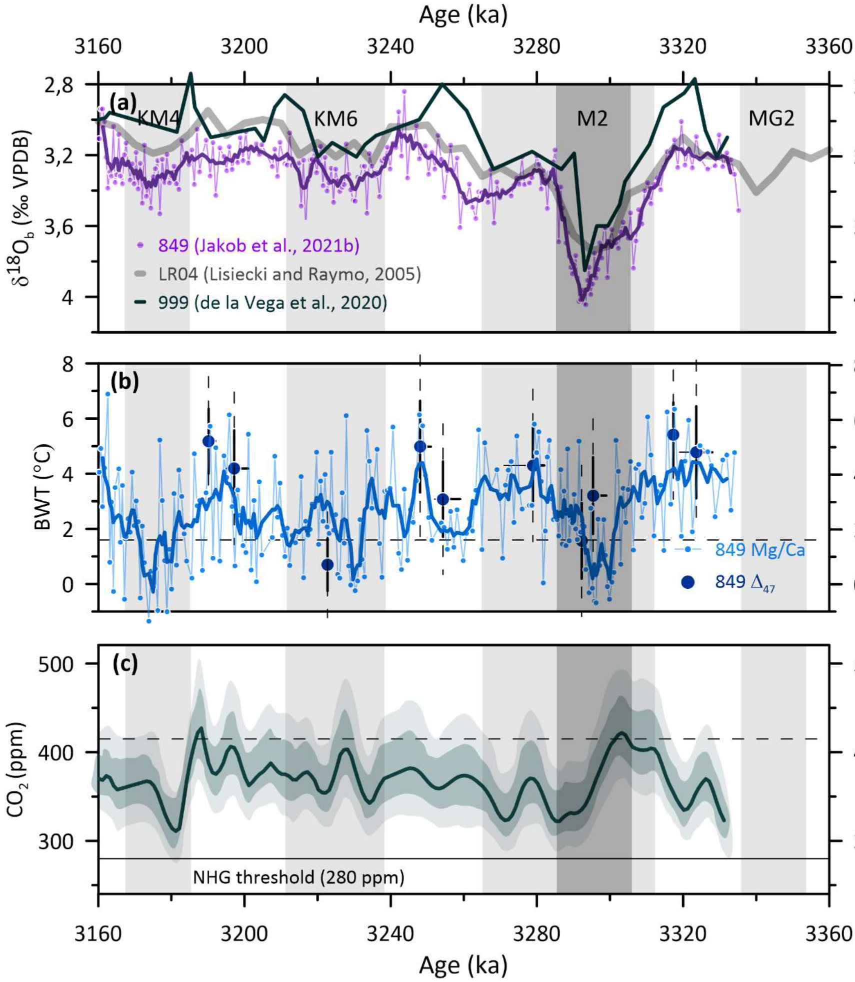


***Fig. S7:*** *a) Benthic foraminiferal $\delta^{18}O$ from Site 849 (purple, 5 pt. running mean, Jakob et al., 2021), Site 999 (green, de la Vega et al., 2020) and the global $\delta^{18}O_b$ stack of Lisiecki and Raymo (2005) (grey), b) Site 849 benthic foraminiferal Mg/Ca and $\Delta_{47}$-based bottom water temperatures (this study) and c) reconstructed atmospheric $CO_2$ from the $\delta^{11}B$-pH proxy from Site 999 (de la Vega et al., 2020). Note the good alignment of Site 849 and 999 $\delta^{18}O_b$ showing that the lag between $\delta^{18}O_b$ at Site 849 and $CO_2$ is not an effect of age model offsets.*

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# Errata for
# Paleoceanographic reconstructions across the Plio-Pleistocene from clumped isotope thermometry

**Anna Hauge Braaten**

Thesis for the degree philosophiae doctor (PhD)

at the University of Bergen

06.11.23

(date and sign. of candidate)

09.11.23

(date and sign. of faculty)

# Errata

Page 113 Missing explanation in figure text. “Vertical shaded areas mark the MIS M2 and MG1 time slices” added at the end of the figure text.

Page 114 Missing explanation in figure text. “Error bars represent 95% CI” corrected to “Temperature uncertainties (95% CI) are expressed as stippled vertical bars”

Page 145 Missing explanation in figure text. “Vertical shaded areas mark the MIS M2 and MG1 time slices” added at the end of the figure text.

Page 146 Error in figure text. “(a) Sites >35°N (b) Sites 35°N-35°S (c) Sites >35°S.” corrected to “(a) Sites >35°N (b) Sites 35°N-35°S”.

Page 146 Missing explanation in figure text. “Vertical shaded areas mark the MIS M2 and MG1 time slices” added at the end of the figure text.

Page 163 Missing explanation in figure text: “68% and 95% confidence intervals are expressed as solid and stippled vertical error bars” corrected to “68% and 95% confidence intervals are expressed as solid and stippled vertical error bars, while horizontal error bars indicate the age range of all individual samples used for each data point”.

Page 165 Missing explanation in figure text. “68% and 95% confidence intervals are expressed as solid and stippled vertical error bars on $\Delta_{47}$ temperatures, while horizontal error bars indicate the age range of all individual samples used for each data point” added to the end of the figure text.

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