Archaenal Membrane Lipid-Based Paleothermometry for Applications in Polar Oceans

By Susanne Fietz, Sze Ling Ho, and Carme Huguet
ABSTRACT. To establish whether ongoing climate change is outside the range of natural variability and a result of anthropogenic inputs, it is essential to reconstruct past oceanic and atmospheric temperatures for comparison with the modern world. Reconstructing past temperatures is a complex endeavor that employs indirect proxy indicators. Over the past two decades, promising paleothermometers have been developed that use isoprenoidal glycerol dialkyl glycerol tetraethers (isoGDGTs) from the membrane lipids of archaea preserved in marine sediments. These proxies are based on the observed relationship between lipid structure and temperature. As with all proxy indicators, observed relationships are often complex. Here, we focus on the application of isoGDGT paleotemperature proxies in the polar oceans, critical components of the global climate system. We discuss the application of and caveats regarding these archaeal membrane lipid-derived proxies and make recommendations to improve isoGDGT-derived polar ocean temperature reconstructions. We also review initial successes using hydroxylated (OH) isoGDGTs proxies in cold Arctic and Southern Ocean regions and recommend that multi-proxy approaches, including both hydroxylated and non-hydroxylated isoGDGTs, be used to contribute to the robustness of paleotemperature reconstructions.

INTRODUCTION
Given the rate and societal impact of ongoing human-caused warming, understanding the geographical extent, magnitude, and frequency of past global climate variations is essential. Ocean temperature is a critical parameter in the climate system. While sea surface temperature reflects heat exchange between the ocean and atmosphere, as well as large-scale ocean circulation, the average temperature of the upper ocean (0–1,000 m) is a useful estimate of upper ocean heat content. Thus, a top priority in paleoceanography is to provide accurate proxy-based ocean temperature reconstructions across all timescales (millions to hundreds of years). This information, gleaned from geological records, is essential for validating numerical models used to project future change and to inform policymakers who are developing strategies for mitigation and adaptation.

Efforts to reconstruct past surface and bottom water temperatures have expanded to include the polar regions (e.g., Shevenell et al., 2011; Fietz et al., 2016), where reliable instrumental temperature data are only available for the past 100 years (e.g., Hansen et al., 2010; IPCC, 2019, and references therein). Part of the impetus for this focus is the relationship that retreating grounding lines accompanied by warming ocean waters are resulting in Antarctic ice sheet mass loss and global sea level rise (Jacob et al., 2012; Rintoul et al., 2018). Furthermore, the Intergovernmental Panel on Climate Change states with high confidence that “both polar oceans have continued to warm in recent years, with the Southern Ocean being disproportionately and increasingly important in global ocean heat increase” (IPCC, 2019).

As calcium carbonate microfossils are not always continuously preserved in high-latitude sediments (e.g., Zamelczyk et al., 2012), paleoceanographers turn to non-carbonate-based molecular fossils to determine past variations in high-latitude ocean water temperatures (e.g., Sluijs et al., 2006; Bijl et al., 2009; Shevenell et al., 2011). Lipids preserved in marine sediments that have been successfully used in paleotemperature reconstructions include algal alkenones and archaeal isoprenoidal glycerol dialkyl glycerol tetraethers (isoGDGTs), which are sensitive to temperature change and relatively resilient to degradation compared to other lipids (e.g., Huguet et al. 2008; Zonneveld et al., 2010; Schouten et al., 2013; Herbert, 2014, and references therein). For example, the most mature of these paleothermometers, the alkenone unsaturation index UK37, was developed in 1986 (Brassell et al., 1986) and is widely used to reconstruct sea surface temperatures (e.g., Ho et al., 2013; Herbert, 2014, and references therein). Subsequently, the archaeal isoGDGT-based paleotemperature proxy known as the TetraEther indeX of 86 carbons, TEX86, was proposed (Schouten et al., 2002) and well received by the organic geochemistry community.

One advantage of proxies that employ archaeal membrane lipids is that these molecules are ubiquitous in globally distributed marine sediments, making them useful for calibration and estimating low-to-high latitude thermal gradients (Schouten et al., 2002). However, as with all proxies, researchers have discovered a number of non-thermal factors that affect the distribution of isoGDGTs in marine sediments. Because archaea occupy almost every niche on Earth, a number of studies have been undertaken to improve our understanding of archaeal distribution, ecophysiology (e.g., Hayes, 2000), and membrane molecular structure (e.g., Chugunov et al., 2015).

Here, we review current knowledge of the archaeal isoGDGT paleotemperature proxies, including the recent hydroxylated isoGDGT (OH-isoGDGTs) paleothermometer. We focus our review on recent insights gained from using these archaeal membrane lipid paleothermometers in the polar regions.

ARCHAEAL MEMBRANE LIPIDS AND PALEOTHERMOMETRY
Membranes are the interfaces between (micro)organisms and their environments. The key roles they play in metabolism (e.g., providing energy to the cell using ion gradients across the membranes; Konings et al., 2002; Zhou et al., 2020) and environmental sensing and signaling (Ren and Paulsen, 2005) require constant composition adjustments (Oger and Cariol, 2013). Archaea synthesize tetraether lipids that span the entire mem-
brane and form a monolayer (Koga and Morii, 2007). The isoGDGTs are a subset of these archaeal tetraether lipids, and their composition is group specific; for example, Thaumarchaeota preferentially synthesize isoGDGTs with cyclopentane rings (Sinninghe Damsté et al., 2002). Archaea also produce OH-isoGDGTs (Lipp and Hinrichs, 2009) that were first discovered in methanotrophic archaea (Hinrichs et al., 1999) and later in Thaumarchaeota (Elling et al., 2017; Bale et al., 2019).

The stability of archaeal membranes increases with ambient growth temperature, especially in thermophilic extremophiles (De Rosa et al., 1980). Yet, it was not until the 2000s that geochemists exploited this observation to develop quantitative temperature proxies (e.g., Schouten et al., 2002; Kim et al., 2010; Ho et al., 2014; Tierney and Tingley, 2014). Of particular importance for understanding isoGDGT-based proxies is that, at all temperatures, archaea must maintain semi-permeability without impacting rigidity (e.g., Chugunov et al., 2015). Most isoGDGTs involved in paleothermometry contain one or more cyclopentane rings, resulting in tighter packing and a more stable membrane (see Figure 1 in Zhou et al., 2020). At low temperatures, archaea reduce the number of cyclopentane rings in their membrane structures, thereby preventing membrane rigidity (Gabriel and Chong, 2000; Schouten et al., 2002). Indeed, Schouten et al. (2002) observed that the cyclization of isoGDGTs in surface marine sediments is correlated globally with measured surface water temperature in mesophilic (non-extreme) environments, resulting in the development of the first archaeal lipid paleothermometer, TEX$_{86}$ (Table 1).

In addition, in Thaumarchaeota, hydroxylation increases membrane fluidity and transport (Huguet et al., 2017), which compensates for increased rigidity at lower temperatures. The observation that the number of rings in hydroxylated isoGDGTs changes with temperature led to the development of ring-number-based OH-isoGDGT proxies (Fietz et al., 2013; Lü et al., 2015; Table 1).

### TEX$_{86}$ RECONSTRUCTIONS IN POLAR OCEANS: OPPORTUNITIES AND CHALLENGES

The general relationship between the number of rings in sedimentary GDGTs and the overlying mean annual sea surface temperature is that the warmer the seawater, the more isoGDGTs there are with higher numbers of cyclopentane rings (e.g., isoGDGT-2 and isoGDGT-3), resulting in higher TEX$_{86}$ index values; incorporation of the isomer of crenarchaeol adds accuracy (Sinninghe Damsté et al., 2002). Kim et al. (2010) proposed a variant of TEX$_{86}$, termed TEX$_{86}^L$, that employs a different GDGT combination (TEX$_{86}^L$; Table 1) and is intended for temperatures below 15°C.

The isoGDGT-derived indices in surface sediments are generally well correlated with seawater temperatures in the overlying upper water column (e.g., Kim et al., 2010; Ho et al., 2014; Tierney and Tingley, 2014; Figure 1). In global calibrations, the standard errors of temperature estimates vary between 4.0°C and 4.8°C.

### TABLE 1. Isoprenoid and hydroxylated GDGT-derived indices proposed for paleotemperature estimates. In the equations, the abbreviation GDGT$_n$ represents GDGTs with $n$ number of cyclopentane rings. For example, isoGDGT-1 represents the non-hydroxylated isoprenoid GDGT with one cyclopentane moiety. The abbreviation OH-GDGT$_n$ stands for hydroxylated isoprenoid GDGTs with $n$ number of cyclopentane rings. The term $\Sigma$isoGDGTs refers to the sum of all non-hydroxylated isoprenoid GDGTs (e.g., isoGDGT-1, isoGDGT-2, isoGDGT-3, crenarchaeol and its isomer, abbreviated in this table as cren'). The term $\Sigma$OH-isoGDGTs refers to the sum of OH-isoGDGT-0, OH-isoGDGT-1 and OH-isoGDGT-2.

<table>
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<tr>
<th>INDEX</th>
<th>EQUATION</th>
<th>REFERENCE</th>
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<tbody>
<tr>
<td>TEX$_{86}$</td>
<td>$\frac{[\text{isoGDGT} - 2] + [\text{isoGDGT} - 3] + [\text{cren'}]}{[\text{isoGDGT} - 1] + [\text{isoGDGT} - 2] + [\text{isoGDGT} - 3] + [\text{cren'}]}$</td>
<td>Schouten et al., 2002</td>
</tr>
<tr>
<td>TEX$_{86}^L$</td>
<td>$\log\left(\frac{[\text{isoGDGT} - 2]}{[\text{isoGDGT} - 1] + [\text{isoGDGT} - 2] + [\text{isoGDGT} - 3]}\right)$</td>
<td>Kim et al., 2010</td>
</tr>
<tr>
<td>OH-GDGT%</td>
<td>$\frac{\Sigma\text{OH-GDGTs}}{2\Sigma\text{OH-GDGTs} + \Sigma\text{isoGDGTs}} \times 100$</td>
<td>Huguet et al., 2013</td>
</tr>
<tr>
<td>OH-GDGT$_{318/336}$</td>
<td>$\frac{\text{OH} - \text{isoGDGT} - 0}{\text{OH} - \text{isoGDGT} - 0 + \text{OH} - \text{isoGDGT} - 1}$</td>
<td>Fietz et al., 2013</td>
</tr>
<tr>
<td>RI-OH</td>
<td>$\frac{[\text{OH} - \text{isoGDGT} - 1] + 2 \times [\text{OH} - \text{isoGDGT} - 2]}{[\text{OH} - \text{isoGDGT} - 0] + [\text{OH} - \text{isoGDGT} - 1] + [\text{OH} - \text{isoGDGT} - 2]}$</td>
<td>Lü et al., 2015</td>
</tr>
<tr>
<td>RI-OH'</td>
<td>$\frac{[\text{OH} - \text{isoGDGT} - 1] + 2 \times [\text{OH} - \text{isoGDGT} - 2]}{[\text{OH} - \text{isoGDGT} - 1] + [\text{OH} - \text{isoGDGT} - 2]}$</td>
<td>Lü et al., 2015</td>
</tr>
<tr>
<td>OHc</td>
<td>$\frac{[\text{isoGDGT} - 2] + [\text{isoGDGT} - 3] + [\text{cren'}] - [\text{OH} - \text{isoGDGT} - 0]}{[\text{isoGDGT} - 1] + [\text{isoGDGT} - 2] + [\text{isoGDGT} - 3] + [\text{cren'}] + \Sigma\text{OH} - \Sigma\text{isoGDGTs}}$</td>
<td>Fietz et al., 2016</td>
</tr>
</tbody>
</table>
5.2°C for TEX$_{86}^L$ and TEX$_{86}$, respectively (Kim et al., 2010). Interlaboratory error (3°–4°C) for TEX$_{86}$ are the same order of magnitude as other commonly used quantitative temperature proxies (Schouten et al., 2013). There is, however, a larger scatter in the TEX$_{86}$–sea surface temperature (SST) relationships at the low temperature end of the calibrations (Figure 1; Kim et al., 2010; Ho et al., 2014; Tierney and Tingley, 2014). The scatter is partly due to bias from terrestrial input, especially in the Arctic Ocean (Ho et al., 2014; Y. Park et al., 2014), and potentially from the use of satellite-assigned sea surface temperatures below the seawater freezing point for some calibrations (Pearson and Ingalls, 2013). Large scatter in TEX$_{86}$–SST relationship is not an issue unique to the polar oceans. It also exists at the high-temperature end in the Red Sea (Figure 1), likely due to an endemic Thaumarchaeota population (Trommer et al., 2009). As such, TEX$_{86}$ and its variants may be affected by environmental conditions other than temperature, such as pH (Elling et al., 2015), oxygen availability (Qin et al., 2015), cellular physiological acclimation including ammonia oxidation rates (Elling et al., 2014; Hurley et al., 2016), and shifts in season and depth of production (Huguet et al., 2007; Ho and Laepple, 2016; Chen et al., 2018). Many of the caveats mentioned above have been reviewed for the global ocean in general (see, for example, comprehensive reviews by Pearson and Ingalls, 2013; Schouten et al., 2013; and Tierney, 2014). Figure 2 illustrates concerns raised for the polar oceans.

A solution for overcoming some of the caveats is to develop a regional calibration. For instance, Shevenell et al. (2011) applied a regionally calibrated TEX$_{86}$ equation instead of TEX$_{86}^L$ to reconstruct Holocene temperature evolution in the Antarctic Peninsula (Figure 1a). Some sources of uncertainty, such as spatial change in the archaeal community, cannot be included in ordinary least squares regression approaches for global calibration. Thus, alternative statistical approaches have also been adopted to improve correlation of TEX$_{86}$ with upper ocean temperature, such as Bayesian regression (BAYSPAR; Tierney and Tingley, 2014) and machine-learning approaches (OPTIMAl; Eley et al., 2019).

Despite calibration challenges, inherent to all paleotemperature proxies, the TEX$_{86}$ paleothermometer revolutionized understanding of past ocean temperature changes in the carbonate-poor polar regions. In the Arctic Ocean, TEX$_{86}$ provided one of the first quantitative temperature estimates for past warm climates characterized by high atmospheric CO$_2$, such as the Cretaceous and the Eocene. TEX$_{86}$ revealed that the Arctic surface ocean during these time peri-

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**FIGURE 1.** Selected global calibrations for paleothermometers (a) TEX$_{86}$ (TetraEther index of 86 carbons), (b) TEX$_{86}^L$ (which employs a different combination of glycerol dialkyl glycerol tetraethers from TEX$_{86}$ and is intended for temperatures below 15°C), and (c) RI-OH' (the weighted average number of cyclopentane rings) against sea surface temperatures. The data for the scatterplots in (a) and (b) are sourced from Tierney and Tingley (2015). A new, extended compilation of published data sets is presented here for RI-OH' (Fietz et al., 2013; Huguet et al., 2013; Lü et al., 2015; Kaiser and Arz, 2016). In (c), linear plots illustrate published calibrations for all three indices as well as a new linear fit for the extended RI-OH' data set.

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- Kim et al., 2010, Calibration
  SST = 81.5 × TEX$_{86}$ − 26.6, n = 396, $R^2 = 0.77$

- Kim et al., 2008, Calibration
  SST = 56.2 × TEX$_{86}$ − 10.8, n = 223, $R^2 = 0.94$

- Shevenell et al., 2011, Calibration
  TEX$_{86}$ = 0.0125 × SST + 0.3038, n = 230, $R^2 = 0.82$

- Kim et al., 2010, Calibration
  SST = 67.2 × TEX$_{86}^L$ + 46.9, n = 396, $R^2 = 0.86$

- Lü et al., 2015, Calibration
  RI-OH' = 0.0382 × SST + 0.1, n = 107, $R^2 = 0.75$

- Linear Fit, This Study
  RI-OH' = 0.0422 × SST − 0.029, n = 167, $R^2 = 0.76$
Methods were as warm as today’s subtropics, a stark contrast to the currently ice-covered Arctic (e.g., Jenkyns et al., 2004; Brinkhuis et al., 2006; Sluijs et al., 2006). Similarly, in the Southern Ocean, $\text{TEX}_{86}$ and its variants have made it possible to reconstruct the temperature evolution from the Jurassic to the Holocene (summarized in Table 2). Thanks to this large body of work, we now know that the surface temperature of the Southern Ocean was once as high as 30°C during the Jurassic (Jenkyns et al., 2012) and has cooled through the Cenozoic, resulting in present-day temperatures surrounding the Antarctic Peninsula (Shevenell et al., 2011; Etourneau et al., 2013). Importantly, $\text{TEX}_{86}$-based reconstructions have helped characterize past greenhouse climates, suggesting that Antarctic surface water temperatures were >10°C during the Early Eocene Climatic Optimum (e.g., Bijl et al., 2009). These reconstructions also improved understanding of temperature magnitude ranges over major climate transitions, including the >4°C cooling across the Eocene-Oligocene transition (e.g., Bijl et al., 2009; Z. Liu et al., 2009). $\text{TEX}_{86}$-based paleotemperature studies also indicate that in climatically sensitive regions, surface ocean temperatures fluctuated abruptly during the Holocene (Shevenell et al., 2011), suggesting the potential for rapid polar ocean temperature fluctuations with continued warming. Furthermore, both long-term cooling and millennial-scale variability on the western Antarctic Peninsula are similar to changes in the low latitudes (i.e., the tropical Pacific) and in regional ice core records (Mulvaney et al., 2012), suggesting climate teleconnections between the low and high latitudes via the Southern Hemisphere westerlies (Shevenell et al., 2011).

### CAVEATS POTENTIALLY ENCOUNTERED IN THE POLAR OCEANS

<table>
<thead>
<tr>
<th><strong>SOLUTIONS</strong></th>
<th><strong>CAVEATS POTENTIALLY ENCOUNTERED IN THE POLAR OCEANS</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Use different isoGDGT index or calibration</td>
<td>Calibration does not perform well at low temperature end (i.e., at high latitudes)</td>
</tr>
<tr>
<td>Including OH-isoGDGTs in toolkit may improve temperature reconstruction</td>
<td>Terrestrial Input</td>
</tr>
<tr>
<td>Monitor relative terrestrial input, e.g., using BIT</td>
<td>Deviation from expected seawater temperature especially in the Arctic</td>
</tr>
<tr>
<td>OH-isoGDGTs may help, but contradictory findings exist on the effect of terrestrial input on OH-isoGDGT distribution</td>
<td>Different Ecotypes</td>
</tr>
<tr>
<td>Regional calibration, e.g., for the Antarctic Peninsula</td>
<td>Depth Origin of the Sedimentary Signal</td>
</tr>
<tr>
<td>Test subsurface calibrations</td>
<td>Subsurface origin reported in several environments, including in the polar oceans</td>
</tr>
<tr>
<td>Be aware where this may be an issue</td>
<td>Physiological Effects</td>
</tr>
<tr>
<td>No definite solution yet</td>
<td>Culture studies reported evidence for and against non-thermal effects on cyclization</td>
</tr>
<tr>
<td>Be aware that it may be an issue when interpreting data</td>
<td>Impact by sedimentary production, e.g., by methanotrophs, methanogens; more likely to affect deep-time records in polar oceans</td>
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</tbody>
</table>

### DOES INCLUDING OH-ISOGDGTs IN TEMPERATURE PROXY INDEX IMPROVE THE ESTIMATES?

At some sites in the Arctic and Southern Oceans, $\text{TEX}_{86}$ and $\text{TEX}_{86}^L$ do not show expected changes. For example, analyses using these proxies do not reflect the warmer conditions during glacial retreat in the Pliocene Arctic (Knies et al., 2014), during the Plio-Pleistocene transition and Pleistocene deglaciations in the Southern Ocean (e.g., McKay et al., 2012; Fietz et al., 2016), and during the late Holocene Arctic sea ice melting (e.g., Fietz et al., 2013). Some inconsistencies in warmer reconstructed temperatures during the deglacials compared to peak interglacials may be attributed to increased meltwater stratification (Shevenell et al., 2011; McKay et al., 2012). Another caveat of particular importance here is the potential lack of $\text{TEX}_{86}$ sensitivity at tempera-
tures below 10°C as observed in mesocosms studies (e.g., Wuchter et al., 2004). In cold waters, archaea adjust the permeability of their membranes by changing the number of rings and adding hydroxyl groups. Including only one of the processes in the proxy index may therefore underestimate the full range of temperature acclimations of archaea in polar oceans. Hence, accounting for both processes by adding OH-isoGDGTs to the paleothermometer index should, in principle, improve the sensitivity of the proxy.

Like isoGDGTs, OH-isoGDGTs are globally distributed in the water column and in sediments (X.-L. Liu et al., 2012; Huguet et al., 2013; Figure 3). X.-L. Liu et al. (2012) suggested that OH-isoGDGTs had potential for paleothermometry, and Huguet et al. (2013) proposed the first OH-isoGDGTs-based temperature proxy after observing a strong correlation between the relative abundance of OH-isoGDGTs and sea surface temperatures in globally distributed seawater and sediment samples. Thereafter, several indices were proposed for applications in the polar oceans (Table 1). While the addition of hydroxylated isoGDGTs in the isoGDGT toolbox was originally proposed as an alternative for cold water paleothermometry (e.g., Fietz et al., 2013; Huguet et al., 2013), it was later suggested that an OH-isoGDGT-temperature relationship also exists globally (Lü et al., 2015). The finding of OH-isoGDGTs in a large set of surface sediments in Chinese coastal seas (n = 70; Figure 3) led Lü et al. (2015) to propose the weighted average number of cyclopentane rings (RI-OH index) as a proxy for sea surface temperatures, as well as a polar variant, the RI-OH’ (Table 1; Figure 1c), with a residual standard error of 6.0°C (compared to 5.2°C for TEX86; Kim et al., 2010). This RI-OH index reasonably reproduced TEX86-derived temperatures dating back 30-40 million years for the US New Jersey shelf (de Bar et al., 2019).

Thus far, OH-isoGDGT-based proxies have been applied to Arctic and Southern Ocean sediments to reconstruct seawater temperatures and to help elucidate ice-ocean dynamics (Fietz et al., 2013, 2016; Knies et al., 2014; Kremer et al., 2018). In these cases, OH-isoGDGT proxies were utilized instead of TEX86 as the latter did not yield changes in accordance with other proxies (Figure 4). For example, in Fram Strait, the gateway to the Arctic Ocean, the OH-isoGDGT-derived indices indicated sea surface cooling of ~5°C (OH-isoGDGT%) and ~3°C (RI-OH’) across the Plio-Pleistocene transition, suggesting an increasing influence of polar water masses (Knies et al., 2018).

### TABLE 2. isoGDGT-inferred Jurassic-Holocene upper ocean temperature evolution in the Southern Ocean.

<table>
<thead>
<tr>
<th>TIME PERIOD STUDIED</th>
<th>GDGT INDEX</th>
<th>MAIN FINDING IN TERMS OF TEMPERATURE CHANGE</th>
<th>REFERENCE</th>
</tr>
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<tbody>
<tr>
<td>Jurassic-Cretaceous</td>
<td>TEX&lt;sub&gt;86&lt;/sub&gt;</td>
<td>Persistent high temperatures of 26°–30°C&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Jenkyns et al., 2012</td>
</tr>
<tr>
<td>Eocene</td>
<td>TEX&lt;sub&gt;86&lt;/sub&gt;</td>
<td>Cooling from ~25°C during early Eocene to ~21°C during late Eocene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Bijl et al., 2009</td>
</tr>
<tr>
<td>Eocene-Oligocene</td>
<td>TEX&lt;sub&gt;86&lt;/sub&gt;</td>
<td>Substantial cooling of &gt;5°C across the Eocene-Oligocene boundary</td>
<td>Z. Liu et al., 2009</td>
</tr>
<tr>
<td>Oligocene-Miocene</td>
<td>TEX&lt;sub&gt;86&lt;/sub&gt;</td>
<td>~5°–6°C cooling from Oligocene to mid-Miocene</td>
<td>Hartman et al., 2018</td>
</tr>
<tr>
<td>Miocene</td>
<td>TEX&lt;sub&gt;86&lt;/sub&gt;</td>
<td>Cold (~1°–3°C) and warm (~6°–10°C) intervals during early to mid Miocene&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Levy et al., 2016</td>
</tr>
<tr>
<td>Miocene</td>
<td>TEX&lt;sub&gt;L86&lt;/sub&gt;</td>
<td>~14°C before the mid-Miocene climatic optimum, and ~8°C thereafter&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Sangiorgi et al., 2018</td>
</tr>
<tr>
<td>Pliocene</td>
<td>TEX&lt;sub&gt;L86&lt;/sub&gt;</td>
<td>Cooling, from ~5°C during early Pliocene to ~2°C during the late Pliocene&lt;sup&gt;d&lt;/sup&gt;</td>
<td>McKay et al., 2012</td>
</tr>
<tr>
<td>Pleistocene</td>
<td>TEX&lt;sub&gt;L86&lt;/sub&gt;</td>
<td>~5°C warming from glacial to deglaciation</td>
<td>Hayes et al., 2014</td>
</tr>
<tr>
<td>Last Glacial-Holocene</td>
<td>TEX&lt;sub&gt;86&lt;/sub&gt;</td>
<td>Warming from ~10°C during the last glacial to ~19°C during the early Holocene&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Kim et al., 2009</td>
</tr>
<tr>
<td>Holocene</td>
<td>TEX&lt;sub&gt;L86&lt;/sub&gt;</td>
<td>~3°C of cooling over the Holocene</td>
<td>Etourneau et al., 2013</td>
</tr>
<tr>
<td>Holocene</td>
<td>TEX&lt;sub&gt;86&lt;/sub&gt;</td>
<td>3°–4°C of cooling over the past 12,000 years; superimposed series of millennial-scale warm and cold events</td>
<td>Shevenell et al., 2011</td>
</tr>
<tr>
<td>Holocene</td>
<td>TEX&lt;sub&gt;L86&lt;/sub&gt;</td>
<td>No long-term trend over the Holocene</td>
<td>Kim et al., 2012</td>
</tr>
<tr>
<td>Holocene</td>
<td>TEX&lt;sub&gt;L86&lt;/sub&gt;</td>
<td>Abrupt warming of ~1.5°C in the early Holocene, possibly associated with ice shelf disintegration</td>
<td>Etourneau et al., 2019</td>
</tr>
</tbody>
</table>

<sup>a</sup> 5.2°C standard error of the estimate for TEX<sub>86</sub> (Kim et al., 2010)
<sup>b</sup> 1.7°C standard error of the estimate for TEX<sub>86</sub> (Kim et al., 2008)
<sup>c</sup> 2.8°C standard error of the estimate for TEX<sub>L86</sub> (Kim et al. 2012)
<sup>d</sup> 4.0°C standard error of the estimate for TEX<sub>L86</sub> (Kim et al. 2010)
In contrast, TEX\textsubscript{13}\textsubscript{86} temperatures did not reveal consistent temporal patterns. Meanwhile, a reconstruction over the past ~120,000 years (Kremer et al., 2018) revealed more reasonable RI-OH\textsuperscript{1} inferred temperatures (~2.5° to 2.5°C; calibration error of 6°C) than TEX\textsubscript{13}\textsubscript{86}-derived temperatures (~17° to 9°C; calibration error of 4°C). Over the Holocene, temperatures based on the OH-isoGDGT\% and RI-OH\textsuperscript{1} indices also followed trends in temperature and water mass changes indicated by multiple proxies, in contrast to the TEX\textsubscript{13}\textsubscript{86}-based temperatures (Fietz et al., 2013; Figure 4).

The reasons for the mismatch between TEX\textsubscript{13}\textsubscript{86}-related temperatures and other proxies in the Arctic are unknown. The isoGDGT-based Ring Index (Zhang et al., 2016) may shed light on the extent of non-thermal bias of the TEX\textsubscript{13}\textsubscript{86}-related reconstructions, especially potential terrestrial input. Ring Index offset values lower than 0.3 at the Plio-Pleistocene transition (Knies et al., 2014) and in the Holocene (Fietz et al., 2013) do not point to a specific non-thermal bias. The factors driving the mismatch between TEX\textsubscript{13}\textsubscript{86}-related temperatures and other proxies in the Arctic do not seem to affect the utility of OH-isoGDGT proxies, as the reconstruction based on them coevolves with other temperature proxies (Figure 4).

The OH-isoGDGT proxy has not been widely tested in the Southern Ocean. E. Park et al. (2019) recently published the very first sediment trap-based study indicating that several OH-isoGDGT-based proxies show promise as temperature proxies for both the Arctic and the Southern Oceans. To date, only one study has applied the OH-isoGDGTs for reconstructions in the Southern Ocean (Fietz et al., 2016). Here, in the subantarctic Atlantic, TEX\textsubscript{13}\textsubscript{86} (Figure 3) suggests warmer conditions during glacial than interglacials in the past 500,000 years, in contrast to other paleotemperature proxies based on the same sediment core (Fietz et al., 2016). Located north of the winter sea ice extent during the last glacial maximum, some inconsistencies of warmer reconstructed temperatures during the glacial and colder temperatures during the interglacial may be attributed to increased meltwater stratification (Shevenell et al., 2011; McKay et al., 2012). Another possible explanation for the “warm” glacial TEX\textsubscript{13}\textsubscript{86}-temperatures in the subantarctic Atlantic record.

**FIGURE 3.** An Ocean Data View (Schlitzer, 2018) map illustrates the progress made since the OH-isoGDGTs were first proposed in 2013 as paleotemperature proxies, including surface sediment sample locations used for calibrations of initial OH-isoGDGT\% (unlabeled filled circles; Huguet et al., 2013). Orange circles roughly indicate the locations of the additional sample sets for calibrations of cyclization variants, such as OH-isoGDGT\textsubscript{13}\textsubscript{18}/13\textsubscript{16} (Table 1) by Fietz et al. (2013; #1), RI-OH and RI-OH\textsuperscript{1} (Table 1) by Lu et al. (2015, #2), and improved calibrations thereof by Kaiser and Arz (2016; #3), as well as for OH\textsuperscript{1} index determination (Table 1) by Fietz et al. (2016, #4). Blue circles highlight focus areas of surface sediment studies that improve our understanding of OH-isoGDGT production, settling, and thus ultimately, distribution in the sediment (#5, Lu et al., 2019; #6, Kang et al., 2017; #7, Davetian et al., 2019). White stars indicate two sediment trap studies (#8, Wei et al., 2019, South China Sea; #9, E. Park et al., 2019, Fram Strait and Southern Ocean). Red circles roughly indicate downcore temperature reconstructions (#1, Fietz et al., 2013; #10, Knies et al., 2014; #4, Fietz et al., 2016; #11, Kremer et al., 2018; #12, de Bar et al., 2019). Circles and stars are not to scale and may not represent 100% of the data set.
could be the bias toward warmer TEX$_{86}$ temperatures caused by low ammonium oxidizing rates (Hurley et al., 2016). However, higher eolian iron input during the glacials (Martinez-Garcia et al., 2009) would contribute to increased oxidation rates (Shafiee et al., 2019) and thus toward a cold bias of the TEX$_{86}$ temperatures and vice versa in the interglacials. This is the opposite of the temporal patterns in the TEX$_{86}$ records and, hence, a bias introduced by such nutrient dynamics does not explain the warm temperatures reconstructed during the glacials.

Adding OH-isoGDGTs in the temperature index improves the reconstruction to some degree. Unlike their counterparts TEX$_{86}$ and TEX$_{L86}$, the OH-isoGDGT indices exhibit temporal patterns that are more consistent with other non-isoGDGT-based proxies (Figure 4) and expectations (lower temperatures during glacials), with the OHc index showing the best match in the temporal trend. In the

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**FIGURE 4.** Multi-proxy based reconstructions of sea surface temperature and related parameters in the polar oceans. (a) Modern annual mean sea surface temperatures (from WOA2013, Locarnini et al., 2013). Black diamonds indicate the two sediment core sites in the Arctic (b–c) and Atlantic Southern Ocean (d–f). (b) Relative abundance of C$_{37:4}$ alkenones and U$_K^{37}$ sea surface temperature (SST) anomalies (Rueda et al., 2013) as well as SST anomalies reconstructed using modern analogue technique (MAT$_{foram}$-SST, Spielhagen et al., 2011). (c) TEX$_{86}$, TEX$_{L86}$, and RI-OH'-derived SST anomalies using calibrations in Kim et al. (2010) and Lu et al. (2015), as well as OH'-derived SST using calibration in Fietz et al. (2016). (d) Benthic δ$^{18}$O stack (Lisiecki and Raymo, 2005), summer SST (SSST) anomalies reconstructed using the modern analogue technique (MAT$_{foram}$-SSST; Becquey and Gersonde, 2002) and U$_K^{37}$ SST anomalies (Martinez-Garcia et al., 2009). (e) Relative abundance of C$_{37:4}$ alkenones to total C$_{37}$ alkenones, indicating cold water mass influence (Martinez-Garcia et al., 2009) and ice rafted debris (IRD) concentration (Becquey and Gersonde, 2002). (f) TEX$_{86}$ and RI-OH'-derived SST anomalies using calibrations in Kim et al. (2010) and Lu et al. (2015) as well as OH'-derived SST (Fietz et al., 2016). Data and graphs (b–c) adapted from Fietz et al. (2013). Data and graphs (d–f) adapted from Fietz et al. (2016). Blue shaded bars in (d–f) denote glacial stages. All index equations are provided in Table 1. All anomalies refer to the core top value as “0.”
OH\textsuperscript{-} index, the assumed cold-water end-member OH-isoGDGT-0 is subtracted from the numerator (Table 1). The fact that this approach improves the reconstruction of temperature evolution suggests that the addition of OH-isoGDGT in the temperature index may help to fully capture the temperature responses of archaean membranes to temperature changes in polar waters. The global calibration of RI-OH (Lü et al., 2015) consists of 107 data points, a far cry from the TEX\textsubscript{86} calibration data set (n >1,000; Tierney and Tingley, 2015). Here, we show that combining recently published data from the TEX\textsubscript{86} calibration data set (n >1,000; Tierney and Tingley, 2015). However, several caveats exist (Figure 2) and structurally different isoGDGTs have been identified, such as OH-isoGDGTs. More work is needed to shed light on these compounds and the proxies based on them, but a few preliminary studies show that incorporating OH-isoGDGTs in the temperature proxy index may lead to improved reconstructions in the polar oceans. We thus recommend that the OH-isoGDGTs be analyzed simultaneously during standard isoGDGTs analysis, as this multi-proxy approach will increase the robustness of paleotemperature reconstructions.

**CONCLUSIONS**

Over the last few decades, the TEX\textsubscript{86} paleothermometer has been used to help reconstruct past changes in sea surface temperatures in the polar regions (e.g., Table 2). However, several caveats exist (Figure 2) and structurally different isoGDGTs have been identified, such as OH-isoGDGTs. More work is needed to shed light on these compounds and the proxies based on them, but a few preliminary studies show that incorporating OH-isoGDGTs in the temperature proxy index may lead to improved reconstructions in the polar oceans. We thus recommend that the OH-isoGDGTs be analyzed simultaneously during standard isoGDGTs analysis, as this multi-proxy approach will increase the robustness of paleotemperature reconstructions.

**REFERENCES**


