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Isoprenoid and branched GDGT-based proxies for surface sediments from marine, fjord and lake environments in Chile

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## ABSTRACT

Proxies based on glycerol dialkyl glycerol tetraether (GDGT) lipids from archaea [isoprenoid GDGTs] and bacteria [branched GDGTs] in 33 surface sediments from marine, fjord and lake systems between 25°S and 50°S in Chile were analyzed. The regional  $\text{TEX}_{86}^{\text{H}}$  calibration obtained from the marine and fjord sediments and mean annual surface temperature ( $T = 59.6 \times \text{TEX}_{86}^{\text{H}} + 33.0$ ;  $r^2$  0.9;  $n = 23$ ) is statistically identical to the global ocean calibration based on suspended particulate material in terms of slope, but not in terms of intercept. The regional surface and subsurface  $\text{TEX}_{86}^{\text{H}}$  calibrations were statistically different from the existing global ocean core top calibrations. The  $\text{TEX}_{86}$  calibration model based on most of the relatively large lakes studied here ( $T = 50.7 \times \text{TEX}_{86} - 11.8$ ;  $r^2$  0.9;  $n = 5$ ) is statistically identical to the global lake calibration. The relatively high  $\text{TEX}_{86}$  values from smaller lakes suggested an additional source for isoprenoid GDGTs, likely terrestrial or aquatic methanogenic archaea. Application of the soil-calibrated MBT'/CBT (methylation and cyclization of branched (br) GDGTs, respectively) temperature proxy to the marine and fjord sediments resulted in an overestimation of continental mean annual air temperature (MAAT), suggesting in situ production of certain br GDGTs in the water column or surface sediment. For the lakes, MBT'/CBT-based surface air temperature estimates were 3 to 6 °C below MAAT. However, temperature estimates from the lake-specific MBT/CBT global calibration were in good agreement with mean annual surface temperature for all the lakes. The results highlight the need for testing local vs. global calibrations of GDGT-based proxies before their application for palaeoenvironmental reconstruction.

**Key words:**

GDGT;  $\text{TEX}_{86}$ ; BIT; MBT'; CBT; calibration; marine; fjord; lake; Chile

## 1. Introduction

Glycerol dialkyl glyceryl tetraethers (GDGTs) are membrane lipids of archaea and bacteria and occur ubiquitously in aquatic environments and soils (reviewed by Schouten et al., 2013). *Thaumarchaeota* (formerly Group 1 Crenarchaeota; Brochier-Armanet et al., 2008; Spang et al., 2010), a specific phylogenetic cluster of the Archaea domain occurring widely in marine and lake systems (e.g. Karner et al., 2001; Keough et al., 2003), biosynthesize isoprenoid (iso) GDGTs (structures in Appendix 1) containing 0-4 cyclopentane moieties and crenarchaeol, which has a cyclohexane moiety in addition to four cyclopentane moieties (Schouten et al., 2000; Sinninghe Damsté et al., 2002; Pitcher et al., 2011a). Another group of GDGTs containing branched (br) instead of isoprenoid alkyl chains (Appendix 1) was initially discovered in peat bogs (Sinningh Damsté et al., 2000) and subsequently shown to be ubiquitous in soils, coastal marine and lake sediments (e.g. Schouten et al., 2000; Hopmans et al., 2004; Weijers et al., 2006a, 2007a; Sinninghe Damsté et al., 2008; Huguet et al., 2010; Loomis et al., 2011). Acidobacteria thriving in soil are a likely source of brGDGTs (Weijers et al., 2006a, 2009; Sinningh Damsté et al., 2011, 2014). Although brGDGTs occur mainly in soil and peat, they are probably also produced in situ in the water column and/or the sediments of marine and freshwater (lake and river) environments (e.g. Peterse et al., 2009; Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; Tierney et al., 2010a; Pearson et al., 2011; Zhu et al., 2011; Loomis et al., 2011, 2012, 2014; Zell et al., 2013; Buckles et al., 2014; De Jonge et al., 2014a; Weijers et al., 2014).

Based on the two types of GDGTs, different indices have been developed as palaeoenvironmental proxies. The branched and isoprenoid tetraether (BIT) index uses the abundance of brGDGTs relative to crenarchaeol to estimate the input of soil-derived organic matter (OM) in sediments (e.g. Hopmans et al., 2004; Huguet et al., 2007; Walsh et al., 2008).

The TEX<sub>86</sub> (tetraether index of GDGTs consisting of 86 carbon atoms) temperature proxy is based on the distribution of aquatic-derived isoGDGTs containing different numbers of cyclopentane moieties (Schouten et al., 2002). Mesocosm incubation studies have shown that the number of cyclopentane moieties in thaumarchaeotal GDGTs increases with growth temperature (Wuchter et al., 2004; Schouten et al., 2007). Global core top marine calibrations suggest that TEX<sub>86</sub> correlates well with the annual mean temperature of the upper oceanic mixed layer (Kim et al., 2010; Tierney and Tingley, 2014) as well as with the 0-200 m temperature (Kim et al., 2008). Since it appeared that the relative abundance of the crenarchaeol regio-isomer (Appendix 1) is insensitive to temperature change in the polar oceans, a new index was introduced, TEX<sub>86</sub><sup>L</sup>, for application to low temperature (< 15 °C) settings, while TEX<sub>86</sub><sup>H</sup> is more suitable for high temperature settings (> 15 °C; Kim et al., 2010). However, observations suggest that the crenarchaeol regio-isomer (cren'), which is not considered for TEX<sub>86</sub><sup>L</sup>, is essential for SST prediction (Shah et al., 2008; Kim et al., 2010) and in certain polar regions does not perform better than TEX<sub>86</sub> (Ho et al., 2014). Surveys of lakes indicate that TEX<sub>86</sub> also correlates with lake surface (Powers et al., 2004, 2010; Blaga et al., 2009) and subsurface temperature (Blaga et al., 2011; Woltering et al., 2012). The relationship between sea/lake surface temperature and TEX<sub>86</sub> may be masked when a large abundance of soil OM is present in marine or lake sediments, since soils also contain isoGDGTs (albeit in low abundance relative to brGDGTs; Weijers et al., 2006b).

The distribution of brGDGTs is influenced by environmental factors such as pH, temperature and humidity. Weijers et al. (2007a) found that the relative number of cyclopentane moieties, expressed in the cyclization of branched tetraether (CBT) index, is related to soil pH, while the relative number of methyl branches, expressed in the methylation of branched tetraether (MBT) index, is related to both soil pH and mean surface air temperature. Combination of these two indices enables reconstruction of mean air temperature (MAT; Weijers et al., 2007).

Peterse et al. (2012) recently extended the soil dataset and proposed a slightly adjusted index, MBT', using the most commonly occurring brGDGTs in soils. Application of the MBT/CBT index to lake sediments results in large underestimation of mean surface air temperature (e.g. Blaga et al., 2010; Tierney et al., 2010a; Zink et al., 2010), likely due to production of brGDGTs in the water column and/or the sediments (e.g. Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; Buckles et al., 2014). A global calibration of MBT/CBT indices with lake surface temperature was established by Sun et al. (2011), while Tierney et al. (2010a) and Pearson et al. (2011) proposed multiple linear regressions based on the fractional abundances of the most dominant brGDGTs in lake sediments for calibration with mean annual surface temperature. Results based on MBT (MBT') and CBT indices should be carefully considered as a recent study has shown that 6-methyl brGDGTs coelute with 5-methyl brGDGTs (De Jonge et al., 2013), which has led to newly defined indices calibrated against pH and air temperature (De Jonge et al., 2014b). Separation of these isomers requires, however, a special analytical set-up for brGDGT analysis (De Jonge et al., 2013, 2014a,b).

Although GDGT-based proxies are being used increasingly for palaeoclimate reconstruction (e.g. Tierney et al., 2008, 2010b; Lopes dos Santos et al., 2010; Tyler et al., 2010; Caley et al., 2011; Peterse et al., 2011; Kabel et al., 2012; Kim et al., 2012a,b; Ménot and Bard, 2012; Blaga et al., 2013), they still require further validation and calibration for different environmental settings in order to constrain their local and regional applicability and accuracy, as shown by different studies based on soils (e.g. Peterse et al., 2012; Birkholz et al., 2013; De Jonge et al., 2013), marine environments (e.g. Kim et al., 2010; Ho et al., 2011, 2014; Kabel et al., 2012; Tierney and Tingley, 2014) and lake settings (e.g. Blaga et al., 2010, 2011; Huguet et al., 2010; Powers et al., 2010; Tierney et al., 2010a, 2012; Zink et al., 2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012). While global calibrations indicate that genetic and/or physiological factors exert a relatively small effect on the relationship

between GDGT production and temperature, and are therefore applicable in most environments, regional and local calibrations, which incorporate the influence of e.g. seasonality, production depth and producers, can provide more accurate reconstruction for particular environments (e.g. Sinninghe Damsté et al., 2008; Tierney et al., 2010a; Zink et al., 2010; Kabel et al., 2012; Kim et al., 2015), bearing in mind that these local factors might not have been the same in the past, recent attempts have been undertaken to accommodate this issue by way of the so-called BAYSPAR calibration, which provides local calibrations by considering only data points from a specific spatial grid into account (Tierney and Tingley, 2014). However, data from the southeast Pacific and Chile are still scarce in the global calibrations of GDGT-based temperature proxies (e.g. Kim et al., 2008, 2010; Pearson et al., 2011; Sun et al., 2011; Tierney and Tingley, 2014; Ho et al., 2014). Therefore, in this study,  $\text{TEX}_{86}$ ,  $\text{TEX}_{86}^{\text{H}}$ , as well as the BIT, CBT, MBT and MBT' indices were measured for 33 surface sediments from marine, fjord and lake systems between 25°S and 55°S in Chile. Characterized by strong north-south temperature and rainfall gradients, resulting in drastically contrasting environments, Chile is a suitable region for testing the need for local vs. global calibrations of GDGT-based proxies.

## 2. Setting

Chile extends between 18°S and 56°S along the southeast Pacific Ocean (Fig. 1). The morphology of the southwestern South American continental margin is characterized by the Andean Cordillera and a coastal range (Weischet, 1970). In southern Chile, the landscape is marked by the presence of the northern and southern Patagonian ice fields, between ca. 46°S and 51°S, and a characteristic fjord system. Often, the fjords are longer than 80 km, with water depth up to 1000 m below sea level (m.b.s.l.) and are separated from the open ocean by shallow sills (up to 70 m.b.s.l.). The water column in the fjords is characterized by a two-layer

structure with a strong halocline, resulting from the substantial input of freshwater from rivers (Killian et al., 2007; Sievers, 2008; Silva, 2008).

The Chilean climate is influenced by the presence of a subtropical high pressure cell in the north (around 27°S), associated with virtually no rainfall in northernmost Chile (Atacama Desert) and a low pressure belt around Antarctica (Cerveny, 1998). The resulting southern westerly winds centred around 45-50°S and the presence of the Andes causes extremely high amounts of precipitation exceeding 7 m/yr in the coastal area of southern Chile. From northern to southern Chile annual mean surface air temperature decreases from 14 to 4 °C (Fig. 1) and the mean seasonal amplitude (summer/winter) is ca. 6 °C. Offshore Chile, the westward-flowing Antarctic circumpolar current splits around 45°S into the southward flowing Cape Horn current and the equatorward flowing Peru-Chile Current (PCC; Strub et al., 1998; Chaigneau and Pizarro, 2005; Fig. 1). Driven by east/southeast winds, the PCC is at the origin of an upwelling system along the Chilean coast from ca. 41°S to the equator (Strub et al., 1998). Sea surface temperature (SST) ranges from ca. 20 °C at 18 °S to 7 °C around Cape Horn, with mean seasonal amplitude (summer/winter) ca. 4 °C.

### 3. Material and methods

The marine, fjord and lake surface sediments (0-1 cm sediment depth) are from an area between 25°S and 55°S (Fig. 1; Table 1). They were recovered during different expeditions: Mascardi lake (December 1993; Ariztegui et al., 1997), ProGlaLakes (January 1994; Chapron et al., 2006), R/V Sonne SO 102 (May-June 1995; Hebbeln et al., 1995), PALATRAS (October 1999; Gilli et al., 2005), R/V Sonne SO 156 (March-May 2001; Hebbeln et al., 2001), Lagos Lanalhue and Lleu Lleu (September 2005), ENDS (March 2006; Waldmann et al., 2010), R/V Gran Campo II cruise in the Chilean Fjords (September 2006), R/V Marion



Dufresne MD 159 PACHIDERME (February 2007) and R/V Gran Campo II expedition to lakes in the Magellanes region (October 2007). The marine sediments ( $n = 13$ ) were obtained at sites between  $25^{\circ}\text{S}$  and  $50^{\circ}\text{S}$  with a water depth up to 1790 m.b.s.l. The fjord sediments ( $n = 10$ ) were from sites between  $41^{\circ}\text{S}$  and  $54^{\circ}\text{S}$  at a depth between 40 and 655 m.b.s.l. The lake sediments ( $n = 10$ ) originate from 6 Chilean lakes and 4 lakes in southern Argentina between  $37^{\circ}\text{S}$  and  $55^{\circ}\text{S}$  at an elevation between 100 and 700 m.a.s.l. (Table 3). The sediments were taken with devices which kept the water-sediment interface undisturbed: multi-corer, short gravity corer and the CASQ gravity corer from the R/V Marion Dufresne.

The total lipid extract (TLE) of the freeze-dried and ground sediment (2-10 g dry weight, dw) was obtained with an accelerated solvent extraction device (DIONEX ASE 200) using dichloromethane (DCM)/MeOH (9:1, v:v) at  $100^{\circ}\text{C}$  and 1000 psi. After adding  $1.0\text{ }\mu\text{g}$  of a  $\text{C}_{46}$  GDGT as internal standard (Huguet et al., 2006), the extract was separated over an  $\text{Al}_2\text{O}_3$  column (activated for 2 h at  $150^{\circ}\text{C}$ ) into an apolar, a ketone and a polar fraction using hexane:DCM (9:1 v/v), hexane:DCM (1:1 v/v) and DCM:MeOH (1:1 v/v), respectively. The polar fraction was analyzed for GDGTs as described by Hopmans et al. (2000) and Schouten et al. (2007). An aliquot was dissolved via sonication (5 min) in hexane:propanol (99:1, v/v) and filtered through a  $0.45\text{ }\mu\text{m}$  PTFE filter. The sample was analyzed using high performance liquid chromatographyatmospheric pressure chemical ionization mass spectrometry (HPLC-APCI-MS; Agilent 1100 series LC-MS instrument; HP 1100 APCI-MS instrument).

Separation was achieved with a Prevail Cyano column (2.1 x 150 mm,  $3\text{ }\mu\text{m}$ ) maintained at  $30^{\circ}\text{C}$ . GDGTs were eluted isocratically with 99% hexane and 1% propanol for 5 min, followed by a linear gradient to 1.8% propanol in 45 min. Flow rate was 0.2 ml/min. Conditions for APCI-MS were: nebulizer 60 psi, vaporizer  $400^{\circ}\text{C}$ , drying gas ( $\text{N}_2$ ) at 6 ml/min and  $200^{\circ}\text{C}$ , capillary voltage -3 kV, corona  $5\text{ }\mu\text{A}$  (ca. 3.2 kV). The GDGTs were detected using single ion monitoring (SIM) of the  $[\text{M}+\text{H}]^{+}$  ions. Quantification was achieved using a relative response

factor value of 1.1 between a C<sub>46</sub> GDGT standard and an isolated crenarchaeol standard (for details see Huguet et al., 2006). Note that in the present study 5- and 6-methyl brGDGTs were not fully separated with the method used (cf. De Jonge et al., 2013, 2014b).

The GDGT-based indices (Table 2) were calculated following Hopmans et al. (2004) for the BIT index (Eq. 1; Table 2), Schouten et al. (2002) for TEX<sub>86</sub> (Eq. 2; Table 2), Kim et al. (2010; Eq. 3; Table 2) for TEX<sub>86</sub><sup>H</sup>, Weijers et al. (2007a) for the MBT and CBT indices (Eq. 4 and 5; Table 2) and Peterse et al. (2012) for the MBT' index (Eq. 6; Table 2). As sea surface temperature (SST) data for the Chilean fjords are scarce, unpublished (punctual CTD - conductivity, temperature, depth - data taken during the above expeditions) and few published data from austral winter and spring (Gonzalez et al., 2010, 2011; Palma and Silva, 2004) were used, together with the World Ocean Atlas 2001 database (WOA; Conkright et al., 2002), which has a spatial coverage of 1° x 1° (lat./long.). Depth integrated annual mean temperatures from 0 to 200 m water depth were calculated from WOA following Kim et al. (2008). The WOA temperatures were chosen in the nearest degree in latitude and longitude to each surface sediment position. For surface air temperature, the high resolution (0.1° x 0.1° grid) World Water and Climate Atlas from the International Management Water Institute (IWMI) was used. The atlas is based on an interpolation (which includes elevation as co-predictor) of data from weather stations around the world for 1961-1990 and provides monthly values (New et al., 2002; data available at the IWMI on-line climate summary service portal; <http://www.iwmi.cgiar.org/>). Mean annual lake surface temperature values were taken from the literature whenever possible (Ariztegui et al., 1997; Parra et al., 2003; Gilli et al., 2005; Pérez et al., 2007; Moy et al., 2011). As both mean annual air and lake surface temperature are similar to each other (Table 3), mean annual air temperature (MAAT) values were used for the lakes when surface water temperature values were not available.

Pearson correlation coefficient analysis and principal component analysis (PCA) were performed with the software PAST (PAleontological STatistics) version 3.04© (Hammer et al., 2001). PCA was performed to identify the dominant factors of the variance in the datasets. Prior to PCA analysis, the data were standardized using mean values and standard deviations to bring all of the variables into proportion with each another. To determine whether the slopes and intercepts of the regression lines were significantly different from each other, *t*-tests were performed using the mean, slope, intercept, standard errors, sum of squared error and sample size for each dataset (Cohen et al., 2003; Wuensch, 2013).

## 4. Results and discussion

### 4.1. GDGT concentration and BIT index

The concentration of isoGDGTs (GDGTs 0-3, crenarchaeol and its regio-isomer; Appendices 1 and 2) ranged between 0.2 and 22.4  $\mu\text{g/g dw}$  (mean 6.5  $\mu\text{g/g dw}$ ) in the marine sediments and between 4.3 and 15.7  $\mu\text{g/g dw}$  (mean 7.4  $\mu\text{g/g dw}$ ) in the fjord sediments (Fig. 2A). The concentration of brGDGTs (summed concentrations of VIII + VII + VI; Appendices 1 and 2) ranged between 0.2 and 0.6  $\mu\text{g/g dw}$  (mean 0.4  $\mu\text{g/g dw}$ ) in the fjord sediments and between 0.02 and 0.4  $\mu\text{g/g dw}$  (mean 0.1  $\mu\text{g/g dw}$ ) in the marine sediments. The concentration of brGDGTs was highest in the lake sediments, between 0.1 and 2.9  $\mu\text{g/g dw}$  (mean 1.1  $\mu\text{g/g dw}$ ), while the mean concentration of isoGDGTs between 0.01 and 1.0  $\mu\text{g/g dw}$  (mean 0.2  $\mu\text{g/g dw}$ ) was lower than in the marine and fjord environments.

The BIT index (Eq. 1; Table 2) for the marine sediments ranged between 0.02 and 0.06 (mean 0.03; Fig. 2B), a common value for open marine settings (Schouten et al., 2013 and references therein). For the fjord sediments, values were between 0.04 and 0.08, on average twofold

higher than for the marine sediments. A cross plot of brGDGT concentration and BIT (Fig. 2B) suggests that elevated BIT values in fjord sediments are primarily related to the increase in concentration of brGDGTs, supporting the idea of an increasing contribution of soil OM towards the coastal area. Such a trend was also inferred on the basis of the interpretation of C/N values from an offshore-inshore transect at ca. 43-47°S. C/N increased from ca. 6 in marine surface sediments (Hebbeln et al., 2000) to 10 and 16 in the outer and inner fjords, respectively (Sepulveda et al., 2011), reflecting an increased input of terrestrial OM, which is characterized by values  $\geq 20$  (e.g. Meyers, 1994 and references therein). The BIT index seems, therefore, to work well as a proxy for the relative input of soil OM to the marine and fjord environments off Chile. However, in situ production of certain brGDGTs cannot be excluded (Section 4.4.).

The lake sediments had much higher BIT values than the marine and fjord sediments, with values between 0.30 and 0.99 (Fig. 2B), i.e. a common range for lake systems (Schouten et al., 2013 and references therein). In comparison with the other lakes, the sediments from Mascardi, Nahuel Huapi, Cardiel and Fagnano lakes (sediments 9, 10, 22, 33, respectively; Tables 1 and 3) had the lowest BIT values. This may be related to their relatively larger size (Table 3) and a higher in situ thaumarchaeotal productivity (Blaga et al., 2009; Powers et al., 2010; Tierney et al., 2010a, 2012). Indeed, the concentration of crenarchaeol was higher in these lakes than in the other, smaller lakes, which were strongly dominated by brGDGTs (Fig. 2C). There was however no correlation ( $r^2$  0.02; not shown) between BIT values and surface/catchment ratio for the different lakes, as would be expected if brGDGTs are predominantly derived from soils. This may indicate in situ production of certain brGDGTs in the lakes (Section 4.4.).

Using a simple two end member mixing model based on data from the Congo River fan, Weijers et al. (2006b) estimated that BIT index values  $> 0.3$  may bias  $\text{TEX}_{86}$ -based SST reconstruction by  $> 2\text{ }^{\circ}\text{C}$ , because isoGDGTs are also present in soils, although in relatively low concentration. Here,  $\text{TEX}_{86}$ -based SST estimates are unlikely to be biased for the marine and fjord sediments, as all BIT values were  $< 0.1$  (Fig. 2B). The relatively high BIT values for the lake sediments indicate that  $\text{TEX}_{86}$ -based lake surface temperature may be influenced by soil-derived input of isoGDGTs (cf. Blaga et al., 2009; Powers et al., 2010). However, since in recent years it has become clear that brGDGTs may also be produced in the water column and sediments of lakes (e.g. Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; De Jonge et al., 2014a; Buckles et al., 2014), the BIT index is less reliable in assessing a significant input of soil material to lake systems. Therefore, we also tested the application of the  $\text{TEX}_{86}$  palaeothermometer to these lakes with BIT values  $> 0.3$ .

#### 4.2. $\text{TEX}_{86}^H$ and temperature in the marine and fjord sediments

Results from water column studies off northern and central-southern Chile have shown that *Thaumarchaeota* are the dominant archaeal group in the Peru-Chile Current system and are predominantly abundant within the upper oxycline (10-100 m depth) of the  $\text{O}_2$  minimum zone (OMZ), where  $\text{NH}_4^+$  attains maximum concentration (Quiñones et al., 2009; Belmar et al., 2011). Similar results were obtained for the OMZ of the Arabian Sea, with a clear maximum in crenarchaeol concentration at the oxycline (Pitcher et al., 2011b; Schouten et al., 2012).

While no data for *Thaumarchaeota* distribution in the water column of the Chilean fjord region were available, the typical two layered structure with an oxycline at ca. 50-75 m and  $\text{NH}_4^+$  maximum between 25 and 100 m (Sievers, 2008; Silva, 2008) suggests a potential subsurface habitat of *Thaumarchaeota* in the fjords, as also suspected in a study of Norwegian fjords (Huguet et al., 2007).

In view of the ecological niche of the *Thaumarchaeota*, we tested the values of  $\text{TEX}_{86}^{\text{H}}$  (Eq. 3; Table 2) against observed temperature of both the sea surface (0 m) and subsurface (0-200 m depth-integrated; see Kim et al., 2008) for the marine and fjord sediments, and compared the resulting regional calibrations with the global ones (Fig. 3; Tables 2 and 4).  $\text{TEX}_{86}^{\text{H}}$  values correlated strongly with both SST and subsurface temperature off Chile, but the  $\text{TEX}_{86}^{\text{H}}$  calibrations were statistically different from the global ocean calibrations in terms of slope and intercept (Fig. 3A, B; Table 4). The surface temperature calibration had a statistically similar slope, but a different intercept from the global calibration based on suspended particulate matter (SPM) from < 100 m water depth and in situ temperature (Schouten et al., 2013; Fig. 3C; Tables 2 and 4). Similar results were obtained with the marine sediments only (data not shown), indicating that the different regional relationship between  $\text{TEX}_{86}^{\text{H}}$  and temperature is not caused by the inclusion of fjord sediments. *Thaumarchaeota* diversity, depth distribution in the water column, as well as seasonality, may explain the difference between the global and our local calibrations. However, the available environmental data are not sufficient to conclude which of these factors cause the observed difference between the calibration off Chile and the global calibration. Our results reveal that the isoGDGT distribution is closely related to surface temperature in both the fjords and the open ocean off Chile, likely because seasonality and depth habitat are similar in both systems. Although *Thaumarchaeota* are probably most abundant at depth (10-100 mwd) off Chile, we recommend using the regional  $\text{TEX}_{86}^{\text{H}}$  surface calibration established here in order to reconstruct annual mean surface palaeotemperature in these environments.

#### 4.3. $\text{TEX}_{86}$ in lakes

While there was an apparent relationship between the  $\text{TEX}_{86}$  values of the sediments of relatively large lakes (water surface  $> 32 \text{ km}^2$ ; sediments 6, 7, 9, 10, 22 and 33; Tables 1 and 3) and mean annual lake (air) surface temperatures, the  $\text{TEX}_{86}$  values for the sediments of relatively small lakes (water surface  $< 0.1 \text{ km}^2$ ; sediments 28, 29, 30 and 32; Tables 1 and 3) were much higher than what would be expected from mean annual surface temperature (Fig. 4). This suggests a source of isoGDGTs in addition to water column-dwelling Thaumarchaeota in the relatively small lakes. In order to test this hypothesis, the GDGT-0/crenarchaeol ratio was calculated (Table 3). Since methanogenic archaea synthesize GDGT-0 (Schouten et al., 1998; Koga et al., 1998), but not crenarchaeol, a GDGT-0/crenarchaeol ratio value  $> 2$  indicates that GDGT-0 (and thus also other isoGDGTs such as GDGT-1 and -2) may originate from methanogenic archaea present in lakes (Blaga et al., 2009). While GDGT-0/crenarchaeol values of sediments 28 and 32 were indeed  $> 2$ , this was not the case for sediments 29 and 30. Therefore, the input of some isoGDGTs produced by terrestrial and/or aquatic methanogens may explain the elevated  $\text{TEX}_{86}^{\text{H}}$  values observed for certain, but not all, small lakes studied here. For the relatively large lakes, a strong correlation ( $r^2$  0.9) was observed between  $\text{TEX}_{86}$  values of the sediments (excluding sediment 6, where the GDGT-0/cren ratio was  $> 2$ ; Table 3) and mean annual lake (air) surface temperatures (Fig. 4). The calibration model [ $T = 50.7 \times \text{TEX}_{86} - 11.8$ ; standard error of estimates (SEE)  $0.6 \text{ }^{\circ}\text{C}$ ] is statistically similar to the global lake calibration of Powers et al. (2010) in terms of both slope and intercept (Tables 2 and 4).

#### 4.4. *MBT'/CBT indices*

The mean BIT values for the marine and fjord sediments ( $< 0.1$ ) suggest that the soil OM input may be too low for the application of the MBT'/CBT proxy (Eqs. 6 and 7), so the signal may be biased by production of brGDGTs in the marine water column and/or in the sediment

itself (Peterse et al., 2009, 2012; Zhu et al., 2011; Weijers et al., 2014). Indeed, MBT'/CBT MAAT estimates did not correlate ( $r^2$  0; not shown) with observed MAAT values of the adjacent continent (where the brGDGTs were assumed to be derived from Fig. 5A) and were generally ca. 2 to 6 °C higher. The high fractional abundances of brGDGTs with one cyclopentane in the marine and fjord sediments compared with lake sediments as revealed by PCA of the fractional abundance of all 12 analyzed brGDGTs (positive loading of GDGT-VIb and GDGT-VIIb on PC 1, which explained 75% of the variance; Fig. 5B) probably indicates in situ production of brGDGTs (Peterse et al., 2009; Weijers et al., 2014). Indeed, because the porewater of marine sediments is typically alkaline, in situ produced brGDGTs are characterized by a higher degree of cyclization (Peterse et al., 2009). Therefore, a low relative concentration and in situ production of certain brGDGTs prevented the application of the MBT'/CBT proxy to most of the fjord and marine sediments off Chile. However, as brGDGTs with 1-2 cyclopentane moieties mainly are produced in situ in marine sediments (Peterse et al., 2009), the BIT index, which is based on brGDGTs without cyclopentane moieties (Hopmans et al., 2004), is likely not affected by in situ production.

In the lake sediments, a high abundance of soil OM could be expected from the relatively high BIT values (Fig. 2; Table 3). However, in situ production of certain brGDGTs in the water column and/or sediment of lakes has been implied from many studies in a wide variety of regions (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; Tierney et al., 2010a, 2012; Bechtel et al., 2010; Loomis et al., 2011; Buckles et al., 2014). When the MBT'/CBT soil calibration (Peterse et al., 2012; Eqs. 6 and 7) was applied to the brGDGTs in the lake sediments, a significant correlation ( $r^2$  0.8) existed between estimated and observed mean annual surface (air and lake) temperatures, but the estimated temperature values were ca. 3 to 6 °C below observed values (Fig. 5A). This agrees with previous studies and is likely due to in situ production of brGDGTs in lakes (see above).



Consequently, specific brGDGT calibrations for lake surface water temperature have been developed using lake surface sediments (Tierney et al., 2010a; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012). The two global calibrations developed by Sun et al. (2011) and Pearson et al. (2011) were tested for the lakes here (Eqs. 20-21; Table 2). While the Pearson et al. (2011) calibration, based on summer MAT, resulted in estimates ca. 2 to 7 °C above observed mean summer temperatures, the Sun et al. (2011) calibration based on MAAT provided temperature estimates closest to observed mean annual surface temperatures (Fig. 5C). With the latter calibration, estimated and observed temperatures correlated significantly ( $r^2$  0.9) and the slope of the linear regression was close to one (0.8; Fig. 5D). The residuals ( $< 0.8$  °C; not shown) were within the calibration error of  $\pm 4.3$  °C (Sun et al., 2011). Therefore, while the absence of water pH data from certain lakes here prevented establishing a MBT/CBT regional calibration, reliable surface temperature estimates could be obtained by applying the global calibration from Sun et al. (2011) for the relatively small lakes, where the TEX<sub>86</sub> proxy was not applicable (Section 4.3.). For the relatively large lakes, both branched and isoprenoid GDGT-based indices potentially allow reconstructing past lake surface temperature.

## 5. Conclusions

Different proxies based on isoprenoid and branched GDGTs in 33 surface sediments from open ocean, fjords and lakes in Chile were measured. The results corroborate the application of these organic proxies to the region. For the marine and fjord environments, the BIT index seemed to work well as a proxy for relative inputs of soil OM, although in situ production of some brGDGTs in the water column and/or the sediment cannot be fully excluded. While GDGT distributions were dominated by brGDGTs in lake sediments, brGDGTs were

probably produced predominantly in situ in the water column and/or the sediment. Therefore, the BIT index should not be used as a proxy for soil OM input to these lakes.

The regional calibration of  $\text{TEX}_{86}^{\text{H}}$  with annual mean surface temperature for the fjord and marine sediments was statistically similar to the SPM global calibration in terms of slope, suggesting that GDGT distribution correlates with Thaumarchaeota growth temperature in surface (< 100 m) water of the fjords and open ocean off Chile. The regional  $\text{TEX}_{86}$  calibration based on most of the relatively large lakes was statistically similar to the global  $\text{TEX}_{86}$  lake calibration. The production of some isoGDGTs by other (methanogenic) archaea prevented the application of  $\text{TEX}_{86}$  to relatively small lakes (water surface < 1 km<sup>2</sup>).

In situ production of brGDGTs containing a relatively high amount of cyclopentane moieties in the water column and/or in the sediment prevented application of the MBT'/CBT palaeothermometer, using the soil-based calibration from Peterse et al. (2012), to the marine, fjord and lake environments. However, the global lake-specific MBT/CBT calibration of Sun et al. (2011) provided temperature estimates close to observed mean annual surface temperatures for all the lakes here.

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#### **Figure, table and appendix captions**

**Fig. 1.** (A) Distribution of mean annual SST (contour lines; data from World Ocean Atlas 2001; Conkright et al., 2002) and air temperature (data from New et al., 2002). Arrows represent the main ocean surface currents in the southeast Pacific region (ACC, Antarctic Circumpolar Current; PCC, Peru-Chile Current; CHC, Cape Horn Current). (B) Detailed map with location of the surface sediments from marine (circles), fjord (triangles) and lake (stars) environments (see Tables 1 and 3).

**Fig. 2.** (A) Concentrations of branched vs. isoprenoid GDGTs of the marine, fjord and lake sediments. (B) BIT index values vs. amount of brGDGTs (log scale). The dotted line represents the upper limit below which TEX<sub>86</sub> indices are assumed not to be biased by soil-derived GDGTs (Weijers et al., 2006b; see text for details). (C) Relative abundance of crenarchaeol and brGDGTs in the lake sediments. Numbers refer to sediments listed in Table 1.

**Fig. 3.** Regional calibration lines for  $\text{TEX}_{86}^{\text{H}}$  and (A) annual mean surface (0 m) and (B) subsurface (integrated depth 0-200 m) temperature in comparison with global calibration curves. Circles and triangles represent marine and fjord sediments off Chile, respectively, and the grey dots the data used in the global calibrations from Kim et al. (2010, 2012a,b). Numbers refer to sediments in Table 1. See Table 2 for the equations of all calibration curves.

**Fig. 4.** Correlation between  $\text{TEX}_{86}$  and mean annual surface temperature for relatively large (black stars) and small (grey stars) lakes. Note that sediment 6 was not included in the linear regression based on relatively large lakes (see text for details). The global correlation curve from Powers et al. (2010; Eq. 12; Table 2) is also shown (grey dashed line). Numbers refer to sediments in Table 1.

**Fig. 5.** (A) Comparison between observed and estimated mean annual surface temperature using the MBT'/CBT soil-based calibration (Peterse et al., 2012; Eq. 14; Table 2) for the marine, fjord and lake sediments. Numbers refer to the sediments in Table 1. (B) PCA of the fractional abundance of brGDGTs in the marine, fjord and lake sediments. Roman numerals refer to structures in Appendix 1 and numbers to the sediments in Table 1. (C) Comparison of observed and estimated surface temperature using the different brGDGT-based indices and lake-specific calibrations from Sun et al. (2011; Eq. 15; Table 2) for mean annual temperature estimates and from Pearson et al. (2011; Eq. 16; Table 2) for mean summer temperature estimates. (D) Linear regression between observed and estimated mean annual surface temperature for the lakes using the global lake calibration from Sun et al. (2011; Eq. 15; Table 2).

**Table 1**

Sediment label, location, observed surface (0 m) and subsurface (0-200 m) mean annual water temperatures and values for the different GDGT-based indices ( n.d., no data).

#### **Table 2**

GDGT-based indices and reported global and regional (this study) calibration curves (fr, fractional abundance; SEE, standard error of estimate; roman numerals refer to structures in Appendix 1).

#### **Table 3**

General characteristics of sampled lakes (m.a.s.l., m above sea level; n.d., no data; BIT is defined in Table 2).

#### **Table 4**

Similarity of slopes and intercepts of different calibration curves considered in this study (see equations 7-13 in Table 2). A *t*-test probability value < 0.05 (in italics) indicates that the slopes/intercepts are significantly different from each other (Cohen et al., 2003; Wuensch, 2013). Tests for the intercepts were not performed when the homogeneity of slope tests were not fulfilled (i.e. no parallel linear relationship between the covariate and the dependant variable) as an invalid analysis of the intercepts may result in inaccurate data interpretation (Hinkle et al., 2003).

**Appendix 1.** Structures of the isoprenoid and branched GDGT membrane lipids.

**Appendix 2.** Abundances (ng/g dw) of isoprenoid (GDGT-0, -1, -2, -3, -4, -4') and branched (GDGT-VI, -VIa, -VIb, -VII, -VIIa, -VIIb, -VIII, -VIIIa, -VIIIb) GDGTs in the surface sediments. See Appendix 1 for the structures of the GDGTs.

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Sediment	Lat.	Long.	Core	Water depth (m)	Environment	0 m water temperature (°C)	0-200m water temperature (°C)	BIT	TEX <sub>86</sub>	TEX <sub>86</sub> <sup>H</sup>	CBT	MBT <sup>*</sup>	MBT
1	25°59'S	70°48'W	GeoB7118-1	460	Marine	17.6	13.3	0.024	0.548	-0.261	0.006	0.324	0.315
2	25°59'S	70°50'W	GeoB7122-2	673	Marine	17.6	13.3	0.016	0.538	-0.270	-0.102	0.298	0.289
3	28°25'S	71°19'W	GeoB7129-1	476	Marine	16.4	12.6	0.023	0.534	-0.273	0.078	0.315	0.307
4	31°58'S	71°40'W	GeoB7147-1	398	Marine	15.6	12.2	0.022	0.514	-0.289	0.190	0.316	0.308
5	36°32'S	73°40'W	GeoB7162-4	798	Marine	14.4	11.5	0.017	0.478	-0.321	0.051	0.395	0.388
6	37°93'S	73°27'W	LA-SL008	15	Lanahue lake	12.5	<i>n.d.</i>	0.950	0.438	-0.359	0.708	0.324	0.322
7	38°17'S	73°33'W	LL-SL002	38	Lieu Lieu lake	12	<i>n.d.</i>	0.917	0.458	-0.339	0.684	0.308	0.304
8	40°59'S	74°33'W	GeoB7197-1	816	Marine	13.3	10.8	0.024	0.453	-0.344	0.151	0.369	0.362
9	41°05'S	71°20'W	NH94-1	50	Nahuel Huapi lake	7.9	<i>n.d.</i>	0.477	0.391	-0.408	0.598	0.223	0.211
10	41°21'S	71°33'W	PMAS93.4	30	Mascardi lake	8.5	<i>n.d.</i>	0.475	0.416	-0.381	1.085	0.288	0.286
11	41°42'S	72°46'W	MD07-3105	329	Fjord	12.8	10.7	0.043	0.427	-0.370	0.362	0.451	0.447
12	41°42'S	72°40'W	MD07-3108	458	Fjord	12.8	10.7	0.062	0.450	-0.347	0.383	0.440	0.436
13	44°09'S	75°09'W	GeoB7182-1	301	Marine	12.1	9.9	0.056	0.472	-0.326	0.321	0.492	0.487
14	44°09'S	75°09'W	MD07-3094	1132	Marine	12.1	9.9	0.026	0.446	-0.350	0.182	0.411	0.404
15	44°17'S	75°23'W	GeoB7187-1	476	Marine	12.1	9.9	0.031	0.436	-0.361	0.146	0.396	0.389
16	44°19'S	75°22'W	GeoB7189-1	868	Marine	12.1	9.9	0.023	0.450	-0.346	0.099	0.362	0.354
17	44°19'S	75°22'W	MD07-3091	481	Marine	12.1	9.9	0.041	0.446	-0.351	0.242	0.393	0.387
18	45°23'S	73°28'W	MD07-3114	294	Fjord	11.7	9.8	0.045	0.419	-0.378	0.438	0.372	0.368
19	47°53'S	74°29'W	MD07-3122	663	Fjord	10.6	9.2	0.069	0.426	-0.371	0.426	0.426	0.426
20	47°53'S	74°29'W	MD07-3120	662	Fjord	10.6	9.2	0.070	0.421	-0.376	0.408	0.430	0.422
21	48°27'S	76°16'W	MD07-3086	1163	Marine	10.5	8.7	0.023	0.435	-0.361	0.127	0.320	0.311
22	48°57'S	71°13'W	CAR99-10P	51	Cardiel lake	8.5	<i>n.d.</i>	0.344	0.402	-0.396	0.091	0.199	0.187
23	49°10'S	76°34'W	MD07-3084	1790	Marine	10.1	8.7	0.022	0.416	-0.381	-0.148	0.281	0.270
24	50°05'S	75°06'W	MDD-1SL	65	Fjord	9.3	9.5	0.041	0.412	-0.385	0.400	0.380	0.373
25	50°19'S	75°22'W	MDD-3SL	65	Fjord	9.3	9.5	0.048	0.408	-0.389	0.170	0.399	0.393
26	50°36'S	74°59'W	Conce-1SL	191	Fjord	9.5	9.5	0.061	0.431	-0.365	0.076	0.368	0.362
27	50°49'S	74°00'W	Peel-4SL	39	Fjord	9.2	9.5	0.080	0.395	-0.403	0.584	0.304	0.301
28	52°49'S	72°54'W	CH-4	16	Chandler lake	9	<i>n.d.</i>	0.996	0.591	-0.228	1.092	0.344	0.341
29	52°53'S	73°46'W	TA-SL1	22	Tamar lake	6.4	<i>n.d.</i>	0.947	0.539	-0.269	1.233	0.273	0.271
30	53°26'S	72°55'W	LH-SL	35	Humphrey lake	4.6	<i>n.d.</i>	0.909	0.485	-0.315	1.200	0.231	0.230
31	53°34'S	70°40'W	MD07-3131	463	Fjord	7.8	7.3	0.042	0.369	-0.433	0.147	0.369	0.361
32	53°36'S	70°55'W	LHAM-SL	23	Hambre lake	5.1	<i>n.d.</i>	0.996	0.561	-0.251	1.030	0.226	0.225



33	54°32'S	67°59'W	LF06-G14	70	Fagnano lake	5.8	<i>n.d.</i>	0.824	0.343	-0.464	0.831	0.236	0.227
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N°	Eq.	r <sup>2</sup>	SEE (°C)	n	Reference
1	BIT = (VI + VII + VIII)/(cren + VI + VII + VIII)				Hopmans et al., 2004
2	TEX <sub>86</sub> = (2 + 3 + cren isomer)/(1 + 2 + 3 + cren isomer)				Schouten et al., 2002
3	TEX <sub>86</sub> <sup>H</sup> = log ((2 + 3 + cren isomer)/(1 + 2 + 3 + cren isomer))				Kim et al., 2010
4	MBT = (VI + VIb + VIc)/(VI + VIb + VIc + VII + VIIb + VIIc + VIII + VIIIb + VIIIc)				Weijers et al., 2007a
5	CBT = -log [(VIb + VIIb)/(VI + VII)]				Weijers et al., 2007a
6	MBT' = (VI + VIb + VIc)/(VI + VIb + VIc + VII + VIIb + VIIc + VIII)				Peterse et al., 2012
7	T <sub>surf</sub> <sup>a</sup> = 68.4 x TEX <sub>86</sub> <sup>H</sup> + 38.6	0.9	2.5	255	Kim et al., 2010
8	T <sub>surf</sub> <sup>a</sup> = 59.6 x TEX <sub>86</sub> <sup>H</sup> + 33.0	0.9	0.8	23	This study
9	T <sub>subsurf</sub> <sup>b</sup> = 54.7 x TEX <sub>86</sub> <sup>H</sup> + 30.7	0.8	2.2	255	Kim et al., 2012a
10	T <sub>subsurf</sub> <sup>b</sup> = 32.1 x TEX <sub>86</sub> <sup>H</sup> + 21.5	0.9	0.6	23	This study
11	T = 59.6 x TEX <sub>86</sub> <sup>H</sup> + 32.0	0.8	2.7	78	Schouten et al., 2013
12	T <sub>surf</sub> <sup>a</sup> = 55.2 x TEX <sub>86</sub> - 14.0	0.9	3.6	12	Powers et al., 2010
13	T <sub>surf</sub> <sup>a</sup> = 50.7 x TEX <sub>86</sub> - 11.8	0.9	0.6	5	This study
14	T <sub>air</sub> <sup>c</sup> = 0.8 - 5.7 x CBT + 31.0 x MBT'	0.6	5.0	176	Peterse et al., 2012
15	T <sub>surf</sub> <sup>a</sup> = 6.8 - 7.1 x CBT + 37.1 x MBT	0.6	5.2	139	Sun et al., 2011
16	T <sub>sum</sub> <sup>d</sup> = 20.9 - 98.1 x fr <sub>GDGT-VIb</sub> - 12 x fr <sub>GDGT-VII</sub> - 20.5 x fr <sub>GDGT-VIII</sub>	0.9	2.0	85	Pearson et al., 2011

a T<sub>surf</sub> = surface water temperature

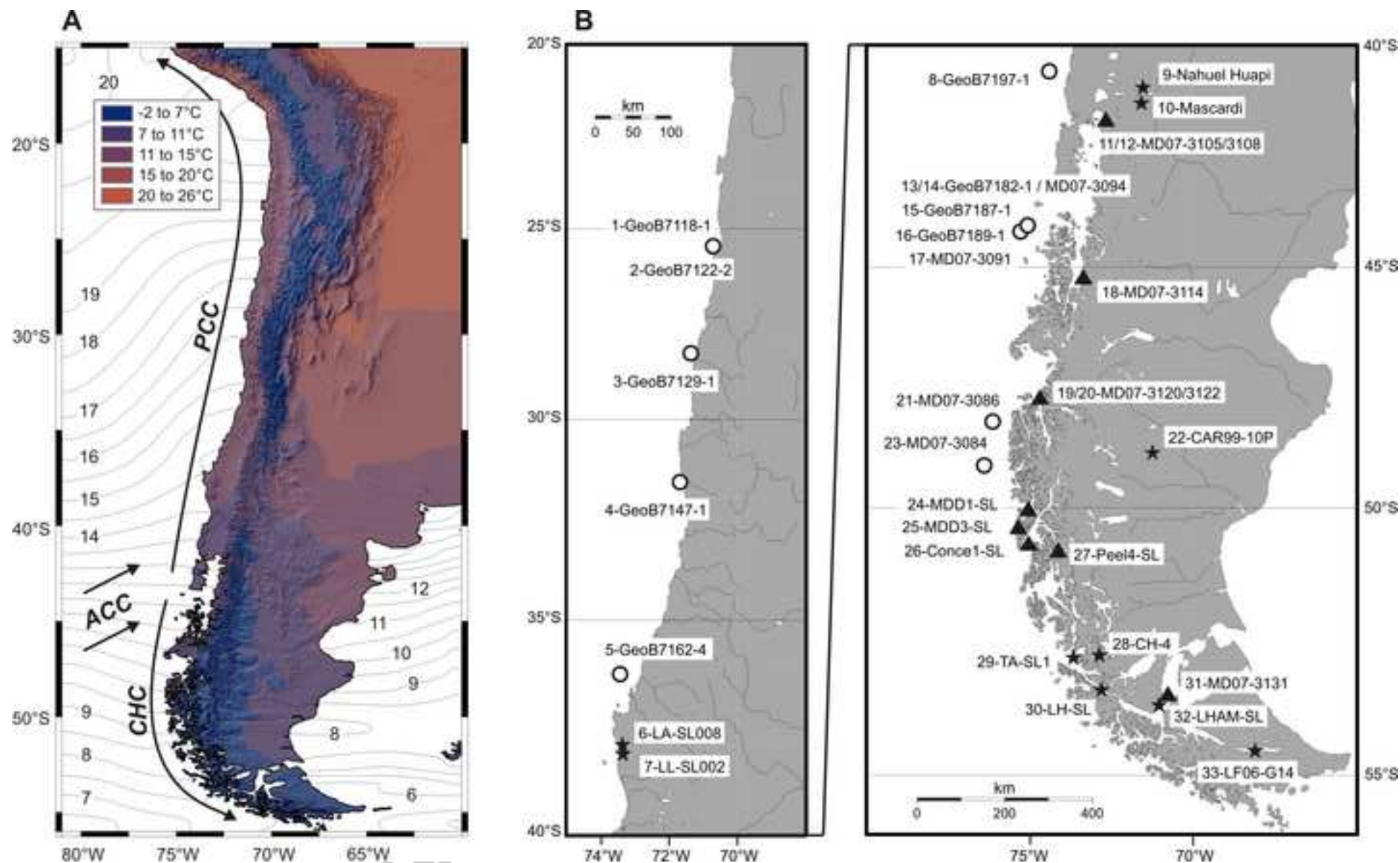
b T<sub>subsurf</sub> = subsurface (0-200m) water temperature

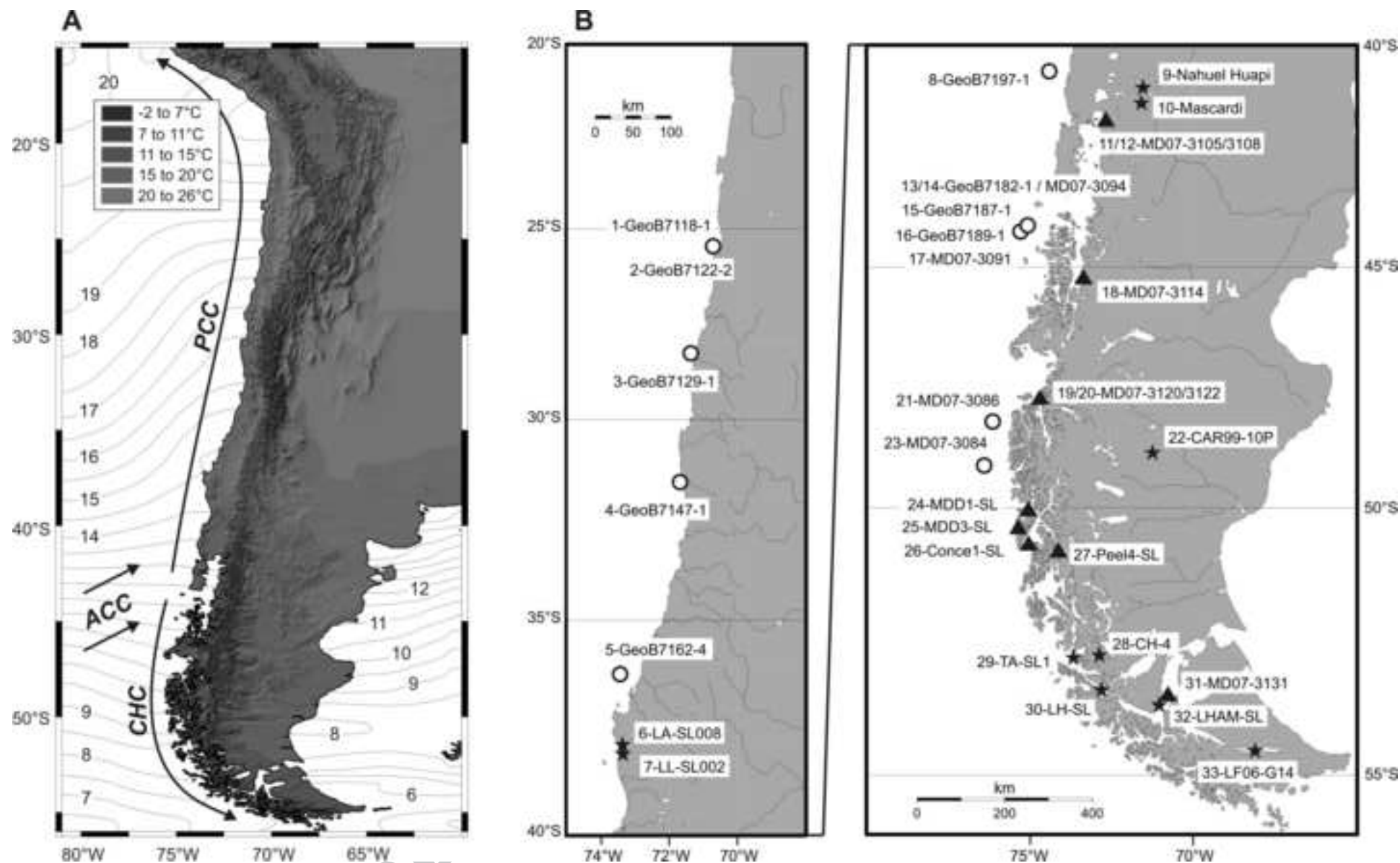
c T<sub>air</sub> = surface air temperature

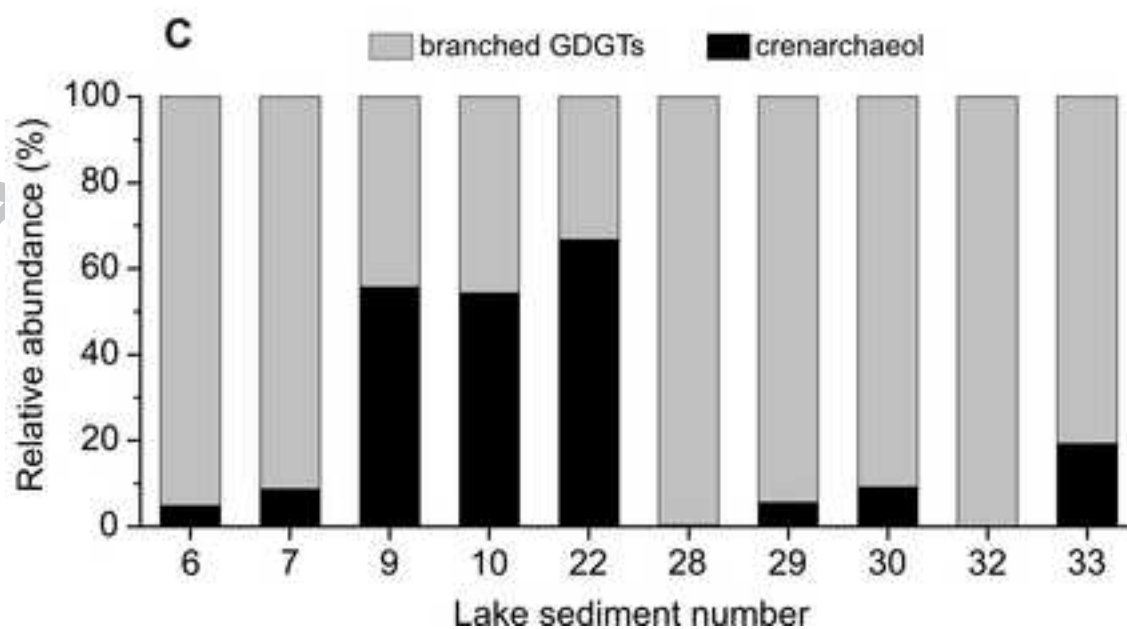
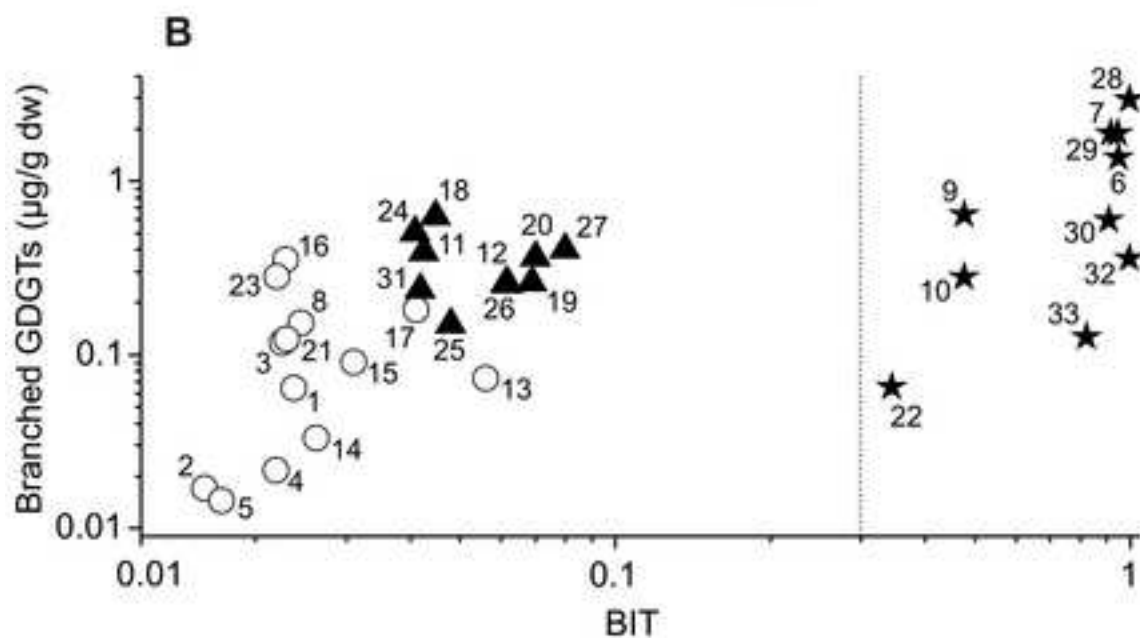
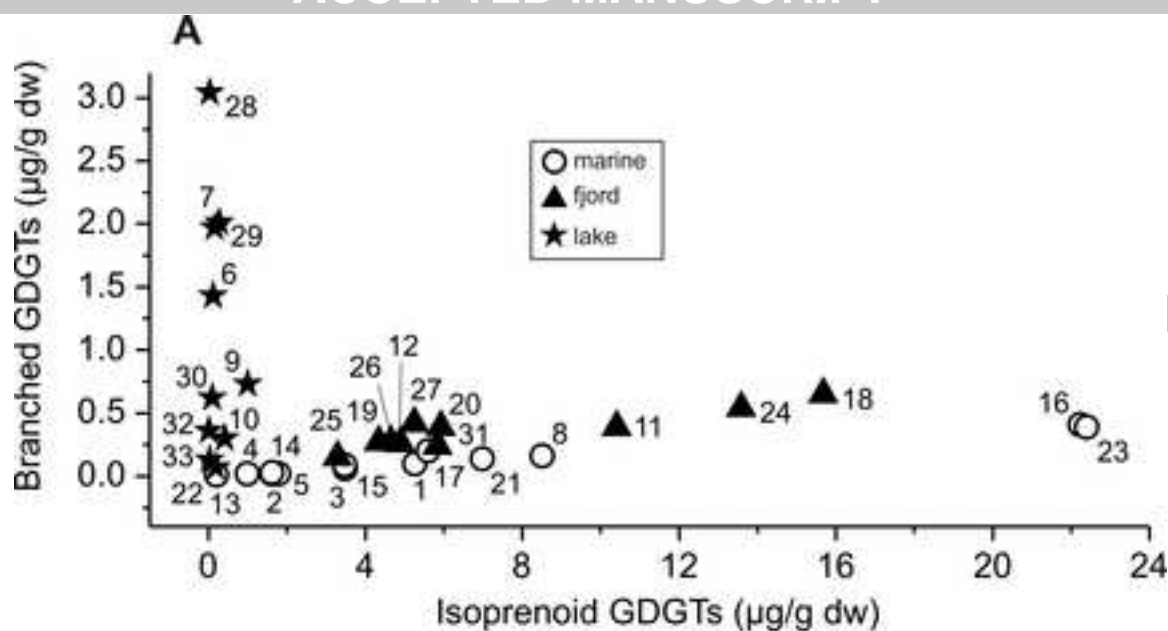
d T<sub>sum</sub> = surface water summer temperature

Lake	Lanahue	Lleu Lleu	Nahuel Huapi	Mascardi	Cardiel	Chandler	Tamar	Humphrey	Hambre	Fagnano
Sediment	6	7	9	10	22	28	29	30	32	33
Latitude	37°33'S	38°17'S	41°05'S	41°21'S	48°57'S	52°49'S	52°53'S	53°26'S	53°36'S	54°32'S
Longitude	73°27'W	73°33'W	71°20'W	71°33'W	71°13'W	72°54'W	73°46'W	72°55'W	70°55'W	67°59'W
Lake altitude (m.a.s.l.)	8	5	770	808	276	45	35	68	68	26
Lake surface (km <sup>2</sup> )	32	37	646	39	370	0.02	0.07	<0.05	0.02	560
Catchment area (km <sup>2</sup> )	360	580	2758	700	4500	0.45	0.81	n.d.	0.11	2900
Surface/catchment ratio	0.09	0.06	0.23	0.06	0.08	0.04	0.09	-----	0.18	0.19
Mean annual air temperature (°C)	12.5	12	7.9	8.5	8.5	9	6.4	4.6	5.1	6
Mean annual lake surface temperature (°C)	11.5	12	7.9	8.5	n.d.	n.d.	n.d.	n.d.	n.d.	5.8
BIT	0.95	0.92	0.48	0.48	0.34	1	0.95	0.91	1	0.82
GDGT-0/cren	3.82	0.84	0.68	0.86	0.43	4.26	0.74	1.07	4642.69	0.63

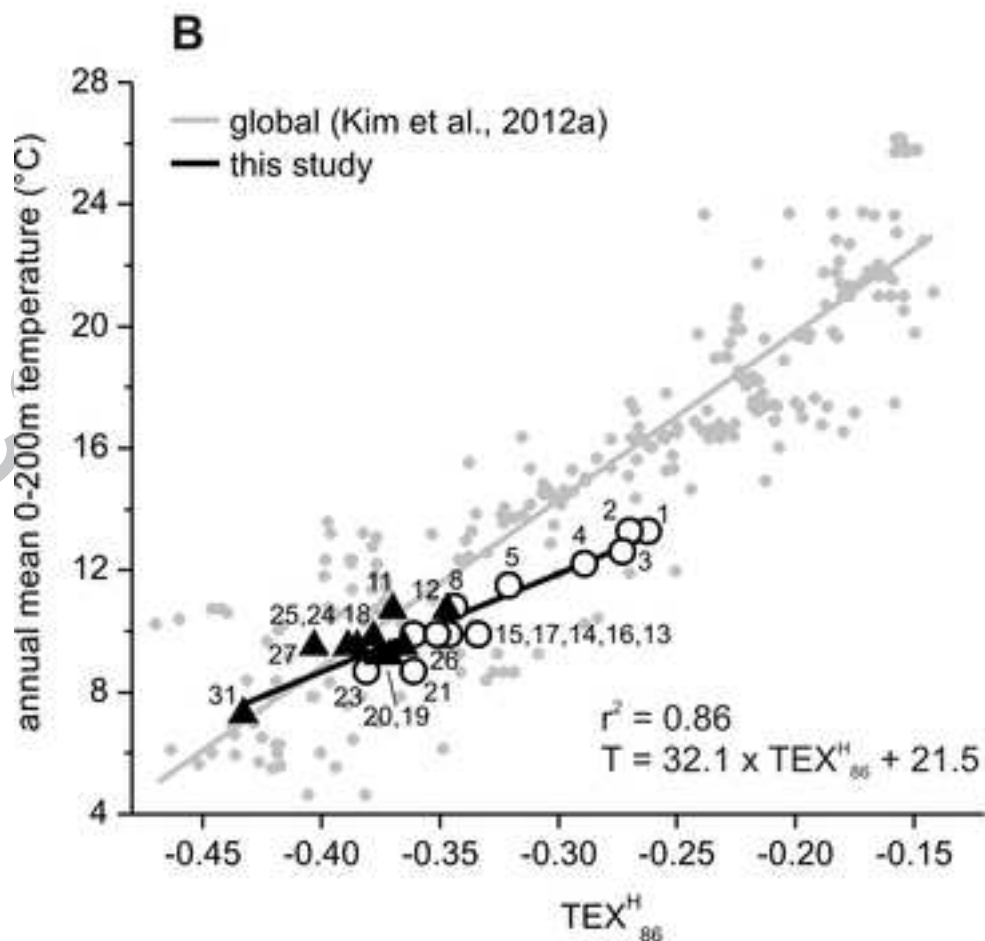
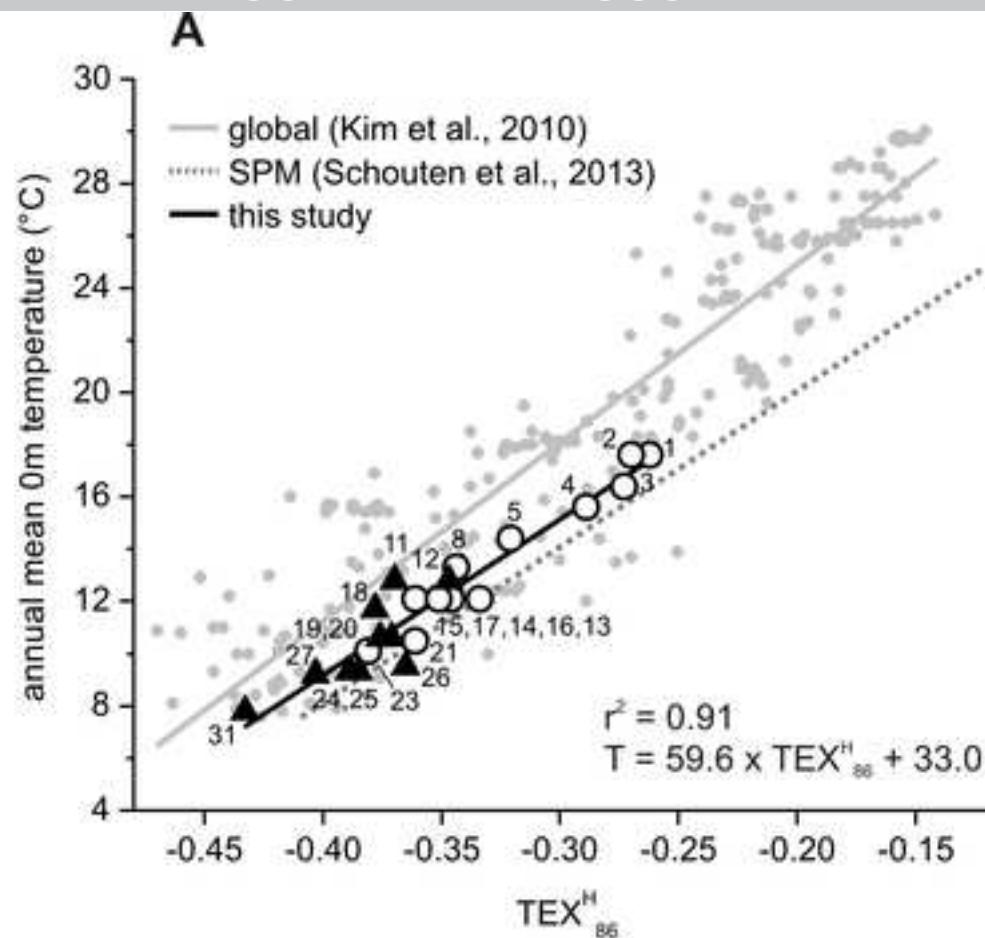
Eq.	Similarity of slope			Similarity of intercept		
	Degree of freedom	<i>t</i> -value	Probability	Degree of freedom	<i>t</i> -value	Probability
TEX <sub>86</sub> <sup>H</sup> <i>surface</i> Kim et al. (2010) vs. this study	274	2.048	0.04	274	-	-
TEX <sub>86</sub> <sup>H</sup> <i>subsurface</i> Kim et al. (2010) vs. this study	274	7.144	0.00	274	-	-
TEX <sub>86</sub> <sup>H</sup> <i>surface</i> Kim et al. (2010) vs. TEX <sub>86</sub> <sup>H</sup> SPM Schouten et al. (2013)	329	2.218	0.03	329	-	-
TEX <sub>86</sub> <sup>H</sup> <i>surface</i> this study vs. TEX <sub>86</sub> <sup>H</sup> SPM Schouten et al. (2013)	97	0.000	1.00	97	2.947	0.00
TEX <sub>86</sub> <sup>H</sup> <i>subsurface</i> Kim et al. (2012a) vs. TEX <sub>86</sub> <sup>H</sup> SPM Schouten et al. (2013)	329	1.256	0.21	329	26.50	0.00
TEX <sub>86</sub> <sup>H</sup> <i>subsurface</i> this study vs. TEX <sub>86</sub> <sup>H</sup> SPM Schouten et al. (2013)	97	6.054	0.00	97	-	-
TEX <sub>86</sub> <i>lake</i> Powers et al. (2010) vs. this study	14	0.038	0.97	14	0.252	0.81



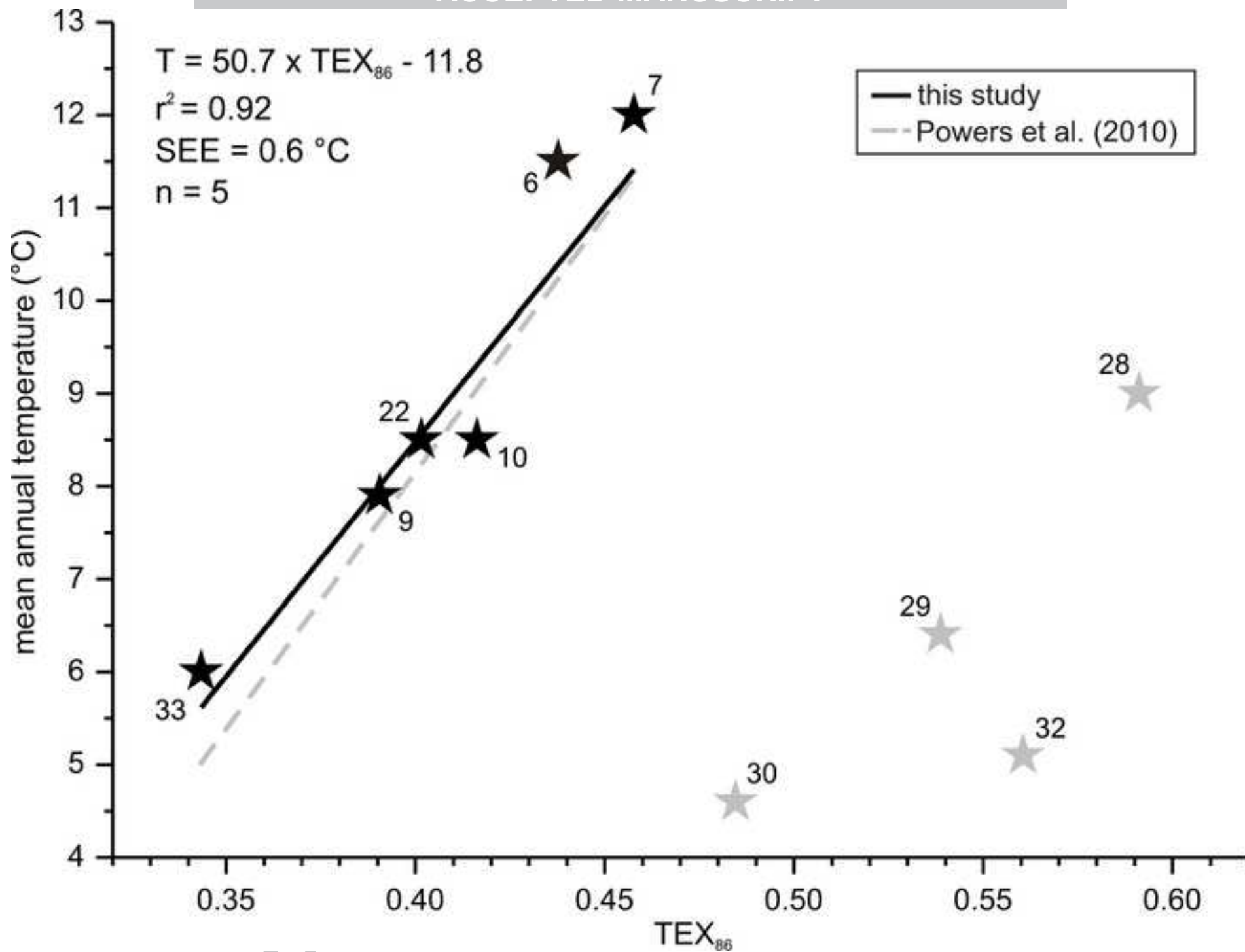


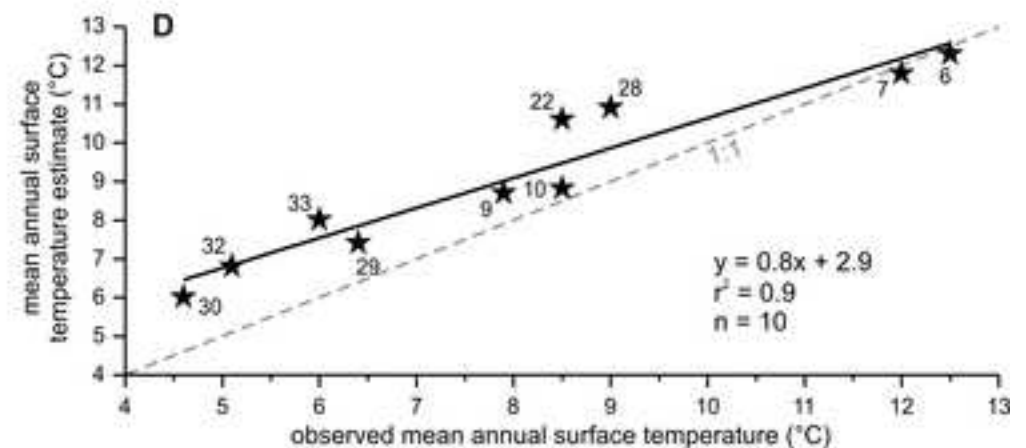
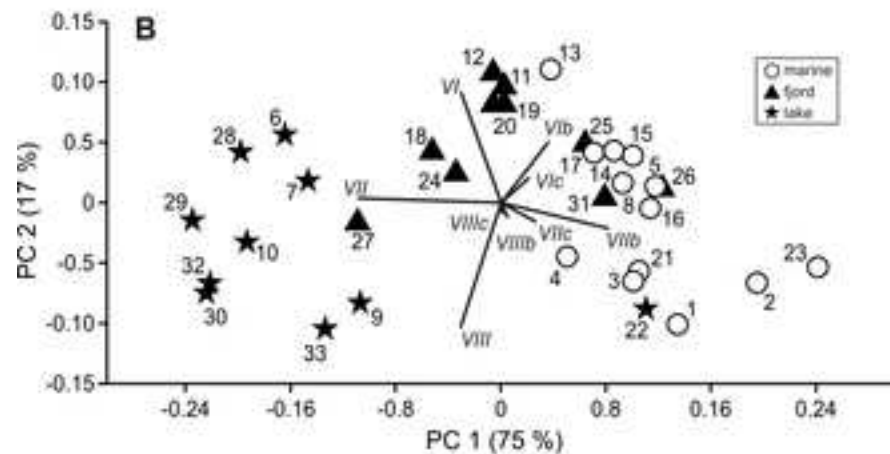
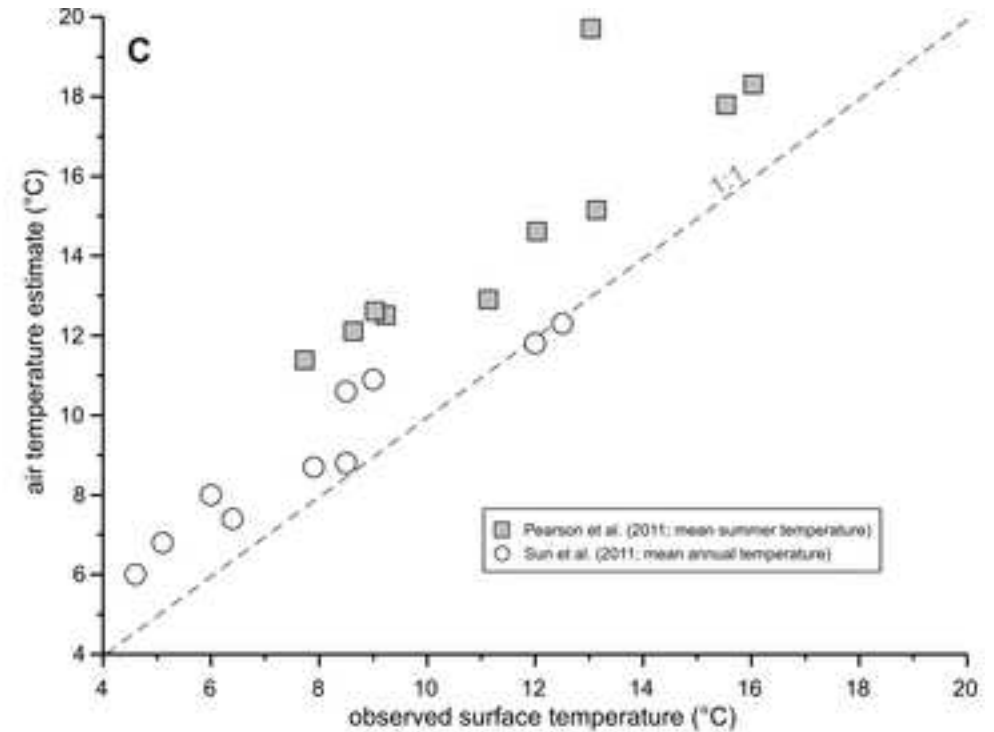
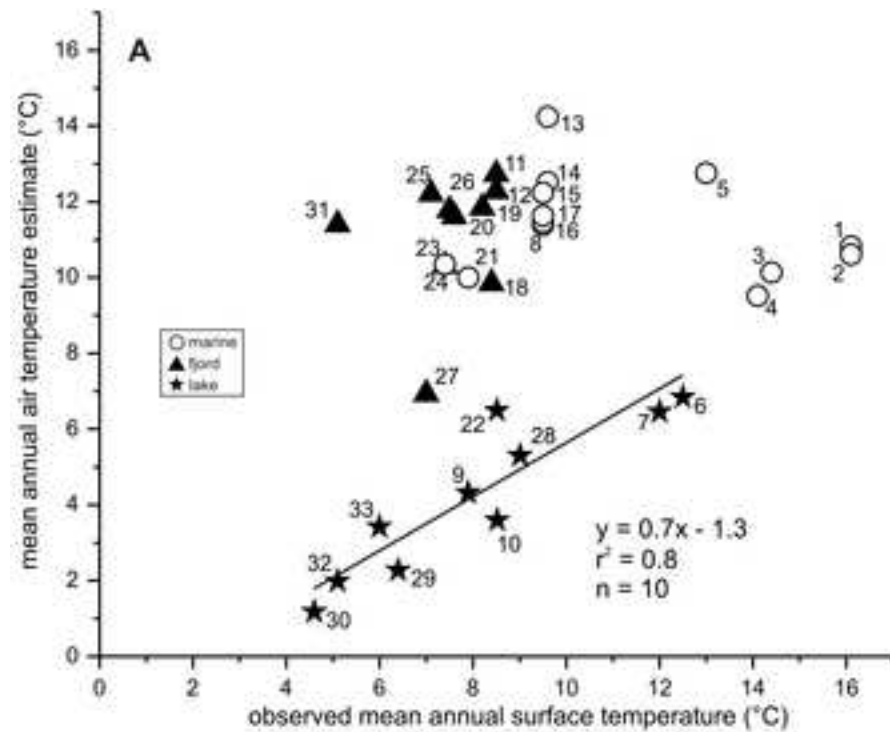












**Highlights**

- Analysis of surface sediments from lake, fjord and marine environments in Chile.
- Development of regional marine  $\text{TEX}_{86}^{\text{H}}$  and lake  $\text{TEX}_{86}$  calibrations.
- Potential in situ production of certain branched GDGTs.

ACCEPTED MANUSCRIPT