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Glycerol dialkyl glycerol tetraethers and the TEX₈₆ index in sinking particles in the western North Pacific

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Seasonal and depth variations in the flux of glycerol dialkyl glycerol tetraethers (GDGTs) and TEX₈₆ (TEX₈₆^H and TEX₈₆^L) values in sinking particles were examined by conducting a 21-month time-series sediment trap experiment at a mooring station (WCT-2, 39°N, 147°E) in the mid-latitude NW Pacific. The aim of the study was to understand the sinking process of GDGTs in the water column and the preservation of the TEX₈₆ signal in the water column and the sediment surface. In the shallow trap, the sinking flux of GDGT showed maxima from May 1998 to February 1999. The maximal

peaks of GDGT sinking flux corresponded to the peaks of the sinking fluxes of organic carbon, opal and lithogenic material. GDGT concentrations in the total fine fraction and the ratio of caldarchaeol to crenarchaeol at three different depths (~1300–4800 m) varied synchronously, implying rapid vertical transport of GDGTs to deeper water with a sinking velocity higher than 260 m d^{-1} below ~1300 m. The changes in TEX₈₆-based temperature were different from those in the contemporary SSTs. The TEX₈₆-based temperature was lower than the SST from May to December and corresponded to the temperature at the thermocline, whereas it was higher than the SST from December to May. The annual average sinking flux of the GDGTs decreased with increasing depth. The GDGT half-depth, the depth range over which half of the GDGT is lost, was calculated to be 3108–3349 m, implying that GDGTs were well preserved during sinking in the water column. The flux-weighted average TEX₈₆-based temperatures were constant with depth and roughly corresponded to mean annual SST. These findings support a previously proposed hypothesis that the GDGTs produced in surface waters are preferentially delivered to the deeper water column by grazing and repackaging in larger particles. The constant TEX₈₆ at different depths indicates that TEX₈₆ is not affected by degradation in the water column. The preservation efficiency of GDGTs was 1.0–1.3% at the water-sediment interface. Despite the significant degradation of the GDGTs, there was a small difference in TEX₈₆ levels between sinking particles and the surface sediment.

Key words: TEX₈₆, glycerol dialkyl glycerol tetraether, sediment trap, Thaumarchaeota, North Pacific

1. Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs) are ubiquitous in marine water and sediments, and are thought to be derived mainly from marine Crenarchaeota Group I (Sinninghe Damsté et al., 2002b), and marine Crenarchaeota Group I was recently classified into a newly-defined archaeal phylum Thaumarchaeota (Brochier-Armanet et al., 2008; Spang et al., 2010). The GDGTs biosynthesized by this group include GDGT-0 (caldarchaeol)–GDGT-3, containing zero to three cyclopentane moieties, and crenarchaeol, which has a cyclohexane moiety in addition to four cyclopentane moieties (Schouten et al., 2000; Sinninghe Damsté et al., 2002b). Schouten et al. (2002) proposed a new palaeotemperature index, TEX₈₆, based on the distribution of GDGTs by way of an empirical correlation between TEX₈₆ values in marine core top sediments and sea surface temperatures (SSTs). Investigation of such a correlation has since been developed using larger data sets (Kim et al., 2008; 2010). The application of TEX₈₆ is increasing in palaeoceanographic studies (e.g. Huguet et al., 2006b).

Multiple proxy approaches to the analysis of cores and surface sediments often show inconsistent patterns when different proxy records are used (e.g., Huguet et al., 2006b, Lee et al., 2008; Lopes dos Santos et al., 2010; Shintani et al., 2011). This phenomenon has been generally attributed to differences in the season or depth that each proxy reflects, physiological bias, or lateral advection. The TEX₈₆ proxy is still under development, and the production season and depth of GDGTs are still not clear. TEX₈₆ must be investigated further for better interpretation of proxy records.

Thaumarchaeota live throughout the water column (e.g., Murray et al., 1999; Karner et al., 2001; Herndl et al., 2005; Baltar et al., 2007; Coolen et al., 2007; Agogué et al., 2008; Beman et al., 2008; Veralá et al., 2008). They occur in highest abundances in the

upper 100 m, but are also present in waters as deep as 5000 m (Karner et al., 2001; Herndl et al., 2005). The physiology of Thaumarchaeota in marine environments is not fully understood, although both heterotrophs (e.g., Ouverney and Furman, 2000; Agogu   et al., 2008; Zhang et al., 2009) and chemoautotrophic nitrifiers (e.g., K  nneck et al., 2005; Hallam et al., 2006; Wuchter et al., 2006a; Coolen et al., 2007; Beman et al., 2008; Park et al., 2010; Blainey et al., 2011; Pitcher et al., 2011) have been recognized. Agogu   et al. (2008) suggested that Thaumarchaeota in subsurface waters (100–150 m) are mostly autotrophic, whereas they live heterotrophically in bathypelagic waters (>1000 m). In the South China Sea, the contribution of Thaumarchaeota to the total prokaryotic community was found to increase with depth and was higher in the upper mesopelagic water column inside than outside cold-core eddies, suggesting that the supply of refractory dissolved organic matter by upwelled water led to a more prominent abundance of Thaumarchaeota (Zhang et al., 2009).

Little is also known about the abundance of GDGTs in the water column. Sinninghe Damst   et al. (2002a) described maxima of crenarchaeol concentrations at 70 m and 500 m in the Arabian Sea. Wuchter et al. (2005) reported a high concentration of GDGTs in particulate organic matter (POM) in the deep-water column below 100 m. The abundance of GDGTs also varies seasonally. A high abundance was reported for winter in the North Sea (Wuchter et al., 2005; Herfort et al., 2006), suggesting that Thaumarchaeota thrive in winter because they do not need to compete with phytoplankton for NH_3 . This hypothesis was recently supported by the observation that the abundance of intact GDGTs and Thaumarchaeota 16S rRNA genes and *amoA* genes showed a seasonal cycle with maxima in winter in the North Sea (Pitcher et al., 2011). Turich et al. (2007) reported the variability in GDGT composition in the water column

in different oceanographic settings and suggested that changes in archaeal ecology, nutrient concentration and oceanographic conditions potentially affect TEX₈₆. Coolen et al. (2007) described a maximum for crenarchaeol concentration in the sulfidic chemocline in the water column of the Black Sea. In order for TEX₈₆ to be a more robust palaeotemperature proxy, a better understanding of the season and depth of GDGT production is required.

It is critical to understand how surface water signals are propagated to deeper waters. Wuchter et al. (2005) reported that the TEX₈₆-derived temperatures of POM at all depths below 100 m correspond to SSTs. On the basis of this observation, they concluded that the GDGTs produced in surface waters were preferentially delivered to the deeper water column by grazing and repackaging in larger particles. Sediment-trap studies conducted in the north-eastern Pacific Ocean and the Arabian Sea demonstrated that the TEX₈₆ values in sinking particles corresponded to SSTs, supporting the above hypothesis (Wuchter et al., 2006b). In the Puget Sound, intact GDGTs are largely present in the free-living particle size fraction (0.2 to 0.7 µm) and core GDGTs are enriched in suspended (0.7 to 60 µm) and aggregate (>60 µm) size fractions, suggesting that archaeal biomass quickly becomes attached or entrained in particles once the archaea are dead or dying (Ingalls et al., 2012). This observation is consistent with the hypothesis of Wuchter et al. (2006b). In contrast, variations in TEX₈₆ values in sinking particles were not coupled to SSTs or deep water temperatures in the Santa Barbara Basin, which was attributed to a complex combination of the contributions of GDGTs produced in different depths and hydrologic conditions (Huguet et al., 2007).

Degradation of GDGTs through the water and sediment columns potentially affects the TEX₈₆ values (Huguet et al., 2009). If this effect is relatively large, it introduces

error into palaeotemperature estimations that are based on TEX₈₆. GDGT degradation through the water column is evaluated based on the decreasing trend of sinking flux with increasing depth. Most sediment trap studies, however, have not detected this decreasing trend because of interference by the lateral influx of allochthonous GDGTs to deeper traps (e.g., Wuchter et al., 2006b). Furthermore, there is very little information on the degradation rate of GDGTs at the water-sediment interface, aside from a few studies (e.g., Sinninghe Damsté et al., 2002a). Evaluation of the preservation rate of GDGTs at the sediment surface is required by methods such as the comparison of the sinking fluxes of GDGTs through the water column and their accumulation rates in the sediment at the same location.

In this study, we examined the seasonal and depth variations in GDGT flux and molecular compositions of sinking particles. We conducted a time-series sediment trap experiment at a mooring station (39°N, 147°E; Fig. 1) in the mid-latitude NW Pacific from November 1997 to August 1999 to understand seasonality, sinking processes and degradation of GDGTs in the water column and the influence on TEX₈₆. Analysis of the underlying sediments was also conducted to evaluate the effects of GDGT degradation at the water-sediment interface on TEX₈₆.

2. Station WCT-2 and previous results

The study site, station WCT-2, is located in the mixing zone between Oyashio and Kuroshio waters (Fig. 1). Cold and warm mesoscale eddies from the Oyashio and Kuroshio, respectively, develop in the mixing zone. The Oyashio–Kuroshio boundary is displaced seasonally. The southern limit of the Oyashio stays at ~38.5°N in April, gradually shifts northward to ~40°N until October, and then moves more rapidly

northward to $\sim 41.5^{\circ}\text{N}$ to December before gradually returning southward until April (Data from Japan Meteorological Agency, <http://www.data.kishou.go.jp/kaiyou/db/hakodate/knowledge/oyashio.html>.) The monthly mean SST ranges from $\sim 9^{\circ}\text{C}$ (March) to $\sim 24^{\circ}\text{C}$ (August) and averages $\sim 15^{\circ}\text{C}$ (Fig. 2a; Conkright et al., 2002). The seasonal SST change reflects both the latitudinal displacement of the Oyashio-Kuroshio boundary and the development of thermal stratification. Thermal stratification develops from summer to fall in this region (Fig. 2b). An ocean general circulation model study indicated that the average surface current velocity was ~ 10 cm/sec (~ 8.6 km/day and ~ 260 km/month) during winters at site WCT-2 (Nonaka et al., 2006); this velocity is much lower than that of the Kuroshio Extension.

Two seasonal cycles were observed in both the compositions and the flux of biogenic matter during the 21 months from November 1997 to August 1999 at station WCT-2 (Mohiuddin et al., 2002; Yamamoto et al., 2007). Opal content ranged from 28% to 63% with an average of 48%, implying that diatom frustules are a major component of the sinking particles at this site. The total fine fraction (< 1 mm diameter), organic carbon, calcium carbonate, and opal fluxes showed strong seasonal variability in traps at each depth. Organic carbon, calcium carbonate, and biogenic opal fluxes began to increase in February–early March and reached a maximum in early May–early July, abruptly decreased in late July, and remained nearly constant after August. Traps at different depths showed similar variations. The biogenic fluxes in the middle and deep traps exceeded those in the shallow trap from April to June, which was attributed to the lateral influx of particles in deeper traps (Mohiuddin et al., 2002).

The alkenone concentration and sinking flux also showed strong seasonal variability in traps at each depth (Yamamoto et al., 2007). The alkenone concentration and sinking

flux increased abruptly in mid-March–April, showed multiple maxima in spring to fall. Traps at the different depths showed similar variations except for the interval between April and May 1999, when the alkenone fluxes in the middle and deep traps exceeded those in the shallow trap. The high alkenone flux from spring to fall corresponded to the high flux of *Emiliana huxleyi* (Yuichiro Tanaka, unpublished data), presumably reflecting the repeated blooms of *Emiliana huxleyi* in this station. Seasonal cycles in alkenone flux lagged behind those of the fluxes in the total fine fraction and bulk biogenic components by about one month. The time lag between bulk biogenic and alkenone fluxes was attributed to the ecological succession of the blooming of alkenone-producing coccolithophores after the blooming of diatoms (Yamamoto et al., 2007).

3. Samples and methods

3.1. Samples

Moored time-series sediment traps were employed at three different depths at the WCT-2 site (39°00'N, 147°00'E) in the western North Pacific from 19 November 1997 to 10 August 1999 (Table 1). The traps were set and recovered during the Western Pacific Environmental Assessment Study (WEST) CO₂ Ocean Sequestration for Mitigation of Climate Change (COSMIC) cruises in 1997, 1998, and 1999 aboard the R/V Daini Hakurei-maru (Mohiuddin et al., 2002). Sample cups at shallow and deep depths were replaced every 13 days from 19 November 1997 to 6 August 1998 and every 18 days from 26 August 1998 to 10 August 1999. The sample cups at middle depths were replaced every 22 days from 19 November 1997 to 10 August 1998 and every 30 days from 27 August 1998 to 10 August 1999. The cups were filled with 1%

HgCl₂ seawater (pH = ~7). Recovered particles were separated into a coarse fraction (>1 mm diameter) and a fine fraction (<1 mm) by filtering. The coarse fraction was made up of scoriae and swimmers. The fine fraction was collected on a membrane filter (0.6 mm pore diameter), dried at 60°C for one day and milled using an agate mortar. Scoriae were picked with tweezers during grinding.

The multiple core CMC18, 30 cm long, was taken at 39°00.0'N, 146°56.0'E, at a depth of 5389 m during WEST COSMIC cruise NH99 of the R/V Daini Hakurei-maru on 7 August 1999. The sediments consist of dark olive brown diatomaceous silty clay from 0 to 10 cm deep and olive black diatomaceous clay with ash patches from 10 to 30 cm deep (Yamamoto et al., 2007). The core was sampled every 0.31 cm, and 10 samples were selected at 0.62 cm interval for analysis.

The age model was created using the calendar ages converted from the AMS ¹⁴C ages of bulk organic matter in six sediment samples (1380–8000 ¹⁴C yrs. BP) using CALIB4.3 software and the marine98 calibration data set (Stuiver and Reimer, 1993) with a 400-year global reservoir correction (Yamamoto et al., 2007).

3.2. Analytical methods

Lipids were extracted from the fine fraction by five 5-min rounds of ultrasonication with 5 ml of dichloromethane-methanol (6:4), then concentrated and passed through a short bed of Na₂SO₄ to remove water. The lipid extract was separated into four fractions (F1: 3 ml of hexane; F2: 3 ml of hexane-toluene (3:1); F3: 4 ml of toluene; F4: 3 ml of toluene-methanol (3:1)) by column chromatography (SiO₂ with 5% distilled water; i.d., 5.5 mm; length, 45 mm).

An aliquot of F4 was trans-esterified with 1 ml 5% HCl/CH₃OH at 60 °C for 12 h

under N₂. The methylated lipids were supplemented with 2 ml distilled water and extracted (3x) with toluene. The extract was back washed (3x) with distilled water, passed through a short bed of Na₂SO₄, and separated into two fractions with SiO₂ column chromatography: F4-1 (acids), 4 ml toluene; F4-2 (alcohols), 3 ml toluene-CH₃OH (3:1). *n*-C₂₄D₅₀ was added as an internal standard to F4-1.

An aliquot of F4-2 was dissolved in hexane-2-propanol (99:1) and filtered. GDGTs were analyzed using high performance liquid chromatography-MS (HPLC-MS) with an Agilent 1100 HPLC system connected to a Bruker Daltonics micrOTOF-HS time-of-flight mass spectrometer. Separation was conducted using a Prevail Cyano column (2.1 x 150 mm, 3μm; Alltech) maintained at 30°C following the method of Hopmans et al. (2000) and Schouten et al. (2007). Conditions were: flow rate 0.2 ml/min, isocratic with 99% hexane and 1% 2-propanol for the first 5 min followed by a linear gradient to 1.8% 2-propanol over 45 min. Detection was achieved using atmospheric pressure, positive ion chemical ionization-MS (APCI-MS). The spectrometer was run in full scan mode (*m/z* 500–1500). Compounds were identified by comparing mass spectra and retention times with those of GDGT standards (obtained from the main phospholipids of *Thermoplasma acidophilum* via acid hydrolysis) and those in the literature (Hopmans et al., 2000). Quantification was achieved by integrating the summed peak areas in the (M+H)⁺ and the isotopic (M+H+1)⁺ chromatograms and comparing these with the peak area of an internal standard (C₄₆ GDGT; Patwardhan and Thompson, 1999) in the (M+H)⁺ chromatogram, according to the method of Huguet et al. (2006a). The correction value of ionization efficiency between GDGTs and the internal standard was obtained by comparing the peak areas of *T. acidophilum*-derived mixed GDGTs and C₄₆ GDGT in known amounts. The standard deviation of a replicate analysis

was 3.0% of the concentration for each compound. TEX_{86} and $\text{TEX}_{86}^{\text{H}}$ (applicable to warm water) were calculated from the concentrations of GDGT-1, GDGT-2, GDGT-3 and a regioisomer of crenarchaeol using the following expressions (Schouten et al., 2002; Kim et al., 2010):

$$\text{TEX}_{86} = \frac{[\text{GDGT-2}] + [\text{GDGT-3}] + [\text{Crenarchaeol regioisomer}]}{[\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}] + [\text{Crenarchaeol regioisomer}]}$$

$$\text{TEX}_{86}^{\text{H}} = \log (\text{TEX}_{86})$$

$\text{TEX}_{86}^{\text{L}}$, applicable in cooler water, was calculated from the concentrations of GDGT-1, GDGT-2 and GDGT-3 using the following expression (Kim et al., 2010):

$$\text{TEX}_{86}^{\text{L}} = \log \left\{ \frac{[\text{GDGT-2}]}{[\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}]} \right\}$$

Temperatures were calculated according to the following equations based on a global core top calibration (Kim et al., 2010):

$$T = 68.4 \text{ TEX}_{86}^{\text{H}} + 38.6 \text{ (when } T > 15^{\circ}\text{C)}$$

$$T = 67.5 \text{ TEX}_{86}^{\text{L}} + 46.9 \text{ (when } T < 15^{\circ}\text{C)}$$

where T = temperature [$^{\circ}\text{C}$]; analytical accuracy was 0.45 $^{\circ}\text{C}$ in our laboratory.

Calculation of mass accumulation rate in core CMC18

The accumulation rate of GDGTs (GDGT AR) was calculated according to the following formula:

$$\text{GDGT AR } (\mu\text{g}/\text{cm}^2/\text{kyr}) = \text{GDGTs } (\mu\text{g}/\text{g-sed.}) \times \text{DBD } (\text{g}/\text{cm}^3) \times \text{LSR } (\text{cm}/\text{kyr})$$

where AR is the accumulation rate, DBD is the dry bulk density, and LSR is the linear sedimentation rate derived from ^{14}C -based age-depth model. The DBD was obtained by the following regression equation between ten measured DBDs and depth (Tatsuo Fukuhara, unpublished data):

$$\text{DBD } (\text{g}/\text{cm}^3) = 0.00780 \times \text{Depth } (\text{cm}) + 0.324$$

3.3. Estimation of chlorophyll concentration and net primary production

Surface chlorophyll-a concentration at the WCT-2 site was extracted from monthly 9 km data of NASA SeaWiFS standard mapped image and take a median values of 3 x 3 pixels. Integrated primary production was calculated with a modified version (Kameda and Ishizaka, 2005) of vertically generalized production model (Behrenfeld and Falkowski, 1997) using SeaWiFS SMI monthly photosynthetically available radiation and AVHRR Pathfinder monthly nighttime SST.

4. Results

4.1. Sediment trap

The concentration of isoprenoid GDGTs, consisting of caldarchaeol (GDGT-0), GDGT-1, GDGT-2, GDGT-3, crenarchaeol, and crenarchaeol regioisomer, varied from

40 to 218 $\mu\text{g g}^{-1}$ in the shallow trap, from 36 to 113 $\mu\text{g g}^{-1}$ in the middle trap and from 21 to 102 $\mu\text{g g}^{-1}$ in the deep trap and showed strong seasonal variability in traps at each depth (Fig. 3a). The GDGT concentration gradually decreased from November 1997 to June 1998, increased from early July to late September, and then gradually decreased to May and June in 1999 (Fig. 3a). Traps at the different depths showed similar variations except for the interval between July and November 1998, when the GDGT concentrations in the shallow trap were two times larger than those in the middle and deep traps.

The sinking flux of GDGTs varied from 4 to 41 $\mu\text{g m}^{-2} \text{d}^{-1}$ in the shallow trap, from 4 to 27 $\mu\text{g m}^{-2} \text{d}^{-1}$ in the middle trap and from 1 to 27 $\mu\text{g m}^{-2} \text{d}^{-1}$ in the deep trap (Fig. 3b). The sinking flux showed strong temporal variability in the shallow traps (~ 1300 m), whereas the sinking fluxes in the deeper traps (~ 2500 – 4800 m) did not vary in harmony with that in the shallow trap. In 1998, the GDGT concentration and sinking flux in the shallow trap increased abruptly in late June/early July and showed maxima in late June/early July, September, early November, and December/January 1999. In 1999, after the maximum in February, GDGT flux was relatively low. The fluxes in the middle and deep traps were relatively unchanged and showed a maximum in late April-early May which exceeded that in the shallow trap (Fig. 3b).

The $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures calculated using the core-top calibrations of Kim et al. (2010) varied from 9°C to 19°C and from 11°C to 21°C, respectively, in the shallow site, from 11°C to 16°C and from 14°C to 18°C in the middle site, and from 10°C to 16°C and from 11°C to 18°C in the deep site (Figs. 3c and 3d). $\text{TEX}_{86}^{\text{H}}$ -based temperatures were 0–3°C lower than $\text{TEX}_{86}^{\text{L}}$ -based temperatures. The $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures fluctuated from November 1997 to June

1998, decreased in early July 1998 and were constantly low from early July 1998 to early November 1998, and then increased in late November 1998 and fluctuated thereafter (Figs. 3c and 3d). This change was different from the changes seen in SSTs (Figs. 3c and 3d, Integrated Global Ocean Services System [IGOSS] weekly SST; Reynolds et al., 2002): the $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures were generally higher than the SST from January to May, whereas it was lower than the SST from May–June to December.

The relative abundance of caldarchaeol and crenarchaeol (Cald/Cren ratio) is assumed to respond to SST (Schouten et al., 2002). The Cald/Cren ratio varied from 0.8 to 1.5. The maximum appeared in late July 1998 and corresponded to a low $\text{TEX}_{86}^{\text{H}}$ - or $\text{TEX}_{86}^{\text{L}}$ -based temperature (Fig. 3e). The minimum appeared in early December 1998 and corresponded to high $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures (Figs. 3c–3e). The ratio had a significant negative correlation with $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures (both $r = -0.69$).

4.2. Core CMC18

The GDGT concentration was highest at the core top, decreased abruptly downwards until 1.6 cm (~1.6 ka) and showed a maximum at 9.1 cm (~2.8 ka) (Fig. 4). The alkenone GDGT AR showed a similar changing pattern with that of GDGT concentration, but it showed an enhanced peak interval from 4.1 to 9.1 cm deep (from ~2.3 ka to ~2.8 ka), and the maximum appeared at 6.6 cm (Fig. 4) due to the high linear sedimentation rate in this interval.

$\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures at the core top were 16.8°C and 16.3°C,

respectively, which are 1–2°C higher than the mean annual SST at this site (15°C, Conkright et al., 2002). TEX₈₆^H- and TEX₈₆^L-based temperatures varied between 15.6°C and 19.0°C and between 12.9°C and 17.9°C, respectively, during the last 5.9 ka (Fig. 4).

4.3. Satellite-based surface chlorophyll concentration and estimated net primary production

Satellite-based surface chlorophyll concentration at the study site showed a seasonal cycle with lower values from July to October (Fig. 5a). The low surface chlorophyll concentrations from summer to fall presumably reflect both the decrease of primary production and the deepening of chlorophyll maximum in the water column. Observations at the A-17 site (39°N, 146.75°E) of A-line monitored by the Fishery Research Agency of Japan revealed the decrease of surface water chlorophyll concentration and the deepening of chlorophyll maximum in early July 1998 (Fig. 4a; Fishery Research Agency of Japan, 2012), supporting this interpretation. Estimated net primary production (NPP) basically showed a similar seasonal pattern with chlorophyll concentration, but the maximal peaks in June shifted one or two months later than the peaks of chlorophyll concentration in April and May, because NPP includes subsurface production enhanced in summer.

5. Discussion

5.1. Season of export production of isoprenoid GDGTs

In the shallow trap, the sinking flux of GDGT showed maxima from May 1998 to February 1999 (Fig. 5c). The maximal peak of GDGT sinking flux corresponded to the peak of the sinking fluxes of organic carbon, opal and lithogenic material (Figs. 5b and

5c). The sinking flux of GDGTs was better correlated with those of organic carbon ($r = 0.80$, $p < 0.01$), opal ($r = 0.59$, $p < 0.01$), lithogenic material ($r = 0.68$, $p < 0.01$), and alkenones ($r = 0.50$, $p < 0.05$) than CaCO_3 ($r = 0.31$) in the shallow trap. This implies that GDGTs sank with the main components of organic matter which are associated with diatom frustules and lithogenic material.

Changes in the sinking fluxes of biogenic opal, CaCO_3 , organic carbon, and GDGTs were generally consistent with changes in chlorophyll concentration and NPP; the sinking fluxes are higher when chlorophyll concentration and NPP were higher (Figs 5a and 5b). Exceptionally, the highest sinking fluxes of opal, organic carbon, GDGTs, and alkenones were found in early July 1998, but surface chlorophyll concentration and NPP were relatively low in this period. It is not clear at this stage whether this was caused by the time lag between the production and sinking of biogenic materials or the subsurface production of primary producers.

The season of GDGT production in the marine environment is still not clear. Wuchter et al. (2005), Herfort et al. (2006), and Pitcher et al. (2011) reported that GDGT concentrations in surface water were higher in winter in the North Sea and suggested that Thaumarchaeota thrive in winter because they do not need to compete with phytoplankton for NH_3 . Wuchter et al. (2006b) showed that the sinking flux of GDGTs was higher in the periods of enhanced primary production in the Arabian Sea and interpreted that the high sinking flux of GDGTs during high marine production was not necessarily caused by higher production of Thaumarchaeota, but by more efficient food web-based scavenging of archaeal cells, attached to aggregates or in faecal pellets. Huguet et al. (2007) found that the sinking flux of GDGTs was reduced in non-upwelling periods in the Santa Barbara Basin. They proposed that reduced primary

production resulted in a decrease in ammonia availability and lower Thaumarchaeota productivity because components of the Thaumarchaeota are nitrifiers (Könneke et al., 2005; Wuchter et al., 2006a) and use ammonia, produced by the decay of phytoplankton and zooplankton, as an energy source.

The present study demonstrated that the sinking flux of GDGTs was enhanced with increasing fluxes of organic matter, diatom frustules and lithogenic materials (Figs. 5b and 5c). This is attributed either to enhanced production of Thaumarchaeota during the phytoplankton bloom or to that the scavenging of GDGTs is enhanced when the organic particulate flux increases after the phytoplankton bloom. In the former case, Thaumarchaeota production would be supported by the supply of ammonia and labile organic compounds derived from decay of plankton. In the latter case, the sinking of GDGTs would be triggered by phytoplankton blooms that accelerated the attachment and entrainment of Thaumarchaeota cells to larger particles. The latter case is more likely to explain the disagreement between TEX₈₆-based temperatures and SSTs observed in this study.

5.2. Depth changes of GDGT sinking fluxes

GDGT concentrations in the total fine fraction varied synchronously at three depths from approximately 1300 m to 4800 m (Fig. 3a). The Cald/Cren ratio also showed synchronous variations at the three different depths (Fig. 3e). The sampling interval was 13 days and no significant time lag was seen in the GDGT concentrations and the Cald/Cren ratio, implying that particles sank ~3400 m within 13 days; the sinking velocity below ~1300 m was calculated to be higher than 260 m d⁻¹. This velocity is in the range of those of faecal pellets and marine snow (Honjo and Roman,

1978; Small et al., 1979; McCave, 1984; Asper, 1987). Recently, settling velocity sediment trap experiments revealed that a large proportion of particulate organic matter sinks 200–500 m d⁻¹ in the north-western Mediterranean Sea (Armstrong et al., 2009; Wakeham et al., 2009). This range is consistent with the velocity estimated in this study.

The annual average sinking fluxes of GDGTs were 12.6–16.4 µg m⁻² d⁻¹ in the shallow trap, 6.8–14.2 µg m⁻² d⁻¹ in the middle trap, and 6.2–7.8 µg m⁻² d⁻¹ in the deep trap (Table 2). The range of sinking flux is of the same magnitude as that in the Arabian Sea (4–12 µg m⁻² d⁻¹; Wuchter et al., 2006b) but is lower than that in the Santa Barbara Basin (~100 µg m⁻² d⁻¹; Huguet et al., 2007).

The annual average sinking flux of GDGTs decreased with increasing depth (Fig. 6). The GDGT flux was almost identical between the NH97 and NH98 intervals. Nearly synchronous variations in the Cald/Cren ratio, TEX₈₆^H, and TEX₈₆^L at the traps of different depths (Figs. 3c–3d) suggest that the incorporation of GDGTs into sinking particles in the middle and deep water column is not significant, and that the sinking particles are mostly transported from the shallow water column. Assuming that the sinking rates are constant in the entire middle and deep water column, and the GDGTs are lost at a constant degradation rate during sinking, the relationship between sinking flux and depth is expressed by the following formula:

$$F_Z = F_0 e^{-kZ}$$

where Z is depth (m), F_Z is the sinking flux at depth Z , F_0 is the presumed extrapolated sinking flux at the sea surface, and k is the decomposition rate constant with depth. The half-depth ($Z_{1/2}$), defined as the depth range over which half of material is lost, is

calculated by the following equation (Wakeham and Lee, 1993):

$$Z_{1/2} \text{ (m)} = \ln 2/k = 0.693/k$$

Table 3 shows the calculated $Z_{1/2}$, F_0 , and F_{5389} (the presumed extrapolated sinking flux at the sea bottom). The half-depths of GDGT flux in the NH97 and NH98 intervals were 3349 m and 3108 m, respectively. The half-depth of GDGT was the same level as that of organic carbon (3655–3738 m; Yamamoto et al., 2007) and higher than that of alkenones (1572–1982 m; Yamamoto et al., 2007). This result indicates that GDGTs are well preserved during sinking in the water column.

5.3. Preservation efficiency of GDGTs at the sediment surface

A comparison between GDGT fluxes at the bottom of the water column and the core-top GDGT AR of Core CMC18 provides a measure of the preservation efficiency of GDGTs at the water-sediment interface. The GDGT fluxes at the bottom of the water column (F_{5389} in Table 3) as estimated by the sediment trap were 5.0 and $6.7 \mu\text{g m}^{-2} \text{ d}^{-1}$ during the NH97 and NH98 sampling intervals, respectively. The NH97 interval did not cover an entire year and did not include the autumn high flux season; thus the GDGT flux was underestimated. The NH98 interval covered an entire year but also included the short period of lateral influx into deeper traps (Yamamoto et al., 2007); thus the GDGT flux was overestimated, although the effect of lateral influx was not significant because the period was short (36 days). Because the core-top GDGT AR of Core CMC18 was $2.40 \mu\text{g cm}^{-2} \text{ d}^{-1}$ ($0.065 \mu\text{g m}^{-2} \text{ d}^{-1}$; Fig. 4), the preservation efficiency of GDGTs is estimated to be 1.0–1.3%. This preservation efficiency was about one third of

that of alkenones (2.7–5.2%; Yamamoto et al., 2007) and one fifth of that of organic carbon (5.5–6.7%; Yamamoto et al., 2007) at the same site.

Prahl et al. (2000) estimated the preservation rates of alkenones (0.8%) and organic carbon (3.3%) at the sediment surface in the central Arabian Sea, based on their concentrations normalized to Al for sediment trap particles and bottom sediments. Wakeham et al. (2002) compared the accumulation rates of organic carbon and biomarkers in the bottom sediments with their sinking fluxes at the deepest sediment traps in the Arabian Sea and estimated that the preservation rates of organic carbon and C_{37:2} alkenone are 3.3–24.0% and 0.1–44.7%, respectively. Sinninghe Damsté et al. (2002a) estimated the relative preservation efficiencies of biomarkers in oxic, suboxic and anoxic environments by comparing their accumulation rates at the same horizon at different locations in the Arabian Sea. They showed that terrestrial n-alkanes are more resistant to degradation than GDGTs and alkenones which are more refractory than steroids. Mollenhauer et al. (2008) suggested that crenarchaeol is more efficiently degraded during lateral transport in oxygen replete environments than are alkenones based on their radiocarbon concentrations. Yamamoto and Polyak (2009) estimated the first-order decomposition rate constants of organic carbon ($1.1 \times 10^{-5} \text{ yr}^{-1}$), C₂₅–C₃₃ n-alkanes ($1.0 \times 10^{-5} \text{ yr}^{-1}$), isoprenoid GDGTs ($2.5 \times 10^{-5} \text{ yr}^{-1}$), and branched GDGTs ($2.0 \times 10^{-5} \text{ yr}^{-1}$), based on the decreasing trends of their concentrations in an Arctic sediment core. These studies indicated that most GDGTs are remineralised at the sediment surface in an oxic environment and that they are less refractory than total organic carbon and n-alkanes and more refractory than steroids. The estimated preservation rates of GDGTs in this study are consistent with this perspective.

5.4. Seasonal variation in TEX_{86}

The changes in TEX_{86}^H - and TEX_{86}^L -based temperatures were different from those of the contemporary SST (Fig. 5d). The TEX_{86}^H - and TEX_{86}^L -based temperatures were lower than the SST from May to December, whereas they were higher than the SST from December to May (Fig. 5d). Disagreement in the seasonal pattern between the TEX_{86} -based temperature of sinking particles and the contemporary SST was reported in the traps below 1500 m in the Arabian Sea (Wuchter et al., 2006b) and in the Santa Barbara Basin (Huguet et al., 2007). The former case was explained by a homogenization of the TEX_{86} SST signal carried by particles from a large area (Wuchter et al., 2006b). The latter case was attributed to a complex combination of the contributions of GDGTs produced in different depths and hydrologic conditions (Huguet et al., 2007).

At the present study site, a similar pattern was observed in seasonal changes in the $U^{K'}_{37}$ -based temperature (Fig. 5d; Yamamoto et al., 2007), which showed parallel changes at each depth. The $U^{K'}_{37}$ -based temperature decreased gradually after October during the low alkenone flux period, abruptly decreased in April at the beginning of the high alkenone flux period, was minimized in April–May, and then increased until September. This change was different from that observed in the SSTs. The $U^{K'}_{37}$ -based temperatures were lower than the contemporary SST during the periods of high alkenone flux from spring to fall, suggesting alkenone production in a well-developed thermocline (shallower than 30 m). During low alkenone flux periods from fall to spring, the $U^{K'}_{37}$ -based temperatures were nearly constant and were higher than the contemporary SSTs. The nearly constant carbon isotopic ratios of $C_{37:2}$ and $C_{38:2}$ alkenones suggest that the source of alkenones was unchanged and that the alkenones

produced in early fall were suspended in the surface water until sinking (Yamamoto et al., 2007).

From May to December, the $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures were a maximum of 9–12°C lower than the contemporary SST (Fig. 5d). Because thermal stratification is developed in summer and fall in the western North Pacific (Fig. 2), the $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures corresponded to the temperatures at the thermocline. When we recovered the sediment traps at the end of the first sampling interval (NH97) in August 1998, we obtained a snapshot profile of water temperatures and chlorophyll concentrations in the water column at the study site. The depth profile indicates that the $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures (9.4°C and 12.7°C, respectively) in the shallow trap corresponded to the water temperatures at 70 m and 40 m depths, respectively (Fig. 7). This correspondence suggests that the depth of GDGT production was 40–70 m if there was no time lag between GDGT production and sinking. The estimated depths overlap depths showing high chlorophyll concentrations (30–70 m; Fig. 7). If there was a time lag, the GDGT production depth would be shallower.

From December to May, the $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures were a maximum of 8–9°C higher than the contemporary SST. A similar pattern was observed in $\text{U}^{\text{K}'}_{37}$ -based temperatures during the low alkenone flux period at the study site (Fig. 5d) and was attributed to the gradual sinking of alkenones that had been produced in the previous period of high alkenone flux. This interpretation is applicable to the case of TEX_{86} , but the Cald/Cren ratio varied significantly from 0.9 to 1.4 during this period (Fig. 3e), suggesting the successive change in GDGT composition. This change is

probably caused by the heterogeneous distribution of GDGTs in the surface water pool, the successive addition of newly-produced GDGTs, and/or the lateral advection of GDGTs by strong surface currents. An ocean general circulation model study indicated that the average of surface current velocity was ~ 10 cm/sec (~ 8.6 km/day and ~ 260 km/month) during winters at site WCT-2 (Nonaka et al., 2006). If particle residence times are long enough, the warm-water detrital GDGTs could be supplied by the Kuroshio Current in winter to spring. It is not clear which process caused TEX_{86} -derived temperatures to be higher than SSTs from winter to spring. Further case studies are necessary to fully understand the phenomenon.

5.5. Depth variations in TEX_{86}

The flux-weighted average $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures were constant with depth ($13.5\text{--}14.2^{\circ}\text{C}$, average 13.8°C and $15.4\text{--}16.3^{\circ}\text{C}$, average 15.9°C , respectively; Fig. 8 and Table 2) and ~ 2 to 0°C lower than mean annual SST in 1998 (15.9°C ; Reynolds et al., 2002). Wuchter et al. (2005) reported a high concentration of GDGTs in POM in the deep water column below 100 m and stated that the TEX_{86} -derived temperatures of POM at all depths correspond to SSTs. On the basis of this observation, they concluded that the GDGTs produced in surface waters were preferentially delivered to the deeper water column by grazing and repackaging in larger particles. Our results show that the flux-weighted average TEX_{86} of sinking particle reflects SST and/or the seasonal thermocline temperature that is affected by SST, like the TEX_{86} of suspended POM does. This finding implies that the particles that give a SST signal are delivered downward, and the suspended POM originated from such sinking particles, which supports the hypothesis of Wuchter et al. (2005). The constant

TEX₈₆ at different depths implies that TEX₈₆ is not affected by degradation in the water column.

The flux-weighted average TEX₈₆^H- and TEX₈₆^L-based temperatures are 2.6–3.3°C and 0–0.9°C lower than the TEX₈₆^H- and TEX₈₆^L-based temperatures at the core top (16.8°C and 16.3°C), respectively. In the case of TEX₈₆^H, the difference in estimated temperatures between traps and core-top sediment (2.6–3.3°C) is larger than the error of TEX₈₆^H palaeothermometry (2.5°C; Kim et al., 2010), whereas in the case of TEX₈₆^L, the difference (0–0.9°C) corresponds to the error. Surface sediment was mixed with subsurface sediments by bioturbation and may contain a preindustrial signal of cooler temperature than contemporary temperature, and the TEX₈₆-based temperature at the core-top sample is possibly biased in the cooler direction. Even considering this bias, TEX₈₆^L shows a better agreement between traps and the bottom sediment than TEX₈₆^H. Whether the degradation at the water-sediment interface did not affect the TEX₈₆ (Kim et al., 2009) or increased the TEX₈₆ (Huguet et al., 2009) depends on the applied parameter TEX₈₆^H or TEX₈₆^L. Kim et al. (2010) recommended that TEX₈₆^H be used in warmer temperature regions (>15°C) and TEX₈₆^L in cooler temperature regions (<15°C). In this study, the flux-weighted average TEX₈₆^L-based temperatures in sediment traps were more consistent with values in the bottom sediment than were TEX₈₆^H-based temperatures. This suggests that TEX₈₆^L is more reliable than TEX₈₆^H in the studied region. The TEX₈₆^L-based temperatures in sediment traps (15.4–16.3°C) and the bottom sediment (16.3°C) correspond to temperatures at the depth range of 0–40 m from July to November in the study site.

6. Conclusions

GDGT and TEX₈₆ analyses of sediment trap and bottom sediment samples revealed that flux-averaged TEX₈₆-based temperatures were 1) nearly constant in sediment traps of different depths, 2) agreed with the value of the bottom sediments, and 3) corresponded to water temperatures at 0–40 m depth from July to November, suggesting that the temperature signal was propagated through the water column by the sinking of GDGTs. The analyses also indicated a rapid vertical transport of GDGTs to deeper water ($> 260 \text{ m d}^{-1}$) and the relatively refractory nature of GDGTs during sinking (the half-depth = 3108–3349 m) and at the sediment surface (preservation efficiency = 1.0–1.3%). These findings suggest that the signal of GDGTs produced in surface or near-surface water is preserved during vertical transport and thus propagated to the sediment surface.

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785 the South China Sea. *Aquatic Microbial Ecology* 56, 65–79.

786

787 Table Captions:

788

789 Table 1 Location, sampling periods and trap depths of the WCT-2 mooring sediment
790 trap system

791

792 Table 2 Averaged sinking fluxes of glycerol dialkyl glycerol tetraethers (GDGTs) and
793 flux-weighted $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures (FWT-H and FWT-L) at
794 site WCT-2.

795

796 Table 3 Half-depths and the estimated fluxes at the sea surface (F_0) and sea floor (F_{5389})
797 of GDGTs at site WCT-2.

798

799 Table 1

Location	Seafloor depth (m)	Duration	Trap depth (m)		
			Shallow	Middle	Deep
39°00.09'N, 146°59.66'E	5356	19 November 1997 to 6 August 1998	1366	3056	4786
39°01.00'N, 147°00.06'E	5322	27 August 1998 to 10 August 1999	1332	2472	4752

800

801

802 Table 2

Sampling interval	Duration	Trap position	Depth (m)	GDGT $\mu\text{g m}^{-2} \text{d}^{-1}$	FWT-H (°C)	FWT-L (°C)
NH97	19 Nov 1997 to 6 Aug 1998	Shallow	1366	12.6	13.5	15.4
	19 Nov 1997 to 10 Aug 1998	Middle	3056	6.8	13.8	16.2
	19 Nov 1997 to 6 Aug 1998	Deep	4786	6.2	13.7	15.6
NH98	27 Aug 1998 to 10 Aug 1999	Shallow	1332	16.4	14.2	16.2
	27 Aug 1998 to 10 Aug 1999	Middle	2472	14.2	14.0	16.3
	27 Aug 1998 to 10 Aug 1999	Deep	4752	7.8	13.5	15.4

FWT-H = flux-weighted $\text{TEX}_{86}^{\text{H}}$ -based temperature.

FWT-L = flux-weighted $\text{TEX}_{86}^{\text{L}}$ -based temperature.

803

804 Table 3

Unit		NH97	NH98
$Z_{1/2}$	m	3349	3108
F_0	$\mu\text{g m}^{-2} \text{d}^{-1}$	15.28	22.11
F_{5389}	$\mu\text{g m}^{-2} \text{d}^{-1}$	5.01	6.65

805

806 Figure Captions:

807

808 Fig. 1 Map showing the location of the study site (WCT-2).

809

810 Fig. 2 (a) Monthly mean temperatures at various depths. (b) The depth profiles of
811 temperature in different seasons at the WCT-2 site (39°N, 147°E). Data from Conkright
812 et al. (2002). MAM = March to May, JJA = June to August, SON = September to
813 November, DJF = December to January.

814

815 Fig. 3 Changes in (a) the concentration and (b) sinking flux of GDGTs, (c and d) $\text{TEX}_{86}^{\text{H}}$
816 - and $\text{TEX}_{86}^{\text{L}}$ -based temperatures, and (e) the ratio of caldarchaeol to crenarchaeol from
817 November 1997 to August 1999. The IGOSS weekly SSTs at 39°N, 147°E are from
818 Reynolds et al. (2002).

819

820 Fig. 4 GDGT concentrations and accumulation rates and $\text{TEX}_{86}^{\text{H}}$ - and $\text{TEX}_{86}^{\text{L}}$ -based
821 temperatures in core CMC18. Arrows indicate the calendar ages converted from the
822 AMS ^{14}C ages of bulk organic matter.

823

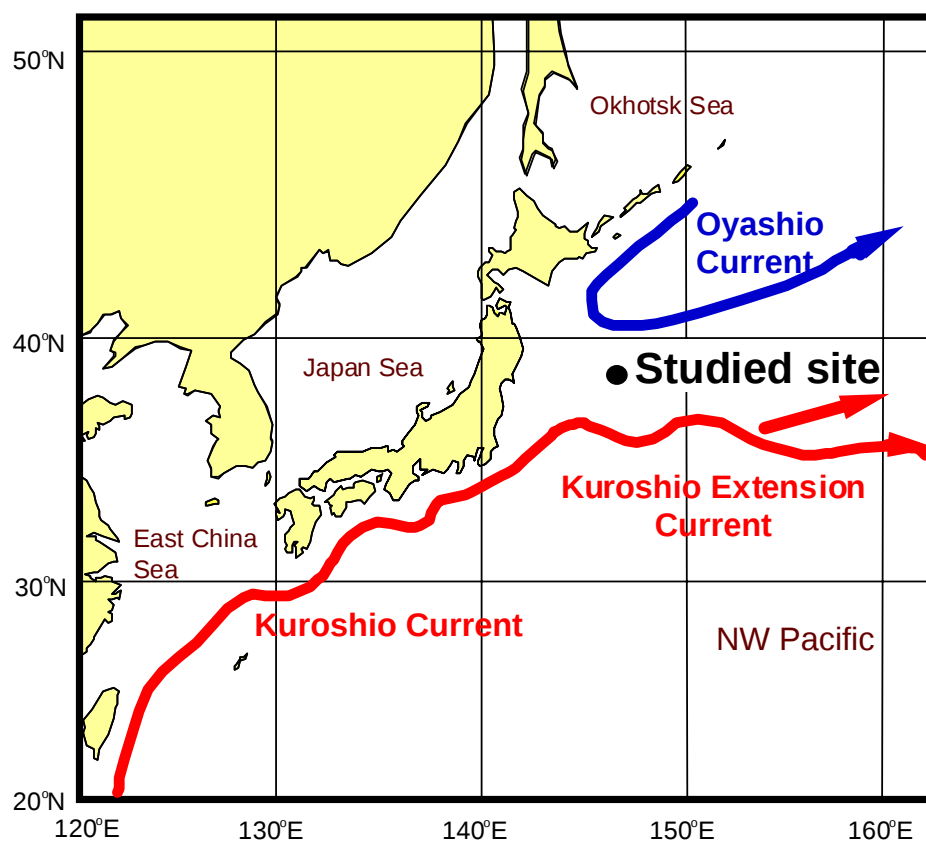
824 Fig. 5 Changes in (a) measured and satellite-based surface chlorophyll-a concentrations
825 and estimated net primary production, the sinking fluxes of (b) CaCO_3 , opal, organic
826 carbon, and lithogenic material and (c) GDGTs and alkenones, and (d) $\text{TEX}_{86}^{\text{H}}$ -, $\text{TEX}_{86}^{\text{L}}$
827 - and U_{37}^{K} -based temperatures in the shallow trap from November 1997 to August 1999
828 at site WCT-2. Data for measured chlorophyll-a concentrations at 0–50 m depth

(average) and 50–100 m depth (average) at nearby site (39°N, 146.75°E) are from the Fishery Research Agency of Japan (2012). Data for CaCO₃, opal, organic carbon and lithogenic material are from Mohiuddin et al. (2002), and data for alkenones and U₃₇^{K'} are from Yamamoto et al. (2007).

Fig. 6 Sinking fluxes of GDGTs at different depths in the water column.

Fig. 7 Depth profiles in the measured temperature and chlorophyll a concentration (Chl-a) when the trap was recovered on 26 August 1998. The TEX₈₆^H- and TEX₈₆^L-based temperatures of the cup from 24 July to 6 August 1998 and the expected production depths (EPD) are also presented.

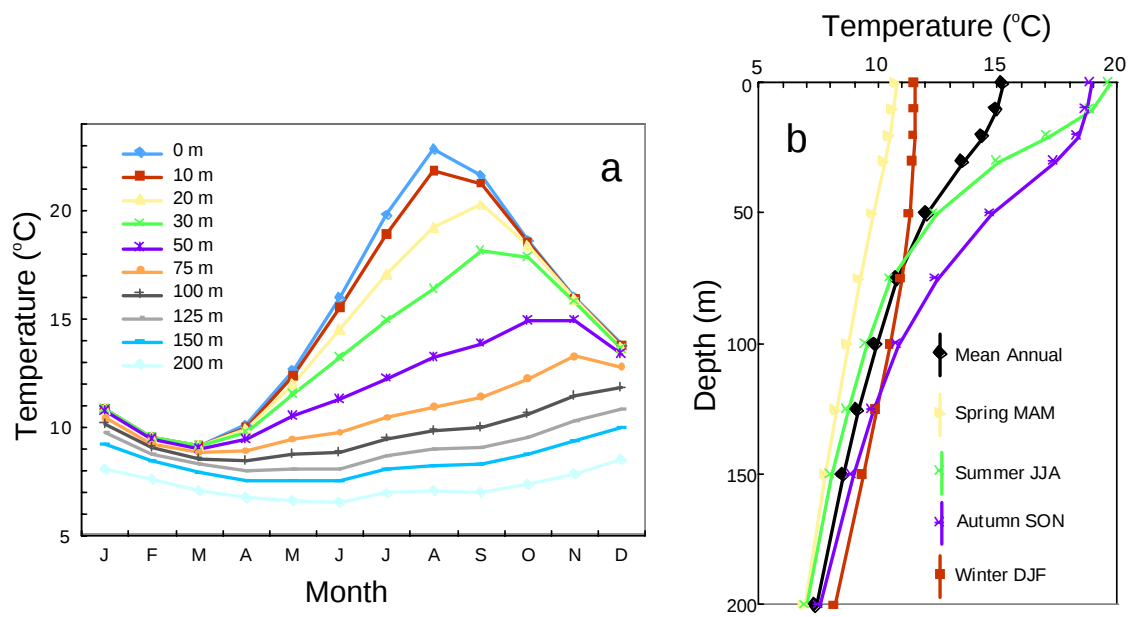
Fig. 8 Flux-weighted TEX₈₆^H- and TEX₈₆^L-based temperatures and mean annual temperature at different depths in the water column. Data for mean annual temperature are from Conkright et al. (2002).



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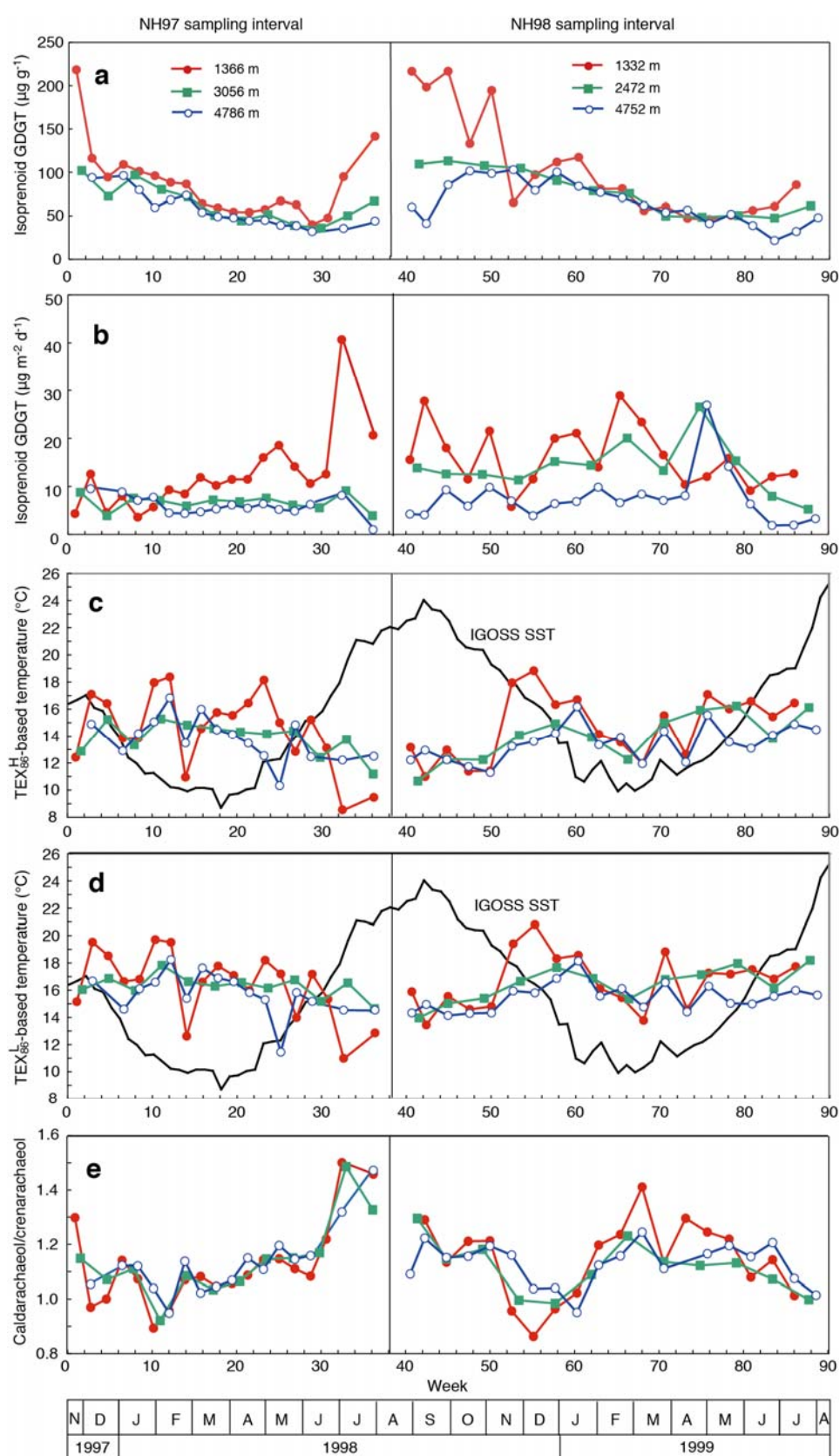
848 Fig. 1



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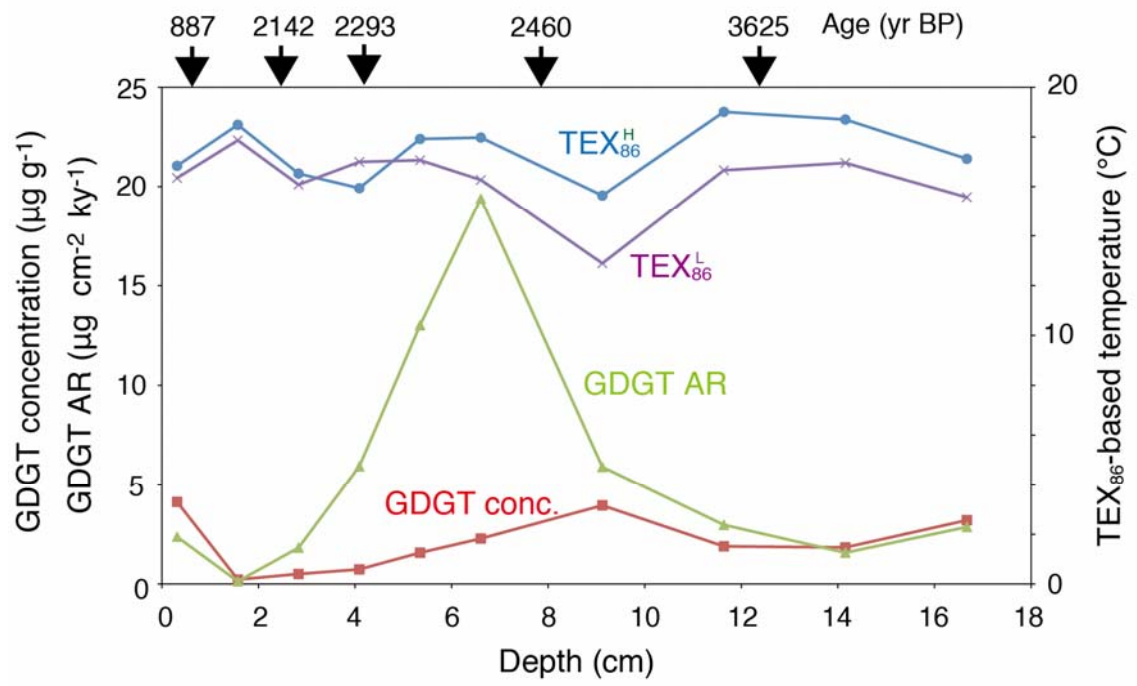
850

851 Fig. 2



852

853 Fig.3



854

855 Fig. 4

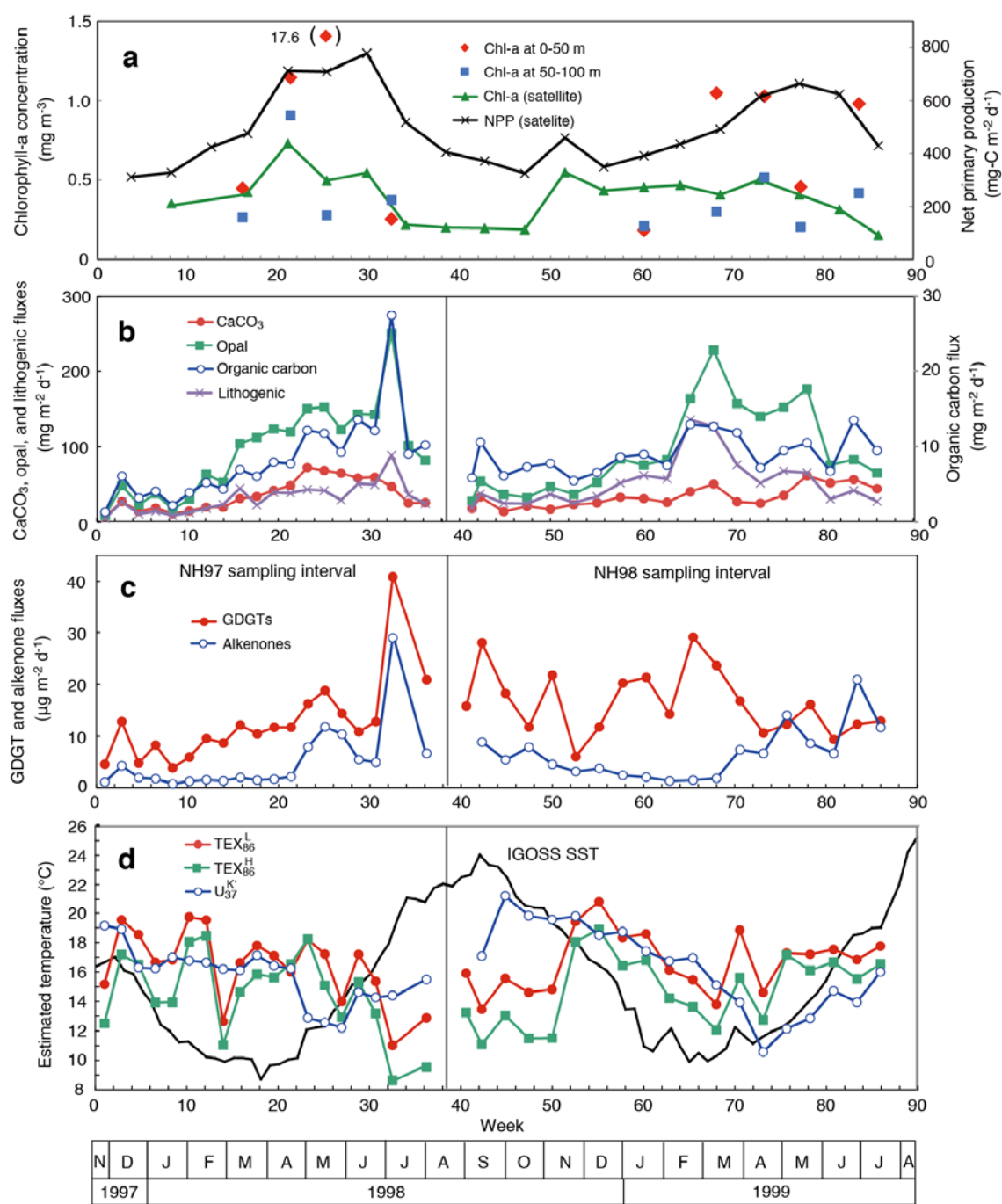


Fig. 5

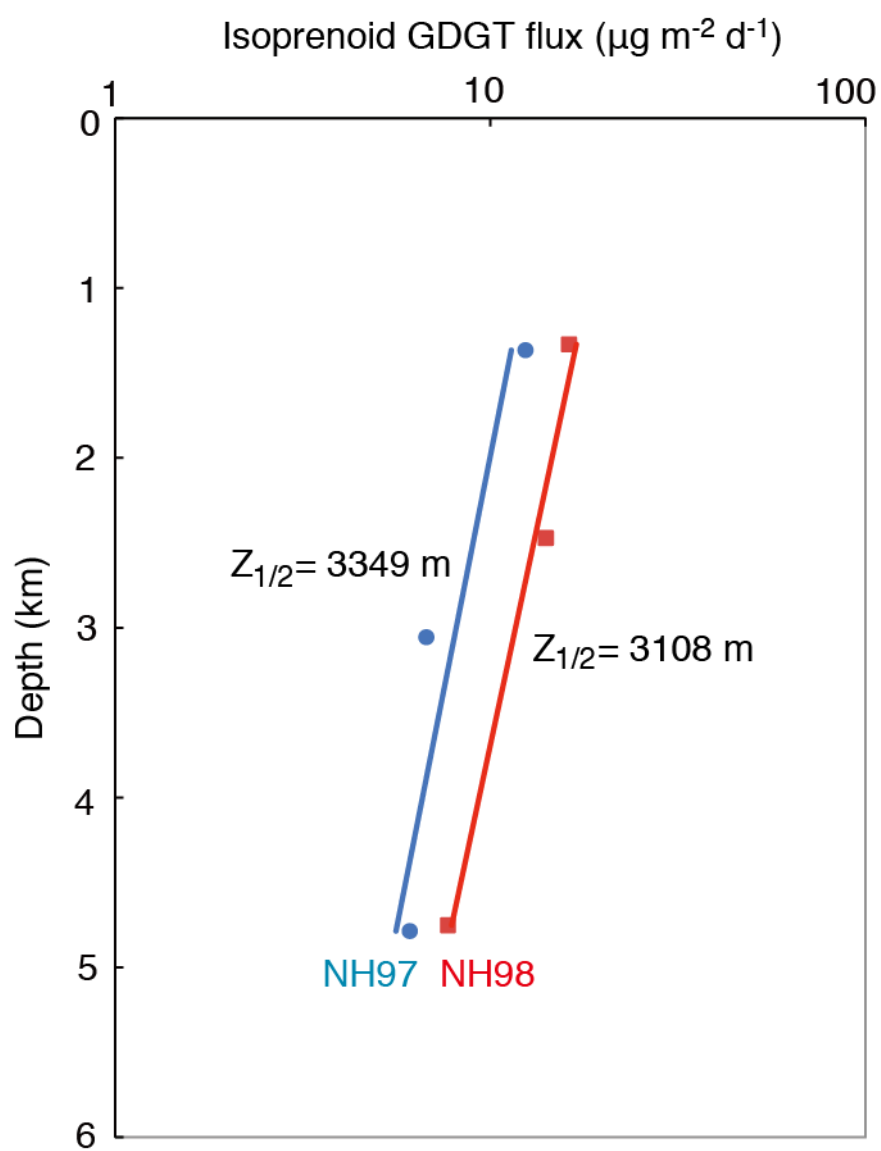
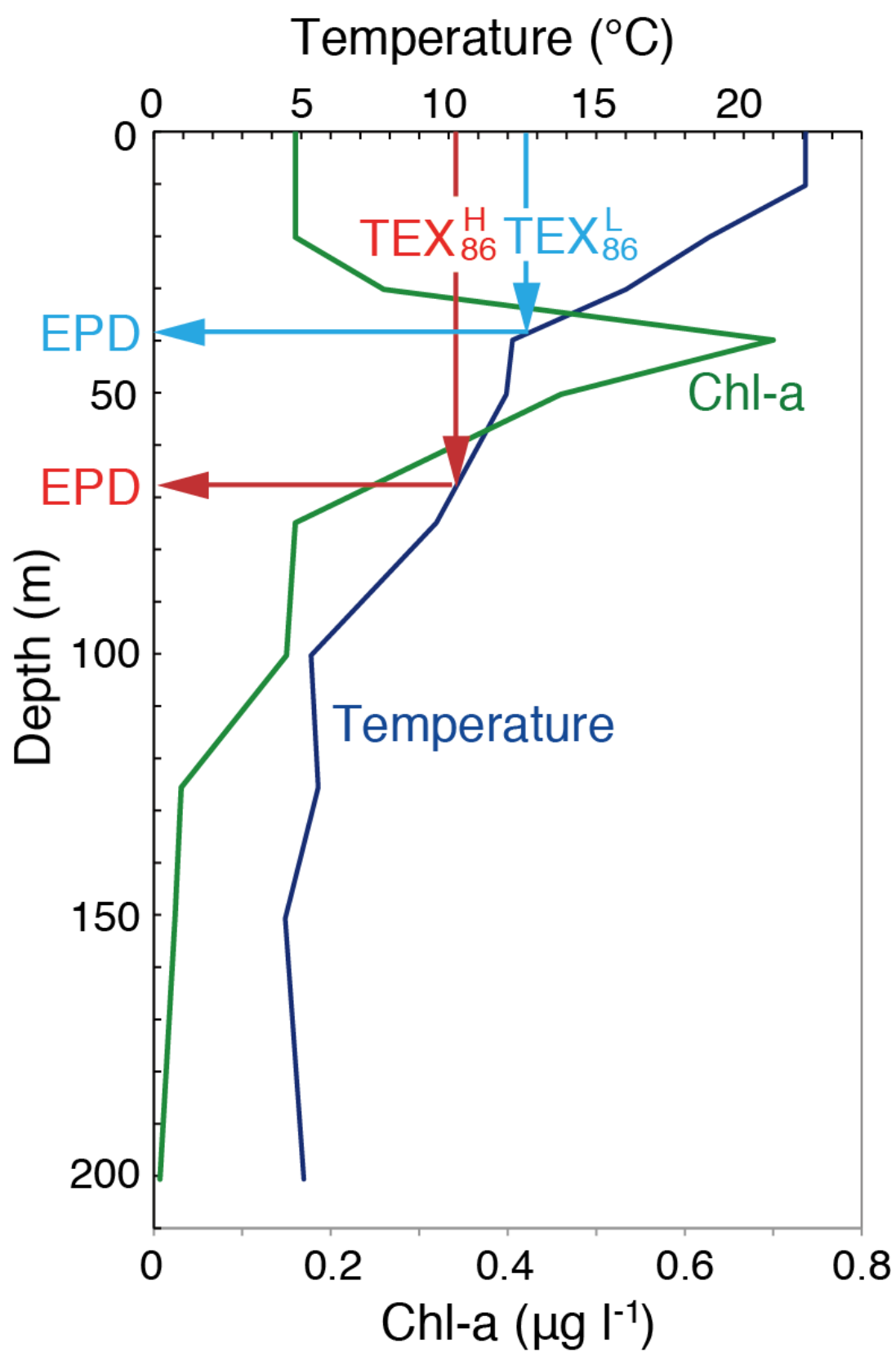


Fig. 6



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863 Fig. 7

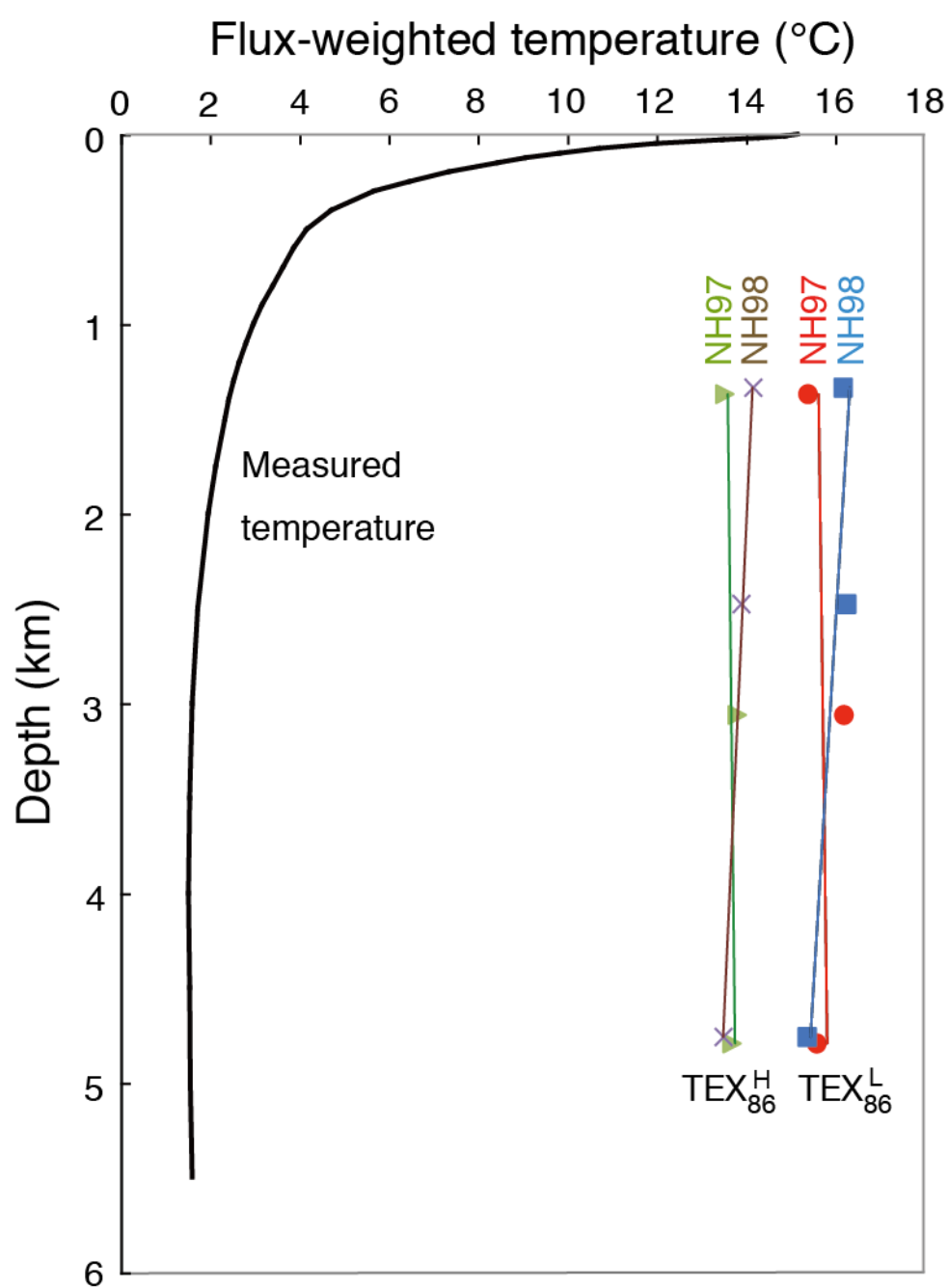


Fig. 8