

1 Core-top calibration of the lipid-based $U^{K'}_{37}$ and TEX_{86} temperature proxies on the southern
2 Italian shelf (SW Adriatic Sea, Gulf of Taranto)

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15

16 **Abstract**

17

18 The Mediterranean Sea is at the transition between temperate and tropical air masses and as
19 such of importance for studying climate change. The Gulf of Taranto and adjacent SW
20 Adriatic Sea are at the heart of this region. Their sediments are excellently suited for
21 generating high quality environmental records for the last millennia with a sub-decadal
22 resolution. The quality of these records is dependent on a careful calibration of the transfer
23 functions used to translate the sedimentary lipid signals to the local environment. Here, we
24 examine and calibrate the $U^{K'}_{37}$ and TEX_{86} lipid-based temperature proxies in 48 surface
25 sediments and relate these to ambient sea surface temperatures and other environmental data.
26 The $U^{K'}_{37}$ -based temperatures in surface sediments reflect winter/spring sea surface

27 temperatures in agreement with other studies demonstrating maximum haptophyte production
28 during the colder season. The TEX_{86} -based temperatures for the nearshore sites also reflect
29 winter sea surface temperatures. However, at the most offshore sites, they correspond to
30 summer sea surface temperatures. Additional lipid and environmental data including the
31 distribution of the BIT index and remote-sensed chlorophyll-*a* suggest a shoreward increase
32 of the impact of seasonal and spatial variability in nutrients and control of planktonic archaeal
33 abundance by primary productivity, particle loading in surface waters and/or overprint by a
34 cold-biased terrestrial TEX_{86} signal. As such the offshore TEX_{86} values seem to reflect a true
35 summer signal to the effect that offshore $U^{K'}_{37}$ and TEX_{86} reconstruct winter and summer
36 temperature, respectively, and hence provide information on the annual temperature
37 amplitude.

38

39 Keywords: Mediterranean climate, Southern Adriatic Sea, Gulf of Taranto, SST, surface
40 sediments, $U^{K'}_{37}$, TEX_{86} , BIT, alkenones, GDGTs

41

42 **1. Introduction**

43

44 A valid and powerful method to better understand short-term environmental and climate
45 change is to study the past. The interactions between atmosphere and ocean are complex so
46 deciphering them requires quantitative and reliable proxies for key environmental parameters
47 such as temperature, air pressure, sea level and the precipitation-evaporation budget. This is
48 also valid for the Mediterranean climate, which is especially sensitive to climate change due
49 to its location between the subtropical high-pressure belt and mid-latitude westerlies (e.g.,
50 Trigo et al., 1999; Xoplaki et al., 2003, 2004).

51 As Sea Surface Temperature (SST) is an important factor in the Earth's climate, its
52 reconstruction is essential for an understanding of past climate change. The commonly used
53 geochemical temperature proxies include $\delta^{18}\text{O}$ and Mg/Ca ratios of planktonic foraminifera
54 (Erez & Luz, 1983; Nürnberg et al., 1996; Elderfield & Ganssen, 2000), the $U^{K'}_{37}$ from
55 alkenones synthesized by haptophytes (Prah1 & Wakeham, 1987) and the TEX₈₆ based on
56 archaeal isoprenoidal tetraether lipids (Schouten et al., 2002; Kim et al., 2008).

57 The $U^{K'}_{37}$ exploits the observation that the abundance of the diunsaturated C₃₇ methyl
58 alkenone, relative to the total of di- and triunsaturated C₃₇ methyl alkenones in surface waters
59 and algal cultures increases with increasing water temperature. These alkenones are produced
60 by a small group of haptophyte algae thriving in the mixed layer: the coccolithophore
61 *Emiliana huxleyi* and related species (Volkman et al., 1980; Marlowe et al., 1984; Brassell et
62 al., 1986; Prah1 & Wakeham, 1987; Conte et al., 1998). Global calibrations of marine core-top
63 $U^{K'}_{37}$ values with mean annual SSTs show a consistent linear relationship with an uncertainty
64 of 1.1°C (Müller et al., 1998; Conte et al., 2006). This led to the establishment of the $U^{K'}_{37}$
65 index as a reliable paleoceanographic tool to estimate SSTs in a variety of oceanic settings
66 (Herbert et al., 2003 and references therein; Haug et al., 2005; Sachs & Anderson, 2005).

67 Nevertheless, some studies reveal clear discrepancies between the $U^{K'}_{37}$ signal in sediments
68 and annual mean SST (e.g., Volkman, 2000). Factors suggested to cause these discrepancies
69 include preferential degradation of the triunsaturated alkenone (Sun & Wakeham, 1994; Gong
70 & Hollander, 1999; Hoefs et al., 2002; Rontani et al., 2006, 2009; Kim et al., 2009b),
71 influence of nutrients and light (Epstein et al., 1998; Versteegh et al., 2001; Prah1 et al.,
72 2003), input of alkenones from remote regions (Benthien & Müller, 2000; Goñi et al., 2001;
73 Ohkouchi et al., 2002; Mollenhauer et al., 2007), differences in species composition
74 (Volkman et al., 1995; Conte et al., 1998), production at greater depths within the euphotic
75 zone (Ternois et al., 1997; Bentaleb et al., 1999; Prah1 et al., 2005) or strong blooming of
76 haptophytes in periods with water temperatures that are significantly different from the annual
77 mean (Sikes et al., 1997; Bentaleb et al., 1999; Prah1 et al., 2001 and references therein; Popp
78 et al., 2006; Versteegh et al., 2007). In spite of these deviations from the global calibration the
79 utility of site-specific calibrations between environment and $U^{K'}_{37}$ is contentious.

80 The TEX_{86} temperature proxy is based on archaeal glycerol dialkyl glycerol tetraethers
81 (GDGT), which are abundant in marine sediments (Schouten et al., 2000, 2002). The
82 biological sources are non-hyperthermophilic cren- and euryarchaeota, a major group of
83 prokaryotes in today's oceans and lakes (Karner et al., 2001; Powers et al., 2004). The relative
84 distribution of these isoprenoidal GDGTs varies with growth temperature and (similar to the
85 $U^{K'}_{37}$) linear regressions of core-top TEX_{86} values to SST enable the use of the TEX_{86} as a
86 temperature proxy (Schouten et al., 2002, 2007a; Wuchter et al., 2005; Kim et al., 2008,
87 2010). The TEX_{86} is considered to reflect annual mean temperatures of the upper mixed layer
88 (Schouten et al., 2002; Kim et al., 2008). Although, the TEX_{86} is increasingly used for
89 reconstructing ancient SSTs, a number of issues remain unresolved (Huguet et al., 2006;
90 Pearson et al., 2007). It appears that the TEX_{86} can be biased due to additional production of
91 GDGTs below the mixed layer (Pearson et al., 2001; Huguet et al., 2007; Lee et al., 2008), by
92 seasonality in crenarchaeotal growth (Schouten et al., 2002; Herfort et al., 2006; Huguet et al.,

93 2006, 2007; Menzel et al., 2006; Wuchter et al., 2006) and by the ecology of planktonic cren-
94 and euryarchaeota due to their presence in different water depths of the ocean and the
95 theoretical possibility of GDGT synthesis by marine euryarchaeota (Wuchter et al., 2005;
96 DeLong, 2006, Turich et al., 2007). Additionally, archaea living in sediments of continental
97 margins and the deep-sea may contribute to the GDGT pool and thus influence the TEX₈₆
98 value (Sorensen & Teske, 2006; Lipp et al., 2008; Shah et al., 2008; Lipp & Hinrichs, 2009).
99 In coastal settings, fluvial input of terrestrial isoprenoidal GDGTs may bias the TEX₈₆
100 (Herfort et al., 2006). Fortunately, this latter bias can be determined by using the Branched
101 and Isoprenoid Tetraether (BIT) index (Hopmans et al., 2004), a ratio between the abundance
102 of branched GDGTs (presumably derived from anaerobic soil bacteria) and crenarchaeol
103 indicating the relative importance of terrestrial organic matter input (Herfort et al., 2006; Kim
104 et al., 2006, Weijers et al., 2006a; Weijers et al., 2006b).

105 Diagenetic overprints of the TEX₈₆ due to changing redox conditions seem to be less
106 important than for other biomarkers (Sinninghe Damsté et al., 2002a; Schouten et al., 2004;
107 Kim et al., 2009b). However, selective degradation during resuspension, transport and
108 redeposition may be significant in some cases and has to be considered for the reliable
109 application of the TEX₈₆ as a SST proxy (Mollenhauer et al., 2007; Kim et al., 2009a).
110 Considering these factors, careful assessment of site-specific relations between U^K₃₇ values,
111 TEX₈₆ and SST is vital to arrive at reliable SST reconstructions.

112 At the Gallipoli shelf (Gulf of Taranto, southern Italy) the influence of the mid-latitude
113 westerlies, represented by the seasonal modes of the Northern Atlantic Oscillation (NAO),
114 have a significant effect on the region causing for example maxima in precipitation during
115 winter and arrival of Atlantic storm tracks in southern Italy (e.g., Hurrell and Van Loon, 1997;
116 Xoplaki et al., 2004). Sediments at the shelf are suitable for high resolution environmental
117 reconstruction (e.g., Cini Castagnoli et al., 1999b; Versteegh et al., 2007) (Fig. 1). Shallow-
118 water cores revealed the unique potential for high-resolution down-core studies of the past

119 two centuries based on radiometric dating and tephroanalysis (Cini Castagnoli et al., 1990;
120 Bonino et al., 1993). Furthermore, carbonate contents (Cini Castagnoli et al., 1992a, 1992b),
121 thermoluminescence (Cini Castagnoli et al., 1997) and the stable carbon and oxygen isotope
122 compositions of the planktonic foraminifer *G. ruber* show significant decadal to centennial
123 components, assumed to be related to solar forcing (Cini Castagnoli et al., 1999, 2000, 2002,
124 2005). An alkenone-based SST reconstruction covering 1305 A.D. to 1979 A.D. proposed
125 that $U_{37}^{K'}$ reflects mainly SST of the cooler part of the year. In the same study an imprint was
126 observed of centennial-scale SST variations consistent with the record of atmospheric $\Delta^{14}C$, a
127 proxy for solar energy variability, suggesting a solar forcing mechanism (Versteegh et al.,
128 2007).

129 Given the suitability of the Gallipoli region for high-resolution climate reconstruction, we
130 carefully calibrated lipid-derived SST proxies in comparison to the most recent environmental
131 conditions over a broader area covering the Italian shelf within the southern Adriatic Sea and
132 Gulf of Taranto, taking into consideration the preservation, transport and other control
133 mechanisms related to these signals.

134

135 **2. Study Area**

136

137 The Adriatic Sea is a narrow semi-enclosed sub-basin of the northeastern Mediterranean Sea
138 which is elongated in NW-SE direction (ca. 200x800 km) (Cattaneo et al., 2003) (Fig. 1).
139 Morphologically its northern part is characterized by shallow and gently sloping shelf
140 (Artegiani et al., 1997a). The southern Adriatic Sea is flanked by a steep slope and narrow
141 shelf, except south of the Gargano Promontory, where the shelf broadens to about 70-80 km
142 and the Strait of Otranto where the Adriatic Sea is separated from the Ionian Sea (Artegiani et
143 al., 1997a; Cattaneo et al., 2003; Zavatarelli & Pinardi, 2003).

144 The circulation of the Adriatic Sea is known to be cyclonic with seasonal variability (Rizzoli
145 & Bergamasco, 1983; Orlić et al., 1992; Artegiani et al., 1997b; Poulain, 2001). There are
146 three main forcing factors affecting the circulation: a) river run-off causing heat loss and low-
147 salinity water gain; b) atmospheric forcing responsible for dense water formation and seasonal
148 differences in circulation; c) exchange via the Strait of Otranto balancing the water budget by
149 intrusion of warm and salty waters from the Ionian Sea (Artegiani et al., 1997a; Cattaneo et
150 al., 2003; Zavatarelli & Pinardi, 2003; Milligan & Cattaneo, 2007).

151 The northern Po-river system and Apennine rivers located north of the Gargano Promontory
152 play the major role in freshwater supply for the western Adriatic Sea by contributing more
153 than 70% of the total runoff, whereas in the south-western Adriatic Sea rivers are nearly
154 absent (Raicich, 1996). On a seasonal scale increased river runoff is observed in late autumn
155 and late spring corresponding to precipitation maxima and snow melting (Cattaneo et al.,
156 2003). This creates the coastal buoyancy-driven Western Adriatic Current (WAC)
157 characterized as Adriatic Surface Water (ASW), which is confined to a narrow coastal strip
158 flowing southwards along the Italian eastern margin through the Strait of Otranto into the
159 Gulf of Taranto where it mixes with Ionian Sea water masses. Its intensity and extension can
160 also be tracked by the development of a thermal front showing low temperatures of Adriatic
161 Surface Water trapped in the western Adriatic coast (e.g., Morović et al., 2006).

162 The southern Adriatic open waters show oligotrophic characteristics comparable to the IS and
163 nutrient supply to the euphotic zone depends strongly on vertical stratification and mixing
164 processes (Viličić et al., 1989). Here, the Western Adriatic Current system plays a crucial role
165 for nutrient supply and drives primary production (PP) of the Adriatic Sea. As a consequence,
166 higher pigment concentrations can be observed in satellite images along the Italian coastal
167 zone (Morović, 2002), the Strait of Otranto, around the Apulian Peninsula into the Gulf of
168 Taranto (e.g. Focardi et al., 2009; Zonneveld et al., 2009). For this region remote-sensing
169 shows a negative correlation between seasonal SSTs to chlorophyll-*a*, whereas SSTs and

170 salinity are positively correlated, indicating that main PP takes place during the colder season
171 and demonstrating the influence of freshwater input and associated heat loss (Zonneveld et
172 al., 2009). Additionally, highest phytoplankton densities in the surface layer of the water
173 column are observed in spring and autumn at the western shelf in the middle Adriatic sub-
174 basin as a consequence of intensified continental water input (Totti et al., 2000). Intrusion of
175 Ionian Surface Water (ISW) is restricted to the eastern coast of the Adriatic Sea, balancing the
176 outflow of Adriatic Surface Water. Advection of nutrient-rich Mediterranean waters into the
177 southern Adriatic Sea is also an important productivity factor (Marasović et al., 1995).
178 Nutrient-rich and high-salinity intermediate waters, with a core at 200 m, form the Levantine
179 Intermediate Water (LIW). The Levantine Intermediate Water invades the southern Adriatic
180 Sea during winter at the western Adriatic shelf, where it mixes with Adriatic Surface Water,
181 affecting the phytoplankton community (Caroppo et al., 2001).

182 Deep-water formation takes place in the northern Adriatic Sea. Here, Northern Adriatic deep
183 Dense Water (NAdDW) occupies the northern shelf, promoted by surface cooling due to wind
184 outbreaks during winter (e.g. Vilibić et al., 2005). Additionally, Adriatic Deep Water (ADW)
185 is formed in the southern Adriatic Sea basin. The two deep waters spread into the Ionian Sea.
186 In the Gulf of Taranto, where the width of the shelf rapidly decreases, dense coastal water is
187 released to depth and transformed by intrusion and mixing with ambient water (Kourafalou,
188 2001; Sellschopp & Alvaréz, 2003; Hainbucher et al., 2006; Bignami et al., 2007).

189 SSTs from satellite and limited available in-situ measurements in the research area vary
190 between 13 °C in winter and 26 °C in summer and show a good agreement (Zavatarelli et al.,
191 1998; Caroppo et al., 1999, 2001; Socal et al., 1999; Boldrin et al., 2002; Zonneveld et al.,
192 2009). Lower SSTs of 13-15 °C during winter and spring are especially observed at the near-
193 coastal locations in the Gulf of Manfredonia due to the influence of the Western Adriatic
194 Current and freshwater input of the adjacent Ofanto river draining into the gulf.

195 In the region the upper water column is well mixed during winter and spring while a
196 thermocline starts to develop at 50-70 m water depth in March leading to open-ocean
197 stratification during summer. This controls nutrient distribution, which is additionally
198 influenced by river input and resuspension due to vertical mixing during winter. As a result,
199 nutrient concentrations in the surface waters decrease from NW to SE (e.g., Civitarese et al.,
200 1998). This seasonality in nutrients and other water column characteristics affects the
201 phytoplankton community structure (Boldrin et al., 2002; Socal et al., 1999).

202 **3. Material and methods**

203

204 **3.1 Surface sediment samples**

205 The sediments analyzed represent the top 2 cm of multicores from 48 stations obtained from
206 the southern Adriatic Sea, Strait of Otranto, Cape St. Maria di Leuca and Gulf of Taranto.
207 They have been collected during P339 POSEIDON cruise ‘CAPPUCCINO’ in June 2006
208 (Fig. 1, Table 1) (Zonneveld et al., 2009). The material was frozen to -20 °C directly upon
209 collection and stayed at this temperature until geochemical processing. ²¹⁰Pb ages imply high
210 sedimentation rates along the Italian shelf (compilation in Zonneveld et al., 2009). Given the
211 high sedimentation rates and sampling strategy, samples represent a record of very recent
212 sedimentation between 2 and 29 years.

213

214 **3.2 Lipid Extraction**

215 For GDGT and alkenone analyses, 5-15 g of freeze dried and homogenized sediment were
216 extracted using an accelerated solvent extractor (ASE 200, DIONEX) with a mixture of
217 dichloromethane (DCM):methanol (MeOH) 9:1 (v/v, three cycles of 5 min each) at 100 °C
218 and 7.6x10⁶ Pa. Before extraction known amounts of *n*-hexatriacontane, 2-nonadecanone, *n*-
219 nonadecanol and *n*-nonadecanoic acid were added as internal standards. The obtained total
220 lipid extracts (TLE) were combined and dried using a Turbovap LV (Zymark Corp.) at 35 °C
221 under a nitrogen stream. The dried TLEs were re-dissolved in DCM and subdivided into two
222 aliquots for further purification.

223

224 **3.3 Alkenone analysis and SST assessment**

225 For alkenone analysis alkenoates were removed by base hydrolysis of the TLE fraction
226 following the procedure described by Elvert et al. (2003). The resulting fraction was separated
227 in DCM-soluble asphaltenes and *n*-hexane-soluble maltenes. The maltenes were desulfurized

228 with activated copper powder and separated by solid phase extraction (Supelco LC-NH₂ glass
229 cartridges; 500 mg sorbent). Four fractions of increasing polarity (hydrocarbons, ketones,
230 alcohols, and fatty acids) were obtained by elution with 4 ml *n*-hexane, 6 ml *n*-hexane:DCM
231 3:1 (v/v), 7 ml DCM:acetone 9:1 (v/v), and 8 ml 2% formic acid in DCM (v/v). The ketone
232 fraction was dissolved in 100 µl *n*-hexane prior to capillary gas chromatography (GC).

233 Gas chromatography was performed by using a Trace GC Gas Chromatograph
234 (ThermoQuest) equipped with a 30 m DB-5MS fused silica capillary column (0.32 mm ID,
235 0.25 µm film thickness) and a flame ionization detector (FID), He as carrier gas with a flow
236 rate of 1 ml/min. The GC temperature program for alkenones used was: injection at 60 °C,
237 1 min isothermal; from 60 °C to 150 °C at 15 °C/min; from 150 °C to 310 °C at 4 °C/min;
238 28 min isothermal with a total oven run-time of 75 min. Peak identification of di- and tri-
239 unsaturated C₃₇ alkenones (C_{37:2} and C_{37:3}) was based on retention time and comparison with
240 parallel GC-MS runs. All samples were analyzed in duplicate and quantification was by peak
241 integration and by assuming the same response factor as the internal standard (2-
242 nonadecanone). Concentrations of di- and triunsaturated C₃₇ alkenones are given as sum in
243 ng/g dw (dry weight) sediment.

244 The U^K₃₇ was calculated using the definition of Prahl & Wakeham (1987) and converted into
245 SSTs by applying the sediment core top transfer function of Conte et al. (2006). Analytical
246 precision of duplicate runs was better than ±0.007 U^K₃₇ units (±0.02 °C).

247

248 **3.4 GDGT analysis and SST assessment**

249 For GDGT analysis, TLE aliquots were separated by alumina oxide column chromatography
250 (activated Al₂O₃, basic, ~150 mesh, 58 Å, Type 5016A, Sigma Aldrich) into an apolar and
251 polar fraction using *n*-hexane:DCM 9:1 (v/v) and DCM:MeOH 1:1 (v/v), respectively. The
252 polar fraction was dried under a stream of nitrogen, weighed and dissolved ultrasonically in *n*-
253 hexane:isopropanol 99:1 (v/v) with a concentration of 2 mg/ml (Schouten et al., 2009). The

254 polar fraction containing the GDGTs was filtered using a 0.45 μm pore size PTFE filter prior
255 to analysis as described by Hopmans et al. (2000, 2004).

256 Analyses were performed by high performance liquid chromatography/atmospheric pressure
257 chemical ionization-mass spectrometry (HPLC/APCI-MS) using an Agilent 1200 series
258 HPLC coupled to an HP 6120 MSD equipped with automatic injector and HP Chemstation
259 software. 20 μl aliquots were injected on to an Alltech Prevail Cyano column (2.1x150 mm,
260 3 μm ; Grace) maintained at 30 $^{\circ}\text{C}$. GDGTs were eluted using the following gradient with
261 solvent A (*n*-hexane) and solvent B (5% isopropanol in *n*-hexane): 80% A:20% B for 5 min,
262 linear gradient to 36% B in 45 min. Flow rate was 0.2 ml/min. After each analysis the column
263 was cleaned by back-flush of *n*-hexane:isopropanol 90:10 (v/v) at 0.2 ml/min for 8 min.

264 Conditions for APCI-MS were as follows: nebulizer pressure 4.1×10^5 Pa, vaporizer
265 temperature 450 $^{\circ}\text{C}$, drying gas (N_2) flow 5 l/min and temperature 350 $^{\circ}\text{C}$, capillary voltage
266 -4 kV, corona 4 μA . For isoprenoidal and non-isoprenoidal GDGTs peak integration of their
267 $[\text{M}+\text{H}]^+$ ions (m/z 1302, 1300, 1298, 1296, 1292, 1022, 1036, 1050) detected in selective ion
268 monitoring (SIM) mode was used (dwell time=76 ms) (Schouten et al., 2007a). The TEX_{86}
269 ratio was calculated according to Schouten et al. (2002). For temperature conversion we used
270 the calibration with annual mean SST using marine sediment core tops after Kim et al. (2008).

271 Additionally, we provide GDGT based temperatures using the recently published calibration
272 from Kim et al. (2010) in the supplementary material (S1).

273 To examine the potential influence of terrestrial archaeal GDGTs we applied the BIT index
274 (Hopmans et al., 2004). Selected samples were analyzed in duplicate and analytical precision
275 was determined by replicate injections of laboratory internal reference material with known
276 TEX_{86} and BIT values. Mean deviation from reference samples was -0.01 TEX_{86} units and
277 mean standard deviation of duplicate samples was ± 0.013 (± 0.72 $^{\circ}\text{C}$). Deviation of duplicate
278 BIT values was better than 0.01 units. Concentrations of GDGTs were not determined.

279

280 **3.5 TOC and Environmental data**

281 Total Organic Carbon (TOC) values of the surface sediments were obtained from parallel
282 multicores taken together with our samples and range between 0.17 and 0.96% (Zonneveld et
283 al., 2009). Seasonal chlorophyll-*a* (Chl-*a*) and SST data were derived from compiled SeaWifs
284 satellite data for 2002-2006 A.D. Data were extracted from the OBPG MODIS-Aqua Monthly
285 Global 9-km database (<http://reason.gsfc.nasa.gov/OPS/Giovanni/ocean.aqua.shtml>) on a
286 0.1 °-grid resolution. Seasonal sea surface salinity (SSS) data were retrieved from the
287 MEDATLAS bottle database (<http://odv.awi.de/data/ocean/medatlasii.html>) spanning the last
288 20 years on a 0.2 °-grid resolution. Data based on the NOAA World Ocean Data Atlas 2005
289 on a 0.25 °-grid resolution were used for: summer-SSS (sites GeoB 10714 and GeoB 10715),
290 autumn-SSS (GeoB 10731, 10732 and 10733), winter-SSS (GeoB 10748 and 10749) and
291 mean annual SSTs (MA SST) and annual salinity data. Seasons were defined as follows:
292 Winter: December – February (DJF), Spring: March – May (MAM), Summer: June – August
293 (JJA), Autumn: September – November (SON)) (Zonneveld et al., 2009).

294

295 **3.6 Correlation analysis, cluster analysis and contour plots**

296 Correlation analysis was performed to interpret the relation between the biomarker and
297 environmental data sets. The software XLStat version 7.5.2[®] was used to create a cross
298 correlation table giving a Pearson correlation coefficient *r*, for significant ($p < 0.05$) and highly
299 significant correlations ($p < 0.0001$). Cluster analysis was performed on abundances of GDGT-
300 0 to GDGT-4' using the software PAST (PAleontological STatistics) version 1.96[®] (Hammer
301 et al., 2001) using euclidian distances and ward linkage. Contour plots were generated with
302 Ocean Data View (ODV) version 4.3.2[®] (Schlitzer, 2010) using a DIVA gridding algorithm
303 (25 per mil x/y length-scale).

304

305 **4. Results**

306

307 **4.1 Alkenone-based temperatures ($SST_{UK'37}$)**

308 The alkenone-based temperatures range from 14.9 to 19.5 °C with lower temperatures at near-
309 coastal sites (Fig. 2b, Table 1). This temperature difference varies between 2 to 4 °C and is
310 largest in transects at the Gargano Promontory sites. At the Strait of Otranto there is no
311 obvious gradient except in the southernmost transect (10744-42; 15.7-17.8 °C). The onshore-
312 offshore gradient also occurs in the eastern part of the Gulf of Taranto. In contrast,
313 temperature differences at the western Gulf of Taranto are not significant (17.5-18.0 °C). The
314 $SST_{UK'37}$ are up to 4 °C lower than the annual average satellite-derived SSTs, and are much
315 closer to the winter/spring SSTs (Fig. 3). Correlation of $SST_{UK'37}$ with seasonal satellite-
316 derived SST is poor with the exception of winter SST (Table 2).

317

318 **4.2 GDGT-based temperatures (SST_{TEX86})**

319 The GDGT-based temperatures vary between 11.0 and 25.8 °C and similar to the alkenone-
320 based SSTs, tend to increase seawards (Fig. 2c, Table 1). Lowest SST_{TEX86} (11.0 and 19.5 °C)
321 occur at near-coastal shelf sites (water depth: <220 m); intermediate values (17.4-22.9 °C) at
322 the outer shelf and shelf break sites (220-733 m) and highest values (23.6-25.8 °C) at the deep
323 ocean sites (>733 m). In the Gulf of Taranto this temperature difference between coast and
324 open ocean approaches 10°C (15.1-25.8°C). The comparison with satellite-derived SSTs
325 shows that neither SST_{TEX86} at shallow-shelf sites nor at the offshore sites agree with annually
326 averaged SSTs (Fig. 2a). The comparison between SST_{TEX86} and water depth shows that
327 calculated temperatures at shallow sites match winter and spring SSTs, whereas sites with
328 water depths exceeding 500 m resemble autumn and summer values (Fig. 3). This pattern also
329 persists when using the recently proposed calibration from Kim et al. (2010; Fig. S1 and Tab.
330 S1). SST_{TEX86} shows a positive correlation with depth (Table 2). It is anti-correlated to
331 chlorophyll-*a*, whereas no correlation exists with $SST_{UK'37}$ and TOC.

332

333 **4.3 Alkenone concentrations**

334 Summed concentrations of the di- and triunsaturated C₃₇ alkenones range between 10 and 500
335 ng/g of dry sediment (Fig. 4b). At the Gargano Promontory highest concentrations of 200-
336 280 ng/g of dry sediment are observed offshore with a cross-shelf decrease towards the near-
337 coastal sites. Similar concentrations are reached in the Strait of Otranto. Maximum
338 concentrations of 400-500 ng/g of dry sediment are observed between Cape St. Maria di
339 Leuca and Gulf of Taranto, where they decrease seawards and to hardly detectable levels at
340 the deepest sites. The normalization of concentrations to TOC (not shown) does not
341 significantly change the above described pattern based on dry sediment.

342

343 **4.4 GDGT distributions and BIT-Index**

344 The relative abundance of isoprenoidal GDGTs within the surface sediments shows the
345 typical distribution of planktonic archaeal GDGTs and is dominated by GDGT-4
346 (crenarchaeol) accounting for 50-55% and GDGT-0 representing 25-40% of total GDGTs
347 (Fig. A2).

348 The BIT index varies between 0.02 and 0.29 (Table 1) with highest values at the near-coastal
349 sites of the Gargano Promontory and decreasing seaward (Fig. 5). At the Strait of Otranto and
350 Gulf of Taranto, BIT is generally lower (0.02 and 0.09), whereas a decrease with increasing
351 distance from the coast was not found. BIT is inversely correlated to SST_{TEX86} and salinity,
352 whereas a positive correlation is present between BIT and chlorophyll-*a* (Table 2).

353

1 **5. Discussion**

2

3 The alkenone- and GDGT-based temperature proxies and recent environmental data clearly
4 demonstrate that in the studied region there is no simple relationship with the annual SST
5 usually observed elsewhere. Of the several mechanisms affecting the temperature proxies we
6 will discuss those, which seem to be of major importance: seasonality, subsurface water
7 production of GDGTs, benthic vs. pelagic origin of GDGTs, and bias caused by the presence
8 of terrigenous GDGTs.

9

10 **5.1 Seasonal alkenone production and alkenone preservation**

11 The observation that the $SST_{UK'37}$ are consistently lower than annual mean SST suggests that
12 alkenone production predominantly takes place during the cooler part of the year along the
13 southern Italian shelf.

14 In the investigated region haptophyte production is dominated by *E. huxleyi* and occurs
15 throughout the whole year with maxima between late autumn and spring based on near-
16 coastal sediment trap stations within the Strait of Otranto and water samples from transects
17 along the southern Adriatic coast (Caroppo et al., 1999; Socal et al., 1999). In the mid
18 Adriatic Sea *E. huxleyi* abundance typically increases in April (Totti et al., 2000). It is also
19 prominent at the Gulf of Manfredonia (Rubino et al., 2009; Balestra et al., 2009). In this
20 region the winter distribution of cold and nutrient-rich Adriatic Surface Water is the main
21 factor promoting phytoplankton growth and controlling the species composition (Socal et al.,
22 1999). Second in importance is the intrusion of nutrient-rich Levantine Intermediate Water by
23 affecting the renewal of water layers during winter turbulence (Caroppo et al., 2001). At the
24 near-coastal stations satellite-derived SSTs for winter and observed $SST_{UK'37}$ are in agreement
25 with each other showing lower temperatures and the influence of Adriatic Surface Water
26 (Fig. 3).

1 In the Mediterranean Sea highest coccolithophore production and fluxes occur during late
2 winter and spring, with *E. huxleyi* as the ubiquitous species in the eastern Mediterranean Sea
3 with its highest abundance within surface waters (Knappertsbusch, 1993; Ziveri et al., 2000).
4 SST_{UK'37} below mean annual values have been reported from particulate material collected in
5 sediment traps and surface sediments of the Mediterranean basin (Ternois et al., 1997; Emeis
6 et al., 2000). Calculating SST_{UK'37} of surface sediments from the northern Ionian Sea (Emeis
7 et al., 2000) and top cm of a sediment core from the Strait of Otranto (Sangiorgi et al., 2003)
8 using the calibration of Conte et al. (2006) provides 16 °C and 14 °C. This also agrees with
9 winter SSTs and with our SST_{UK'37} range of our nearby samples 10716 (14.9 °C) and 10742
10 (17.8 °C). We estimated the expected sedimentary alkenone composition as a flux-weighted
11 mean on the basis of seasonal cell abundances of *E. huxleyi* and seasonal SSTs from a
12 sediment trap at the Italian shelf in the Strait of Otranto showing maximum cell abundances in
13 November and February (Socal et al., 1999). The estimates are consistent with the alkenone
14 composition in the surface sediments and show a substantially lower SST compared to annual
15 mean SSTs (Table 3).

16 Satellite-derived surface pigment concentrations for the years 2002-2006 of the investigated
17 sites show a negative correlation with SSTs also suggesting that the major portion of PP takes
18 place during the colder seasons with systematically higher chlorophyll-*a* concentrations at the
19 near-coastal sites (Table 2; Zonneveld et al., 2009). Additionally, TOC and concentrations of
20 alkenones appear higher at near-coastal stations, suggesting a higher PP for this region (Fig.
21 4b).

22 In general, chlorophyll-*a* concentrations in the water column follow phytoplankton density.
23 Typically, low values, implying oligotrophic conditions, occur throughout the year, except
24 during winter along the southern Adriatic coast (Caroppo et al., 2001). During winter, highest
25 chlorophyll-*a* concentrations are found within the near-coastal surface layer. This is consistent
26 with high phytoplankton concentrations promoted by the nutrient-rich surface waters of the

1 Western Adriatic Current. Additionally, vertical mixing during winter months brings nutrients
2 into the surface waters (Zonneveld et al., 2009). In summer a deep chlorophyll maximum
3 exists, which can result in underestimation of haptophyte production during warmer seasons
4 as surface waters are depleted in nutrients and alkenone producers may concentrate at the
5 nutricline (Knappertsbusch, 1993). However, observations at the Strait of Otranto imply that
6 coccolithophorids thrive within the surface waters even during summer (Boldrin et al., 2002).
7 Further evidence of the influence of near-coastal Adriatic Surface Water can be observed in
8 the seaward increase in satellite-derived SST during winter (e.g., Gulf of Manfredonia) (Fig.
9 3). This partly may explain the seaward increase of $SST_{UK'37}$. Since, the $SST_{UK'37}$ increase
10 appears to be 2 °C higher than that observed by satellites an additional explanation is needed.
11 However, considering the calibration error of 1.1 °C, this temperature increase is not
12 significant. Selective degradation of tri-unsaturated alkenones in well oxygenated bottom
13 waters of the Northern Adriatic deep Dense Water and/or Adriatic Deep Water at the deeper
14 sites could lead to an increase of $SST_{UK'37}$ (e.g. Hoefs et al., 1998; Gong & Hollander, 1999;
15 Kim et al., 2009b). The influence of early diagenetic processes at the deeper sites was also
16 considered as a factor affecting the dinoflagellate cyst associations in the region, but since
17 oxygen penetration depth is not significantly related to the cyst accumulation rates, this
18 mechanism appears to be unlikely (Zonneveld et al., 2009). Therefore, we propose that
19 selective degradation of alkenones plays a minor role. Instead we conclude that the observed
20 alkenone-based SSTs are consistent with the general productivity patterns recording primarily
21 the SST during the colder part of the year when biomass is highest.

22

23 **5.2 Seasonality in production of planktonic archaea**

24 For the offshore sites, the GDGT-derived temperatures agree best with summer SST. The
25 SST_{TEX86} are 7 °C higher than annual mean SST and 10 °C higher than $SST_{UK'37}$ (Fig. 3). That
26 leads to the hypothesis that, in contrast to the haptophytes, offshore the export of biomarker

1 signals from planktonic archaea predominantly takes place during the warm season. During
2 this season oligotrophic conditions in the open Adriatic and Ionian Sea prevail, which is also
3 reflected by minimum concentrations of chlorophyll-*a* in surface waters (Socal et al., 1999).
4 Consequently, maxima in growth of planktonic archaea occur when PP is at a minimum. Such
5 inverse correlations between archaeal abundance and chlorophyll-*a* have also been observed
6 elsewhere such as in the polar oceans (Murray et al., 1998), the Santa Barbara Channel
7 (Murray et al., 1999) and the North Sea (Wuchter et al., 2005; Herfort et al., 2007). GDGT-
8 based SSTs in eastern Mediterranean Sea sediments also agree with our observation that the
9 offshore ‘open-sea’ sites reflect summer conditions (Menzel et al., 2006; Castañeda et al.,
10 2010). Thus we propose that also for the offshore sites in our study the SST_{TEX86} reflects
11 summer planktonic archaeal production.

12 In contrast, the much lower SST_{TEX86}, at the near-coastal sites, which agree with winter SST,
13 suggest that the maximum archaeal production takes place during the colder part of the year;
14 the period with maximum PP. This is especially pronounced at the Gargano Promontory sites
15 under the direct influence of the Western Adriatic Current. Nutrient concentrations and
16 particle loading in the surface waters appear higher during the colder period (Socal et al.,
17 1999). These conditions may favor the presence of planktonic archaea as reported for coastal
18 waters in the Black Sea (Stoica and Herndl, 2007) and the Canadian Arctic (Wells et al.,
19 2006). Wuchter et al. (2005) observed a positive correlation between chlorophyll-*a* and
20 archaeal lipids in surface waters from the Bermuda Atlantic Time-Series (BATS). At the
21 BATS site, wind-induced convective mixing results in nutrient enrichment of surface waters
22 which promotes PP during winter and possibly also growth of planktonic archaea. At the
23 coastal sites in our region, chlorophyll-*a* concentrations are higher than offshore during the
24 whole year (Table 1) and even in summer they exceed offshore winter levels. Consequently,
25 in contrast to the offshore sites, archaeal blooming during the oligotrophic season, as a
26 strategy of minimizing the competition for nutrients (Murray, 1998) is unlikely to occur at the

1 coastal sites. Instead the winter signal may become relatively more important. A crucial
2 process may be the concomitant increased transport of phytoplankton to depth due to
3 aggregation of cells and other suspended matter occurring during higher PP in this coastal
4 shallow setting (Socal et al., 1999). This larger amount of marine snow in combination with a
5 shallow water column would promote an efficient vehicle to carry the GDGTs to the sea floor
6 and primarily export the SST signal during this time of the year (Wuchter et al., 2005; Huguet
7 et al., 2006a, 2007). Further evidence may lie in the biology of planktonic archaea with some
8 members participating in the oxidation of ammonia (Könneke et al., 2005; Wuchter et al.,
9 2006). Especially in shallow and photic estuarine sediments, phytoplankton and
10 microphytobenthos can contribute organic nitrogen (Caffrey et al., 2007). If this nitrogen
11 becomes mineralized to ammonia it supports nitrification by crenarchaeaota (Francis et al.,
12 2005; Nicol & Schleper, 2006).

13 Alternatively, it is known that crenarchaeaota can reside in deeper water (e.g., Karner et al.,
14 2001) and low reconstructed temperatures could result from subsurface production of
15 GDGTs, which seems to play a major role in upwelling areas where TEX_{86} systematically
16 underestimates SSTs (Huguet et al., 2007; Lee et al., 2008). However, as our data show, for
17 stations with depths below the thermocline (> 75 m, i.e., the vast majority of our samples), the
18 observed pattern cannot be explained by invoking a substantial contribution of GDGTs
19 produced below the thermocline. Likewise, deep water production is not relevant for the
20 shallowest, coldest stations (< 75 m) that do not reach below the thermocline.

21 Our observations suggest that there are two modes of planktonic archaeal growth, which are
22 spatially and temporally separated on the southern Italian shelf. One is consistent with the
23 general observation of preferred oligotrophic conditions accompanied by low PP at the
24 offshore sites. The other mode is directly linked to higher nutrient concentrations at the near-
25 coastal sites, where planktonic archaea are rather associated with particle-rich waters of the
26 Adriatic Surface Water and vertical mixing during the colder season.

1 Future studies on the seasonal abundances and community structure of planktonic archaea
2 within the water column as well as the distribution of GDGTs for near-coastal and offshore
3 sites are required.

4

5 **5.3 GDGTs from benthic and pelagic archaeal communities**

6 All samples showed a characteristic marine archaeal GDGT profile, with abundant GDGT-0
7 and crenarchaeol and lower contributions of GDGT-1 to GDGT-3 and the crenarchaeol
8 regioisomer. Shallow sites show a higher contribution of GDGT-0 than offshore sites and vice
9 versa (Fig. A1). Although crenarchaeol is a predominant marker for planktonic crenarchaeota
10 affiliated with Marine Group 1 (MG1) (Sinninghe Damsté et al., 2002b), it also is
11 biosynthesized by a thermophilic crenarchaeota living in hot springs (Pearson et al., 2004;
12 Zhang et al., 2006; Schouten et al., 2007b; Pitcher et al., 2009). GDGT-0 has been interpreted
13 as a general archaeal core lipid that is synthesized by members distributed throughout the
14 archaeal domain (Koga et al., 1993). In the oceanic water column this compound is probably
15 derived from both planktonic eury- and crenarchaeota. Furthermore, it is likely that cren- and
16 euryarchaeota, including sedimentary affiliates of the MG1 archaea (Inagaki et al., 2006) and
17 other benthic archaea (Teske & Sorensen, 2008) produce similar lipids as their water column
18 relatives (Biddle et al., 2006; Lipp & Hinrichs, 2009). In our region benthic cren- and
19 euryarchaeotal communities were found in sediments located off the Cape of St. Maria di
20 Leuca and bottom waters east off the Gulf of Manfredonia (Yakimov et al., 2006; Martin-
21 Cuadrado et al., 2008), but their influence on the TEX₈₆ signal still remains unclear. Turich et
22 al. (2007) differentiated between GDGT abundances in epi- and mesopelagic waters based on
23 a data set of particulate organic matter (POM), where higher abundances of GDGT-0
24 compared to GDGT-1 to GDGT-4 are observed in epipelagic waters indicating a contribution
25 of group II euryarchaeota. Being aware that studies on POM reflect only snapshots it is
26 striking that we observe a similar pattern in the surface sediments. However, without DNA

1 data, a robust link between the microbial ecology of planktonic archaea and GDGT lipids
2 cannot be established.

3

4 **5.4 Cold-biased signature from the terrestrial realm**

5 The BIT values in the range of 0.02-0.29 with a seaward decrease are consistent with
6 previously observed values for coastal to open marine environments (Hopmans et al., 2004;
7 Kim et al., 2006). BIT values for coastal marine settings with a high input of OM from rivers
8 are up to 0.98 (Hopmans et al., 2004; Kim et al., 2006). In comparison BIT values of lake
9 sediments from Italy showed a wide range between 0.08 and 0.99 and a highly variable
10 degree of soil OM input (Blaga et al., 2009). Hence, the values at the southern Adriatic Sea
11 and Gulf of Taranto suggest the sediments contain a low contribution of soil OM; implying
12 that the TEX₈₆ reflects largely a marine signal. Elevated BIT values occur at locations with
13 higher chlorophyll-*a* concentrations and lower salinity (Table 2), a pattern which is
14 particularly pronounced at the inner shelf of the Gargano Promontory. This indicates an
15 increased supply of terrestrial OM and nutrients, due to the influence of the Western Adriatic
16 Current that stimulates PP. However, the supply of terrestrial GDGTs by nearby local rivers
17 south of the Gargano Promontory (e.g. Ofanto River) cannot be excluded. The generally
18 lower BIT values in the remainder of the southern Adriatic Sea and Gulf of Taranto, even at
19 near-coastal sites, can be related to the absence of river input due to the lack of major rivers
20 on the Apulian Peninsula (Raicich, 1996). It also indicates that the input of land-derived
21 material from the north is low and, more specifically, that the soil-derived fraction of
22 terrestrial OM is low for the region (Walsh et al., 2008). The latter situation is typical for
23 southern Italy since the landscape of the Apulian peninsula is characterized by complex karst
24 landforms. Additionally, variations in autochthonous crenarchaeol production can affect the
25 BIT as observed from discrepancies between BIT and other soil markers (Schmidt et al.,
26 2009). Interestingly, higher BIT values are associated with low SST_{TEX86} predominantly at the

1 Gargano Promontory area (Table 2). This is in contrast to the general observation that
2 terrestrial isoprenoid GDGTs may alter the TEX₈₆ signal leading to an increase of estimated
3 temperature with higher BIT values (Herfort et al., 2006; Weijers et al., 2006). Instead our
4 observations suggest the possibility of an allochthonous, cold TEX₈₆ signal that is transported
5 from the continent to shelf sediments. Further investigations on the soils and river sediments
6 in the research area are necessary to reveal their influence on the marine realm.

7

8

1 **6. Conclusions**

2

3 Calibration of the $U^{K'}_{37}$ and TEX_{86} temperature proxies using core-tops along the southern
4 Italian shelf to local SSTs shows that both proxies reflect SSTs that considerably differ from
5 annual mean SSTs. $SST_{UK'37}$ values appear lower than annual mean SSTs. This is attributed to
6 predominant production and export of alkenones during winter and spring fuelled by the
7 Adriatic Surface Water and vertical mixing. SST_{TEX86} increases with distance from shore
8 suggesting that at offshore sites the peak of planktonic archaeal production and the export of
9 related signals take place during summer when conditions are oligotrophic. In contrast,
10 SST_{TEX86} at near-coastal sites is low. This is explained by either one or a combination of the
11 following factors: different timing of archaeal production due to particle-rich surface waters
12 and prevailing higher nutrient contents (no oligotrophic conditions) and/or terrestrial input
13 leading to a cold-biased TEX_{86} signal. Our study demonstrates the importance of constraining
14 regional factors to arrive at a robust interpretation of past temperature signals and that care
15 has to be taken in applications of SST proxies in near-coastal environments. We suggest that
16 regional studies are needed in coastal to marine transitions showing contrasting water column
17 characteristics. As a corollary, interpretation of molecular SST signals in terms of absolute
18 temperature in ancient environments that are not accessible to an evaluation of regional and
19 seasonal factors will remain problematic. Here, a combination of both molecular temperature
20 proxies provides an opportunity to differentiate between seasonal and/or spatial characteristics
21 of the water column in the past.

22

23

24

25

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2

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17 southern Italy, Eastern Mediterranean). *J. Sea Res.* 62, 189-213.

18

19

1 **Caption of Figures**

2

3 **Fig. 1** Map of the Adriatic and Ionian Sea indicating the study area and general circulation
4 pattern (ISW: Ionian Surface Water, ASW: Adriatic Surface Water, LIW: Levantine
5 Intermediate Water, NAddW: Northern Adriatic Deep Water; ADW: Adriatic Deep Water;
6 redrawn from Artegiani et al., 1997b, Poulain et al., 2001, Vilibić et al., 2004). Right zoom in
7 3D-map showing the locations of the surface sediment analyzed in this study (GP: Gargano
8 Promontory; G. of Manfredonia: Gulf of Manfredonia; St.ML: Cape Santa Maria di Leuca).
9 Samples were grouped in accordance to their spatial distribution within the southern Adriatic
10 Sea (circles: GP and G. of Manfredonia, triangles: Strait of Otranto) and Gulf of Taranto
11 (diamonds: E Gulf of Taranto, squares: W Gulf of Taranto).

12

13 **Fig. 2** Contour plots of SST values for surface sediments along the southern Italian shelf: a)
14 satellite-derived annual mean SST (AM SST); b) alkenone-based temperature ($SST_{UK'37}$); c)
15 GDGT-derived temperature (SST_{TEX86}). Dashed lines are water depth contours (250 m and
16 1000 m).

17

18 **Fig. 3** Seasonal SST and proxy variations for the surface sediment sample locations versus
19 multicore top depth. Curves indicate annual mean (AM SST; solid) and seasonal (Wi SST, Sp
20 SST, Su SST, Au SST; dashed) satellite derived SST. Seasons are defined as: Wi SST: Dec-
21 Jan-Feb, Sp SST: Mar-Apr-May, Su SST: Jun-Jul-Aug, Au SST: Sep-Oct-Nov. SSTs based
22 on $U^{K'}_{37}$ are indicated by filled symbols and TEX_{86} by open symbols, respectively. Different
23 symbols represent the spatial sample distribution within the research area (Fig. 1; circles: GP
24 and G. of Manfredonia, triangles: Strait of Otranto, diamonds: E Gulf of Taranto and squares:
25 W Gulf of Taranto). Errors of temperature estimate based on the calibration of Conte et al.
26 (2006) and Kim et al. (2008) are 1.1 °C and 1.7 °C.

1 **Fig. 4** Distribution of a) TOC values and b) content of summed di- and triunsaturated
2 alkenones (in $\mu\text{g/g dw}$) in surface sediments along the southern Italian shelf. Dashed lines are
3 water depth contours (250 m and 1000 m).

4
5 **Fig. 5** Contour plot of BIT index values in surface sediments along the southern Italian shelf.
6 Dashed lines are water depth contours (250 m and 1000 m).

7 8 **Caption of Figures in Appendix**

9
10 **Fig. A1** Cluster analysis and bar plot of relative GDGT abundance in the analyzed surface
11 sediment samples. Numbers correspond to samples listed in Table 1.

12 13 **Caption of Tables**

14
15 **Table 1** Station data and results of alkenones and GDGT analysis for core top sediments

16
17 **Table 2** Pearson correlation coefficient (r) detected between biomarker and environmental
18 data ($p < 0.05$ and **$p < 0.0001$**)

19
20 **Table 3** Comparison of seasonal abundance of *E. huxleyi*, influence on the SST signal by
21 calculated weighted SST and $\text{SST}_{\text{UK}'37}$ of surface sediments

22 23 **Caption of supplementary material (electronic annex)**

24
25 **Figure S1** SST estimates resulting from the calibration by Kim et al. (2008; x-axis) vs. SST
26 estimates according to two new calibrations by Kim et al. (2010; y-axis; open and black

1 circles are $\text{TEX}_{86}^{\text{L}}$ and $\text{TEX}_{86}^{\text{H}}$, based respectively) for the dataset from the southern Italian
2 shelf. The solid line gives the 1:1 line between both temperature estimates. The dashed lines
3 give the linear regression based on the dataset

4

5 **Table S1** Comparison of TEX_{86} indices and derived temperatures based on the calibrations
6 from Kim et al. (2008, 2010)

*Research Highlights

- SSTs based on $U^{K'}_{37}$ and TEX_{86} disagree with each other
- SST $U^{K'}_{37}$ seem to reflect maximum alkenone production during colder part of the year
- SST TEX_{86} increase with distance to coast (=water depth)
- Spatially and temporally separated modes of crenarchaeotal growth

Figure1
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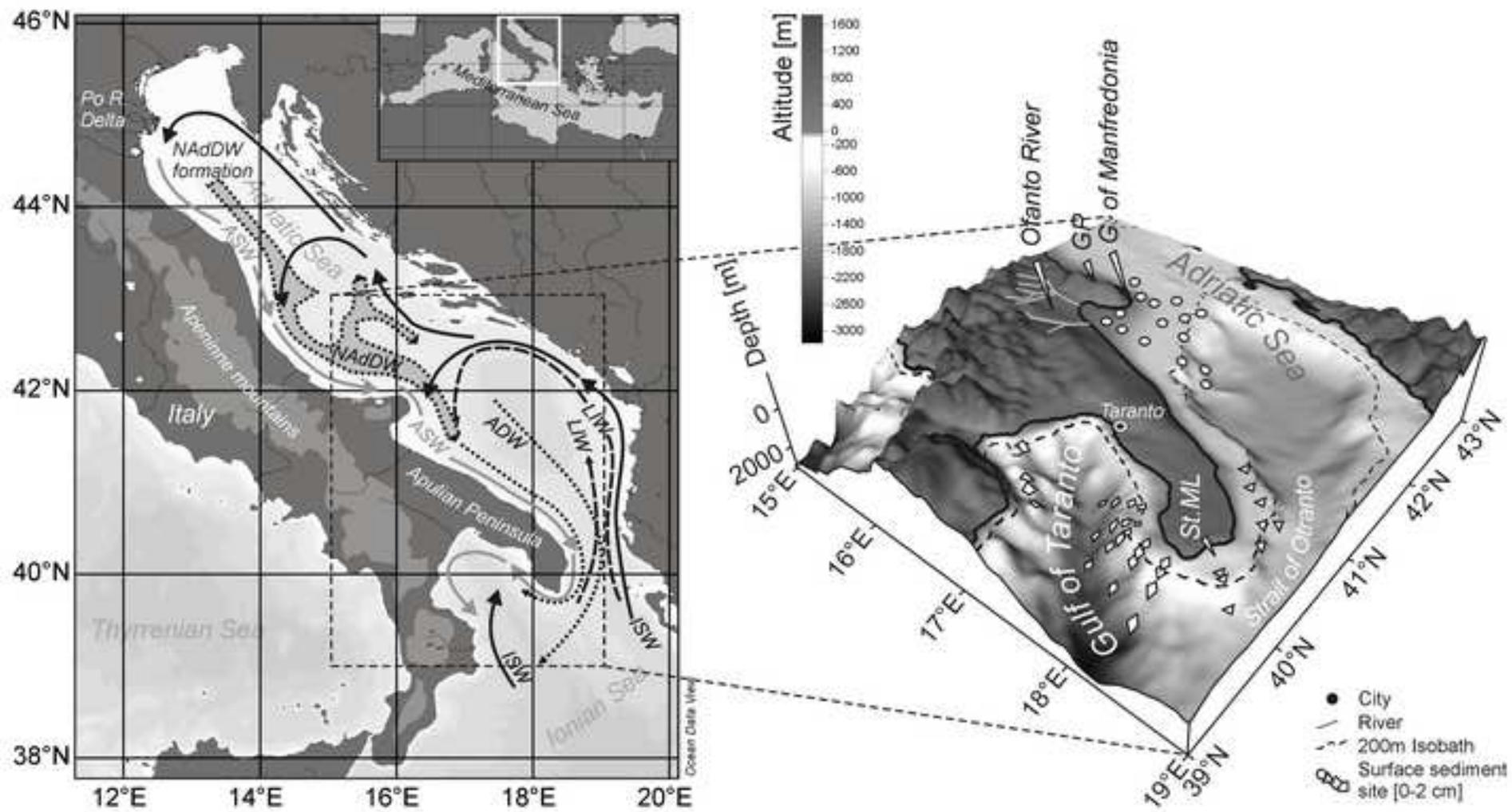


Figure2

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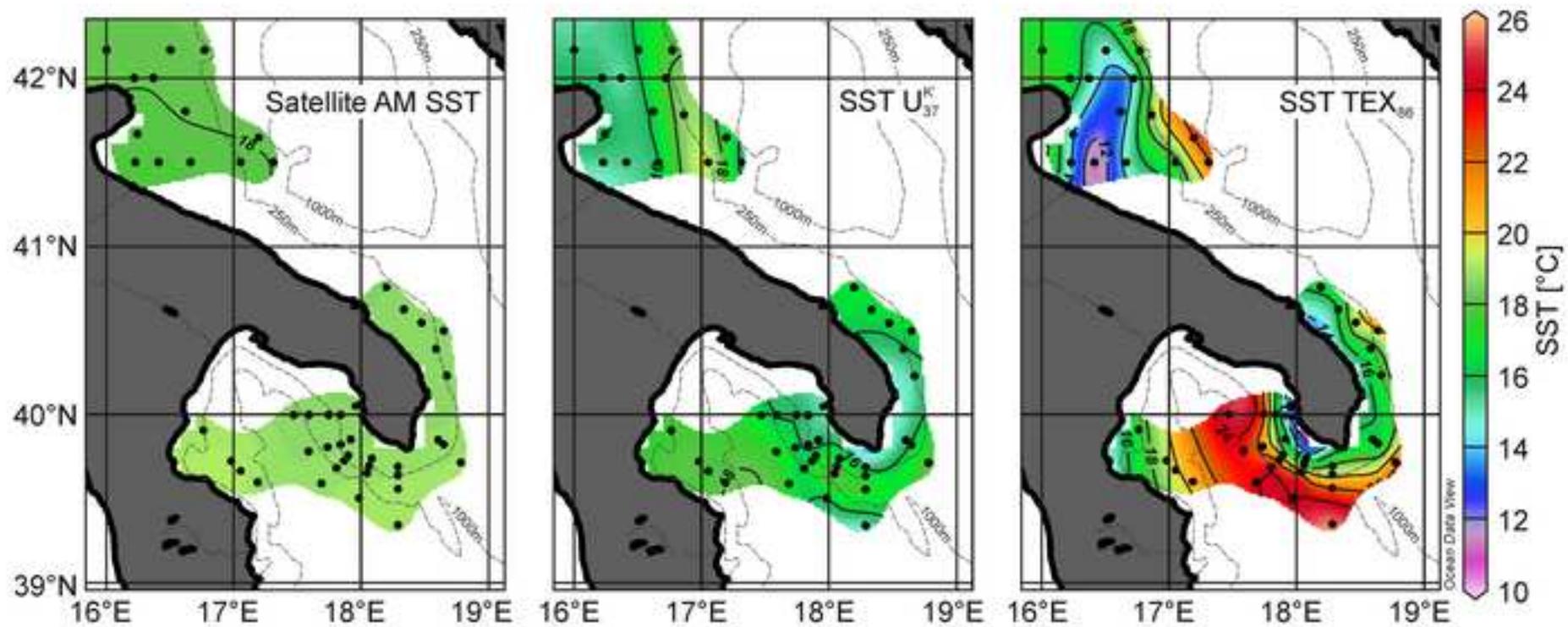


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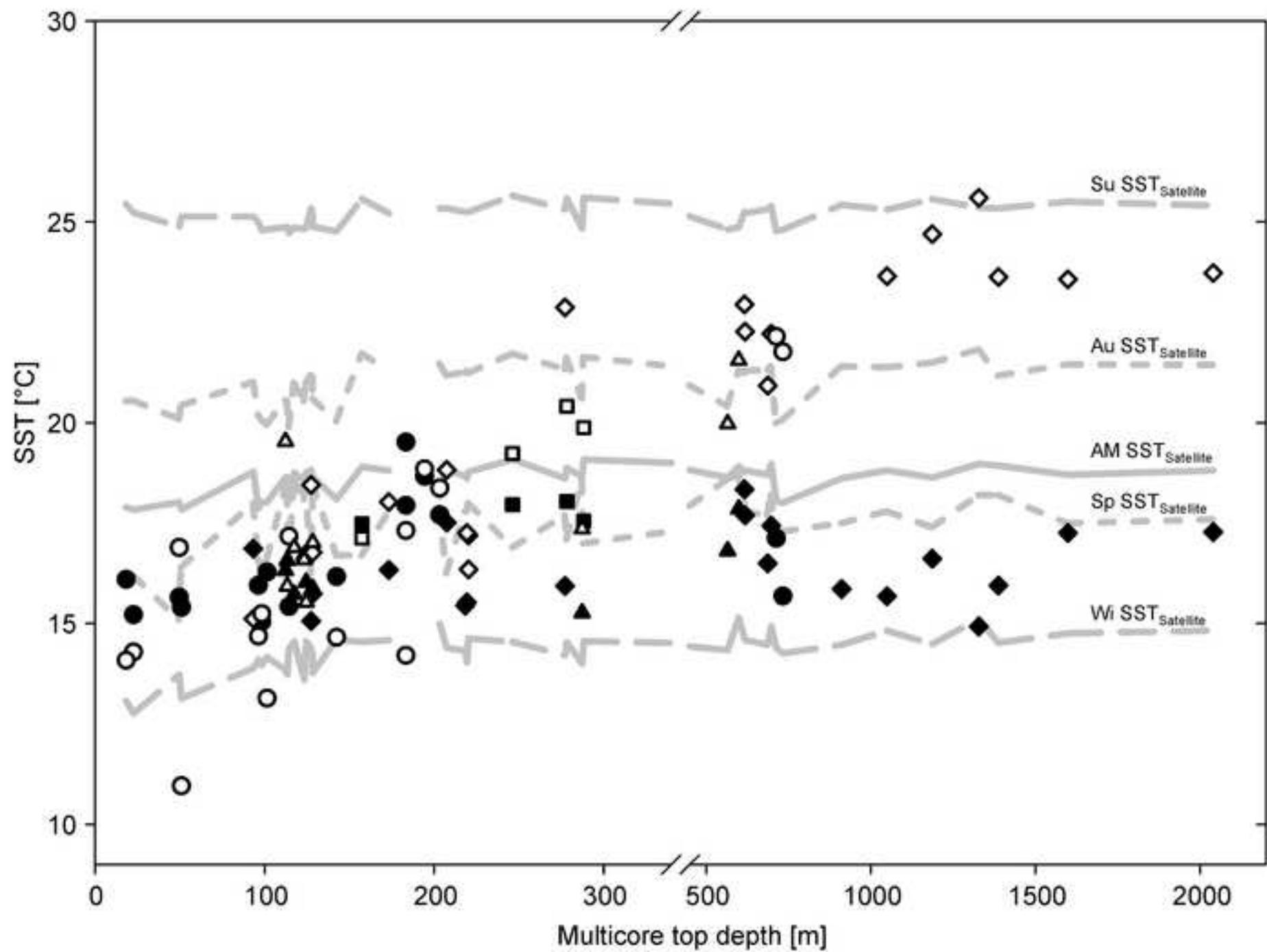


Figure4

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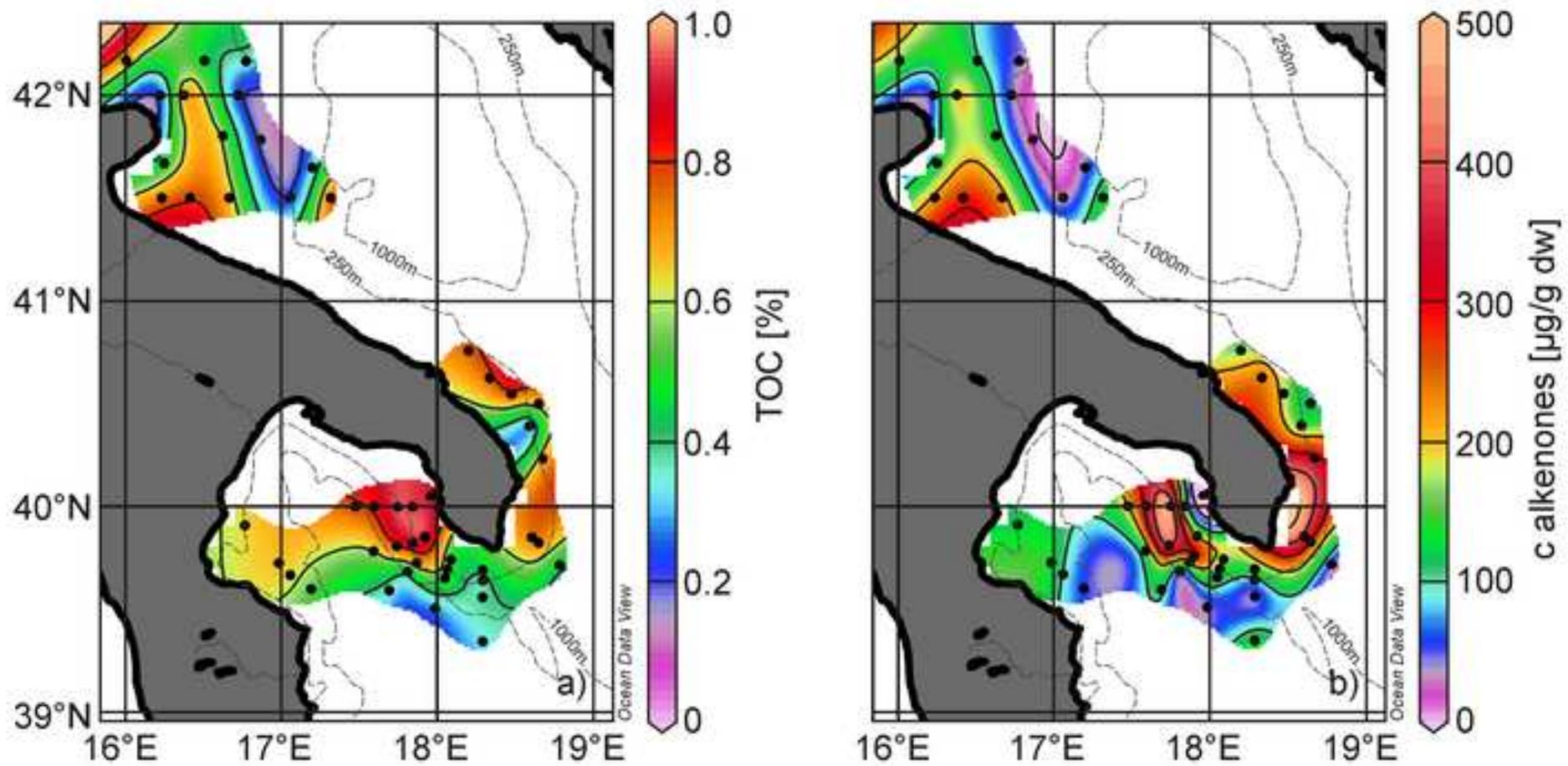


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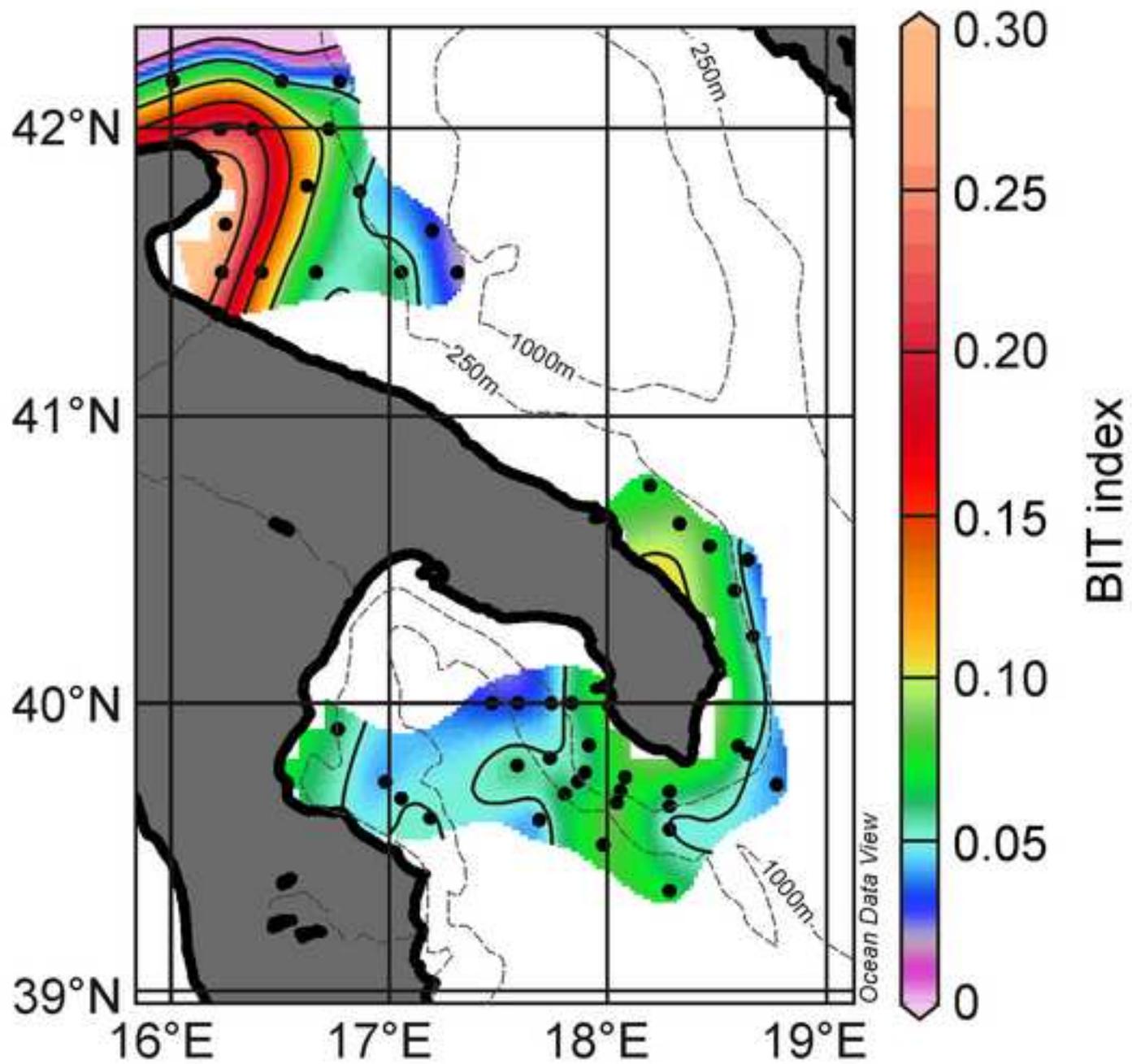


Table1

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Sample [GeoB]	Lat [°N]	Lon [°E]	Water Depth [m]	U ^K ₃₇	SST _{UK37} ^a [°C]	TEX ₈₆	SST _{TEX86} ^b [°C]	BIT index	Conc alkenones [µg/g dw]	TOC [%]	SST satellite [°C] ^c					Chl _a [mg/dm ³] ^c				SSS [psu] ^c				
											an	sp	su	au	wi	sp	su	au	wi	an	sp	su	au	wi
10701	40.000	17.467	1186	0.601	16.61	0.63	24.70	0.03	194	0.79	18.64	17.40	25.57	21.50	14.49	0.30	0.15	0.22	0.26	38.21	38.58	38.43	38.47	37.96
10702	40.000	17.586	911	0.575	15.86	n.d.	n.d.	0.03	311	0.81	18.62	17.50	25.43	21.41	14.47	0.30	0.16	0.24	0.29	38.20	38.54	38.43	38.46	37.94
10703	40.000	17.742	277	0.578	15.93	0.60	22.86	0.04	502	0.96	18.62	17.70	25.32	21.34	14.21	0.35	0.17	0.25	0.34	38.20	38.52	38.31	38.50	38.46
10704	40.000	17.833	219	0.564	15.52	0.50	17.25	0.06	109	0.92	18.61	17.80	25.26	21.30	14.03	0.35	0.18	0.26	0.37	38.18	38.37	38.31	38.54	38.46
10705	39.853	17.913	128	0.572	15.74	0.49	16.76	0.06	175	0.94	18.67	17.90	25.16	21.14	14.19	0.32	0.18	0.27	0.32	38.18	38.36	38.31	38.52	38.35
10706	39.825	17.833	218	0.561	15.44	n.d.	n.d.	n.d.	n.d.	0.88	18.67	17.80	25.25	21.26	14.31	0.31	0.16	0.25	0.28	38.18	38.42	38.31	38.54	38.35
10707	39.783	17.583	1598	0.622	17.26	0.61	23.57	0.06	125	0.59	18.70	17.50	25.50	21.46	14.75	0.29	0.13	0.21	0.24	38.21	38.64	38.36	38.41	38.24
10708	39.808	17.733	686	0.597	16.50	0.56	20.92	0.05	438	0.81	18.70	17.70	25.32	21.33	14.47	0.29	0.15	0.23	0.27	38.21	38.61	38.46	38.55	38.35
10709	39.757	17.893	173	0.591	16.33	0.51	18.03	0.06	396	n.a.	18.81	17.60	25.22	21.30	14.59	0.28	0.15	0.22	0.25	38.23	38.33	38.31	38.51	38.35
10710	39.592	17.683	2040	0.623	17.27	0.61	23.72	0.04	125	0.37	18.81	17.80	25.41	21.44	14.82	0.26	0.12	0.19	0.22	38.23	38.61	38.61	38.59	38.24
10711	39.683	17.800	1049	0.569	15.68	0.61	23.65	0.07	43.9	0.38	18.81	17.80	25.31	21.38	14.82	0.26	0.13	0.20	0.23	38.23	38.55	38.60	38.55	38.37
10712	39.727	17.862	618	0.637	17.69	0.59	22.27	0.05	112	0.71	18.81	17.80	25.22	21.30	14.59	0.28	0.15	0.22	0.25	38.23	38.55	38.60	38.55	38.37
10713	39.692	18.283	127	0.549	15.06	0.52	18.45	0.07	149	0.46	18.83	16.26	25.34	21.18	14.39	0.28	0.16	0.24	0.31	38.24	38.18	37.98	38.31	37.73
10714	39.640	18.283	207	0.631	17.51	0.53	18.83	0.05	82.0	0.33	18.83	16.26	25.34	21.18	14.39	0.28	0.16	0.24	0.31	38.24	38.18	37.98	38.31	37.73
10715	39.559	18.283	697	0.628	17.43	0.59	22.21	0.05	34.4	0.40	18.98	18.20	25.39	21.41	14.92	0.24	0.14	0.18	0.23	38.27	38.30	38.28	38.53	38.12
10716	39.345	18.283	1328	0.544	14.92	0.65	25.60	0.07	133	0.33	18.98	18.20	25.36	21.83	15.11	0.23	0.11	0.15	0.21	38.27	38.38	38.28	38.51	38.34
10717	39.742	18.080	93	0.609	16.86	0.46	15.11	0.08	192	0.45	18.78	18.00	25.14	21.02	13.88	0.33	0.18	0.30	0.39	38.23	38.19	38.31	38.50	38.46
10718	39.693	18.058	220	0.620	17.19	0.48	16.34	0.06	120	0.62	18.78	18.00	25.25	21.24	14.62	0.28	0.15	0.24	0.30	38.23	38.20	38.60	38.52	38.46
10719	39.653	18.042	616	0.658	18.34	0.60	22.95	0.09	143	0.53	18.78	18.00	25.25	21.24	14.62	0.28	0.15	0.24	0.30	38.23	38.27	38.88	38.48	38.72
10720	39.507	17.978	1387	0.578	15.95	0.61	23.63	0.08	38.4	0.28	18.93	18.20	25.34	21.18	14.52	0.26	0.12	0.18	0.23	38.25	38.37	38.88	38.45	38.55
10721	42.166	16.767	203	0.637	17.70	0.52	18.37	0.04	41.6	0.36	18.16	17.90	25.34	21.48	14.99	0.23	0.14	0.20	0.24	38.19	38.36	38.06	38.44	38.44
10722	42.167	16.500	142	0.586	16.17	0.45	14.65	0.05	105	0.45	18.09	16.70	24.76	20.05	14.60	0.25	0.17	0.25	0.28	38.18	38.25	38.11	38.22	38.40
10723	42.167	16.000	114	0.561	15.42	0.50	17.16	0.07	159	0.67	18.06	16.50	24.73	19.90	14.37	0.32	0.23	0.40	0.44	38.10	37.65	37.85	37.88	38.25
10724	42.001	16.217	50	0.568	15.65	0.49	16.89	0.21	54.8	0.21	18.02	15.10	24.89	20.10	13.73	0.40	0.28	0.48	0.70	38.17	37.04	37.86	37.42	37.90
10725	42.000	16.367	98	0.548	15.04	0.46	15.24	0.20	205	0.70	18.02	16.30	24.79	20.06	13.97	0.34	0.24	0.41	0.43	38.17	38.28	37.92	38.15	38.36
10726	42.000	16.717	183	0.645	17.94	0.44	14.20	0.09	40.6	0.21	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
10727	41.801	16.617	101	0.589	16.27	0.43	13.14	0.11	122	0.59	18.03	16.60	24.82	19.96	14.16	0.30	0.21	0.32	0.36	38.26	38.02	37.72	38.21	38.47
10728	41.783	16.858	194	0.669	18.66	0.53	18.85	0.05	11.5	0.17	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
10729	41.647	17.191	712	0.618	17.12	0.59	22.14	0.03	40.6	0.32	18.05	17.10	24.77	20.00	14.39	0.27	0.13	0.18	0.21	38.27	38.31	38.23	38.48	38.53
10730	41.500	17.050	183	0.698	19.52	0.50	17.30	0.06	24.9	0.21	17.93	17.00	24.66	19.96	14.47	0.26	0.13	0.19	0.22	38.28	38.32	38.10	38.37	38.36
10731	41.500	16.658	96	0.578	15.94	0.45	14.68	0.06	224	0.65	17.87	16.60	25.00	20.19	14.10	0.33	0.26	0.39	0.45	38.27	37.92	37.63	38.07	37.08
10732	41.500	16.407	51	0.560	15.40	0.39	10.96	0.14	283	0.79	17.83	16.40	25.13	20.44	13.14	0.59	0.39	0.58	0.91	38.25	37.60	37.42	38.03	37.08
10733	41.500	16.225	23	0.554	15.22	0.45	14.28	0.25	213	0.73	17.83	16.20	25.23	20.56	12.76	0.79	0.47	0.83	1.43	38.29	37.25	37.31	38.29	37.08
10734	41.667	16.242	18	0.583	16.09	0.44	14.08	0.29	127	0.48	17.89	16.20	25.44	20.54	13.07	1.15	0.67	1.00	1.89	38.29	33.93	37.24	37.59	37.97
10735	41.500	17.308	733	0.569	15.68	0.58	21.77	0.02	129	0.74	18.01	17.30	24.81	20.08	14.25	0.29	0.12	0.18	0.21	38.28	38.58	38.24	38.49	38.59
10736	40.758	18.192	123	0.603	16.69	0.49	16.58	0.07	164	0.76	18.57	18.10	24.82	20.54	13.59	0.36	0.22	0.37	0.54	38.21	38.10	38.00	37.86	37.40
10737	40.625	18.329	113	0.599	16.56	0.48	15.93	0.09	236	0.76	18.64	18.30	24.88	20.56	13.73	0.32	0.20	0.30	0.47	38.18	38.12	37.94	37.93	37.45
10738	40.546	18.467	112	0.591	16.31	0.54	19.54	0.08	189	0.80	18.64	18.40	24.87	20.56	13.84	0.32	0.20	0.31	0.46	38.18	38.28	37.86	37.88	37.45
10739	40.500	18.642	565	0.607	16.80	0.55	19.97	0.04	106	0.66	18.64	18.60	24.82	20.42	14.33	0.26	0.16	0.24	0.30	38.17	38.24	38.09	37.96	37.67
10740	40.392	18.583	128	0.576	15.87	0.49	17.01	0.06	143	0.26	18.66	18.50	24.88	20.60	13.76	0.32	0.19	0.32	0.47	38.16	38.19	38.06	37.79	37.56
10741	40.233	18.667	287	0.556	15.26	0.50	17.35	0.05	330	0.67	18.66	18.60	24.84	20.61	14.00	0.29	0.18	0.29	0.40	37.99	38.18	38.07	37.85	37.64
10742	39.716	18.776	599	0.642	17.85	0.58	21.56	0.04	47.2	0.43	18.91	18.70	24.87	21.30	15.14	0.24	0.14	0.18	0.23	38.26	38.25	37.95	38.37	38.08
10743	39.825	18.642	124	0.581	16.02	0.47	15.52	0.05	271	0.75	18.76	18.60	24.86	21.00	14.55	0.26	0.16	0.21	0.30	38.22	38.10	38.03	38.27	37.66
10744	39.850	18.600	117	0.571	15.72	0.49	16.88	0.07	405	0.72	18.76	18.60	24.86	21.00	14.55	0.26	0.16	0.21	0.30	38.22	38.08	38.02	38.20	37.72
10746	39.908	16.758	157	0.630	17.48	0.50	17.12	0.06	120	0.63	18.90	16.70	25.58	21.73	14.54	0.45	0.21	0.27	0.33	38.26	38.26	38.66	38.38	28.39
10747	39.725	16.975	246	0.646	17.95	0.53	19.23	0.04	134	0.65	19.08	16.90	25.65	21.72	14.54	0.39	0.18	0.24	0.27	38.29	38.27	38.66	38.32	28.39
10748	39.667	17.050	288	0.632	17.55	0.55	19.88	0.05	95.9	0.63	19.08	17.00	25.61	21.64	14.56	0.33	0.16	0.23	0.27	38.29	38.27	38.59	38.29	38.20
10749	39.600	17.183	278	0.648	18.03	0.55	20.41	0.05	55.0	0.54	18.87	17.10	25.59	21.62	14.53	0.32	0.16	0.22	0.26	38.26	38.26	38.66	38.37	38.16

n.d.: not detected

n.a.: not available

^aSST_{UK'37} calculated after Conte et al., 2006

^bSST_{TEX86} calculated after Kim et al., 2008

^cEnvironmental Data: Chl *a*=Chlorophyll *a*. SSS=Salinity; su=summer (Jun-Jul-Aug), wi=winter (Dec-Jan-Feb) (Zonneveld et al., 2009)

Table2[Click here to download Table: table2.doc](#)

	SST _{UK37}	Conc alkenones	SST _{TEX86}	BIT
Conc alkenones	-0.415			
SST _{TEX86}	0.201	-0.145		
BIT	-0.300	0.036	-0.483	
TOC	-0.372	0.437	-0.107	-0.065
Water Depth	0.076	-0.134	0.789	-0.317
SST satellite an	0.237	0.007	0.532	-0.515
SST satellite sp	0.099	0.157	0.350	-0.537
SST satellite su	0.192	-0.052	0.382	-0.069
SST satellite au	0.234	0.023	0.522	-0.368
SST satellite wi	0.381	-0.222	0.637	-0.695
Chl <i>a</i> sp	-0.191	0.070	-0.438	0.789
Chl <i>a</i> su	-0.271	0.098	-0.573	0.853
Chl <i>a</i> au	-0.308	0.097	-0.570	0.878
Chl <i>a</i> wi	-0.275	0.091	-0.510	0.859
SSS an	0.331	-0.269	0.111	0.118
SSS sp	0.166	0.042	0.448	-0.783
SSS su	0.382	-0.144	0.652	-0.609
SSS au	0.251	-0.046	0.499	-0.545
SSS wi	-0.183	0.009	0.127	0.014

TOC=Total Organic Carbon; Chl *a*=Chlorophyll *a*; SST=satellite-derived SST; SSS=Salinity; an=annual, sp=spring (Mar-Apr-May), su=summer (Jun-Jul-Aug), au=autumn (Sep-Oct-Nov), wi=winter (Dec-Jan-Feb) (Zonneveld et al., 2009)

Table3[Click here to download Table: table3.doc](#)

	Average occurrence of <i>E. huxleyi</i> ^a		SST	SST References
	[cells/dm ³]	[%]	[°C]	
February	22779	47.7	11.2	Socal et al. (1999)
May	8825	18.5	18.8	OBPG MODIS-Aqua 2002-2006*
August	4412	9.2	28.5	Socal et al. (1999)
November	11767	24.6	18.9	OBPG MODIS-Aqua 2002-2006*
MA SST			19.4	
Weighted SST			16.1	
SST _{UK37}			16.2±0.7	this study (10743 and -44)

^aSurvey from 1994 Socal et al. (1999)

*Monthly means of OBPG MODIS Aqua 2002-2006 for area at Latitude 39.4-39.5 °N/ Longitude 18.3-18.4 °E

Figure A1
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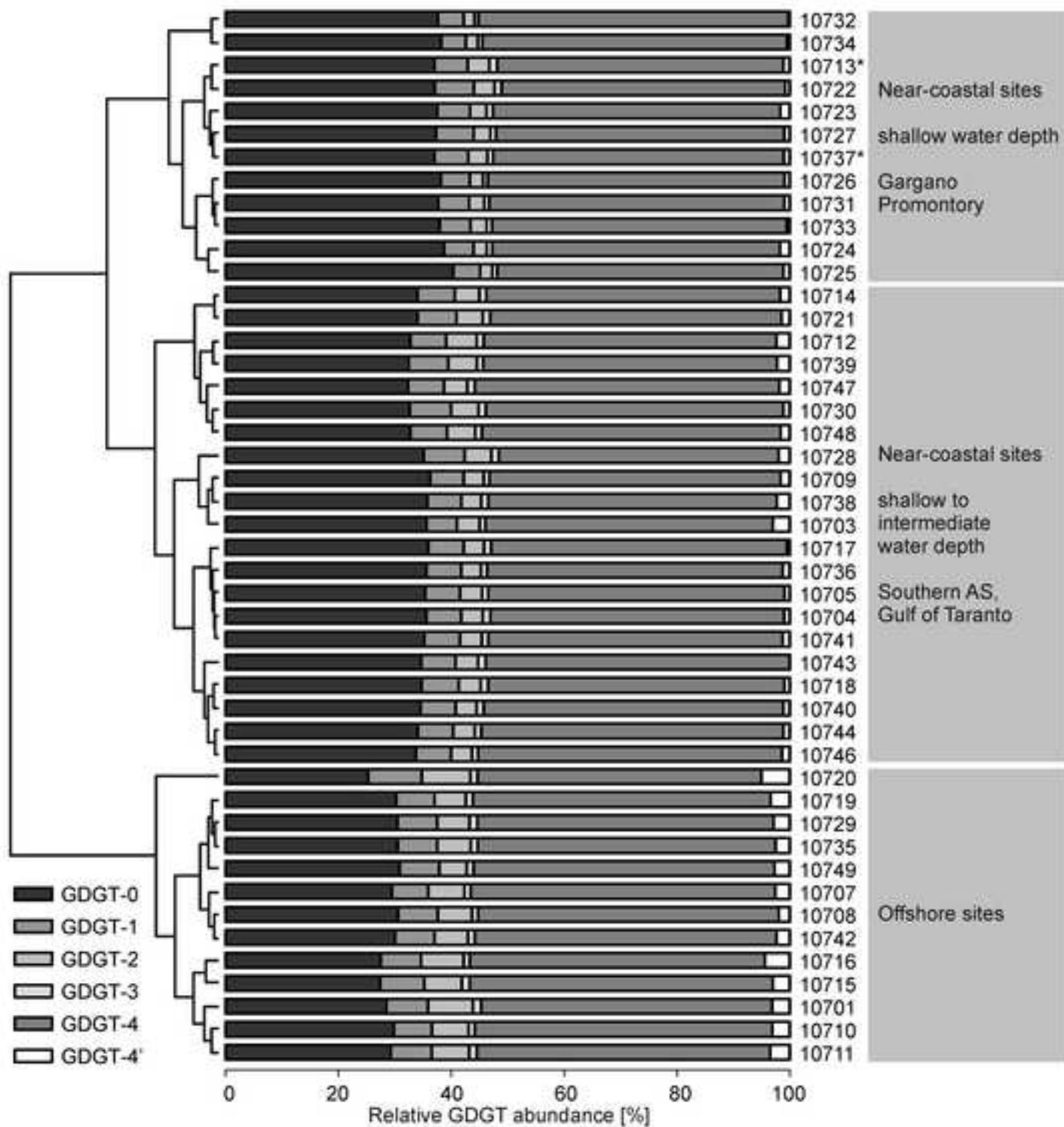


Figure S1

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Table S1
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