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1 **A radiocarbon-based assessment of the preservation characteristics of crenarchaeol and**
2 **alkenones from continental margin sediments**
3

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10

11 **Abstract**
12 Crenarchaeotal glycerol dibiphytanyl glycerol tetraether (GDGT) lipids and alkenones are two
13 types of biomarkers derived from planktonic marine micro-organisms which are used for
14 reconstruction of sea-surface temperatures. We determined the radiocarbon contents of the archaeal
15 GDGT crenarchaeol and of alkenones isolated from continental margin sediments. Systematic
16 differences were found between the two biomarkers, with higher radiocarbon contents in crenarchaeol
17 than in the phytoplankton-derived alkenones. These differences can be explained by variable
18 contributions of pre-aged, laterally advected material to the core sites. Crenarchaeol appears to be
19 more efficiently degraded during transport in oxygen-replete environments than alkenones. Whether
20 this reflects the influence of chemical structure or mode of protection (e.g., particle association) is not
21 yet known.
22

23 **1. Introduction**
24 Compound-specific and compound-class-specific radiocarbon analyses of co-occurring
25 biomarkers have revealed systematic differences in the radiocarbon age of the lipids preserved in
26 marine sediments (Eglinton et al., 1997; Pearson et al., 2001; Smittenberg et al., 2004). These
27 discrepancies in radiocarbon content, and the corresponding radiocarbon age, can be related to the
28 radiocarbon signature of the carbon used for metabolism of the precursor organisms. In several cases,

1 however, they appear to reflect differences in the resistance of the individual compounds to
2 degradation during lateral and vertical transport to the sediments and during early sedimentary
3 diagenesis (Mollenhauer and Eglinton, 2007). This effect appears to be particularly pronounced for
4 compounds such as short-chain *n*-alkanoic acids that are synthesized by a multitude of organisms in
5 both terrestrial and marine environments. In compounds with these characteristics, those of terrestrial
6 origin deposited in marine sediments appear to be preferentially preserved over their marine
7 counterparts. The apparent superior preservation of terrigenous lipids may be related to chemical
8 recalcitrance (e.g., *n*-alkanes), enclosure in resistant cell walls, or to the protective effect of adsorption
9 of the lipids to the surface of detrital mineral particles, which may be more effective for terrigenous
10 material that has been subject to transport over long distances (Huguet et al., 2007a).
11 Significant differences in radiocarbon content are, however, also observed when radiocarbon
12 analyses are restricted to lipids exclusively derived from marine plankton (Eglinton et al., 1997;
13 Pearson et al., 2001; Smittenberg et al., 2004). Variations in the reactivity of the individual
14 compounds may also play a role if the lipids preserved in the sediment contain a mixture of material
15 that was synthesized at different times (recent vs. pre-aged; Sun and Wakeham, 1994). Material older
16 than the vertically settling plankton debris could reflect lateral advection of re-suspended sediment
17 (Ohkouchi et al., 2002) or could be supplied by vertical mixing within the sediment (bioturbation;
18 Mollenhauer et al., 2007). If lateral supply is an important factor, the compound's ability to survive
19 transport in oxygenated water masses may play a key role in determining the relative contribution of
20 radiocarbon-depleted material to the lipids preserved in the sediment.
21 Here we present radiocarbon (^{14}C) contents of crenarchaeol, a glycerol dibiphytanyl glycerol
22 tetraether (GDGT) with four five-membered rings and one six-membered ring, which is
23 biosynthesized by planktonic marine group I crenarchaeota (Sinninghe Damsté et al., 2002b). The
24 membrane lipids of this group of organisms have been used to reconstruct sea-surface temperatures via
25 an index termed TEX_{86} and expressing the degree of cyclization of GDGTs (Schouten et al., 2002).
26 The data are compared with published and two new ^{14}C-contents data of haptophyte-derived alkenones
27 isolated from the same continental margin sediments (Mollenhauer et al., 2005a; Mollenhauer et al.,

2007). We find that crenarchaeol is systematically less depleted in ^{14}C than alkenones and attribute this difference to a greater propensity of alkenones to survive lateral transport following re-suspension.

2. Methodology

2.1 Material

We analyzed samples from two sediment cores from continental margins with contrasting depositional regimes. Core GeoB3313-1 was recovered from the upper continental slope off southern Chile (41.00°S, 74.75°W, 852 m water depth). This location is influenced by westerly winds, freshwater supply through the Chilean fjord systems, and high primary productivity (Lamy et al., 2002). The extraordinarily high sedimentation rates (~1 m/kyr) at this location are partly explained by sediment focusing in the small basin where the core was recovered from (Mollenhauer et al., 2005a).

The second sediment core GeoB5546-2 was retrieved from the upper continental slope of NW Africa (27.53°N, 13.73°W, 1072 m water depth). Sedimentation rates at this core location are approximately 20-30 cm/kyr. The location is influenced by the coastal upwelling area to the south of it, and by eolian supply of terrigenous material from the adjacent arid continent.

2.2. Analytical methods

Dried and homogenized sediment samples were extracted in a Soxhlet apparatus for 48 h using dichloromethane (DCM) and methanol (97:3). Crenarchaeol and alkenones were isolated from total lipid extracts of sediments that were dried by rotary evaporation and subsequently saponified using a 0.5 M solution of potassium hydroxide (KOH) in methanol. The procedure involves liquid extraction of neutral lipids from the saponified total lipid extracts using hexane followed by SiO_2 column chromatography into three successively more polar fraction using hexane, DCM:hexane (2:1, v/v), and methanol. Alkenones were purified from the second fractions as described in Ohkouchi et al., (2005). The third, most polar fraction was further fractionated and archaeal lipids were collected by liquid chromatography using methods similar to those described by Hopmans et al. (2000) and Smittenberg et al. (2002). In brief, this procedure involved pre-filtering of the polar fraction through a 4-mm-diameter PTFE filter (0.45 µm pore size) using hexane:isopropanol (99:1; v/v) as solvent. Filtered

1 samples were dried, weighed, and re-dissolved in hexane:isopropanol (99:1; v/v) to create solutions
2 with concentrations of ~5-10 mg/ml total material. Crenarchaeol was purified using an Agilent 1100
3 series HPLC instrument by repeated injection of 50 µl aliquots onto an Alltech NH_2 5 µm column (250
4 x 10 mm) maintained at 30 °C. GDGTs were eluted using the following gradient program, where A =
5 hexane and B = propanol: 1 % B from 0-5 min; a linear gradient to 1.8 % B from 5 to 50 min,
6 followed by column cleaning by backflushing with 10 % B. Flow rate was 3 ml/min. Eluents were
7 collected in 1 min fractions. The retention time of crenarchaeol under these conditions was
8 approximately 26 min. Contents of individual fractions were checked by analyzing small sub-fractions
9 by flow-injection analysis (FIA)-atmospheric pressure chemical ionization mass spectrometry (APCI-
10 MS) using an identical HPLC system coupled to an HP 1100 MSD mass spectrometer as described by
11 Smittenberg et al. (2002). GDGTs and possible co-eluting compounds were screened using a mass
12 range of *m/z* 300-1400. Crenarchaeol-containing fractions were re-combined and purified in a second
13 HPCL separation step using a 250 x 4.6 mm Alltech Prevail CN (5 µm) column and a flow rate of 1
14 ml/min. Injection volume was 25 µl, and 30 second fractions were collected. Fractions were again
15 screened for crenarchaeol using FIA/APCI-MS using a scan range of *m/z* 1225-1325.
16 Fractions containing crenarchaeol were further purified to remove potential column-bleed by
17 elution from an Al_2O_3 column using ethyl acetate as solvent. Purified samples of crenarchaeol and
18 alkenones were combusted in evacuated pre-combusted quartz ampoules in the presence of CuO at
19 850 °C for 5 h. Resulting CO_2 was dried by passage through a vacuum line equipped with a water trap,
20 which was cooled in a slurry of dry ice and propanol, and quantified by expansion into a calibrated
21 volume. Subsequently, CO_2 was converted to graphite using standard methods (Pearson et al., 1998).
22 Graphite was pressed into targets for radiocarbon analysis by accelerator mass spectrometry (AMS).
23 The latter two steps were performed at the National Ocean Sciences Accelerator Mass Spectrometer
24 (NOSAMS) facility at the Woods Hole Oceanographic Institution.
25 Radiocarbon contents are reported as fraction modern carbon (fMC) (Stuiver and Polach, 1977).
26 It is likely that the combustion process is the major source of blank carbon (Pearson et al., 1998; Shah
27 and Pearson, 2007). Since both sample sets were combusted using identical methods and equipment,

1 addition of blank carbon to crenarchaeol samples during the combustion process was corrected for as
2 described in Mollenhauer et al. (2007) for alkenone samples.
3
4 **3. Results and discussion**
5 Radiocarbon contents of crenarchaeol and corresponding alkenones are presented in Table 1 and
6 Figure 1. Alkenones were found to be slightly radiocarbon-depleted relative to co-occurring
7 crenarchaeol in both the core off Chile and the NW African core. Larger offsets with more
8 radiocarbon-depleted alkenones than crenarchaeol were observed on the Namibian margin as
9 previously presented in Mollenhauer et al. (2007). These offsets could either derive from primary
10 differences due to the carbon source utilized by the precursor organisms, or could be due to
11 differences in the relative amount of pre-aged biomarkers contributing to the total alkenones and
12 crenarchaeol deposited at the respective core sites.
13 Primary differences due to the carbon source utilized could most likely only account for offsets
14 in the opposite direction than what is observed. Crenarchaota are more likely to thrive in deeper water
15 masses than phytoplanktonic alkenone producers, as the former are reported to occur at all depths
16 (Karner et al., 2001), and furthermore have been shown to record ^{14}C-levels of ambient DIC (Ingalls et
17 al., 2006). DIC of deeper waters is more radiocarbon-depleted than DIC in near-surface waters.
18 Therefore primary differences due to differences in depth habitat are not likely to produce
19 radiocarbon-offsets in the same sense as observed. Heterogeneity in haptophyte and archaeal
20 productivity, resulting variability in vertical supply of their lipids to the sediments, and seasonal
21 variations in radiocarbon levels of surface waters cannot be ruled out. However, we observe offsets in
22 radiocarbon content in the same direction in three very different settings, southern Chile, NW Africa,
23 and the Namibian margin. Similar heterogeneity in productivity at all settings is considered unlikely.
24 Admixture of variable amounts of material synthesized at different times than the time of
25 deposition (i.e., "pre-aged" material) is an alternative explanation. In a previous study of radiocarbon
26 ages of alkenones and co-occurring foraminifera it was shown that lateral advection of pre-aged
27 material is likely operative at some of the locations investigated in the present study, in particular off
28 Chile and on the Namibian margin (Mollenhauer et al., 2005a). Our data indicate that crenarchaeol

1 preserved in oxygen-replete marine sediment samples is composed to a large percentage of material
2 deposited shortly after its formation by the precursor organisms, whereas alkenones may contain larger
3 proportions of laterally advected, pre-aged material as previously shown (Ohkouchi et al., 2002;
4 Mollenhauer et al., 2003). This observation requires that proportionally more crenarchaeol is
5 delivered from overlying surface waters than alkenones, which implies that crenarchaeol is entrained
6 in particles that are less susceptible to mobilization and transport or that crenarchaeol is less able to
7 survive lateral transport than alkenones.

8 One way in which the apparent higher recalcitrance of alkenones than crenarchaeol could be
9 explained is the mode of association of the compounds to mineral particles. Organic matter can be
10 protected from oxic degradation by adsorption to mineral surfaces or pores (Mayer, 1994; Mayer,
11 1999; Mayer et al., 2004), sorption to macromolecular organic matrices, or by entrainment in
12 aggregates (Hedges et al., 2001). The alkenone-forming phytoplankton organisms are likely
13 consumed by secondary producers such as copepods, and may preferentially be exported within faecal
14 pellets, and GDGTs have also been found in stomachs and intestinal tracts of planktonic decapods
15 (Huguet et al., 2006). Export to depth via sinking of faecal pellets therefore seems likely for both
16 types of compounds. However, both compounds could also be entrained in marine snow particles,
17 which upon settling on the sea-floor re-aggregate to form clay-organic-rich aggregates (Ransom et al.,
18 1998).

19 The observations implying greater lateral supply of pre-aged alkenones than crenarchaeol,
20 particularly on the Namibian continental margin, could also be explained if crenarchaeol is associated
21 with particles that are less susceptible to re-suspension. Since lateral transport following re-suspention
22 primarily affects the fluffy aggregates forming bottom nepheloid layers (Thomsen and Gust, 2000),
23 this scenario would either require the type of feacal pellets produced by organisms consuming archaea
24 being less easily disaggregated than those produced by coccolithophorid consumers, or a different
25 likelihood of the lipids to become entrained in clay-organic-rich aggregates of the bottom nepheloid
26 layer. Based on our data, this cannot be resolved at present.

27 If crenarchaeol was more chemically labile than alkenones, the third explanation suggested
28 above could apply. Both types of compounds are well preserved in marine sediments. In previous

studies, preservation of alkenones was found to be only slightly superior to preservation of crenarchaeol (Sinninghe Damsté et al., 2002a; Huguet et al., 2007a). Both studies focused on degradation after deposition. It is known, however, that the oxygen exposure time is an important parameter determining preservation of organic matter (Hartnett et al., 1998). Total oxygen exposure time includes exposure during transport in oxygenated water masses (Keil et al., 2004). It is interesting to note that the largest differences between radiocarbon contents of alkenones and crenarchaeol were found off Namibia, which is also the area in which the largest ^{14}C-offsets between alkenones and foraminifera were reported and attributed to lateral transport (Mollenhauer et al., 2005a). We consider the most likely explanation for our observed age offsets that alkenones are selectively preserved during lateral transport, while crenarchaeol is more rapidly degraded in oxygenated water masses.

Within our limited data set, there are two exceptions from the general trend of more radiocarbon-depleted alkenones relative to co-occurring crenarchaeol. One exeption is an “old” sample from the NW African margin (GeoB5546-2, 485-490 cm). In this and a second sample from this site (GeoB5546-2, 550-555 cm) we cannot rule out strong influences of blank carbon, as the radiocarbon contents are lower than fMC = 0.27, which was determined as the lower limit of highly accurate radiocarbon dating of alkenone samples (Mollenhauer et al., 2005b). By inference, we consider dates of crenarchaeol samples to be similarly accurate within the same ranges of ^{14}C contents. The second sample where crenarchaeol is more radiocarbon-depleted than alkenones is a core-top sample from the inner shelf off Namibia (Mollenhauer et al., 2007) deposited under oxygen-deficient conditions. The difference could indicate that archaea thrive in a depth habitat deeper than that of the alkenone producing phytoplankton at this particular location with high nutrient dynamics, or it could reflect different seasonalities of coccolithophorids and crenarchaeota in this coastal upwelling region, where surface water reservoir ages are likely to vary with the strength of upwelling. In core-top samples from the inner shelf off Namibia, alkenone radiocarbon contents >0.95 fMC are higher than expected pre-bomb reservoir levels, which implies the presence of “bomb-radiocarbon” in these samples and hence rapid sedimentation with little or no addition of pre-aged material (Mollenhauer et al., 2003, 2007).

In a previous study from the oxygen-deficient depo-center of the Santa Monica Basin on the California margin, radiocarbon contents of biphytanes derived from archaeal GDGTs were analysed for their radiocarbon contents (Pearson et al., 2001). Radiocarbon contents were lower than in those of planktonic foraminifera shells from the same sediments, where the latter reflect surface water $DI^{14}C$. This observation was attributed to a deeper habitat of the archaea in this particular location, possibly associated with a nitricline. In a later study of crenarchaeotal lipids and the TEX_{86} index in sediment traps and core-top sediments from nearby oxygen-deficient Santa Barbara Basin, the occurrence of substantial abundances of crenarchaeota in deeper habitats was confirmed (Huguet et al., 2007b). ^{14}C-contents of GDGT-derived biphytanes in the Santa Monica Basin reported by Pearson et al. (2001) were similar to those of the alkenones in corresponding sediments, which were determined to contain pre-aged carbon in a subsequent study (Mollenhauer and Eglinton, 2007). This observation is in contrast to our finding of ^{14}C-enriched crenarchaeol relative to alkenones in the oxic continental margin settings described above. This contrasting behavior therefore suggests that either the addition of pre-aged alkenones to Santa Monica Basin sediments compensates for the expected habitat-derived primary difference in ^{14}C contents of these lipids, or, if these expected primary differences were not present, that preferential degradation of crenarchaeol could be much more efficient in oxygen-replete environments.

4. Conclusions

Our study using sediment samples collected on the continental margins of NW Africa, Chile, and Namibia implies that alkenones tend to be more radiocarbon-depleted than co-occurring crenarchaeol. The differences are larger at the sites that were previously identified as locations which are affected by lateral sediment transport. This observation is consistent with a greater lateral supply of allochthonous pre-aged alkenones to the sample site relative to crenarchaeol. Preferential preservation of alkenones during lateral transport in oxygenated water masses is regarded as the most likely explanation for these offsets. In order to elucidate the causes of this preferential preservation, further studies of the mineral and particle-type association of these and other biomarkers need to be undertaken.

1

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1 Table caption:
2
3 Table 1: Radiocarbon concentrations expressed as fMC and as $\Delta^{14}C_{initial}$ for crenarchaeol and alkenone
4 samples from GeoB3313-1 and GeoB5546-2. Foraminifera ages in parentheses are from $\delta^{18}O$
5 stratigraphy (H. Meggers, unpublished).
6
7 Figure caption:
8
9 Figure 1: Radiocarbon data of co-occurring crenarchaeol and alkenones from the S Chilean
10 (GeoB3313-1), NW African (GeoB5546-2), and Namibian continental margins. Data from the
11 Namibian margin are from (Mollenhauer et al., 2007). The 1:1 line is marked, and data plotting in the
12 grey shaded areas correspond to less than 500 ^{14}C yr difference in the conventional radiocarbon ages
13 calculated from fMC values. The dashed lines fMC values of 0.27, which was found to be the lower
14 limit of reliable alkenone ^{14}C dates (Mollenhauer et al., 2005b).
15

1 Table 1:
2
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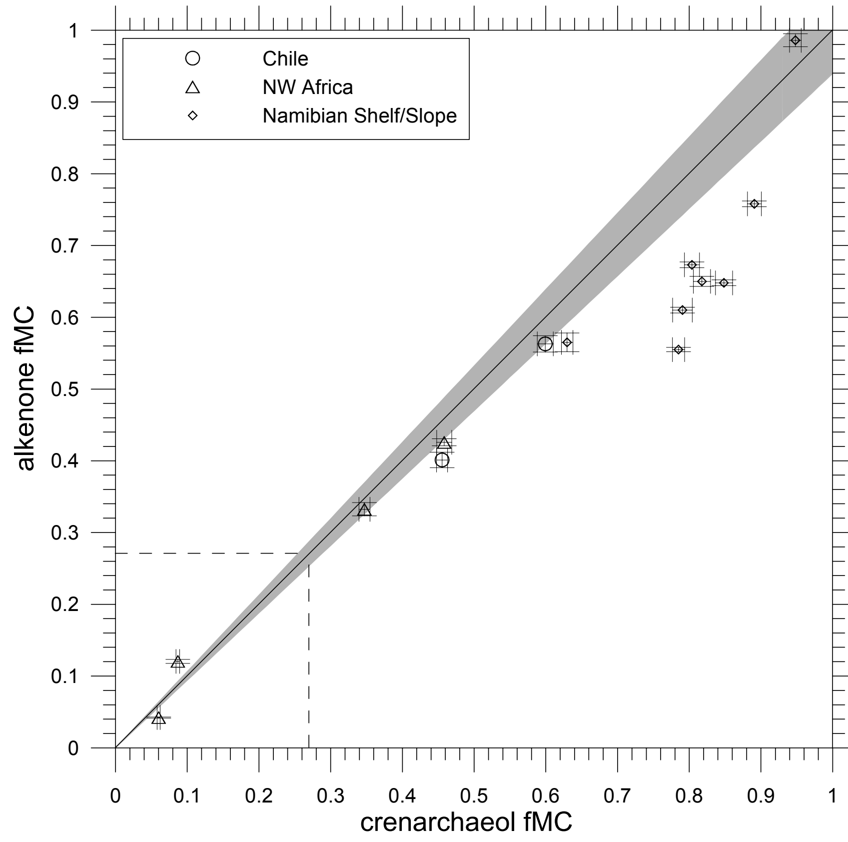
Location	Core	Depth (cm)	crenarchaeol fMC	alkenones fMC	Foram age cal. yr BP
S Chile	GeoB3313-1	404-407	0.599±0.011	0.563±0.011[a]	3810[a]
	GeoB3313-1	757-759	0.455±0.008	0.401±0.011[a]	7080[a]
NW Africa	GeoB5546-2	75-80	0.458±0.010	0.426±0.005[a]	7330[a]
	GeoB5546-2	126-131.5	0.347±0.008	0.333±0.009[a]	9680[a]
	GeoB5546-2	485-490	0.087±0.003	0.120±0.003	(27700)
	GeoB5546-2	550-555	0.060±0.002	0.042±0.001	(32100)
Namibian shelf and slope	WW24005	0-1	0.948±0.008[b]	0.986±0.009[b]	
	WW24005	13-15	0.630±0.008[b]	0.565±0.013[b]	
	WW24040	14-16	0.891±0.010[b]	0.758±0.004[b]	
	WW24060	8-10	0.818±0.013[b]	0.650±0.007[b]	
	WW24080	0-1	0.843±0.014[b]	0.648±0.004[b]	
	WW24080	14-16	0.785±0.009[b]	0.555±0.003[b]	
	RCOM2506	0-1	0.804±0.011[b]	0.673±0.004[b]	
	RCOM2506	14-16	0.791±0.016[b]	0.612±0.004[b]	

4 [a] from Mollenhauer et al. (2005a)
5 [b] from Mollenhauer et al. (2007)

1 Figure 1:
2
3



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