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TEMPERATURE CONTROL ON LADDERANE LIPID CHAIN LENGTH IN ANAMMOX BACTERIA

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A recent addition to the pool of source diagnostic biomarkers are the membrane lipids of anaerobic ammonium oxidizing (anammox) bacteria. Anammox bacteria oxidize NH_4^+ with NO_2^- to N_2 under anoxic conditions and create the intermediate compound hydrazine. Anammox bacteria have a prokaryotic organelle surrounded by a membrane bilayer composed of unusual 'ladderane' lipids. Ladderanes consist of C_{18} and C_{20} alkyl chains possessing 3 or 5 linearly concatenated cyclobutane rings, bound by ether and/or ester linkages to a glycerol backbone. Modelling experiments have shown that ladderane lipids may provide a denser cell membrane than conventional lipids (Sinninghe Damsté et al., 2002). The increased density is believed to prevent proton and hydrazine loss from the organelle. Ladderane lipids have been shown to be excellent tracers for the presence of anammox bacteria in water columns, sediment traps and sediments (e.g. Kuypers et al., 2003). However, the factors controlling the relative abundance of the different ladderane lipid isomers (i.e. genetic and/or environmental) were unknown until now.

In this study we analysed the ladderane lipid composition of enrichment cultures (four genera of anammox bacteria), particulate organic matter and surface sediments to ascertain the impact of environmental conditions on the relative distribution of ladderane lipids. Analyses were conducted using our recently developed novel HPLC-APCI-MS/MS technique (Hopmans et al., 2006). On plotting a ratio between ladderane lipids containing 5 cyclobutane rings and hydrocarbon chain lengths of 18 and 20 carbon atoms, respectively, a highly significant sigmoidal relationship (R^2= 0.93) is observed between ladderane lipid chain length and *in situ* temperature (Figure 1). This relationship indicates that there is an increase in the concentration of ladderane lipids containing shorter alkyl chains at lower temperatures and vice versa, particularly between 10 and 25°C. Phylogenetic analysis showed that different genera contribute to the different ladderane pools, suggesting that this mechanism of temperature adaptation is present in all anammox bacteria. Temperature stimulated production of shorter chained lipids has been previously documented in other bacteria and is thought to lead to increased membrane fluidity under cold conditions by reducing carbon to carbon interaction between lipid chains (Russell et al.,1990). Our results may be used to discriminate between the origin of ladderane lipids in marine sediments, i.e. if ladderanes are produced *in situ* in cold surface sediments or if they originate from the warmer upper water column.

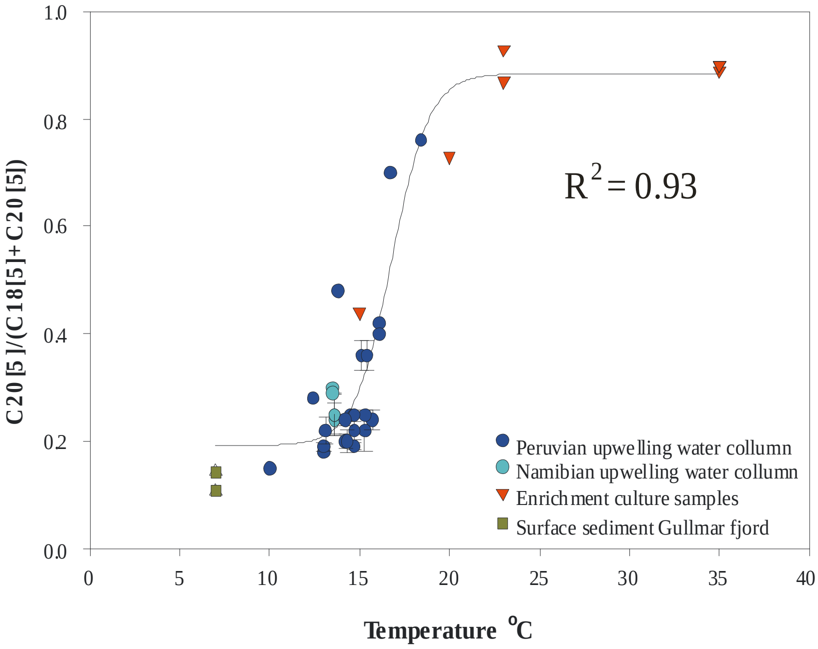

Figure 1. Sigmoidal relationship between ladderane lipid ratio and *in situ* water column, reactor medium and sediment temperature

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ALKENONES IN LACUSTRINE SEDIMENTS AS PALEOCLIMATE INDICATORS

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Long-chain alkenones (LCAs) are a key class of biomarkers for certain members of the algal class Prymnesiophyceae (i.e., prymnesiophytes). These compounds are ubiquitous in ocean sediments where they are extensively used for paleotemperature reconstructions. Alkenones have also been reported in about 20 lakes around the world, but their paleoclimate significance is only beginning to be realized. In this study we report the occurrence of alkenones in sediments from a series of lakes in Greenland, western United States, western China and Alaska and discuss their paleoclimate applications.

We have previously reported unusually high concentrations of long-chain alkenones (LCAs) in sediments from a suite of laminated lakes in the Sondre Stromfjord region of southwestern Greenland (D'Andrea and Huang, 2005). Decadal-scale alkenone unsaturation UK37 records from three of these lakes depict remarkable coherence, providing unique records of regional temperature variability for the mid- to late Holocene. Comparison of these records with other highly-resolved temperature reconstructions from the North Atlantic suggests millennial-scale oscillations in the dominant mode of NAO over the past ~6000 yrs. Records of sedimentary LCA concentration from the lakes also imply regional control over the productivity of prymnesiophyte algae. While total organic carbon (TOC) records can yield clues to the overall productivity of a lake basin, LCAs are purely aquatic in origin and therefore represent ideal biomarkers for autochthonous productivity and facilitate refined paleolimnologic and paleoclimatic interpretation. Sediment traps were deployed in the saline lakes in April 2006, collecting discrete seston samples during spring and summer at 10 day intervals. We are presently using water temperature data collected over the same time interval (which included the spring thaw) to create an absolute UK37 temperature calibration specific to the Greenland lakes.

We established a quantitative reconstruction of temperature and salinity changes over the past 3500 years, based on alkenone distribution patterns in Lake Qinghai sediments (Liu et al., 2006). We show that alkenone proxies $U^{k'}_{37}$ and $\%C_{37:4}$ faithfully record temperature and salinity changes in Lake Qinghai, China (Fig.1). During the late Holocene, our $U^{k'}_{37}$ record indicates up to a 1ºC change in mean annual air temperature or a 2ºC change in summer lake water temperature, in which the 20th century warm period, LIA, MWP, DACP and RWP have been identified. As suggested by %$C_{37:4}$, warm periods are associated with periods of lake water freshening. The coupled surface temperature and salinity changes in Lake Qinghai suggest that Asian monsoons strongly influenced regional climate, and experienced significant changes in their strength during the late Holocene. Alkenones provide a rare opportunity to study the relationship between climatic and hydrological changes independent of chronology. A regional salinity calibration using surface sediments from Tibetan Plateau allows a robust quantification of salinity changes based on %$C_{37:4}$ values.

We are also establishing downcore records from Brush Lake, Montana, and several Alaskan lakes where we have found alkenones in lake surface sediments. The sediments of Brush Lake are varved, allowing high resolution reconstruction of lake water temperature for the entire Holocene.

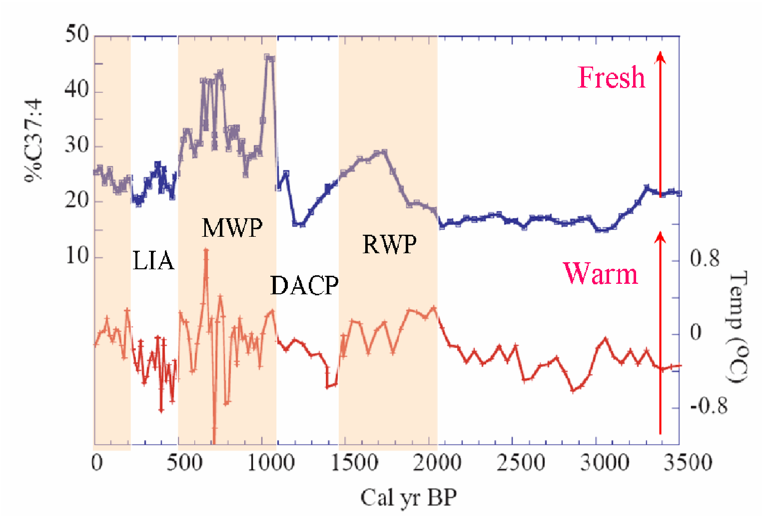

Figure 1. Late Holocene temperature and salinity records from Lake Qinghai, west China.

(Top) Salinity change based on %C37:4.

(Bottom) Temperature reconstruction based on $U^{k'}_{37}$. LIA = Little Ice Age; MWP = Medieval Warm Period; DACP = the Dark Ages Cold Period; RWP = Roman Warm Period.

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