The paleolimnologist's guide to compound-specific stable isotope analysis – an introduction to principles and applications of CSIA for Quaternary lake sediments

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ABSTRACT

The stable isotope composition of key chemical elements for life on Earth (e.g., carbon, hydrogen, nitrogen, oxygen, sulfur) tracks changes in fluxes and turnover of these elements in the biogeosphere. Over the past 15 to 20 years, the potential to measure these isotopic compositions for individual, source-specific organic molecules (biomarkers) and to link them to a range of environmental conditions and processes has been unlocked and amplified by increasingly sensitive, affordable and wide-spread analytical technology. Paleoenvironmental research has seen enormous step-changes in our understanding of past ecosystem dynamics. Vital to these paradigm shifts is the need for well-constrained modern and recent analogues. Through increased understanding of these environments and their biological pathways we can successfully unravel past climatic changes and associated ecosystem adaption.

With this review, we aim to introduce scientists working in the field of Quaternary paleolimnology to the tools that compound-specific isotope analysis (CSIA) provides for the gain of information on biogeochemical conditions in ancient environments. We provide information on fundamental principles and applications of novel and established CSIA applications based on the carbon, hydrogen, nitrogen, oxygen and sulfur isotopic composition of biomarkers. While biosynthesis, sources and associated isotope fractionation patterns of compounds such as *n*-alkanes are relatively well-constrained, new applications emerge from the increasing use of functionalized alkyl lipids, steroids, hopanoids, isoprenoids, GDGTs, pigments or cellulose. Biosynthesis and fractionation are not always fully understood. However, although analytical challenges remain, the future potential of deeper insights into ecosystem dynamics from the study of these compounds is also emerging.

KEYWORDS: stable isotopes, global, paleoclimatology

1 INTRODUCTION

The key elements that form organic matter on Earth, carbon, hydrogen, oxygen and nitrogen, occur in the form of two (C, H, N) or three (O) stable isotopes as determined by the number of neutrons in their nuclei, with the lighter isotope dominating. Each chemical reaction during the formation of organic matter and each phase transition (e.g., evaporation) changes the isotope distribution of the product (organic molecule, water vapour) by discriminating against the heavier (C, H, O) or, in some cases, lighter (N) isotopes. Thus, as these elements, and others such as sulfur, pass through biogeochemical cycles, their isotopic composition in a specific molecular and environmental context carries information on where they originally came from and how they got there. The determination of stable isotope ratios in an organic molecule therefore provides a tool to investigate and understand modern-day elemental cycling, thereby aiding our ability to reconstruct the variability of past element fluxes and the associated environmental drivers (for an introduction to stable isotope geochemistry see, e.g., Galimov, 1985; Hoefs, 2004). On a global scale, isotope distributions of carbon, oxygen and hydrogen vary over time, depending on the amounts of carbon dioxide and water stored in the major reservoirs, ocean water, atmosphere and polar ice caps or, on geological time scales, in rocks. Over the past five decades, stable carbon and oxygen isotope data from marine carbonates and ice cores, for example, has been fundamental in improving our understanding of the biogeosphere's response to external and internal forcing and associated changes in elemental fluxes such as the transfer of carbon from the atmosphere to the ocean. More recently, isotope analysis of individual biological compounds, i.e. compound-specific isotope analysis (CSIA) has allowed geoscientists to zoom in on processes involving organic matter transformation on much smaller scales and to study element cycling within individual ecosystems, from primary producer to ultimate microbial degrader and mineralisation. The improved understanding of how certain ecosystem changes can modify the isotopic fingerprint of organic molecules in sedimentary archives has resulted in the development of CSI-based proxies that document the adaption of the biosphere to the variability of key environmental parameters such as temperature or moisture supply. Some CSI proxies in fact respond to changes in these parameters directly, such as the hydrogen and oxygen isotope composition of meteoric water that is reflected in the isotope composition of biomarkers synthesized through the uptake of water and a carbon substrate (e.g., leaf-wax lipids, cellulose; Sauer et al., 2001a; Wolfe et al., 2001, 2007; Sachse et al., 2012). Many of the concepts, methodologies and paleoenvironmental proxies have originally been developed and applied in marine research, due to the fact that the global ocean is the most extensive ecosystem on Earth, with relatively well understood ecological boundary conditions, as compared to lakes, which feature specific ecological conditions that rarely match from one lake to another. However, since analytical facilities have become more widely available and the calibration of CSI data for applications in diverse lacustrine systems more affordable, an increasing number of lacustrine paleoenvironmental research projects now include CSIA, supporting established palynological or bulk geochemical data and thereby also bridging the (still existing) gaps between the various scientific communities.

This review aims to introduce CSIA as a prospective and increasingly popular tool to scientists in the field of paleolimnology who are practitioners of paleolimnology rather than specialized biogeochemists, involved in interdisciplinary studies and aiming for an improved understanding of the basic principles that control the proxy data they are dealing with or might want to produce themselves. The rapid expansion of diverse applications of CSIA has produced a plethora of research outputs, including recent reviews (i.e., Castañeda and

Schouten, 2011; Sessions, 2016; Diefendorf and Freimuth, 2017) that provide detailed information on either individual isotopes or specific compound classes in both marine and terrestrial settings. Here we provide an encompassing overview of CSIA (C,N,H,S) from an extensive spectrum of compounds for reconstructing Quaternary environmental change specifically from limnic settings, guiding the reader towards a more focused literature base with key case studies (summarized in Table 1). We include an introduction into the biosynthesis of the relevant biomarkers since isotope fractionation during biosynthesis is a key factor with regard to the ultimate stable isotope distribution in an organic molecule, in addition to the environmental factors driving the isotopic composition of the substrates used by primary producers. The desire for an improved understanding of proxy variability and sensitivity links paleoenvironmental sciences to studies of biogeochemical processes in modern ecosystems and food webs. Some of the CSI applications introduced here, for example, those using amino acids, pigment or sulfur-containing compounds, still are at the stage of development where further study of modern biogeochemical processes alongside pioneering paleoenvironmental research and methodological advances will help to develop their full potential, which also means that there are merits still to be gained. We thus hope our approach will help investigators new to the field to understand the relevance and power of isotope-based proxies and potentially inspires new ventures into one of the most dynamic realms of paleoenvironmental sciences.

In the following, we first provide an overview of the fundamental principles of isotope fractionation in biogeochemical cycles, followed by sections that introduce and discuss specific compound classes for which environmental proxies are well established (e.g., alkyl lipids) and less well-known compound classes or individual compounds (e.g., cellulose), with information on their various sources and CSIA applications. Although bulk elemental isotope analyses ($\delta^{13}C$, $\delta^{15}N$) provide useful paleoenvironmental information, particularly in combination with compound-specific isotopes, we will not review this area as it is well covered by other recent contributions (e.g., Sessions, 2016; Diefendorf and Freimuth, 2017).

2 STABLE ISOTOPE DISTRIBUTION, FRACTIONATION AND ANALYSIS

2.1 Isotopes in the biogeosphere

Photosynthetic and chemoautotrophic primary producers form the ultimate base of aquatic and terrestrial food chains, transforming molecular or elemental inorganic substrates (e.g., CO_2, CH_4, NH_3, H_2) and water into biomass. Biochemically speaking, life on Earth is essentially composed of carbon, hydrogen, oxygen, nitrogen and phosphorous, with a bulk stoichiometry, e.g., of the most important autotrophic producers of biomass, marine algae, of $C_{106}H_{263}O_{110}N_{16}P$ (Redfield, 1958). Each autotrophic organism taps into specific reservoirs of the elements required in which the heavier stable isotopes, i.e. ^{13}C, ^{2}H, ^{18}O, ^{15}N, are present in specific proportions. These proportions vary for each reservoir, depending on physical conditions and variable exchange with other reservoirs (e.g., proportions of CO_2 with heavy carbon and/or oxygen atoms in the atmosphere or the ocean vary across glacial-interglacial cycles, depending on temperature and evaporation rates; e.g., Hayes et al., 1999). Once a substrate has been taken up by an organism it will be fully or partially incorporated into organic molecules by enzymes. Enzymatic activity discriminates against the heavier (C, H, O) or, in case of nitrogen, lighter isotopes of reactants, leading to a different relative abundance of the light and heavy isotopes of the product, i.e. the isotope fractionation factor ε (Hayes et al., 1989; Popp et al., 1989), discussed in more detail below. Hydrogen and nitrogen are also frequently exchanged between the compound that is biosynthesized and the operating enzyme. For example, during the biosynthesis of major lipid compound classes in a photosynthetic organism, enzymatic reactions involving nicotinamide adenine dinucleotide phosphate (NADPH) lead to repeated addition of isotopically light hydrogen (i.e. ^1H rather than ^2H) to the synthesized lipid (e.g., Smith and Epstein 1970; Luo et al., 1991; see also Fig. 1).

Thus, the isotope composition of an element in biomass from primary production reflects the specific isotope composition of the reservoir and substrate and, through the fractionation factor between original substrate and synthesized biomass, the level and pathway of metabolic processing. Heterotrophic organisms consuming biomass of a certain isotope composition will again increase the fractionation factor to a certain extent when incorporating organic compounds into their own body tissue, either directly (little fractionation) or through further metabolic processing (additional fractionation; see, e.g, DeNiro and Epstein, 1978; Peterson and Fry, 1987).

Reactions between reduced inorganic sulfur and organic compounds in sediments are considered to be important for organic matter preservation. The fractionation of sulfur is a useful tracer of sulfurization reactions post-deposition, which often occur in the presence of strong pore water isotopic gradients, typically driven by microbial sulfate reduction, active during deposition and sedimentation (Habicht and Canfield, 1997; Kraal et al., 2013). Prior studies have looked at bulk sedimentary OM to understand fractionation as a function of sulfidization reactions between authigenic sulfide, and residual organosulfur compounds (Amrani and Aizenshtat, 2004; Riedinger et al., 2017; Pärn et al., 2018). However, enhanced ability to measure compound-specific sulfur isotopic compositions of volatile organosulfur compounds, co-eval pore water, sulfides forming, and the residual organic matter has greatly enabled our ability to understand the processes that govern sulfur cycling and diagenetic processes in both modern and ancient sediments.

2.2 Compound-specific isotope analysis (CSIA)

Compound-specific isotope analysis (CSIA) provides the opportunity to trace the basic elements (C, H, N, S) through primary biosynthetic processes, food web dynamics and heterotrophic microbial degradation to burial in the sedimentary archive (Matthews and Hayes, 1978). Quantifying these elemental fluxes underpins reconstructions of environmental dynamics and is key to the field of paleoenvironmental science. In recent years, applications of CSIA proxies to paleoenvironmental studies have gained increasing traction as our understanding of the biological and physical/chemical controls of isotopic fractionation improves (e.g., through studies of isotope fractionation in modern systems and mesocosm experiments). At the same time, analytical facilities are becoming more sensitive, automated and economical and therefore more widely available.

CSIA has now been successfully used to reconstruct changes in organic matter sources as well as to record the response of organisms to changes in temperature and moisture supply, air mass handling, shifts in food webs and diets, phytoplankton community shifts, water chemistry, redox chemistry, carbon cycling, methane cycling, vegetation change, and paleohydrology (see Table 1 for references).

Many CSIA methods start with common lipid extraction techniques such as microwave-assisted extraction (MAE), accelerated solvent extraction (ASE), ultrasonication, or Soxhlet extraction, using a range of organic solvent combinations and in some cases an added aqueous buffer. The protocols mainly differ in the processing of the total lipid extract (TLE) in order to purify the various target compounds, which typically includes separation of polar and non-polar compounds or of aliphatic hydrocarbons, aromatic hydrocarbons and alcohols (e.g., Sauer et al., 2001b). Individual compounds are commonly identified by gas chromatography–mass spectrometry (GC-MS) through their specific mass spectra and analysed by gas chromatography-isotope ratio mass spectrometry, with either a combustion or thermal conversion interface (GC-C-IRMS, GC-TC-IRMS; Hayes et al., 1989; Freeman et al., 1990; Hilkert et al., 1999), and by high-performance liquid chromatography-isotope ratio mass spectrometry (LC-IRMS; Boschker et al., 2008) to determine their isotopic composition. The latter is expressed as the divergence of the ratio of the heavier isotope over the lighter isotope from the equivalent ratio in a standardised reference material (δ-annotation) as shown for carbon below (Eq. 1):

$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1\right) * 1000 \qquad \textbf{\textit{Equation 1}}$$

The international reference standards are Vienna Peedee Belemnite (VPDB) for ^{13}C, Vienna Standard Mean Ocean Water (SMOW) for ^{2}H, atmospheric N_2 (AIR) for ^{15}N and Vienna

Canyon Diablo Troilite (V-CDT) for ^{34}S. A comprehensive compilation of CSIA methodologies, including details on instrumentation, has been published by Jochmann and Schmidt (2011).

2.3 Isotopic fractionation: from substrate to compound

The basics of isotope fractionation apply to organic compounds biosynthesised by organisms across the phylogenetic tree in virtually every aquatic and terrestrial environment. Responsible for the variable isotopic composition of organic molecules is biochemical processing during biosynthesis, which discriminates against the heavier carbon, hydrogen and oxygen isotopes and lighter nitrogen isotope and results in the more processed molecules being isotopically lighter (i.e. depleted in ^{13}C, ^{2}H, ^{18}O) or heavier (enriched in ^{15}N) compared to less processed molecules. An example for such a process is enzymatic carbon chain elongation, which leads to long-chain *n*-alkyl compounds produced by higher plants being depleted in the heavy carbon and hydrogen isotopes compared to short-chain *n*-alkyl compounds, even within the same plant (Diefendorf and Freimuth, 2017, and references therein). Typically, plants are responsible for a fractionation factor (ε) of -10 to -30 ‰ for carbon and -100 to -170 ‰ for hydrogen between substrate and *n*-alkyl compounds (Collister et al. 1994; Chikaraishi et al., 2004; Hou et al., 2007; Sachse et al., 2012; Sessions, 2016). An exception to the general depletion of the heavy isotope in products of enzymatically controlled reactions has been observed in some microbes, with inverse hydrogen isotope fractionation, i.e. enrichment of ^{2}H, widely occurring in lipids of aerobic heterotrophs (Zhang et al., 2009; Osburn et al., 2016; Kümmel et al., 2016).

Prior to fractionation during biosynthesis, however, it is the isotopic composition of the substrates providing the key elements for primary production, e.g., CO_2, HCO_3^-, H_2O and NO_3^- for photoautotrophs, that determines the baseline isotopic composition of an organic compound, and this is where information on paleoenvironmental conditions can be gained.

Atmospheric CO_2 is taken up by the vast majority of primary producers through photosynthetic carbon fixation, a process that strongly fractionates against ^{13}C (e.g. Körner et al., 1991; Diefendorf and Freimuth, 2017). For land plants, water availability is one of the parameters that significantly influences fractionation rates during carbon fixation as it exerts a strong control on plant stomatal conductance, which in turn influences biosynthetic fractionation during photosynthesis. Variability of $\delta^{13}C$ values of compounds from higher plants is likely to represent water availability, at least qualitatively, when $\delta^{13}C$ values are determined for time intervals when vegetation changes were minimal and where no major shifts in atmospheric CO_2 took place (Diefendorf and Freimuth, 2017). Interpreting changes in *n*-alkane $\delta^{13}C$ values as precipitation indicators has been established as a paleoclimatic tool in certain settings (see Kohn, 2010 and references therein).

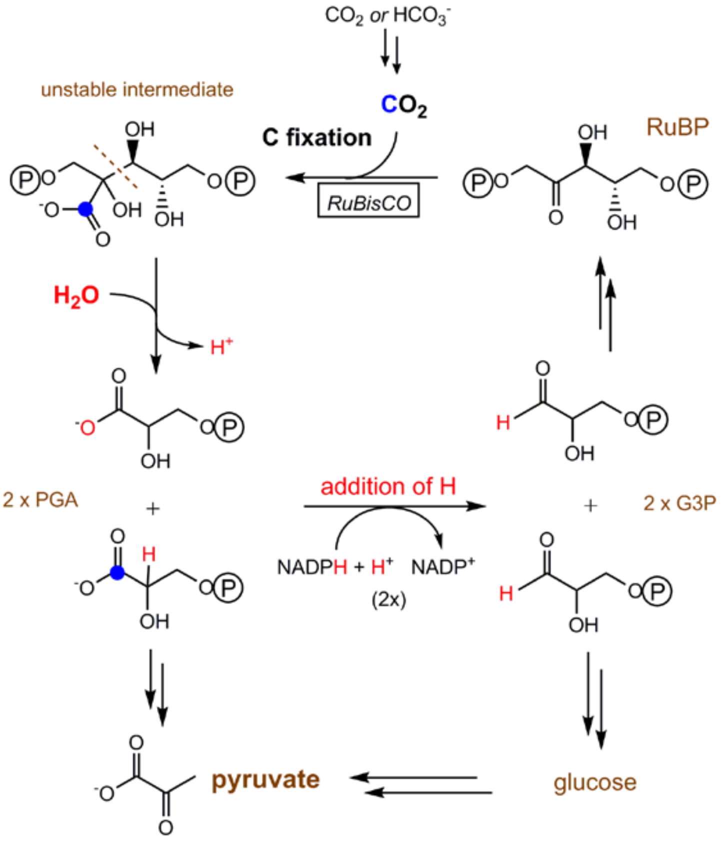


Figure 1: Fixation of carbon dioxide through the Calvin cycle during photosynthesis and biosynthesis of pyruvate, the starting material for the biosynthesis of many of the compounds discussed in this review (after Calvin and Benson, 1948; Sachse et al., 2012; Berg et al., 2015). CO_2 and meteoric water are taken up by the photosynthesizing organism for carboxylation and hydrolysis of Ribulose 1.5-biphosphate (RuBP). This process produces two molecules of 3-phosphoglycerate (PGA) and discriminates against the heavy isotopes (blue dot: added carbon from CO_2; added hydrogen atoms in red). PGA can be turned into pyruvate either through a 10-step mechanism (not shown) or via the biosynthesis of simple sugars such as glucose (shown on the right), the first step of which is the formation of glyceraldehyde-3-phosphate (G3P). Five out of six G3P molecules produced from three initial RuBP molecules are needed to recover three RuBP molecules while one G3P molecule can be used for the formation of glucose. Thus, six CO_2 molecules are taken up for the formation of one sugar molecule.

Most plants fix carbon directly through the Calvin cycle of photosynthesis (Fig. 1), requiring stomatal gas exchange with the atmosphere for CO_2 uptake in the process, i.e. during daytime. As the first metabolic product contains three carbon atoms (3-phosphoglycerate) these plants are called C3 plants. Under arid conditions, however, some plants fix CO_2

temporarily through the Hatch-Slack pathway by forming oxaloacetate, a molecule containing four carbon atoms, before shifting it into bundle sheath cells where the CO_2 is released to facilitate the Calvin cycle (for details see Berg et al., 2015). This allows the plants to shift stomatal gas exchange for CO_2 uptake into the night and, thus, minimise water loss. Again, with reference to the first metabolic product, plants following this strategy are called C4 plants. They mainly represent tropical grasses, including maize, for example. Importantly, the C4 metabolic adaption discriminates less strongly against ^{13}C, leading to a difference in fractionation ($\Delta^{13}C$) between terrestrial C3 and C4 plants that is significantly greater than 10 ‰, with bulk $\delta^{13}C$ values of C3 plants ranging from -22 to -37 ‰ (average of -27 ‰) and of C4 plants from -9 to -15 ‰ (average of -12 ‰; O'Leary, 1988; Kohn, 2010). Therefore, $\delta^{13}C$ values of bulk organic matter and individual terrestrial lipids such as leaf wax-derived long-chain *n*-alkyl compounds (see Fig. 2 for *n*-alkane $\delta^{13}C$) can generally be used to reconstruct spatiotemporal changes in C3 and C4 vegetation, in particular, the relative abundance of tree and shrub-dominated vegetation compared to grasslands (e.g., Huang et al., 2001; Castañeda et al., 2007; Sinninghe Damsté et al., 2011a; Magill et al., 2013; Freeman and Pancost, 2014; Garcin et al., 2014; Johnson et al., 2016). However, apart from the above-mentioned modifying influence of water availability, interspecies differences in isotope fractionation and leaf wax production associated with changes in the plant community will also have to be considered, alongside past variations in the $\delta^{13}C$ value of atmospheric CO_2 (Garcin et al., 2014; Diefendorf and Freimuth, 2017).

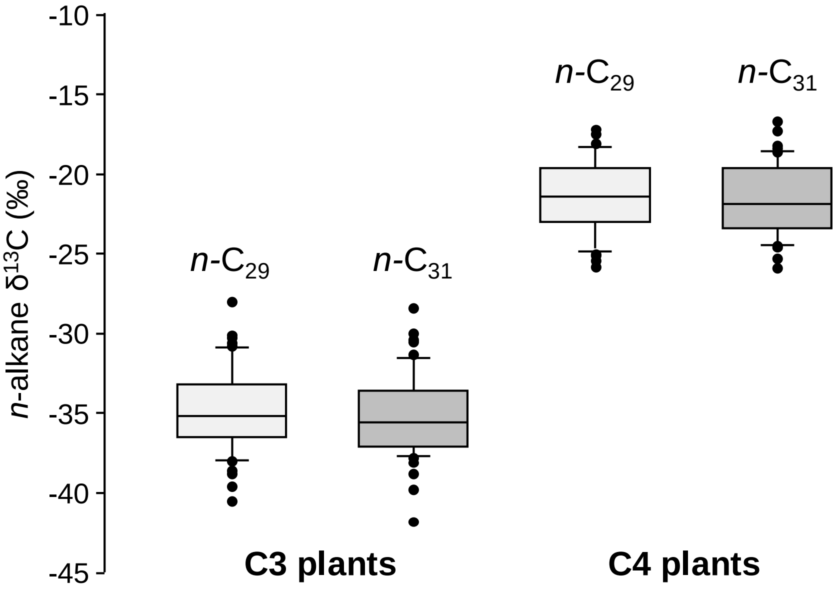


Figure 2: Box and whisker diagram of CSI data of plant-wax derived C_{29} and C_{31} *n*-alkanes of C3 and C4 plants illustrating their potential for reconstructions of vegetation changes in tropical settings (modified from Castañeda and Schouten, 2011, data from Castañeda et al.,

2009).

Aquatic primary producers use dissolved carbon dioxide ($CO_{2[aq]}$) or, under $CO_{2[aq]}$-limited conditions, bicarbonate (HCO_3^-) as inorganic carbon sources for photosynthesis (Lucas, 1983; Prins and Elzenga, 1989). In freshwater lakes, $CO_{2[aq]}$ is typically not limited and derives to variable extent from heterotrophic respiration in the water column or sediment and exchange with the atmosphere (Cole and Prairie, 2009). This means that freshwater photoautotrophs, which are C3 plants, and terrestrial C3 plants partly use the same inorganic carbon substrate, resulting in bulk organic carbon isotope ratios (bulk $\delta^{13}C_{org}$) of freshwater algae that are indistinguishable from those of terrestrial C3 plants (Meyers and Teranes, 2001; Lamb et al., 2006 and references therein).

The primary source of hydrogen for biosynthesis in photosynthetic organisms is environmental water, and the major determinant of the δ^2H value of lipids is the δ^2H value of the source water used by the organism (Yapp and Epstein, 1982; Sternberg, 1988; Sessions et al., 1999; Sachse et al., 2012; Rach et al., 2017). Water vapour contained by a specific air mass becomes isotopically depleted in ^2H as more water precipitates, i.e. with distance from the evaporation centre as well as with cooling and increasing altitude (Craig, 1961; Darling et al., 2005). The basic application of δ^2H values in environmental archives is, therefore, paleohydrology, i.e. the reconstructions of changes in the moisture content of the air mass delivering precipitation or an altogether change in the trajectory and source of the air mass (air mass tracking). Higher plants take up meteoric water (through soil water; Sachse et al., 2012), and evaporation processes during plant respiration (e.g., loss of leaf water) subsequently modify the isotopic composition of the water before it is used in biosynthetic reactions (e.g. Kahmen et al., 2013a, 2013b; Rach et al., 2017). δ^2H values derived from lipids of terrestrial plants will therefore reflect a combined precipitation and evapotranspiration signal (Sachse et al., 2004, 2012). By contrast, submerged aquatic macrophytes and algae use water from the surrounding water column as their hydrogen source. This means that, e.g., in a lake system with no significant fluvial inflow of water from distant areas, the δ^2H values of lipids from submerged macrophytes and algae will mainly reflect the average δ^2H value of local precipitation (Sachse et al., 2004; Fig. 3), unless it is modified by elevated lake water evaporation rates under more arid climate regimes. In this case, the difference between the δ^2H values of macrophyte-derived mid-chain and terrestrial long-chain *n*-alkanes (Δ^2H) can potentially be used to assess changes in lake water evaporation (Mügler et al., 2008; Aichner et al., 2010a) although this approach still needs further testing (Aichner et al., 2010a; Rao et al., 2014). Nevertheless, many studies have illustrated the generally strong relationship between modern-day climate and δ^2H in lipids in settings with pronounced hydrological gradients (e.g., Huang et al., 2004; Sachse et al., 2004; Nieto-Moreno et al., 2016).

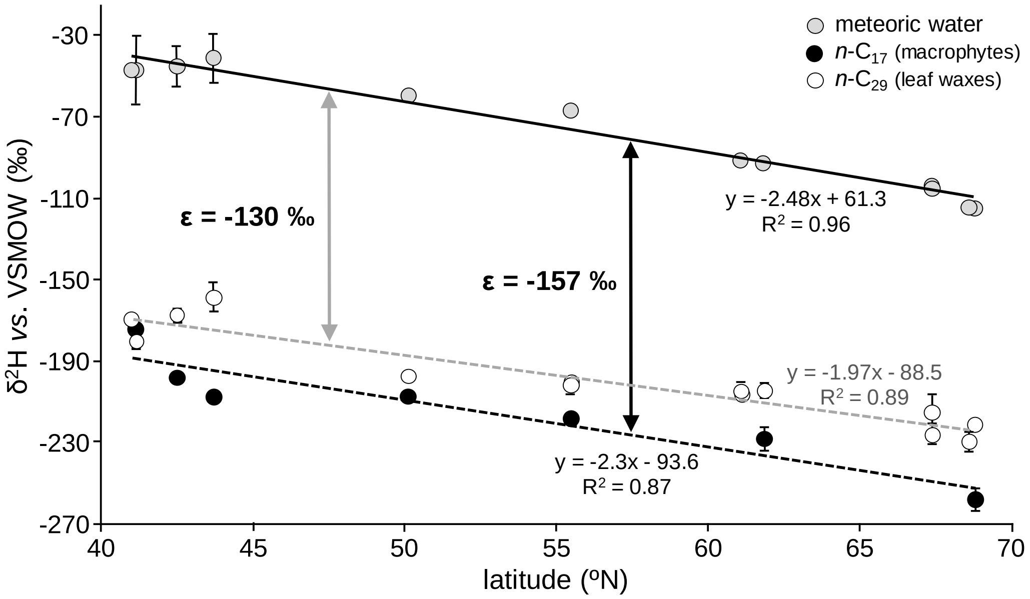


Figure 3: Correlation between the δ^2H values of lake water from a European N-S transect and the δ^2H values of the C_{17} and C_{29} *n*-alkanes from macrophytes and terrestrial plants in the catchments, illustrating the close control of lake water isotopic composition on leaf wax δ^2H values (modified from Sachse et al., 2004).

The main nitrogen substrates for eukaryotic algae are nitrate (NO_3^-) and ammonium (NH_4^+), while prokaryotic cyanobacteria can directly fix dissolved nitrogen ($N_{2(aq)}$; Harvey, 1940, 1953; Stal, 2015; Glibert et al., 2016). There is little to no fractionation involved in biological nitrogen fixation (Hoering and Ford, 1960; Minagawa and Wada, 1984), allowing phytoplankton communities dominated by cyanobacteria to be differentiated from eukaryote-dominated communities. As N_2 can be fixed in both terrestrial and aquatic environments, nitrogen from both of these sources contribute to the lacustrine nitrogen cycle. Isotopic fractionation can occur during many of the transformations nitrogen undergoes, including N_2 dissolution, nitrification and denitrification, nitrate and ammonium assimilation, and ammonia volatilisation (Collister and Hayes, 1991; Talbot, 2001). Thus, the absolute δ^{15}N value of the substrates provides limited environmental information compared to the absolute δ^{13}C and δ^2H values of atmospheric and dissolved CO_2 and meteoric water, respectively. Instead, information on environmental change may be gained from the difference in the isotope values of source amino acids, retaining the isotope composition of the initial substrate, and trophic amino acids, determined by fractionation along each trophic step, with implications for changes in the lacustrine food web structure (see Section 3.2 for details).

The transfer of sulfur between different reservoirs typically involves a change in the oxidation state, which is mediated either through abiologically or biologically induced processes

(Strauss, 1997; Farquhar et al., 2000). The main source of sulfur in sediments is derived from sulfate in the overlying water column or pore waters via downward diffusion in the sediments. Typically, sulfate is reduced to sulfide by bacterial sulfate reduction (BSR), active just below the sediment-water interface, leading to sedimentary sulfide typically depleted with respect to ^{34}S (e.g., Jørgensen, 1978; Habicht et al., 1998). Isotopic fractionation between sulfate in the water, sulfide, and organic sulfur compounds is fundamentally a function of the availability of sulfate to be reduced and the efficiency of the bacterium present (i.e. large amounts of easily metabolizable organic matter aids the sulfate reduction process; e.g. Kaplan et al., 1963; Canfield and Thamdrup,1994; Habicht and Canfield, 1997). Favourable conditions for BSR and an open source of sulfate can result in large isotopic fractionation between sulfate and the sulfide product. In the context of restricted settings, such as lakes, sulfate is not readily replenished and may undergo seasonal variation resulting in variations in the range of isotopic fractionation of the sulfate and the product sulfide (i.e. Urban et al., 1999; Zerkle et al., 2010; Oduro et al., 2013, discussed later). Furthermore, the bio-mediated uptake of sulfur into organosulfur compounds in organic matter leads to variable enrichment of ^{34}S with respect to sulfide phases formed, as well as variability of ^{34}S across different organic sulfur compounds present (Andreae, 1990; Kharasch, 2013). Typically, studies have focussed on the isotopic variation between original sulfate, the sulfide and bulk organic matter. Utilisation of compound-specific analysis in the examples discussed here is able to better deduce the physical and biochemical processes that lead to sulfur fractionation in sediments.

The basic physiological and substrate-related drivers of isotopic fractionation in primary producers during diagenesis are thus relatively well constrained. However, as illustrated by many examples in the remaining sections of this review, a range of environmental and source-specific factors such as temperature, seasonality and salinity or vegetation change and associated changes in evapotranspiration can further modify the isotopic composition of organic compounds. These need to be understood in order to improve the interpretation of CSI data variability in environmental archives. On the other hand, new proxies can be developed that target additional and more specific aspects of ecosystem change, once such causal relationships are established, and it is this improved understanding of isotope fractionation in modern biogeochemical cycles that brings to light the potential of CSIA in future paleoenvironmental studies. The compounds most frequently studied for their CSI values in paleoenvironmental research are alkyl lipids. Therefore, these compounds also provide many examples of the complex relationship between environmental factors, diverse sources and compound-specific carbon and hydrogen isotope ratios, some of which are presented in the following. A more comprehensive introduction to alkyl lipid CSI applications is provided in Section 3.1.

The $\delta^{13}C$ values of alkyl lipids are susceptible to more specific and often local factors. Eley et al. (2016) demonstrate that *n*-alkane $\delta^{13}C$ values of C3 and C4 plants from a temperate saltmarsh show a significant variability of $\delta^{13}C$ values, with differences between C3 species of up to 10 ‰ and pronounced intra-species differences across the growing season. In a tropical wetland setting, Yamoah et al. (2016) observe large-scale variability in *n*-alkane $\delta^{13}C$ values, with long-chain compounds becoming isotopically enriched during drier periods. The authors attribute this finding to a shift in the main substrate from dissolved CO_2 to isotopically heavier bicarbonate rather than changes in the overlying vegetation and enhanced C4 plant input. Significant differences in the $\delta^{13}C$ value between mid- and long-chain compounds have been reported, with the reason behind the offset remaining elusive. An apparently climatically controlled systematic offset of up to 6 ‰ between suberin-derived C_{22} *n*-fatty acid and leaf wax-derived long-chain fatty acids in Late Quaternary lake sediments (see supplement to Holtvoeth et al., 2017) could either point to an age-offset between lipids from leaf litter and soils (root material) or to differences in CO_2 uptake by plants for the formation of leaf and root tissue under variable climatic regimes and different rates of microbial respiration in the soil. C_{22} ω-hydroxy acid found in Miocene lake sediments is reported to be depleted by 4-5 ‰ relative to the long-chain ω-hydroxy acids (Huang et al., 1996). In this case, the authors hypothesised this compound to derive from anoxic bacterial biomass. The examples above illustrate the need for an improved understanding of carbon isotope fractionation in natural systems. A detailed review of environmental factors that can influence the $\delta^{13}C$ values of fatty acids has recently been published by Reiffarth et al. (2016).

The range of factors that can further modify the $\delta^{2}H$ values of alkyl lipids is even more complex. Additional environmental and physiological variables such as secondary hydrogen exchange reactions and effects of algal growth rates or metabolic differences can influence the isotopic fractionation between hydrogen in environmental water in aquatic and terrestrial lipids (see review by Sachse et al., 2012). Extensive growth experiments have shown that C3 and C4 grasses not only discriminate significantly different against ^{13}C but also differ in the $\delta^{2}H$ values of their *n*-alkanes by 40 ‰, on average (Gamarra et al., 2016). This could be attributed to the metabolic differences in the way NADPH is produced, i.e. in the bundle sheaths in C4 grasses rather than in the chloroplasts in C3 grasses, with the NADPH then providing the hydrogen for lipid biosynthesis (Gamarra et al., 2016). Studying the leaf wax *n*-alkane hydrogen isotope distribution of riparian trees, Oakes and Hren (2016) describe significant interspecies variation of $\delta^{2}H$ values that can exceed 50 ‰ throughout the growing season. Similarly, Tipple and Pagani (2013) found differences in the correlation between precipitation and *n*-alkane $\delta^{2}H$ values between tree species. However, such interspecies differences appear to be averaged out in the soil as *n*-alkanes from soil samples did show a good correlation between precipitation and CSI δ^2H values. On the other hand, short-term fluctuations in δ^2H of the leaf wax C_{28} *n*-fatty acid reported from the sedimentary record of an Alpine lake may be due to local factors such as length of growing season, amount of snowfall or anthropogenic modification of the local vegetation (Wirth and Sessions, 2016), factors that are not always well constrained. Ladd et al. (2017) investigated the influence of growth rate and temperature on the δ^2H value of algal lipids (fatty acids and brassicasterol) in an oligotrophic and a eutrophic lake. Although the authors found significant variability in the δ^2H values of fatty acids throughout the growing season the average δ^2H value of the C_{16} *n*-fatty acid matched the δ^2H value of the lake water and was also preserved in the surface sediment. An in-depth discussion of the factors that can modify δ^2H values of *n*-alkanes exceeds the objectives of our introduction to CSIA and we therefore refer to the very detailed recent review on this matter provided by Sessions (2016).

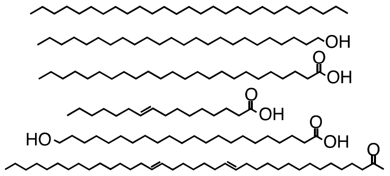
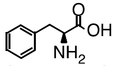
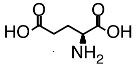
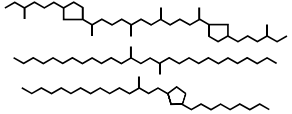
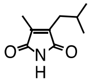
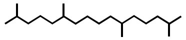
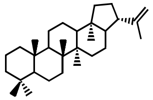
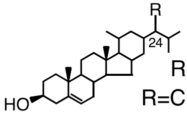
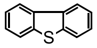
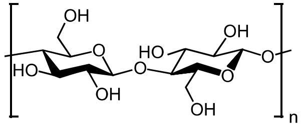
Compound class	Structures	Application / Indicative for…	Isotope-Proxies	Analytical Technique	Refs.
Alkyl lipids: n-alkanes, n-fatty acids, n-alcohols, unsaturated fatty acids, hydroxy acids, alkenones (structures top to bottom)		meteoric water source / air mass tracking, seasonality, evaporation rates,climate change vegetation change (C3 vs. C4 plants) compound source (terrestrial, aquatic, bacterial) potentially: salinity	δ^{2}H δ^{13}C δ^{2}H, δ^{13}C δ^{2}H	GC-IRMS	1 - 4 5 - 7 4 8 9
Amino acids	 phenylalanine  glutamic acid	food web structure, trophic level compound source	δ^{15}N δ^{13}C, δ^{15}N	GC-IRMS	10, 11 12
Glycerol-dibiphytanyl-glycerol tetraethers (GDGTs)	GC-amenable cleavage products* 	terrestrial vs. aquatic sources (brGDGTs, iGDGTs)	δ^{2}H, δ^{13}C δ^{13}C	GC-IRMS SWiM-IRMS	13 - 15 16
Chlorins Maleimides	 maleimide	photic zone euxina source	δ^{15}N δ^{13}C	GC-IRMS	17 18 19. 20
Isoprenoids	 crocetane	paleoenvironment autotrophy vs. heterotrophy	δ^{2}H δ^{13}C	GC-IRMS	21 22, 23
Hopanoids	 diploptene	bacterial autotrophy vs. heterotrophy methanotrophy	δ^{13}C	GC-IRMS	24 25
Steroids	 R=CH$_3$: campesterol R=CH$_2$CH$_3$: β-sitosterol	meteoric water source, hydrology change, salinity compound source (e.g., terrestrial, aquatic)	δ^{2}H δ^{13}C, δ^{2}H	GC-IRMS	26, 27 28
Sulfurised compounds	 dibenzothiophene	S cycling in active redox zones pathways of DMS formation VOCS production and release	δ^{34}S	MC-ICPMS	29 30 31 32
Cellulose		source (terrestrial vs. aquatic) carbon cycling, lake-water balance	δ^{18}O δ^{13}C	GC-IRMS	33 34

Table 1: Overview of compound classes, representative structures and isotope applications with key references (reviews where applicable). References are: 1. Sauer et al. (2001b); 2. Nichols et al. (2009); 3. Sachse et al. (2012); 4. Sessions (2016); 5. Huang et al. (2001); 6. Sinninghe Damsté et al. (2011a); 7. Garcin et al. (2014); 8. Reiffarth et al. (2016); 9. Schouten et al. (2006); 10. Chikaraichi et al. (2009); 11. Ohkouchi et al. (2017); 12. Larsen et al. (2015); 13. Wuchter et al. (2004); 14. Weijers et al. (2010); 15. Lengger et al. (2014); 16. Pearson et al. (2016); 17. Boreham et al. (1994); 18. Hayes et al. (1987); 19. Grice et al. (1996a, 1996b); 20. Wolfe et al. (2001); 21. Grice et al. (2005); 22. Koopmans et al. (1996); 23. Whiteside and Grice (2016); 24. Coolen et al. (2008); 25. Talbot et al. (2014); 26. Sauer et al. (2001b); 27. Schwab and Sachs (2011); 28. Chikaraishi et al. (2005); 29. Amrani et al. (2012); 30. Raven et al. (2015); 31. Oduro et al. (2013); 32. Greenwood et al. (2018); 33. Edwards and McAndrews (1989); 34. Street-Perrot et al. (2018). *for intact molecules see Figures 9 and 10.

3 SOURCES AND CSI APPLICATIONS OF BIOMARKER COMPOUND CLASSES

3.1 Alkyl lipids (*n*-alkanes, *n*-fatty acids, *n*-alcohols, alkenones)

Alkyl lipids of variable carbon chain lengths are ubiquitous building blocks in the formation of organic tissue. They form the hydrophobic part of cell membrane lipids in bacterial, plant and animal tissue (e.g., phospholipids, glycolipids, sphingolipids), function as storage fats (triacylglycerides, steryl esters) or contribute to protective layers such as the wax ester and cutin layers on the outer surfaces of plant cells, mainly on leaves, or suberin on the inside of plant cells, mainly in roots. This wide functional range of alkyl lipids involves different levels of biosynthetic processing, an understanding of which greatly improves the interpretation of CSI values from the various compounds found in a TLE. It also increases the range of paleo-environmental information to be gained, and we therefore briefly introduce the basics of alkyl lipid biosynthesis in the following.

All alkyl lipids produced by primary producers, i.e. mainly photosynthesizing organisms, are based on *de novo* biosynthesis of fatty acids and formed using environmental water and either atmospheric CO_2 or, in case of aquatic organisms, dissolved CO_2 and bicarbonate (HCO_3^-) as sources for hydrogen and carbon, respectively. Fatty acid biosynthesis follows the acetogenic pathway, using pyruvate derived from the breakdown of sugars (e.g., glucose) to first form an acetyl molecule bound to the co-enzyme A (acetyl CoA), then combining it with malonyl CoA to form a 4-carbon unit (acetoacetyl-ACP), with the reducing agent nicotinamide adenine dinucleotide phosphate (NADPH) replacing an oxygen atom by a hydrogen atom (Fig. 4). Repeated reactions with malonyl CoA and NADPH extend the molecule by two CH_2 units at each step. This process typically ends with the formation of C_{16}

and C_{18} fatty acids and results in a characteristic dominance of even over odd fatty acid chain lengths in most organisms (for further details on fatty acid biosynthesis see, e.g., Sachse et al., 2012).

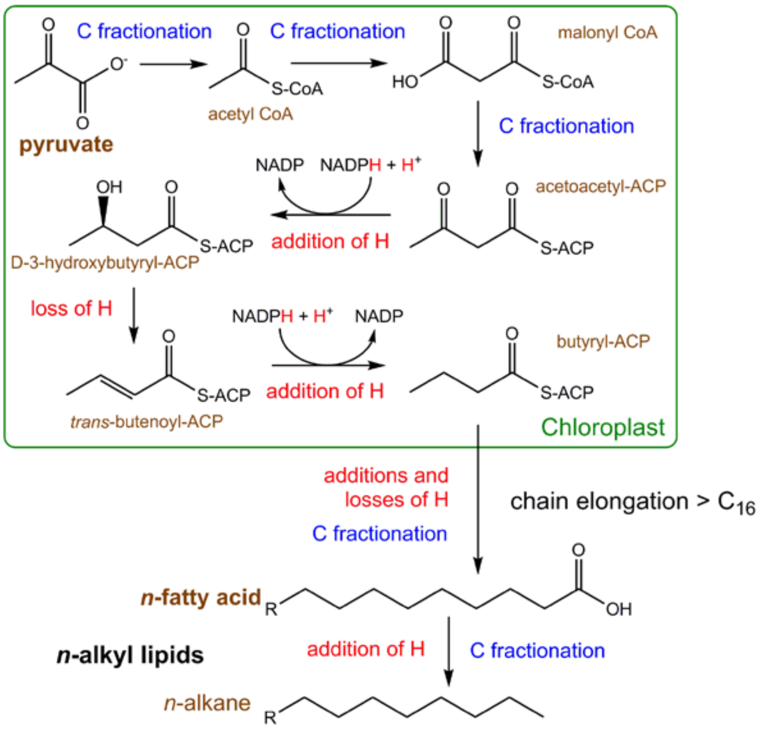


Figure 4: The “acetogenic pathway” of fatty acid biosynthesis, using pyruvate produced through the Calvin-Benson cycle after CO_2 uptake. Addition and loss of C or H during reactions as well as reactions between molecules discriminate against ^{13}C and ^{2}H, i.e. fractionation occurs at each of these steps; ACP = acetyl carrier protein, CoA = co-enzyme A, NADPH = nicotinamide adenine dinucleotide phosphate (partial scheme modified from Sachse et al., 2012).

The C_{16} and C_{18} *n*-fatty acids, also known as palmitic and stearic acid, respectively, are basic building blocks for a vast range of molecular structures, in particular, membranes. They are modified according to specific requirements such as membrane fluidity through further enzymatic processing, inserting, e.g., double bonds into the carbon chain (unsaturated fatty acids), adding alkyl branches or further functional groups (branched fatty acids, hydroxy acids) or forming cyclopropane units (cyclopropane fatty acids). Higher plants apply further enzymatic processing in epidermal cells to extend the chain lengths of palmitic or stearic acid for the formation of hydrophobic epicuticular wax esters and biopolyesters such as cutin and suberin in the protective layers of leaves and roots (Millar and Kunst, 1997). The activity of fatty acid elongase adds two CH_2 units to the starting molecule (C_{16}, C_{18} *n*-fatty acid) at each step, resulting again in the dominance of even- over odd-numbered fatty acid chain lengths in plant biomass. *n*-Alcohols and *n*-alkanes are formed through stepwise enzymatic reduction and decarboxylation of *n*-fatty acids (e.g., Coursolle et al., 2015). Because of the removal of an aldehyde (-CHO) *n*-alkanes are one carbon atom shorter than the original fatty acid, leading to a strong odd over even dominance among *n*-alkanes. Several calcifying and non-calcifying marine and lacustrine haptophytes produce long-chain alkenones, with chain lengths of 37 to 40 carbon atoms and 2 to 4 double bonds, using the same chain-elongating process as land plants initially, followed by desaturation steps (Rontani et al., 2006), during which first di- and then tri-unsaturated alkenones are formed (Kitamura et al., 2018) as opposed to all double bonds being formed at once.

3.1.1 Sources

3.1.1.1. n-Alkanes, n-fatty acids, n-alcohols

Generally, individual *n*-alkyl lipids are not species-specific. However, as different groups of organisms produce different types of homologous series of alkyl lipids, peaking at different chain lengths, shifts in chain-length distributions observed in a sedimentary archive can point towards changes in the major lipid sources and, hence, towards ecosystem adaption to environmental change. Long-chain *n*-alkyl lipids (> C_{24}) are almost exclusively produced by land plants as part of the cuticular wax layer that protects leaves from disease and ultraviolet light, and functions as a barrier to inhibit water loss (e.g., Eglinton and Hamilton, 1967; Volkman et al., 1998; Jetter et al., 2000; Diefendorf and Freimuth 2017 and references therein). Although lower concentrations of these compounds also occur in waxes on the surface of other parts of plants, leaf waxes are commonly assumed to be the dominant source of long-chain *n*-alkyl lipids delivered to lake sediments (e.g., Gamarra and Kahmen, 2015; Diefendorf and Freimuth, 2017). By contrast, alkyl lipids produced by bacteria and aquatic taxa are mainly membrane lipids or storage fats and are dominated by the short-chain compounds, typically by C_{16} and C_{18} fatty acids as well as alcohols. Storage fats frequently include unsaturated compounds with chain lengths up to 20 or 22 carbon atoms, such as the essential poly-unsaturated fatty acids eicosapentaenoic acid (EPA) and docosahexaenoic (DHA). However, these biologically highly desirable and labile compounds are usually not preserved in sedimentary records. *n*-Alkanes in aquatic algae and bacteria are dominated by the C_{17} or C_{19} homologues (e.g., Gelpi et al., 1970; Sachse and Sachs, 2008) while some macrophytes tend to produce a mid-chain range of *n*-alkanes (C_{21} - C_{25}; e.g., Ficken et al., 2000; Aichner et al., 2010b). Depending on the investigated setting, a fairly robust marker for the supply of *n*-alkanes from peat moss (*Sphagnum* spp.) is the C_{23} *n*-alkane (see review on *n*-alkane distributions by Bush and McInerney, 2013), although root material of some sedges can be another wetland-related source (Ronkainen et al., 2013). Mid-chain alkyl compounds (C_{22} and C_{24} *n*-fatty acids, hydroxy acids, diacids and *n*-alcohols) characterize the alkyl fraction of suberin, an important biopolyester in root material (Molina et al., 2006, Pollard et al., 2008). They can thus indicate soil organic matter supply (Holtvoeth et al., 2016, 2017). Next to differences in *n*-alkyl chain lengths between species, there are also differences in the overall amounts of plant wax that are produced by land plants. Van den Bos et al. (2018), for example, showed that the concentration of the most abundant *n*-alkane homologues in *Betula pendula* (birch) exceeded 100 µg/g dry leaf material, whereas *Quercus robur* (oak) contained concentrations of around 10 µg/g per homologue or less. Diefendorf et al. (2011) and Diefendorf and Freimuth (2017) show that conifers typically produce significantly smaller amounts of *n*-alkanes than broad-leaved species.

3.1.1.2. n-Alkenes

Occasionally, mid-chain mono-unsaturated alkenes maximising at C_{25} and C_{27} are preserved in lake sediments (Jaffé et al., 1996; van Bree et al., 2014). Investigating their origin, van Bree et al. (2014) found these compounds in sinking particles collected in a shallow sediment trap in Lake Challa, but they were absent in terrestrial organic matter sources in the catchment, which suggests an origin in the oxygenated water column of the lake. Analysing the carbon isotope composition of the $C_{25:1}$ and $C_{27:1}$ *n*-alkenes, van Bree et al. (2014) were able to confirm an aquatic origin for these compounds as their $\delta^{13}C$ values were consistent with the expected range for algal biomass in Lake Challa. However, the exact source of the mid-chain *n*-alkenes still has to be identified.

3.1.1.3 Long-chain alkenones

Long-chain alkenones are produced by several calcifying and non-calcifying haptophyte species in marine and saline lacustrine environments (Volkman et al., 1980a,b; Marlowe et al., 1984; Li et al., 1996; Thiel et al., 1997) and serve as energy storage lipids in these algae (e.g., Eltgroth et al., 2005). They have also been found in freshwater systems (Cranwell, 1985; Zink et al., 2001). However, in contrast to marine settings, the source of alkenones in lakes is generally not well defined as lacustrine haptophyte species show great biodiversity that significantly varies between lakes (Theroux et al., 2010; Toney et al., 2010). One of the non-calcifying haptophyte species found in saline lakes is *Chrysotila lamellosa* (Sun et al., 2007) while other alkenone producers appear genetically related to the coastal species *Isochrysis galbana* (Coolen et al., 2004a; D'Andrea et al., 2006; Theroux et al., 2010). For freshwater systems, Zink et al. (2001) speculate that also other, not yet identified non-haptophyte algae may produce alkenones. Nevertheless, alkenones can be abundant alkyl lipids in lake sediments (e.g., Zink et al., 2001; D'Andrea and Huang, 2005; Toney et al., 2011), they are relatively resistant towards diagenetic degradation (Sikes et al., 1991; Prahl et al. 2000, 2003; Freitas et al., 2017) and can thus be targeted as an algal biomarker by CSIA.

3.1.2 Applications

First and foremost, the isotopic composition of an individual alkyl compound can identify or confirm its presumed source, with the largest differences in biosynthetic isotope fractionation (ε) separating terrestrial and aquatic plant matter sources as well as distinguishing between C3 and C4 plants (review by Castañeda and Schouten, 2011) or pointing to methanotrophic bacterial sources (e.g., Summons et al., 1994). Variability in the isotopic composition of a specific compound over time typically reflects ecosystem response to a wide range of potential environmental drivers, including changes in hydrology, seasonality, temperature, and nutrient supply that affect species distribution and diversity. Accordingly, CSI data are ideally combined with further proxy data to narrow down the key system drivers. For example, palynological data may complement CSI proxy records by identifying changes in plant abundance or diversity that reflect the adaption of the vegetation to changes in hydrology or temperature (e.g., Huang et al., 2006; Tierney et al., 2010).

Many studies applying CSIA focus on *n*-alkanes as they are easy to isolate from the TLE, do not require further sample preparation or correction for added carbon or hydrogen during derivatisation and their source is relatively specific, with their main source in sedimentary archives being cuticular plant waxes. Thus, *n*-alkane CSI data interpretation can focus on a limited number of reasonably well understood environmental drivers. For example, Sinninghe Damsté et al. (2011a) used the δ^{13}C values of the C_{31} *n*-alkane in sediments of Lake Challa (Mt. Kilimanjaro) to reconstruct glacial-interglacial vegetation change from C4 grass-dominated savannah to C3 vegetation in response to hydrological changes in East Africa over the past 25 ka (Fig. 5).

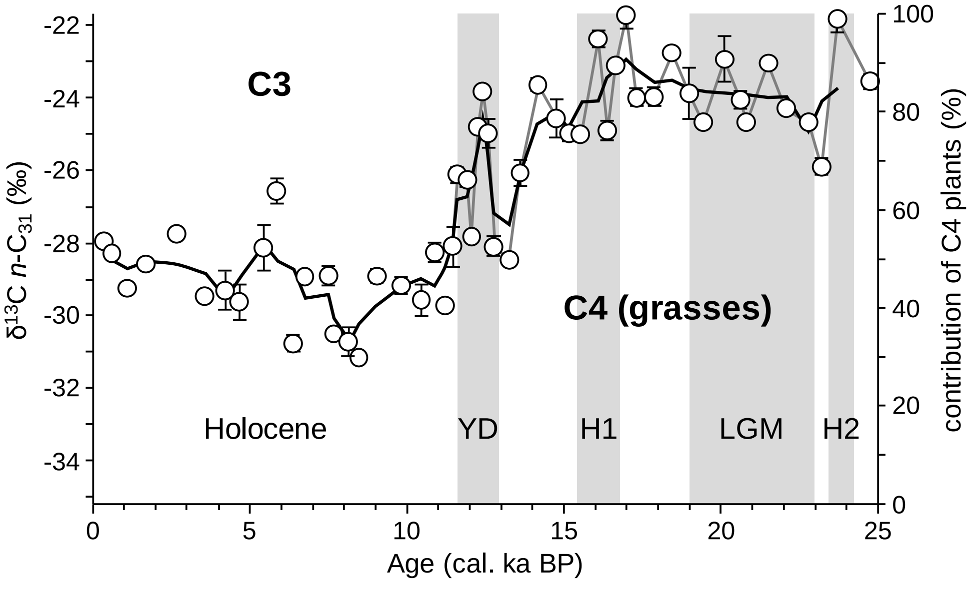


Figure 5: Reconstruction of changing proportions of C3 and C4 vegetation based on δ^{13}C

values of the C_{31} *n*-alkane in sediments of Lake Challa, East Africa for the past 25 ka, revealing the transition from C4 grass savannah during the last glacial to mixed C3/C4 vegetation in the Holocene (black line: 3-point moving average, H1/H2 = Heinrich event 1/2, LGM = last glacial maximum, YD = Younger Dryas; modified from Sinninghe Damsté et al., 2011a).

In Lake Koucha on the eastern Tibetan Plateau, Aichner et al. (2010b) found $\delta^{13}C$ values of macrophyte-derived C_{23} *n*-alkanes (mainly from *Potamogeton*) diverging from the $\delta^{13}C$ values of the terrestrial C_{31} *n*-alkane but following an equivalent shift towards heavier values in bulk inorganic carbon (TIC) $\delta^{13}C$ values, which the authors interpreted as evidence for dissolved CO_2 limitation due to enhanced productivity at least in the littoral zone of the lake (Fig. 6). This coincided with a shift from a macrophyte-dominated saline ecosystem to a phytoplankton-dominated freshwater ecosystem as indicated by other biomarkers and micropaleontological data.

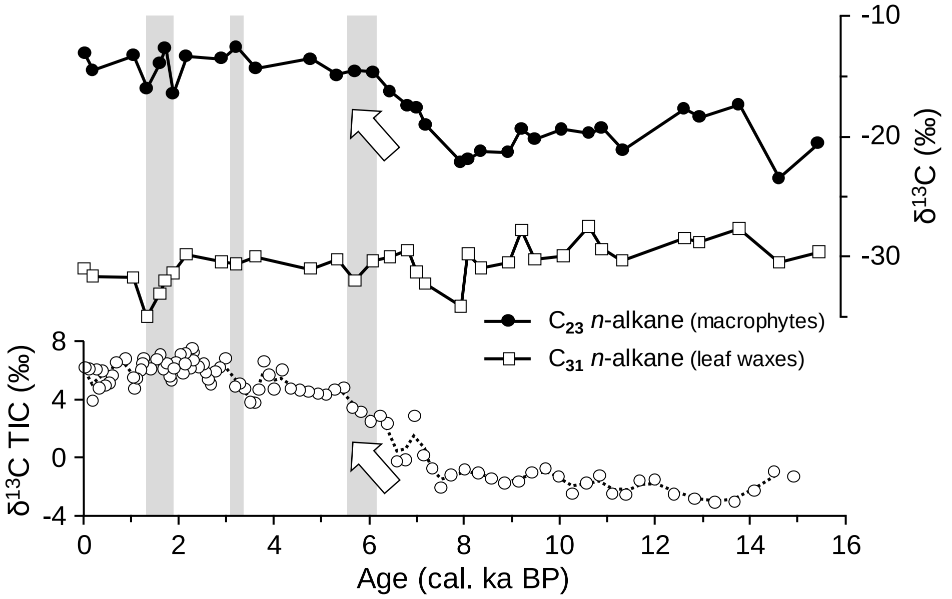


Figure 6: CSI data of the C_{23} *n*-alkane from macrophytes and the terrestrial C_{31} *n*-alkane compared to the $\delta^{13}C$ values of bulk TIC in Lake Koucha (eastern Tibetan Plateau), suggesting CO_2 limitation due to enhanced productivity after 7 cal ka BP (grey bars: cold periods, dashed line: 3-point running average; modified from Aichner et al., 2010b).

The widened scope and an improved understanding of isotope fractionation affecting *n*-alkyl lipids in modern ecosystems has led to a rapid increase in studies targeting a wider range of alkyl lipids for the gain of more specific paleoenvironmental information in recent years. An increasing number of studies apply *n*-alkyl lipid $\delta^{2}H$ values for paleohydrological reconstruction, illustrating the substantial promise of this novel method (Sachse et al., 2012).

Rach et al. (2014) studied the precisely dated varved sediment record from Lake Meerfelder Maar (Germany) to reconstruct changes in hydroclimate over Western Europe at the onset of the Younger Dryas, using *n*-alkane δ^2H values. By comparing the δ^2H records of the terrestrial C_{29} *n*-alkane and the aquatic C_{23} *n*-alkane (assumed to derive from macrophytes such as *Potamogeton* sp.) the authors were able to differentiate between the effects of temperature changes, aridification, and moisture source changes and could confirm a 170-year delay between atmospheric cooling in Greenland and hydrology change over Western Europe, which is also backed by palynological data from the site. A later study by Rach et al. (2017) of the Holocene section of the same sedimentary record focussed on the Subboreal-Subatlantic climate transition around 2.8 ka and found terrestrial *n*-alkane δ^2H values to confirm the establishment of cooler and wetter conditions, potentially associated with a change in atmospheric trajectories. A sediment record spanning the same time interval obtained from the Netherlands (Engels et al. 2016; van den Bos et al., 2018) shows an opposite δ^2H-trend around this time, which could be explained by a change in the atmospheric circulation pattern resembling the negative phase of the North Atlantic Oscillation. Notably, Rach et al. (2017) also observe a large change in δ^2H values of aquatic lipid biomarkers (C_{21} and C_{23} *n*-alkane) of up to 30 ‰, which the authors assume to result not just from hydrological change but also from ecosystem change as it coincides with a strong increase in aquatic plants and algal remains in the palynological record.

The combination of δ^2H and $\delta^{13}C$ values of the C_{29} *n*-alkanes in a Norwegian peatland was used to reconstruct Holocene changes in the seasonality of rainfall, one of the more elusive factors determining CSI data outside the monsoon regions (Nichols et al., 2009; Fig. 7).

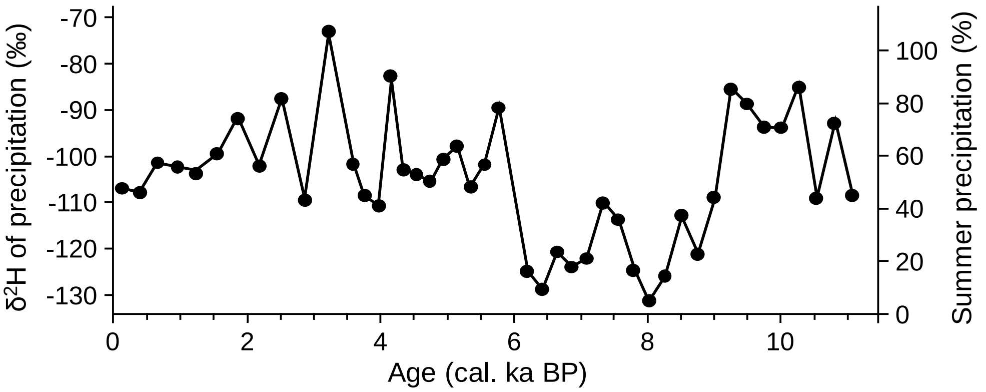


Figure 7: Seasonality of precipitation in NW Norway during the Holocene, expressed as the proportion of summer precipitation and reconstructed from *n*-C_{29} alkane δ^2H values (modified from Nichols et al., 2009).

Although *n*-alkanes are well established as target compounds for CSIA they frequently are a minor TLE fraction compared to *n*-fatty acids or *n*-alcohols (see, e.g., Cranwell, 1981; Otto and Simpson, 2005; Berke et al., 2012; Holtvoeth et al., 2016), which can provide valuable alternative data when the amount of sample material and extractable *n*-alkanes are too low for CSIA. Tierney et al. (2008), for example, applied hydrogen isotope (δ^2H) analysis of the leaf wax-derived C_{28} *n*-fatty acid to sediment cores from Lake Tanganyika (East Africa) to reconstruct variations in precipitation patterns over the past 60,000 years in order to better understand the processes that control climate in the tropics. Their data show that this understudied region experienced abrupt paleohydrological changes coeval with orbital and millennial-scale events recorded in Northern Hemisphere monsoonal climate records (Fig. 8). These results provide sound evidence for a strong control of Indian Ocean surface temperatures and winter Indian monsoon on precipitation in southeast Africa.

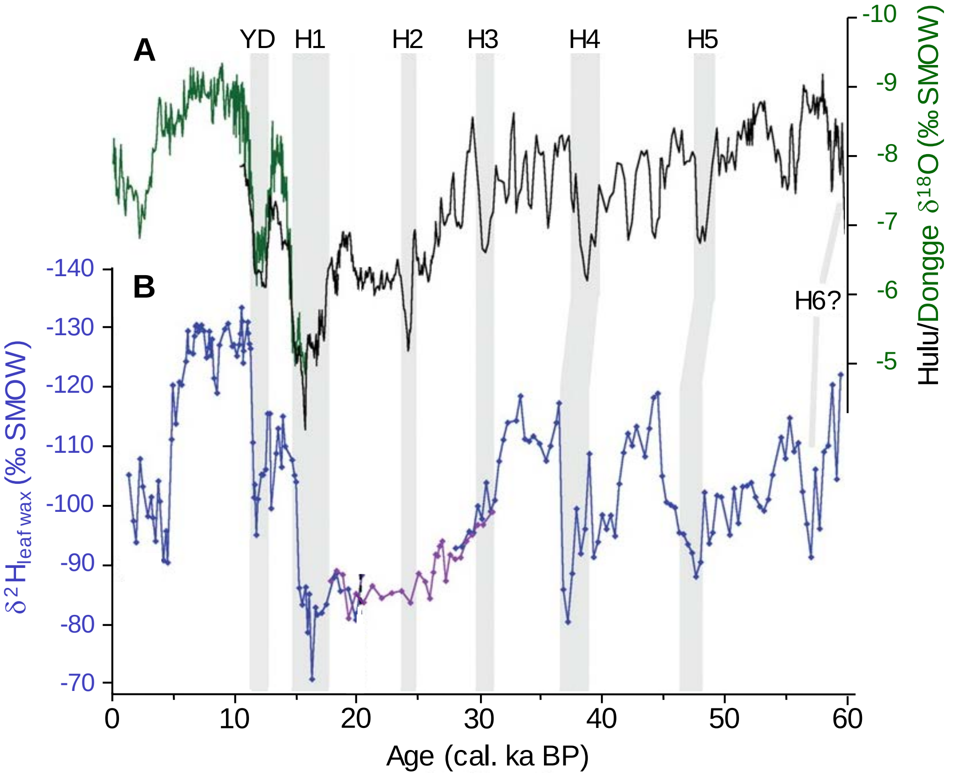


Figure 8: The close correlation of the δ^2H values of leaf wax-derived C_{28} *n*-fatty acid in sediments of Lake Tanganyika (B) with the $\delta^{18}O$ records of the Hulu and Dongge caves (A) reveal the close linkage between Northern Hemisphere monsoon variability and East African hydrology over the past 60,000 years (YD = Younger Dryas, H1-6 = Heinrich events 1-6; modified from Tierney et al., 2008).

A study by Berke et al. (2012) on sediments of the past 14 kyrs from Lake Victoria combines $\delta^{13}C$ data of the C_{29} *n*-alkane and, due to the relatively low abundance of *n*-alkanes, δ^2H data of the C_{28} *n*-fatty acid with a biomarker-based temperature proxy (TEX_{86}; Section 3.3) in order to reconstruct hydrologically controlled changes in the catchment, in particular, changes in the proportion of C3 and C4 plants. The data are then compared to equivalent data from other African settings, specifically, δ^2H data of the C_{28} *n*-fatty acid from Lakes Challa (Tierney et al., 2011), Tanganyika (Tierney et al., 2008) and Malawi (Konecky et al., 2011) and of the C_{29} *n*-alkane from higher plants of the Congo Basin (Schefuß et al., 2005) and the Zambezi River catchment (Schefuß et al., 2011). Berke et al. (2012) find their reconstruction in good agreement with other African records and illustrated the spatiotemporal propagation of drier and cooler conditions across East and North Africa after a warm and humid early Holocene as well as the influence of monsoonal moisture supply in periods of maximum seasonal contrast between Northern and Southern Hemisphere insolation. Notably, the authors observe a mismatch between their *n*-alkane δ^{13}C values and palynological data which they attribute to different source vegetation for leaf waxes and pollen from around the lake, underscoring the value of multiproxy approaches. The δ^2H values of the *n*-fatty acids, on the other hand, should be independent of this as they are determined by the δ^2H value of meteoric water rather than interspecies differences in biosynthetic processing. Accordingly, the δ^2H values of the *n*-fatty acids do indeed appear coherent with the changes in the amount of precipitation and associated biome adaption postulated by Berke et al., (2012).

Due to the strong control of meteoric water isotope composition over leaf wax δ^2H values that is particularly pronounced in regions with distinct seasonal changes in moisture source a similar approach was taken by Cisneros-Dozal et al. (2014) for a reconstruction of North American monsoon intensity during the late Pleistocene (540 - 360 ka BP). In the sediments of a paleolake in the southwestern US, δ^2H values of the C_{28} *n*-fatty acid reflect the changing intensity of monsoonal moisture supply from the Gulf of Mexico and the Gulf of California, which is seasonally alternating with moisture supply from the cooler North Pacific Ocean. The CSI data resolves the orbitally controlled monsoon variability during interglacials, specifically, during marine isotope stage 11, and thus provides the mechanism driving equivalent changes in pollen, bulk δ^{13}C and GDGT-based temperature data from the same record.

Studying the isotopic composition of *n*-alkyl lipids that are part of tissue types other than cuticular waxes widens the application of CSI data considerably towards aquatic ecosystems as well as towards other terrestrial OM sources such as soil OM (suberin-derived alkyl compounds). In fact, soil OM is the larger carbon reservoir compared to living biomass by a factor of ~2 (Post et al., 1977). The amounts and isotopic composition of suberin-derived α,ω-diacids or C_{22} and C_{24} ω-hydroxy acids can provide evidence for the dynamics of the soil carbon pool (Mendez-Millan et al., 2010) ascribed to changes in vegetation cover or land use change and, thus, support established CSIA of leaf wax *n*-alkanes tracking changing proportions of C3 and C4 plants. Even within a pure C3 river catchment, Alewell et al. (2016), for example, were able to distinguish between contributions to river sediment from different OM sources (forest, agricultural land) using CSI data and concentrations of *n*-fatty acids. In order to investigate the links between the isotopic composition of the major limnic carbon pools, i.e. dissolved inorganic and organic carbon (DIC, DOC), $CO_{2(aq)}$, particulate organic carbon (POC) and algal and bacterial biomass, on the one hand, and lake water pCO_2, food web structure and nutrient regime in lakes of different trophic status, on the other hand, de Kluijver et al. (2014) combined bulk substrate isotope values with CSI data of algal and bacterial fatty acids and glucose. This approach revealed complex interdependencies between carbon pool dynamics and isotope values, with nutrient level being a major factor. In order to assess aerobic methanotrophic bacterial production that is responsible for relatively low methane outgassing in Lake Kivu, Morana et al. (2015) interpreted $\delta^{13}C$ values of *n*-fatty acids, mono-unsaturated and branched fatty acids alongside $\delta^{13}C$ values of methane, DIC and POC from water column profiles. Studying methane production in and outgassing from surface sediments of West, Central and North European lakes, Stötter et al. (2018) found correlations between in-lake methane concentrations and the relative abundance of ^{13}C-depleted mono-unsaturated fatty acids in the sediments that appeared to derive mainly from methane-oxidising bacteria. However, the authors also find that oxygen availability at the sediment-water interface is a major factor affecting the abundance of these compounds. Thus, although reconstructing changes in methane outgassing from lakes would contribute significantly to the understanding of methane cycling in the past, the extension of such approaches into the paleorecord remains a challenge. Glucose has a low preservation potential, for example, and disentangling the sources of microbial biomarkers from communities living in the water column or *in situ* will be an issue. However, in any such attempt, CSIA will provide an essential tool due to the strong fractionation resulting from the consumption of microbial methane, whichever biomarker from a methanotrophic organism one would be studying. We would like to point out the research opportunities that follow from the relations described above between environmental factors and the isotope composition of certain lipids and glucose in soils and modern aquatic ecosystems since the potential of many of these relations for paleoenvironmental proxy development has yet to be explored.

CSIA of long-chain alkenones from incubation experiments with the dominant marine haptophyte species, *Emiliania huxleyi* and *Gephyrocapsa oceanica*, and the coastal species *Isochrysis galbana* demonstrated that the δ^2H value of the alkenones is generally determined by the δ^2H value of the water and, to a significant extent, by salinity (e.g., Englebrecht and Sachs, 2005; Schouten et al., 2006; M'boule et al., 2014; Weiss et al., 2017). Haptophyte growth rate is another modifying factor (Schouten et al., 2006; M'boule et al., 2014). The concept of alkenone δ^2H values tracking salinity was applied, e.g., by van der Meer et al. (2007) to sedimentary alkenones in the eastern Mediterranean where the alkenone δ^2H value strongly correlates with enhanced freshwater supply during sapropel formation. In a Holocene sediment core from an estuarine site on the west coast of Florida, alkenone δ^2H values also appear to have varied to some extent with salinity (van Soelen et al., 2014), however, such relation was not seen, e.g., in alkenones in suspended particles and surface sediment from the Chesapeake Bay estuary on the east coast of the US (Schwab and Sachs, 2011). A shift in haptophyte species distribution along with change in salinity is one of the likely reasons for the weak or absent correlation between alkenone δ^2H values and salinity in brackish coastal settings. In North American saline lakes, Nelson and Sachs (2014) observe a correlation, particularly, of the δ^2H value of the $C_{37:4}$ alkenone in the surface sediment with lake water δ^2H, although this appears weaker than in the marine realm. As far as we are aware at the time of writing, the applicability of alkenone δ^2H for reconstuctions of salinity changes in a lacustrine setting has yet to be tested, ideally, for an extant lacustrine environmental archive where the evolution of both salinity and algal species can also be determined by other means.

Schouten et al. (2001) and D'Andrea and Huang (2005) determined the δ^{13}C values of alkenones in sediments of Antarctic and Arctic saline lakes and found further ^{13}C depletion in the alkenones relative to other biomarkers such as fatty acids, sterols and steranes, with δ^{13}C values of the alkenones of -35 ‰ (Schouten et al., 2001) to -42 ‰ (D'Andrea and Huang, 2005). These offsets are not straightforwardly explained and low growth rates and high concentrations of dissolved CO_2 due to the low water temperatures in the investigated settings remain hypothetical causes for enhanced fractionation during alkenone biosynthesis. D'Andrea and Huang (2005) again refer to the uncertain source of the alkenones in Arctic lakes but point out the possibility that the isotopic fingerprint of the alkenones may relate to specific ecological conditions. Similarly, a 1 ‰ shift in alkenone δ^{13}C values in mid-Holocene sediments from a restricted estuary (Charlotte Harbour, Florida) may also derive from a shift in species distribution and an associated change in fractionation as isotopic change in DIC could be ruled out based on δ^{13}C values of carbon from foraminifera (van Soelen et al., 2014). We are currently not aware of CSIA of alkenones in pure freshwater systems, for which the potential of such application for paleoenvironmental reconstructions remains to be explored.

3.2 Amino acids

3.2.1 Sources

Amino acids are biologically ubiquitous compounds present in all organisms, both in the form of proteins (polypeptides, i.e. chains of amino acids) and as precursors and intermediates in the biosynthesis of other essential biomolecules, such as porphyrins, neurotransmitters in animals, and lignin in plants. Heterotrophic organisms typically cannot biosynthesise all amino acids they require, i.e. some amino acids have to be assimilated through food sources. These are known as essential amino acids or source amino acids. By contrast, nonessential amino acids are synthesised by heterotrophs through enzymatically controlled addition of ammonia (NH_3^+) to metabolic intermediates, commonly pyruvate, oxaloacetate, α-ketoglutarate, in a process called transamination (for details see, e.g., Lengeler et al., 1999; Chikaraishi et al., 2009). Like many enzymatically controlled biosynthetic reactions, transamination and deamination (removal of ammonia) inherit isotope fractionation (Gaebler et al., 1966) and, in this case, result in ^{15}N enrichment of the nonessential (or trophic) amino acids (McClelland and Montoya, 2002; Chikaraishi et al., 2007). Thus, the nitrogen isotopic composition of essential and nonessential amino acids in heterotrophic organisms is determined by the source (essential amino acid) and by the level of metabolic processing (nonessential amino acid). Phenylalanine (Phe), for example, is an essential amino acid in mammals and undergoes few metabolic steps in which fractionation could occur, therefore, $\delta^{15}N_{Phe}$ values represent those of the diet, and ultimately the base of the food web. Phe is therefore referred to as a source group amino acid. On the other hand, glutamic acid (Glu) plays a central role in amino acid biosynthesis, and so $\delta^{15}N_{Glu}$ values reflect the amount of N metabolic cycling between the base of the food web and the consumer tissue, and is referred to as a trophic group amino acid (McClelland and Montoya, 2002; O'Connell, 2017).

It is thus possible to estimate the trophic position of organisms in aquatic and terrestrial ecosystems using an equation based on the differing trophic ^{15}N enrichments of Glu and Phe, of approximately 8 ‰ and 0.4 ‰, respectively (Eq. 2):

$$\mathrm{TL}_{\mathrm{Glu-Phe}} = \frac{\delta^{15}\mathrm{N}_{\mathrm{Glu}} - \delta^{15}\mathrm{N}_{\mathrm{Phe}} - \beta}{7.6} + 1$$ ***Equation 2***

where β is the difference between Glu and Phe at the base of the food web being studied (Chikaraishi et al., 2009; Chikaraishi et al., 2010; Yamaguchi et al., 2017). This method has benefits over using a bulk method, as the $\delta^{15}N$ values of these amino acids provide an internal trophic position measure, without the need to measure the flora and fauna contributing to the diet (Chikaraishi et al., 2007, 2009).

3.2.2 Applications

CSIA of amino acids has developed into a tool to improve our understanding of nitrogen transfer in modern aquatic food webs (e.g., Uhle et al., 1997; McClelland and Montoya, 2002; McCarthy et al., 2007; Yamaguchi et al., 2017). An increasing number of studies successfully apply nitrogen as well as carbon CSIA of amino acids to track amino acid production in the limnic water column as well as microbial processing during sinking and in surface sediments (e.g., Carstens et al., 2013). In paleolimnological contexts, the application of CSIA of amino acids has so far been limited due to the relatively low preservation potential of amino acids and the uncertainties associated with nitrogen fractionation affecting individual amino acids during and after entering the sedimentary record. Carstens et al. (2013) observe an early diagenetic decrease of amino acid-bound nitrogen relative to the total nitrogen from 38 to 10 % in the top 6 cm of sediment in two Swiss lakes as well as changes in the δ^{15}N values of amino acids that are also likely to result from *in situ* microbial processing rather than changing inputs over time. Further evidence for heterotrophic alteration of selected amino acids from detrital organic matter leading to a scattered amino acid δ^{15}N pattern is provided in a critical review of amino acid nitrogen CSIA in environmental contexts by Ohkouchi et al. (2017), with the authors concluding that understanding how exactly microbial activity alters amino acid δ^{15}N patterns “remains a frontier area of CSIA-AA applications”. Thus, while amino acid δ^{15}N values may provide information on both organic matter sources and microbial degradation, these processes will have to be understood before any proxy can be reliably applied.

3.3 Glycerol-dibiphytanyl-glycerol tetraethers (GDGTs)

3.3.1 Sources

Isoprenoidal etherlipids, in particular archaeol and hydroxyarchaeol (diethers) or glycerol dibiphytanyl glycerol tetraether lipids (iGDGTs, Fig. 8A) are the predominant membrane lipids of archaea (Langworthy, 1982, 1977; Langworthy et al., 1972; Schouten et al., 2013). Archaea are widespread in mesophilic settings: marine and lake sediments (MacGregor et al., 1997; Vetriani et al., 1998), soils (Hershberger et al., 1996; Leininger et al., 2006), and the ocean (DeLong, 1992; Fuhrman and Davis, 1997; Karner et al., 2001). Isotopic fractionation has been studied on only a small proportion of cultured organisms (Könneke et al., 2012; van der Meer et al., 2001). The membranes of some bacteria can also consist of diether lipids and tetraether lipids, containing non-isoprenoidal, sometimes methylated, hydrocarbon chains (glycerol dialkyl glycerol tetraetherlipids or branched GDGTs, (brGDGT, Fig. 8B; Sinninghe Damsté et al., 2011b, 2014; Weijers et al., 2006). Sources of brGDGTs comprise microorganisms thriving in lacustrine and riverine environments (Blaga et al., 2010; Tierney and Russell, 2009; De Jonge et al., 2014), peats (Weijers et al., 2006) and soils (Weijers et al., 2007).

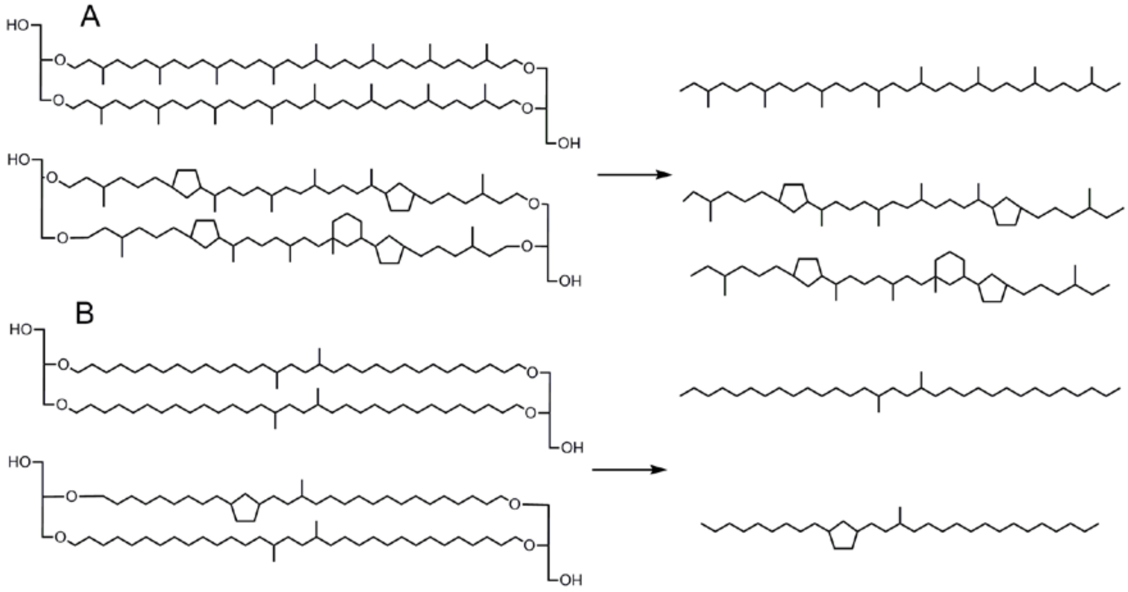


Figure 9: Glycerol-dibiphytanyl-glycerol tetraether lipids (GDGTs) and cleavage products; A: common isoprenoidal GDGTs (iGDGTs) and biphytanes, B: common branched GDGTs (brGDGTs) and branched and cyclic alkanes (modified from Schouten et al., 1998).

$\delta^{13}C$ values of GDGTs are most commonly measured after chemical degradation to biphytanes and branched alkanes (Schouten et al., 1998; Fig. 9), but can also be determined for intact molecules by a spooling-wire microcombustion device interfaced with an isotope-ratio mass spectrometer (SWiM-IRMS*;* Pearson et al., 2016) or possibly by high-temperature GC-IRMS (Lengger et al., 2018). Analytical challenges in the determination of the stable hydrogen isotopic composition are large and only a limited amount of CSI studies focusing on GDGTs have been carried out, so far (e.g., Kaneko et al., 2011).

3.3.2 Applications

The applicability of carbon isotopes of GDGTs for lacustrine environmental reconstructions still has to be tested. However, $\delta^{13}C$ values of GDGTs have been the subject of a significant number of studies of modern environments that work towards the development of GDGT-based paleoenvironmental proxies. These include stable isotope probing experiments aiming to study origin and metabolism of GDGTs (Wuchter et al., 2003; Lengger et al., 2014), and the determination of natural $\delta^{13}C$ values of GDGTs. GDGTs are highly abundant in lakes, and their distributions are well studied as they are used in paleothermometers such as TEX_{86} and MBT (Castañeda and Schouten, 2011). Some are produced *in situ* in the lakes, while others are exogenous and derived from surrounding soils or riverine influx. Provided sources and net carbon isotope fractionation factors for archaeal, planktonic iGDGTs such as crenarchaeol are further constrained, $\delta^{13}C_{biphytane}$ could potentially be used as a paleo-DIC proxy in lakes, as suggested for marine settings (Hoefs et al. 1997, Kuypers et al. 2001, Pearson et al. 2016). Bacterial brGDGTs, on the other hand, have been reported to be depleted by 1 ‰ in ^{13}C compared to the bulk organic carbon in a peat (Weijers et al., 2010); consistent with a heterotrophic lifestyle. However, in lakes (sediments and water column), brGDGTs were found to be varying with $\delta^{13}C$ of POM, but strongly depleted in $\delta^{13}C$ in anoxic bottom waters, with values of -43 to -47 ‰ (10 ‰ depleted compared to TOC, Weber et al., 2015) and -42 ‰ (Weber et al., 2018). Weber et al. (2018) attributed this depletion to uptake of ^{13}C-depleted organic carbon ultimately derived from biogenic methane by the source bacteria living in and below the redox transition under hypoxic and methanotrophic conditions. Thus, $\delta^{13}C$ values of brGDGTs in lake sediments can shed light on organic matter sources and lake biogeochemistry.

$\delta^{13}C$ values of iGDGTs produced by archaea can also be used to study present and past settings of anaerobic oxidation of methane. GDGTs with unusually negative $\delta^{13}C$ values have been found mostly in methane seep environments and euxinic water columns, and are strong evidence for anaerobic methanotrophs (ANME; Hinrichs et al., 1999, 2000; Wakeham et al., 2004; Niemann and Elvert, 2008). Recently, these have been used for the first time to trace anaerobic oxidation of methane in sediments of a freshwater wetland (Segarra et al., 2015).

In summary, there are several potential applications for $\delta^{13}C$ values of GDGTs as proxies in lacustrine and freshwater environments. These range from establishing the presence of anaerobic methane oxidising archaea, to constraining paleo-DIC and organic matter sources.

3.4 Pigment transformation products

Key compounds for photosynthesis, chlorophylls and bacteriochlorophylls are the most abundant pigments on the planet. Their transformation products, chlorins, porphyrins, and maleimides can be preserved in lacustrine and marine sediments. Another important group of pigments in plants and microbes are carotenoids. Pigments contain chromophore groups, typically conjugated double bonds that absorb portions of the visible solar spectrum and give molecules their distinctive colours. Many of the pigments integrate oxygen functional groups that provide sites for microbial degradation, making these compounds particularly sensitive to post-depositional alterations. The major forms of stabilizing alterations are complete aromatization of the chlorophyll tetrapyrrole ring to lead to porphyrins and hydrogenation of carotenoids carbon-carbon double bonds to form isoprenoid alkanes (Fig. 10).

The various chlorophylls differ principally in the alkyl sidechains attached to the central tetrapyrrole ring. The most important sidechain of chlorophyll *a*, the most common photosynthetic pigment, is the ester-linked diterpenoid alcohol, phytol (Fig. 10, see Fig. 11

for biosynthesis). As chlorophylls absorb red wavelengths of solar energy, aquatic phototrophs have evolved different carotenoid compounds as accessory pigments to broaden the range of wavelengths useful for photosynthesis (c.f. Swain, 1985; Sanger, 1988). Many of the accessory pigments are characteristic of different photoautotrophs and this can be used to help identify past sources, synthesis, taphonomy, and freshness of organic matter in limnic records (Naeher et al., 2013).

Chlorophylls undergo minor to major transformations within the water column and in the sediment. These continue during diagenesis and lead to the formation of porphyrins and maleimides (Grice et al., 1996, 1997; Pancost et al., 2002). The reactivity of pigments makes them sensitive indicators of changes in aquatic environments. For example, the diagenetic conversion of chlorophyll to pheophytin is enhanced by acidic conditions, as shown by Guilizzoni et al. (1992) when employed in the reconstruction of the progressive acidification of lakes in the Central Alps.

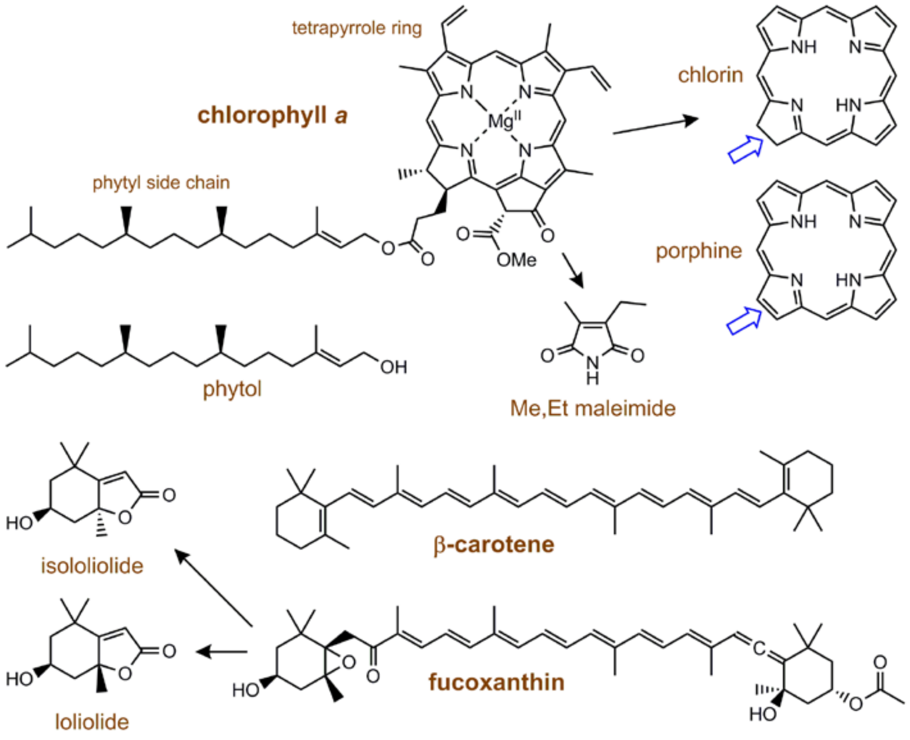


Figure 10: Molecular structures of common pigment types and representative degradation products in limnic settings. Chlorophyll *a* is the dominant chlorophyll and primary photosynthetic pigment. Secondary pigments such as carotenoids (e.g., β-carotene, fucoxanthin) are present in various amounts in plants and algae as well as dinoflagellates. Pigments are rarely preserved intact whereas degradation products such as chlorin, porphyrins (parent structure: porphine) and maleimides from chlorophylls or loliolide/isololiolide from fucoxanthin are frequently observed in lake sediments and can be

used as indicators for photoautotrophs.

3.4.1. Chlorins and porphyrins

3.4.1.1 Sources

Chlorins are broadly defined as chlorophylls and their phaeopigment derivatives central to photosynthesis (Fig. 10) and thus inherently linked to primary producers (Sanger, 1988). As they quickly degrade in light and oxygen, chlorins extracted from water or surface sediments are thought to be derived from synthesis at or close to the collection site, reducing the influence of transport. Degradation of chlorins during diagenesis and transport biases limnic sediments toward autochthonous sources, although chlorins are also synthesized by land plants (Sanger, 1988). Chlorins contain four nitrogen atoms to each molecule (Fig. 10), offering the opportunity for compound-specific $\delta^{15}N$ analysis.

Intensively studied since the 1930s (e.g., Treibs, 1936) porphyrins are aromatic organic compounds that consist of carbon and nitrogen and sometimes contain a metal atom such as magnesium at their centre (e.g., chlorophyll). Whereas chlorins comprise the immediate diagenetic products of chlorophylls, geoporphyrins result from long-term diagenesis (cf. Callot et al., 1990). They have vanadium or nickel in their centre and can be preserved in a wide range of sediments for hundreds of millions of years (Eglinton et al., 1985; Callot and Ocampo, 2000).

3.4.1.2 Applications

The nitrogen isotopic composition of chlorins has been determined from contemporary waters and cultured algae (Sachs and Repeta, 1999; York et al., 2007), as well as from late Quaternary marine and limnic sediments (Sachs and Repeta, 1999; 2000; Higgins et al., 2010), e.g., to provide insights into the marine N-cycle in the Mediterranean sapropel formation. These studies, however, relied upon phaeopigments (Sachs and Repeta, 1999, 2000) or on the coalescence of several chlorin fractions (Higgins et al., 2010). Coupled $\delta^{13}C$ and $\delta^{15}N$ from chlorins extracted from last glacial-interglacial transition sediments of Lake Suigetsu, Japan (Tyler et al., 2010) emphasize both the potential (e.g., the response of aquatic primary productivity to post-glacial environmental change) and further work needed for chlorin-specific isotopes as tracers in lake sediments.

Where ancient sediments are concerned, $\delta^{15}N$ measurements of diagenetic products of chlorins are more prevalent, e.g. metalloalkylporphyrins (Hayes et al., 1987; Ohkouchi et al., 2006 for nitrogen fixation/assimilation) and maleimides (Grice et al., 1996a; Pancost et al., 2002; see Section 3.4.3).

3.4.2 Aromatic carotenoids and maleimides

3.4.2.1 Sources

Carotenoids are usually yellow- to red-coloured lipids formally derived from the irregular C_{40} isoprenoid lycopene carbon skeleton by hydrogenation, dehydrogenation, cyclization and oxidation reactions (Pfenning, 1978). Biosynthesized *de novo* by all photosynthetic bacteria, eukaryotes, halophilic (high salt) archaea, and a large variety of non-photosynthetic organisms, over 600 different carotenoid structures have been identified in modern organisms (Goodwin, 1976; Liaaen-Jensen, 1979; Summons and Powell, 1986). In aquatic sedimentary environments, the only significant biological sources for aromatic carotenoids are green and purple sulfur bacteria, anoxygenic photoautotrophic prokaryotes that inhabit the sulfide-rich, light-limited, and oxygen depleted bottom waters of some lakes and ocean basins (Grice et al., 1996a; Koopmans et al., 1996; Schaeffer et al., 1997).

Maleimides are the oxidation products mainly of the tetrapyrrole nuclei from chlorophyll and/or bacteriochlorophyll related pigments (Fig. 10) and potentially from other sources, e.g., cytochromes (Paoli et al., 2002) and phycobilins from cyanobacteria and rhodophytes (Glazer et al., 1976; Brown et al., 1990), possibly by a transformation pathway involving the oxidation of vinylic chlorophyll substituents and the formation of an aldehyde intermediate during early diagenesis under anoxic conditions (Pickering and Keely, 2011; Naeher et al., 2013). Bacteriochlorophyll (bchl) pigments *c, d,* and *e* (1 and 2; M = Mg, R3 = farnesyl) are exclusively made by green sulfur bacteria (Pfennig, 1978).

3.4.2.2. Applications

Although their multiple double bonds make them reactive compounds that should be interpreted cautiously, source-specific chlorophyll-derived pigments (e.g., carotenoids and maleimides) can be robustly preserved in sediments thousands to millions of years old (as reviewed in Brocks and Summons, 2005), yielding unparalleled information for paleolimnological reconstructions, including details on lake evolution, redox transitions, changing patterns of aquatic primary productivity, and environmental conditions.

The presence of aromatic carotenoids (or bchl derived porphyrins) in lakes provides evidence of anoxygenic photosynthesis in contemporary environments and in sediments, a vast array of diagenetic aromatic components have been identified (Grice et al., 1997; Koopmans et al., 1996) that are derived from green sulfur bacteria (e.g. aromatic compounds isorenieratene/ chlorobactene with a 2.3,6 methyl aromatic substitution pattern) or from okenone from purple sulfur bacteria (e.g. with a 2, 3, 4 methyl aromatic substitution pattern; Brocks and Summons, 2005.) These carotenoids and bchl-derived porphyrins serve as a marker for photic zone euxinia in the past. (Grice et al., 1996a,b; Koopmans et al., 1996; Hartgers et al., 1995; Grice et al., 1997; Grice et al., 2005a; Ocampo et al., 1985;

Whiteside and Grice, 2016).

Furthermore, changes in primary producers can be inferred from the types of pigments that are present in sediments. For example, progressive eutrophication of Esthwaite Water in the English Lake District is recorded by increases in the concentrations of the carotenoids indicative of cyanophytes (Griffiths, 1978). Similarly, in other lake settings, relative abundance changes of bchl *a* relative to bchls *c* and *d* indicate development-related changes in the structure of the bacterial community, leading to increased competition for light or nutrients (Abella et al., 1980; Parkin and Brock, 1980; Rodrigo et al., 2000). Differences in the proportions of bchl *e* and bchls *c* and *d* indicate if brown or green species of green sulfur bacteria dominate in lakes of different depths and where different light regimes and chemical conditions prevail (Vila and Abella, 1994). Wilson et al. (2004) looked at the impact of stratigraphic resolution of sediment depth profiles of bchls *c* and *d*, as revealed by methanolysis, in Kirisjes Pond, Antarctica, and a finely laminated microbial mat from Les Salines de la Trinitat, Spain and showed that bacterial communities are highly sensitive to changing conditions and respond quickly. With regard to primary productivity sources on longer timescales, Kimble et al (1974) demonstrated that the major extractable tetraterpane in the ~50 million-year-old lacustrine Green River Formation is the β-carotene derivative perhydro-β-carotene, suggesting that algal photosynthesis was the primary source of organic matter to this paleolimnologic system.

A recent modern calibration study for past biogeochemical cyclicing of redox-stratified lakes by Fulton et al. (2018) observed distinctive $\delta^{13}C$ and $\delta^{15}N$ values of pigments and nutrients in the water column and surface sediments of Fayetteville Green Lake (New York, USA), which they attribute to seasonally variable populations of cyanobacteria, purple sulfur bacteria and green sulfur bacteria at the chemocline. Informed by these data, and $\delta^{13}C$ and $\delta^{15}N$ values for pyropheophytin and bacteriochlorophyll from the Black Sea deposited during its transition to a redox-stratified basin ~7.8 ka, the authors proposed an isotopic mixing model for nutrient evolution that shows pigment decomposition to a common porphyrin derivative can produce non-specific sedimentary isotope signatures. This model underlines the need for caution and further refinement in paleobiogeochemical interpretations from basins with diverse microbial populations near a shallow chemocline.

Most maleimide studies have looked at the oxidation products of porphyrins in crude oil (e.g., the Quirke et al., 1980 investigation of the Cretaceous Boscan crude oil) and petroleum source rocks (e.g., studies by Grice et al., 1996, 1997 on the Australian Permian Kupferschiefer and Mid-Triassic Serpiano shales that used Me,n-Pr and Me,**i**-Bu maleimides and the Me,**i**-Bu/Me,Et ratio as indicators for Chlorobi and hence, for the occurrence of photic zone euxinia across the end-Permian extinction). In a recent study, Naeher et al. (2013) linked Me,**i**-Bu maleimide to the presence of photic zone euxinic and anoxic conditions in Swiss lake Rotsee during the last 150 years and throughout the Romanian Black Sea history, including the limnic phase. A further need remains for the detection and characterization of maleimides in recent lake bodies and sediments to determine their partly unidentified precursors, their formation processes during chlorophyll/bacteriochlorophyll degradation and importance in terms of environmental conditions, particularly the impact of oxygen. In a recent study towards this end, (Naeher et al,. 2013) proposed Me,Me and Me,Et indices as novel proxies for estimating the degree of organic matter degradation, which are applicable for longer timescales than e.g. the chlorin index.

Carotenoid and maleimide diagenetic products are easily distinguished by CSIA. For example, bacterially derived green sulfur products are ca. 15 ‰ more enriched in ^{13}C than phytoplankton biomarkers (e.g., steranes, hopanoids and steroids) due to the assimilation of CO_2 by the reversed TCA cycle (Quandt et al., 1977) rather than the C3 carbon fixation pathway. Purple sulfur bacteria differ from green sulfur bacteria in that they fix CO_2 by the C3 pathway and are typically depleted in ^{13}C due to assimilation of the lighter carbon that characterises the deeper water column (Hollander et al., 1993; Schaeffer et al., 1997).

3.4.3 Biomarkers derived from porphyrin pigments

3.4.3.1 Regular and irregular isoprenoids

Pristane (Pr) and phytane (Ph), are C_{19} and C_{20} regular isoprenoid alkanes, respectively, that are largely derived from the phytyl side chain of chlorophyll *a* (Fig. 10, phytol biosynthesis in Fig. 11) in many photosynthetic organisms, as well as from bacteriochlorophylls *a* and *b* of purple sulfur bacteria (Pfenning, 1978). Tocopherols are also precursors or pristane in plants (Goossens et al., 1984). Studies from Dead Sea Basin halites and other hypersaline sediments reveal other sources to be ether-linked membrane lipids of halophiles (Ph) and the C_{21} to C_{25} regular isoprenoids (Grice et al., 1998). The C_{15} regular isoprenoid farnesane is largely derived from the side chain of bacteriochlorophylls *c, d, e* in green sulfur bacteria (Pfennig, 1978). Other sources for phytane include methanotrophic bacteria (Freeman et al., 1990).

The C_{20} irregular isoprenoids crocetane (structure in Table 1) and pentamethylicosane (PMI) have been detected in sediments (e.g., Thiel et al., 1999; Barber et al., 2001; Greenwood and Summons, 2003), modern cultures and microbes (Summons et al., 1996). Crocetane can be a thermally formed product of either archaeal biphytane or isorenieratene from green sulfur bacteria (Maslen et al., 2009). PMI is derived from methanotrophic archaea that live in symbiosis with sulfate-reducing bacteria, allowing the oxidation of methane under strict anoxic conditions (Schouten et al., 1997).

3.4.3.2 Applications

The $\delta^{13}C$ of crocetane can reveal whether it stems from a precursor that was biosynthesized by green sulfur bacteria indicative of photic zone euxinia, (values of 11 and -6 ‰) that use the reverse tricarboxylic acid (TCA) cycle (Summons and Powell, 1986) or by archaea engaging in the anaerobic oxidation of methane (AOM; Orphan et al., 2001; values of -150 ‰). Although $\delta^{13}C$ of crocetane has not been measured in Quaternary lake sediment records, a novel study by Tulipani et al. (2015) used relative abundances of methyltrimethyltridecylchromans (MTTCs) and $\delta^{13}C$ values with other biomarker parameters as indicators of riverine freshwater incursions (i.e., a freshwater lens) into Middle to Late Devonian paleoreefs (Canning Basin, Western Austalia), characterised by prevailing anoxia, persistent photic zone euxinia (Spaak et al., 2018) and water column stratification.

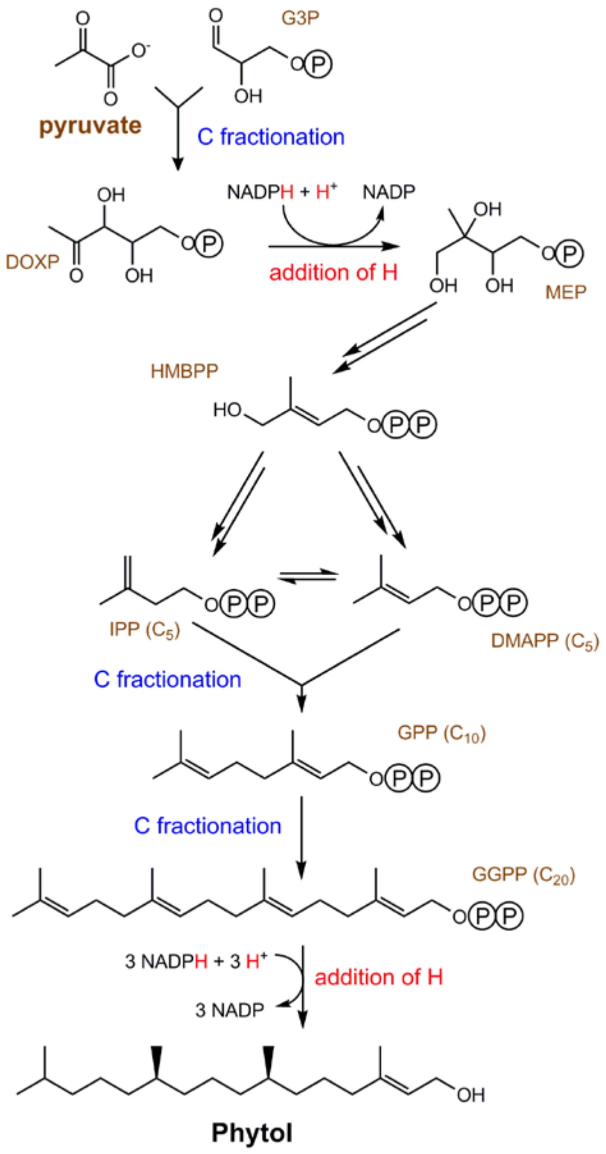


Figure 11: The mevalonate-independent pathway ("DOXP/MEP pathway") for the biosynthesis of phytol via the isoprenoid precursors dimethylallyl pyrophosphate (DMAPP) and isopentenyl diphosphate (IPP), starting with pyruvate produced through the Calvin cycle after CO_2 uptake (Fig. 1); DOXP = 1-deoxy-D-xylulose, G3P = glyceraldehyde-3-phosphate, GPP = geranyldiphosphate, GGPP = geranylgeranyldiphosphate, HMBPP = (*E*)-4-hydroxy-3-methyl-but-2-enyl pyrophosphate, MEP = 2-methyl-erythroyl-4-phosphate, NADPH = nicotinamide adenine dinucleotide phosphate (after Sachse et al., 2012).

3.5 Isoprenoid biomarkers of *Botryococcus braunii*

3.5.1 Sources

Three races of the unicellular green microalga *Botryococcus braunii* are reported (A, B and L), and are characterized by their hydrocarbon lipids. The B race makes C_{30} to C_{37} branched isoprenoidal hydrocarbons called botryococcenes, giving rise to the isoprenoidal biomarkers botryococcane (e.g. Maxwell et al., 1968; Metzger and Largeau, 1999; Grice et al., 1998) and a range of cyclic botryococcenes (Metzger et al., 1985) and polymethylatedsqualenes (Summons et al., 2002). Botryococcane is biosynthesized by the mutual action of separate and distinct squalene synthase enzymes (Niehaus et al., 2011), whereas the L race biosynthesise a C_{40} isoprenoid hydrocarbon, lycopa-14(E),18(E)-diene (Grice et al., 1998 and references therein). B-race biomarkers are indicative of freshwater to brackish lakes and saline seas (e.g. Maxwell et al., 1968; Metzger and Largeau, 1999; Grice et al., 1998; Summons et al., 2002) from varying latitudes (Tyson, 1995).

3.5.2. Applications.

Biomarkers derived from *Botryococcus* are more enriched in ^{13}C compared to other phytoplankton biomarkers in both sediments (Huang et al., 1995; Grice et al., 1998; Huang et al., 1999; Audino et al., 2001; Summons et al., 2002) and culture (Summons et al., 1996). Potential explanations include (1) isotopic fractionation associated with photosynthesis may not be fully expressed due to limiting internal pCO_2 in these microalgae, (2) the thick outer walls may limit the CO_2 diffusion rates, thereby enriching biomass in ^{13}C (Boreham et al., 1994), and (3) *Botryococcus braunii* utilize a ^{13}C-rich bicarbonate source (Huang et al., 1999 and references therein). Sediments recovered from the last glacial maximum have *Botryococcus* biomarkers (Huang et al., 1999) that are significantly enriched in ^{13}C ($\delta^{13}C$ = 5%). These values are attributed to low atmospheric pCO_2 and accompanying depletion of dissolved CO_2 causing these microalgae to assimilate isotopically heavier bicarbonate from their lacustrine environment. The δ^2H of lipids (e.g., alkadienes, botryococcenes, heptadecenes, fatty acids, and phytadiene) from *Botryococcus braunii*, closely follow the δ^2H of the assimilated water (Zhang et al., 2007), and have been used alongside n-alkanes in lacustrine oil shales (torbanites) of Permian to Carboniferous age to disentangle dual-source systems in tropical and glacial environments (Dawson et al., 2004).

3.6 Bacterial hopanes and hopenes

3.6.1 Sources

Bacterial hopanes and hopenes are a class of pentacyclic triterpenoids that comprise membrane lipids produced by bacteria (Rohmer et al., 1984). Although only about ~10% of bacterial types produce bacteriohopanoids, it is generally not possible to link a given hopanoid to a specific bacterial source (Pearson et al., 2007). The use of compound-specific isotopes, however, offers tremendous power for distinguishing among potential bacterial sources of hopanes and hopenes (Freeman et al., 1990). Hopanoid-producing bacteria in limnic settings include photo- and chemoautotrophs, and heterotrophs able to grow on a wide variety of carbon sources (Freeman, 1990; Pancost and Sinninghe Damsté, 2003; Sessions, 2016). Bacterial hopanoids have long been considered functional analogues of eukaryotic sterols (Rohmer et al., 1984), although the specifics of their roles in membranes remain the subject of extensive investigation (e.g. Poralla et al., 1984; Welander et al., 2009; Blumenberg et al., 2012; Eickhoff et al., 2013; Ricci et al., 2017).

Bacteria produce hopanoids from squalene via the mevalonic pathway of squalene biosynthesis as shown in Figure 12, starting with pyruvate and followed by cyclization of squalene to form the C_{30} compounds 17β,21β(H)-hop-22(29)-ene (diploptene; Table 1) and diplopterol, and may build upon the diploptene structure via adenosylhopane to synthesize diverse C_{35} bacteriohopanepolyols (BHPs, Rohmer, 1993; Bradley et al., 2010).

Modifications to the hopanoid structure (methylation at C-2 or C-3, unsaturation within the ring structure, side-chain length and composition) have traditionally been interpreted as indicators of specific bacterial lineages (e.g. Summons et al., 1999; Talbot et al., 2014). However, further research indicates it is increasingly likely that the specific distribution of hopane and BHP structures reflects environmental conditions or metabolic processes rather than, or in addition to, phylogeny (e.g. Ricci et al., 2014; Osborne et al., 2017). Source attribution may yet prove more specific for some compounds (e.g. 35-aminobacteriohopane-30,31,32,33,34-pentol in Type I methanotrophic bacteria; Neunlist and Rohmer, 1985; Talbot et al., 2003; but see van Winden et al., 2012; Rush et al., 2016) or some settings (e.g. hop-17(21)-ene and 2-methylhop-17(21)-ene in methanotrophic *Sphagnum* symbionts; van Winden et al., 2010). Nonetheless, elucidating the relationships between bacterial hopanoid synthesis and environmental conditions will further enhance the information that can be derived from these compounds.

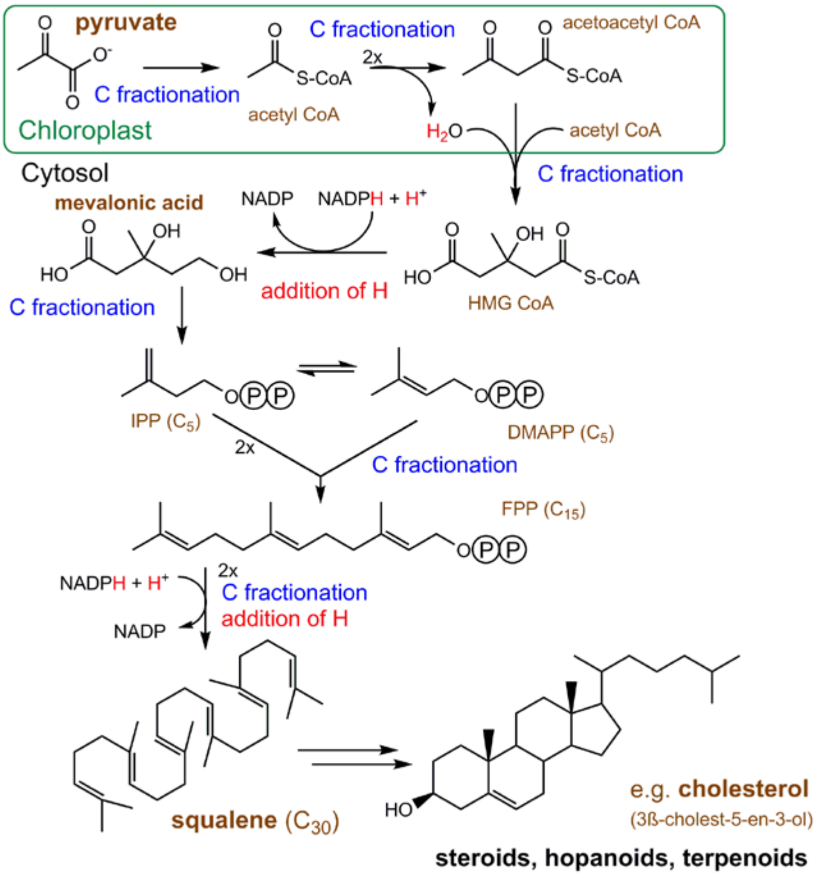


Figure 12: The "mevalonic pathway" for the biosynthesis of squalene, starting with pyruvate produced through the Calvin cycle after CO_2 uptake (Fig. 1); CoA = co-enzyme A, DMAPP = dimethylallyl pyrophosphate, FPP = farnesyl pyrophosphate, HMG = 3-hydroxy-3-methylglutaryl, IPP = isopentenyl diphosphate, NADPH = nicotinamide adenine dinucleotide phosphate (after Sachse et al., 2012).

In marine and freshwater nitrogen cycling, anaerobic oxidation of ammonium (anammox) to dinitrogen gas (N_2) with nitrate as an electron acceptor is an important microbial process performed exclusively by anammox bacteria. A stereoisomer of bacteriohopanetetrol (BHT), BHT II, has been unequivocally identified in culture enrichments of anammox bacteria and oxygen minimum zone waters, microbial hotspots responsible for fixed nitrogen removal (Sáenz et al., 2011; Rush et al., 2014). Given the residence time in geological sediments, the BHT isomer is a potential biomarker for past anammox activity (Matys et al, 2017; and potential expansion of OMZs in warmer worlds of Earth's deep past), which has heretofore eluded detection through ladderane fatty acid abundances in sediments older than 140 ky (Jaeschke et al., 2009).

Carbon isotopic analysis of hopanes and hopenes is by far the most commonly exploited isotope system for bacterial hopanoids (Pancost and Sinninghe Damsté, 2003). In order to deconvolve bacterial hopane and hopene sources, studies often focus on the stable carbon isotopic compositions of C_{29} to C_{31} 17β,21β(H)-hopanes and hopenes (e.g. Aichner et al., 2010b; Davies et al., 2016; Zheng et al., 2014). Analysis of functionalized hopanols (e.g. diplopterol) can be accomplished through derivatization with BSTFA (e.g. Hollander and Smith, 2001), however a correction must be applied to account for carbon added with the trimethyl silica moiety (Jones et al., 1991). Although δ^2H analyses promise to provide substantial further information (Osburn et al., 2016; Zhang et al., 2009), few environmental studies measuring δ^2H in hopanoids have been conducted to date (Sessions 2016; Li et al., 2009). As the topic of stable hydrogen isotopes in paleoenvironmental research has been thoroughly discussed in a recent review (Sessions, 2016), this section focuses on stable carbon isotopes.

3.6.2. Applications

Because carbon source and biosynthetic pathway can have substantial impacts on hopane and hopene carbon isotopic composition, the carbon isotopic composition of hopanes and hopenes is often used to differentiate photoautotrophic and heterotrophic bacterial sources from chemoautotrophic and methanotrophic bacterial sources. This can provide valuable insight into lacustrine carbon cycling, sources of sedimentary organic carbon, cryptic changes in bacterial community composition, and changes in water column structure. For example, Hollander and Smith (2001) demonstrated a striking increase in recycling of carbon associated with the post-1900 AD extreme eutrophication of Lake Mendota through the carbon isotopic composition of hopanol in tandem with other markers of lacustrine primary producers. A similar approach, using compound-specific carbon isotope analyses of hopanes as well as other sedimentary lipids (steranes, pristane, phytane) in the ~50 million-year old lacustrine Green River Formation clearly demonstrated protracted meromixis and abundant chemoautotrophic and menthanotrophic bacteria (Collister et al., 1992).

Many studies that seek qualitative assessment of intensive methane cycling in wetlands and lakes utilize carbon isotope analyses of hopanes. Incorporation of biogenic methane-derived carbon into bacterial biomass results in hopanes with substantial depletions in ^{13}C (Summons et al., 1994; Jahnke et al., 1999; but see also Sakata et al., 2008; and Kool et al., 2014). Although absence of ^{13}C-depletion in hopanes and hopenes is inadequate to exclude methane cycling, the presence of hopanes or hopenes with carbon isotopic compositions of < -40 ‰ is often explained as at least a partial contribution from methanotrophic bacteria (e.g., Freeman et al., 1990; Schoell et al., 1994). This is particularly true in wetland deposits where hopanes are more depleted in ^{13}C than ~-34 ‰ are rarely observed (van Winden et al., 2012; Pancost et al., 2000). For example, in a study of Holocene wetland deposits, Zheng et al. (2014) observed that increased diploptene concentrations with lower $\delta^{13}C_{diploptene}$ (from ~-32 ‰ to -42 to -50 ‰ around 6.4 to 4 thousand years ago) coincided with decreased abundances of lipids derived from methanogens and locally dry conditions. Zheng et al., (2014) attribute this combination of observations to increased efficiency of aerobic methane oxidation and bacterial incorporation of methane-derived carbon under drier conditions. Consequently, drier phases had a two-fold impact on wetland methane emissions through decreased methanogenesis as well as more efficient aerobic methanotrophy.These findings provide a mechanism linking changes in wetland water balance and the Asian monsoon with the mid-Holocene decrease in atmospheric methane concentrations, findings which have been robust to further study over a longer timescale (18kyr; Huang et al., 2018). For glacial-interglacial cycles, Talbot et al. (2014) showed the highest abundance of highly specific BHP biomarkers for aerobic methane oxidation, 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol) from the Congo River Basin correlated with warm intervals. CSIA for BHPs indicate aminopentol was likely supplied by terrestrial watershed or gas hydrates/subsurface reservoirs. This study is a demonstration of the large potential of aminoBHPs to trace and, once better calibrated and understood, quantify past methane sources and fluxes.

In lacustrine settings, methane incorporation into bacterial biomass is greatest in localized areas of diffusive methane flux, rather than plant-mediated or ebullition (Davies et al., 2016). Even so, several studies have effectively documented changes in incorporation of methane derived carbon in hopanoids as a function of climatic conditions (water balance, temperature) or anthropogenic factors (eutrophication). Elvert and colleagues (2016) demonstrate that the Holocene Thermal Maximum is associated with enhanced methane processing in a North American Arctic thermokarst lake. Aichner et al. (2010b), as part of a broad paleolimnologic investigation of Lake Koucha in the eastern Tibetan Plateau, observe an increase in the concentration of ^{13}C-depleted hopanoids, including diploptene (-45.5 to -62.7 ‰), beginning around 7,000 cal BP. The authors attribute this increase in both bacterial contribution to sedimentary organic matter and incorporation of methane-derived carbon into bacterial biomass to lake freshening. Naeher et al. (2014) utilize the previously determined eutrophication history of Lake Rotsee, Switzerland to examine trends in biomarkers associated with methane cycling. This analysis indicated that increased primary productivity and stratification led to an increase in the concentrations of ^{13}C-depleted diploptene (-60 to -43 ‰) and homohopanoic acid (-64 to -45 ‰), although the two compounds' concentrations and isotopic compositions exhibit a complex relationship, suggesting a larger role for methane oxidizing bacteria from the 1930s onward in Lake Rotsee (Fig. 13). While some lake hopanoid CSIA datasets indicate active incorporation of methane-derived carbon for long timescales (e.g., Street et al., 2012), this is not the case for all lakes (e.g., Huang et al., 1999; Sarkar et al., 2014).

Despite the insights afforded by CSIA of bacteriohopanoids into relative changes in the intensity of assimilatory methane oxidation, diverse sources of uncertainty and the idiosyncratic natures of lakes and wetlands impede efforts to devise a generalizable or quantitative proxy for assimilatory methane oxidation or methane emissions. Consequently, much additional work remains to be done to refine the use of hopanoid carbon isotopes to assess past changes in limnic carbon cycling.

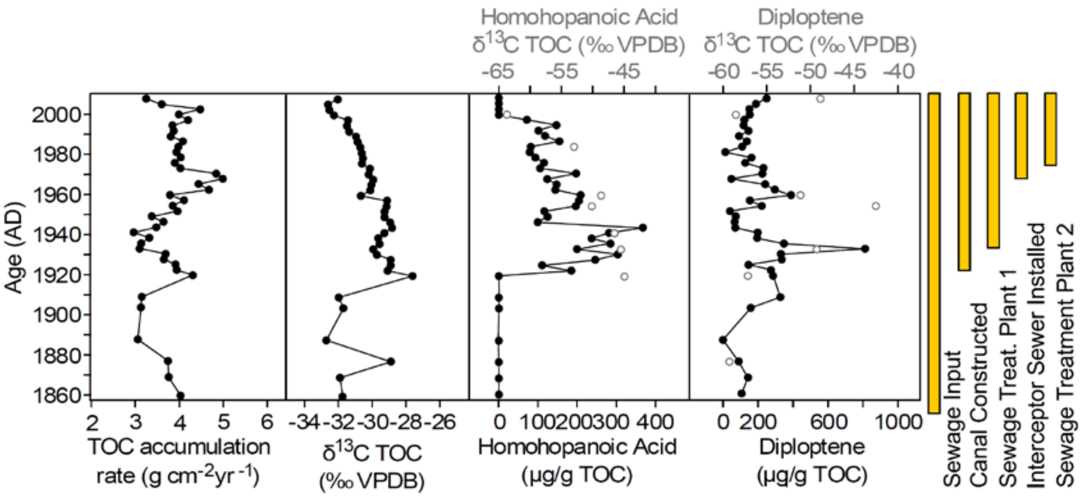


Figure 13: Homohopanoic acid and diploptene reflect changes in methane cycling as a function of anthropogenic impacts on Lake Rotsee, Switzerland (modified from Naeher et al., 2012; 2014). Persistent nutrient inputs associated with sewage inputs, coupled with water balance and sedimentation impacts of canal construction triggered eutrophication and stratification. This increased organic matter supply combined with anoxia drove increases in bacterial productivity (hopanoid concentrations) and incorporation of biogenic methane into bacterial biomass (carbon isotopic composition of hopanoids).

3.7 Steroids

3.7.1 Sources

Sterols, the biological precursors of steranes commonly found in sedimentary rocks, are a diverse group of polycyclic isoprenoids (tetracyclic triterpenoids) characteristic of Eukarya (Rohmer et al., 1979; Volkman, 1986). Sterols represent a significant fraction of the lipid pool in marine algae (Jones et al. 1994), and play a key structural role in organisms, including control of cell membrane fluidity, cell signaling, phagocytosis, and stress tolerance (Bloch, 1991; Castoreno et al., 2005; Volkman, 2005). Like hopanoids, sterols are biosynthesized following the same mevalonate pathway that produces the C_{30} isoprenoid squalene (Figure 12, section 3.6). Biosynthesis continues with the epoxidation of squalene (C_{30}) to oxidosqualene, followed by a subsequent cyclization to two intermediate molecules (protosterols), cycloartenol and lanosterol, respectively (e.g., Volkman, 2005; Summons et al., 2006). A series of enzymatic oxidation and decarboxylation steps leads to the formation of animal and fungal steroids (e.g., cholesterol [C_{27}] and ergosterol [C_{28}]) from lanosterol, and the formation of plant sterols (e.g., sitosterol [C_{29}]) from cycloartenol. In contrast to hopanoids, the biosynthesis of sterols is oxygen-dependent (e.g., Summons et al., 2006). Although Eukarya are the primary producers of sterols, a limited number of steroid structures have also been reported in a small number of bacteria, including cyanobacteria (e.g., Pearson et al. 2003; Volkman 2003, 2005). A recent study, however, indicates that the potential for bacterial sterol synthesis may occur more widely than previously thought (Wei et al., 2016).

The diversity of sterols is determined by the number of carbon atoms in their skeleton (e.g., C_{26-30}), the position of hydroxyl (alcohol) functional groups in the ring system, the position of unsaturations (double bonds) in the ring structure and side chain, and differences in ring and/or side-chain alkylations (e.g., Volkman, 1986; Volkman, 2005). While some sterols can be considered characteristic of a given algal class, many of them are widely distributed and less diagnostic. For instance, 24-norcholesterol (C_{26}) has been reported in some diatom and dinoflagellate species (Rampen et al., 2007); cholesterol (C_{27}) is typically found in red algae and metazoa (Volkman, 1986, 2003; Volkman et al., 1998; Kodner et al., 2008); 24-methylcholesterol (C_{28}) is present in chlorophyll-c containing algae (dinoflagellates, coccolithophores, diatoms) and prasinophytes (Volkman, 1986, 2003; Volkman et al., 1998; Kodner et al., 2008; Rampen et al. 2010); 24-ethylcholesterol (C_{29}) is found in green algae, prasinophytes, diatoms and land plants (Volkman, 1986, 2003; Volkman et al., 1994, 1998; Kodner et al., 2008; Rampen et al. 2010); 24-*n*-propyl-cholesterol (C_{30}) is present in Chrysophytes and pelagophytes (Moldowan, 1984; Volkman et al., 1998). Additionally, 23,24-dimethyl-cholesterols are present in dinoflagellates and haptophytes, while 4-

methylsterols and 4,23,24-trimethylcholesterol (dinosteranes) derive mostly from dinoflagellates (de Leeuw et al., 1983; Summons et al., 1987; Withers 1987; Mansour et al., 1999).

The diagenesis of sterols leads to modifications in their molecular structure as a result of photo oxidation, oxidation, reduction, dehydration, rearrangement, hydrogenation, and aromatization (e.g., Mackenzie et al., 1982; Meyers and Ishiwatari, 1995; Peters et al., 2005). These reactions result in the loss of double bonds and/or hydroxyl groups, and the generation of stanols, stanones, sterenes, and aliphatic and aromatic steranes. Due to their broad diversity, relative specificity, and stability in sediments, the distribution and abundance of sterols and steranes preserved in sedimentary records have been long used in paleoenvironmental reconstructions (e.g., Grantham and Wakefield, 1988; Meyers and Ishiwatari, 1993; Hinrichs et al., 1999; Menzel et al., 2003; Knoll et al., 2007; Kasprak et al., 2015; Brocks et al., 2017).

3.7.2 Applications

While sterols have been successfully applied in paleolimnological studies to trace changes in algal and other organic matter sources (e.g., Aristegui et al., 1996; Matsumoto et al., 2003; Tani et al., 2009) or redox changes (Matsumoto et al., 2003), few studies have explored the full potential of the ecological and environmental information encoded in their stable isotopic composition. The stable carbon isotope composition ($\delta^{13}C$) of sterols, as well as other algal lipids, is controlled by multiple biological and environmental factors, including the isotopic composition of dissolved inorganic carbon (DIC), carbon transport mechanisms, isotopic fractionation during carbon fixation and biosynthesis, growth rates, cell geometry, and nutrient availability, among others (Pancost et al., 1999; Popp et al., 1999, Schouten et al., 1998, Hayes, 2001; Pancost and Pagani, 2006, Cernusak, et al., 2013). Thus, if some of the factors controlling their stable isotope composition can be constrained, the $\delta^{13}C$ of sterols present in aquatic environments can be used to, for instance, disentangle changes in biological sources (e.g., algal *vs*. land plants; Matsumoto et al., 1982; Canuel et al., 1997; Neunlist et al., 2002; Chikaraishi et al., 2005; Chikaraishi and Naraoka, 2005), the diagenetic transformation of sterols to stanols (Neunlist et al., 2002), the possible sources of other algal lipids such as alkenones (D'Andrea and Huang, 2005), and prevailing biogeochemical conditions (e.g., nutrient availability, carbon cycling, primary productivity, the concentration and isotopic composition of inorganic carbon pools, changes in column stratification; Hollander and Smith, 2001; Villinski et al., 2008). A step forward in tracing the specific sources of organic matter preserved in lacustrine environments is the paired analysis of carbon and hydrogen stable isotopes in sterols ($\delta^{13}C$-$\delta^{2}H$). By using the $\delta^{13}C$-δD sterols present in Lake Haruna, Japan, Chikaraishi and Naraoka (2005) were able to disentangle the complexity of single and mixed (aquatic vs. terrestrial) sources in this setting. For instance, while the $\delta^{13}C$-$\delta^{2}H$ values of sedimentary 24-methylcholesta-5,22-dien-3β-ol corresponded well to those of planktonic algae, the $\delta^{13}C$-$\delta^{2}H$ of sterols such as 24-ethylcholest-5-en-3β-ol indicated a mixture of sources from terrestrial C_3 plants and planktonic algae (Fig. 14). Overall, the results from this study confirmed observations that $27\Delta^{5,22}$, $27\Delta^{5}$, $27\Delta^{0}$, and $28\Delta^{5,22}$ sterols are algal products, while $28\Delta^{5}$, $29\Delta^{5,22}$, and $29\Delta^{5}$ sterols can derive from multiple sources, thus allowing their more reliable use in paleolimnological and paleoclimatic reconstructions.

The $\delta^{13}C$ of sterols, along with other algal and bacterial biomarkers preserved in lake sediments, has also been utilized to develop eutrophication models over time (Hollander and Smith, 2001). By studying the diversity, mass accumulation rate, and $\delta^{13}C$ of biomarkers present in sediment from Lake Mendota (south-central Wisconsin, USA), in addition to the present-day isotopic dynamics in the lake water column, these authors produced eutrophication models (from moderate to severe) that take into account changes in eukaryotic- and microbially-derived productivity over time. Notably, these models allow to explain how microbially-mediated carbon cycling processes can influence the $\delta^{13}C$ record of bulk sedimentary organic carbon, and thus provide insight into interpreting carbon isotopic trends preserved in lacustrine records. Additionally, the presence of ^{13}C-depleted sterols in sediment of Ace Lake in Antarctica was used to constrain the presence of aerobic methanotrophic bacteria and an active methane cycle in this setting during the Holocene (Coolen et al., 2004b).

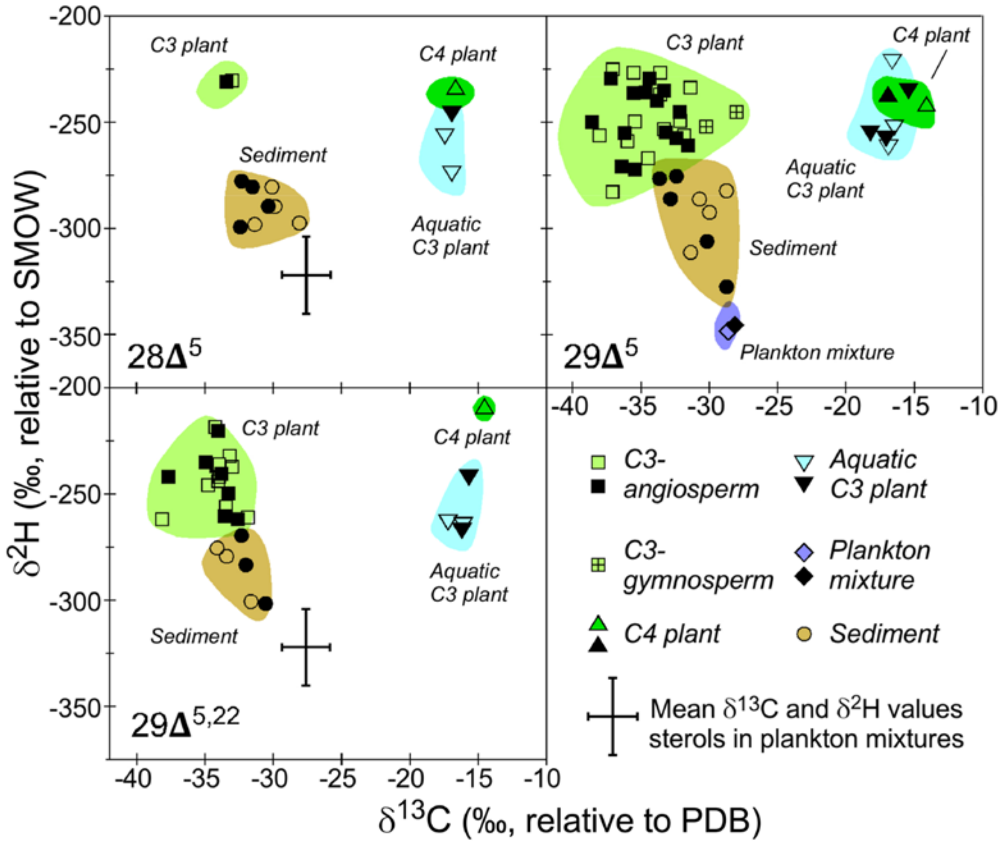


Figure 14: Cross plots of δ^{13}C-δ^{2}H of 28Δ^{5}, 29Δ^{5,22}, and 29Δ^{5} sterols from the Lake Haruna environment. Open and filled symbols indicate the naturally occurring i.e. "free" sterols and bound forms, respectively (modified from Chikaraishi and Naraoka, 2005).

More recently, along with other algal lipids such as alkenones (Section 3.2), the δ^{2}H of sterols present in aquatic environments has increasingly been used as a proxy for the δ^{2}H of environmental water ($\delta^{2}H_{water}$, see review by Sachse et al., 2012). Sauer et al. (2001b) first showed that the δ^{2}H of 24-methylcholest-3-ol, 24-ethylcholest-5,22-dien-3-ol, and 4,23,24-trimethylcholesterol extracted from aquatic sediments exhibited a rather constant fractionation (around ~201±10‰) with respect to environmental water. Since then, a growing body of research has demonstrated that, besides $\delta^{2}H_{water}$, biological factors such as biosynthetic pathways, secondary hydrogen exchange, growth rates, in addition to environmental factors such as salinity, temperature, and nutrient availability can influence hydrogen isotope fractionation and the δ^{2}H of sterols (Sessions et al. 1999, Li et al. 2009, Chikaraishi et al. 2004, Zhang and Sachs 2007; Zhang et al., 2009; Sachse et al., 2012; Romero-Viana, 2013; Nelson and Sachs, 2014). Over the past few years, the δ^{2}H of source-specific sterols such as dinosterol have also been shown to be controlled by salinity. The δ^{2}H of dinosterol present in suspended particles and surface sediment from the Chesapeake Bay (salinity range of 10–29 PSU) exhibits a ^{2}H /^{1}H fractionation that decreases by 0.99 ±

0.23 per unit increase in salinity (Schwab and Sachs, 2011). While the exact mechanism controlling isotopic fractionation under varying salinity remains elusive, the observed relationship in sterols and other lipids supports qualitative to semi-quantitative reconstructions of past salinities from sedimentary dinosterol δ^2H values. For example, the δ^2H of dinosterol preserved in sediments from a brackish lake in Palau (Sachs et al., 2009; Richey and Sachs, 2016) and an endorheic lake in Galápagos (Atwood and Sachs, 2014; Nelson and Sachs, 2016), have been used to infer variations in salinity and precipitation associated with latitudinal shifts in the position of the Intertropical Convergence Zone during the Late Holocene. The information embedded in the δ^2H of sterols in sedimentary records, however, is gradually lost over geologic timescales due to hydrogen exchange with increasing thermal maturity (Sessions, 2016).

3.8 Sedimentary cellulose

3.8.1 Sources

Cellulose is a structural carbohydrate and plays an essential role for cell growth and development of higher plants forming a major component of vascular plant organic matter (Khezami et al., 2005). Non-vascular plants, such as bryophytes and some algae (Rho and Litzky, 1979; Koyama et al., 1997), and bacteria (Ross et al., 1991) are also capable to synthesize cellulose. Potential sources for sedimentary cellulose are therefore terrestrial plants, soils, aquatic macrophytes, bacteria, and algae. Cellulose is biosynthesized from initial photosynthates (trioses) converted to hexoses and condensed to form cellulose (Hayes, 2001). Cellulose microfibrils, consisting of bundles of cellulose molecules, are completely embedded into a matrix of polysaccharides (hemicellulose) and small amounts of structural proteins in cell walls (Showalter, 1993; Popper et al., 2011) and, thus, not easily accessible for decomposing organisms.

3.8.2 Applications

The isotopic composition of oxygen, carbon, and hydrogen in the molecular structure of aquatic cellulose provides information on cellulose origin, the lacustrine carbon cycle and the lake-water balance. Here, we focus on the determination of the oxygen isotope composition of sedimentary cellulose ($\delta^{18}O_{cell}$), which either can be of terrestrial (litter, plant debris, soil) or aquatic origin (aquatic macrophytes, algae, bryophytes). The δ^{18}O value of aquatic cellulose is closely linked to the host water isotopic composition (Sauer et al., 2001a; Sternberg et al., 2007; Zhu et al., 2014a; Mayr et al., 2015), while terrestrial cellulose is generally more ^{18}O-enriched due to soil evaporation and leaf water transpiration (Roden et al., 2000). In many cases, aquatic and terrestrial cellulose sources contribute to bulk sediment $\delta^{18}O_{cell}$ values, which is a challenge for paleoenvironmental interpretation. In this respect, multiple-proxy approaches, including analyses of C/N ratios of bulk sediment and $\delta^{13}C$ of cellulose, can give valuable clues for interpretation (Heyng et al., 2014, c.f. Figure 15). Alternatively, identifiable cellulose-containing macrofossils can be extracted from the sediment and analysed. Hence, some studies focus on cellulose extracted from aquatic moss remains in sedimentary sequences (Mayr et al., 2013; Zhu et al., 2014b). In other cases, the environmental setting precludes major terrestrial cellulose input, e.g. for lakes with very small or scarcely vegetated catchments (Heyng et al., 2014).

The $\delta^{18}O$ values of cellulose, calcite and diatom opal from the Last Glacial to Holocene time intervals of the sediment record of Polish Lake Gosciaz were analysed to disentangle host water isotope variations from temperature changes (Rozanski et al., 2010). While at least two unknowns, temperature and host-water $\delta^{18}O$, influence calcite and opal $\delta^{18}O$ values, $\delta^{18}O_{cell}$ was used to directly reconstruct host-water $\delta^{18}O$ and thus resolve temperature-$\delta^{18}O$ equations of the other proxies. A similar approach was used for a 6000-year long, Holocene record from Lake Pupuke, New Zealand (Heyng et al., 2015). In that study, $\delta^{18}O$ values of biogenic opal and $\delta^{18}O_{cell}$ were combined to reconstruct fluctuations of lake-water temperatures and compared with independent temperature reconstructions using GDGTs. Both temperature reconstructions matched comparatively well. In dry regions, the lake-water-isotope composition is strongly influenced by evaporative heavy-isotope enrichment. Host-water-isotope reconstructions from $\delta^{18}O_{cell}$ can then provide information about past lake-water balance and regional hydrology in such areas. Zhu et al. (2014b) used $\delta^{18}O_{cell}$ of submerged aquatic mosses from sediments of Laguna Potrok Aike to reconstruct lake-water $\delta^{18}O$ of this Patagonian steppe lake during the last deglaciation.

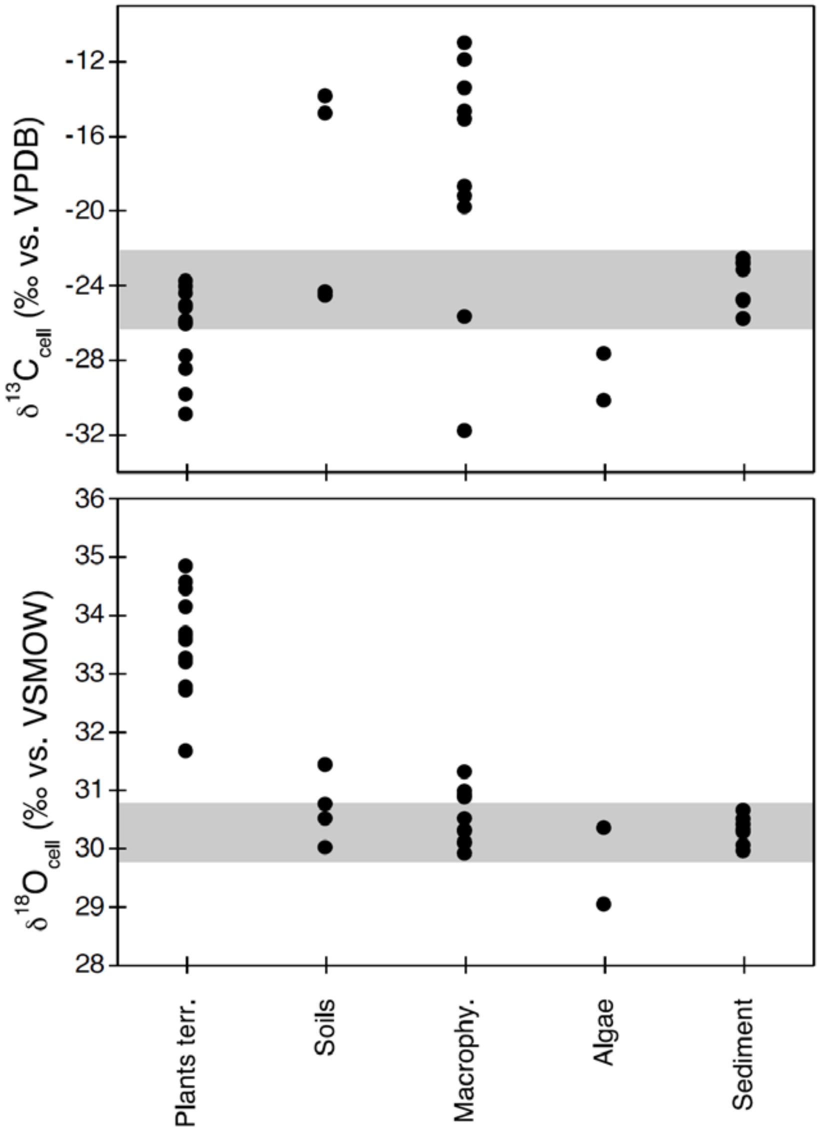


Figure 15: Stable isotope composition of cellulose from autochthonous and allochthonous sources and sediment from a modern survey at Lake Pupuke (Heyng et al., 2014). Shown are $\delta^{13}C_{cell}$ (upper) and $\delta^{18}O_{cell}$ (lower) values from terrestrial plants, soils, aquatic macrophytes, lacustrine algae, and lake sediments (upper 30 cm). Grey bars indicate the range of Lake Pupuke's sediments. Note the ^{13}C enrichment of aquatic macrophytes in that lake, while terrestrial plant cellulose is strongly ^{18}O enriched compared to other sources and sediments.

3.9 Organic sulfur compounds

3.9.1 Sulfur sources

The use of stable isotopes to understand the biogeochemical cycling of sulfur in oceanic (Rees et al., 1978; Jørgensen et al., 2004; Böttcher et al., 2006), freshwater (Fry, 1986; Canfield et al., 2010; Zerkle et al., 2010), and terrestrial systems (Goldhaber and Kaplan, 1980; Habicht and Canfield, 2001) has principally focussed on the dynamics of inorganic sulfate, sulfide and their intermediate species. Organic sulfur compounds (OSCs) in sedimentary organic matter are predominantly incorporated via secondary processes (Werne et al., 2008). The major sulfurization pathway involves an abiotic reaction of reduced inorganic sulphur species during diagenesis (e.g., pore water HS^-; or polysulfides, S_x^{2-}) that is produced by microbial sulfate reduction (Kaplan and Rittenberg, 1964; Fry et al., 1986). OSCs deposited from biological sources (e.g., the amino acid cysteine), which are synthesized through direct reduction and assimilation of dissolved sulfate, are very labile to diagenetic loss (Hedges, 1992; Hedges and Keil; 1995), but may still contribute to sedimentary organic matter which commonly has $\delta^{34}S$ values that range between those of biotic (relatively high $\delta^{34}S$) and abiotic (lower $\delta^{34}S$) end members (Canfield et al., 1998; Passier et al., 1999; Werne et al., 2003; Aizenshtat and Amrani, 2004). Few studies (e.g., Amrani et al., 2009; Oduro et al., 2011, 2012) have looked at the S isotope composition of OSC.

Thermochemical sulfate reduction (TSR) can also contribute high concentrations of OSCs in gas (i.e., high H_2S) reservoirs. TSR is a high temperature redox process in which sulfates, such as gypsum or anhydrite, are reduced and organic matter oxidised (Krouse et al., 1988; Cross et al., 2004). TSR can significantly influence the $\delta^{34}S$ of OSCs, which will gradually inherit the $\delta^{34}S$ value of the mineral sulfates utilised, these are typically relatively heavy compared to OSCs from reduced S sources (Amrani et al., 2012).

In recent years the advent and utilization of quadruple sulfur isotopes (^{32}S, ^{33}S, ^{34}S, and ^{36}S) has allowed for increased resolution and fingerprinting of the biological and abiotic processes that govern sulfur cycling. The minor isotopes (^{33}S, and ^{36}S) are subject to inorganic and organic fractionation mechanisms that are similar to those for ^{34}S. Experimental studies have shown that biological S metabolisms produce minor isotope patterns, with characteristics attributed to differences in the individual step controls of the metabolic pathways (Farquhar et al., 2003, 2007; Johnston et al., 2005, 2007, 2008; Ono et al., 2006). The incorporation of minor isotopes into studies allows for fuller characterisation within biogeochemical systems (at both the cellular and ecosystem level) and as such can be used to assess the contribution of different pathways (enzymatic or biogeochemical) to the measured isotopic values.

3.9.2 Applications

Early biogeochemical applications of CSIA of sulfur-containing compounds have included studies of the mechanism and timeframes of diagenetic organic sulfurization and cycling in sediments, the characterisation of ocean-derived sulfur aerosols, exploration for oil and mineral resources and other paleo-environmental reconstructions. Further details of the first of these, as applied to modern settings, follow:

Diagenetic sulfurization pathways

A combination of syngeneic (water column) and diagenetic (sediment) S sources in immature sediments from the Cariaco Basin were identified by $\delta^{34}S_{OSCs}$ (Raven et al., 2015). These two main organic sulfurization mechanisms consisted of:

i) Reaction of dissolved HS^- with OM resulting in the intra-molecular addition of available S. Difficulties in releasing intra-molecularly bound S make this a relatively irreversible reaction. The incorporation of ^{32}S would be kinetically favored, thus, leading to organic S lower in ^{34}S than HS^- and more similar to co-existing pyrite.

ii) Reaction of OM with polysulfides (S_x^{2-}) resulting in an intermolecular addition and formation of S_x-bridges between different organic units. A reverse of this process could subsequently release the S_x-bridges from the organic moiety, such that $\delta^{34}S$ of this organic S would be reflective of the equilibrium status of these reactions.

Raven et al. (2015) considered pathway ii) to be most likely responsible for the relative ^{34}S enrichment (e.g. Amrani and Aizenshtat, 2004) traditionally attributed to organic sulfurization and the formation of the kerogen fraction.

Tracing organic sulfur cycling in modern lakes

Oduro et al. (2013) and Zerkle et al. (2010) utilized quadruple S isotope systematics and zero-valent sulfur (ZVS), volatile organic sulfur compounds (VOSCs) and acid-volatile sulfur (AVS) profiles as part of a multi-year study on the meromictic Fayetteville Green Lake (FGL, Fig. 16). Stratification in the lake is mainly controlled via the inflow of highly saline groundwater, resulting in a strongly developed chemocline, while the source of both organic and inorganic sulfur is from high sulfate concentration in the water column. These conditions make the site a natural analogue for ancient environments.

Zerkle et al. (2010) showed that at the chemocline sulfide is enriched in ^{34}S as a result of sulfide oxidation via reaction with O_2, from the oxidized freshwater above, in spite of the high population of phototrophic S-oxidizing organisms observed at the chemocline. They further suggested that the production of product sulfur species, e.g., thiosulfate, sulfite, or zero-valent sulfur, was a result of very fast turnover of S-intermediates by oxidation and/or disproportionation processes around the chemocline. Their data also showed seasonal variations in isotopic enrichment at the chemocline as a result of greater contribution from phototrophic S-oxidation reactions under higher light availability in spring and summer. ZVS in the chemocline in autumn is suggested to reflect production and re-oxidation by phototrophic processes, including intercellular isotope exchange between S_0, polysulfides, and sulfide, and further oxidation of ZVS to sulfate. Smaller fractionations between sulfide and zero-valent sulfur in April suggest a metabolic rate control on the extent of fractionation, similar to that of sulfate-reducing prokaryotes.

Oduro et al. (2013) built upon this study by quantifying VOSCs in the lake and highlighting the various biotic and abiotic pathways available for methylated and non-methylated VOSCs production and cycling in sulfidic freshwater environments (Fig. 16). These applications, while focused on modern-day lakes, have implications for our abilities to identify such processes in the preserved horizons of paleolakes and similar environments. While such studies of VOSCs in the ancient rock record are limited due to issues of maturity, the overprints and alteration, greater understanding of these processes in modern analogues may provide a new way to fingerprint products of these processes that are identifiable in the rock record. Further, with the development of new analytical techniques, greater machine resolution, the ability to screen, and reduce, post-deposition organic contaminants, and better sample processing (e.g., Brocks et al., 2008; Brocks and Hope, 2013) we can hope to soon be able to readily identify these compounds in the rock record.

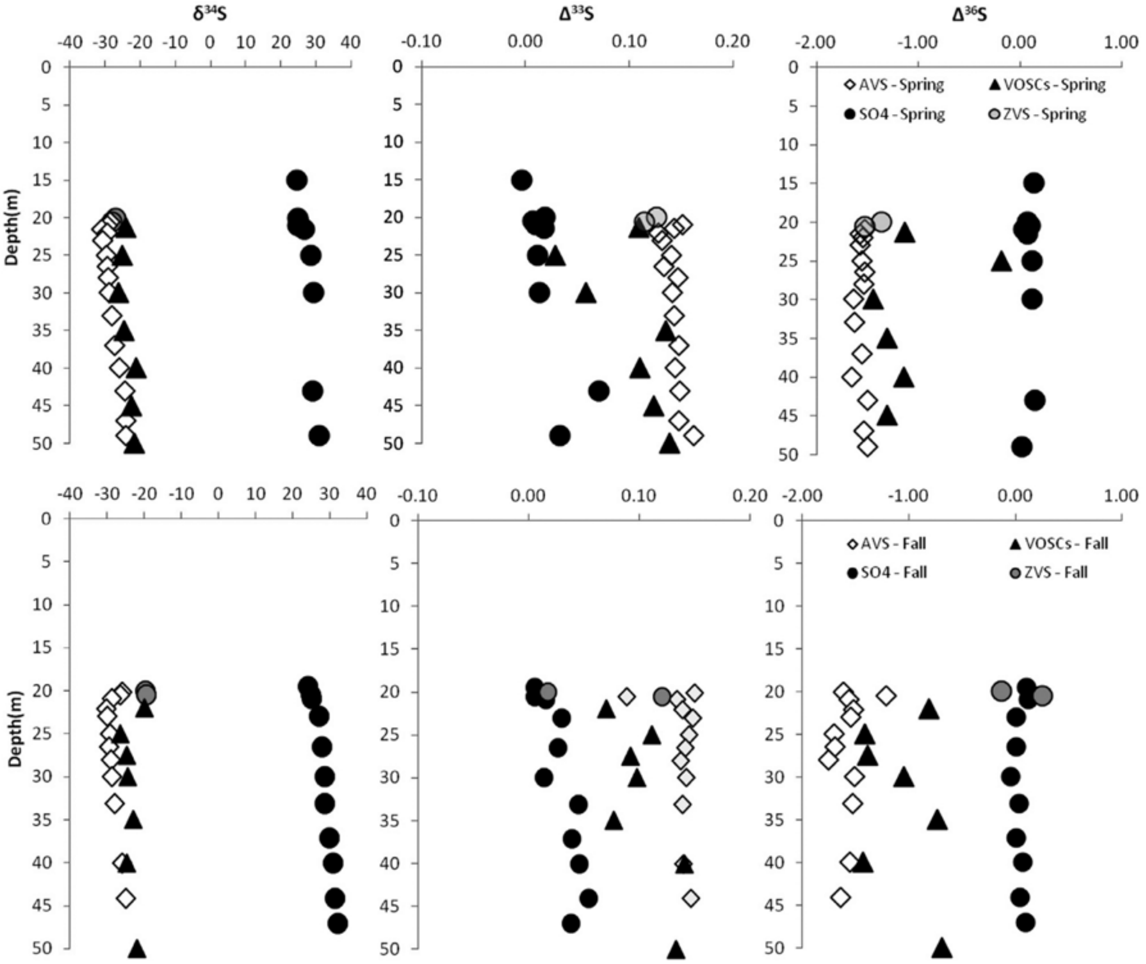


Figure 16: Depth profiles of the multiple sulfur isotope composition of different sulfur species (Sulfate – SO_4^{2-}, Acid Volatile Sulfur - AVS, Volatile Organic Sulfur Compounds –

VOSCs, and Zero-Valent Sulfur – (ZVS) in Fayetteville Green Lake (FGL) for Spring, 2009 and Fall, 2008. From Oduro et al., 2013, including data from Zerkle et al., 2010)

In addition, the studies discussed above highlighted the role of simultaneous biological and abiotic processes in freshwater environments that promote the formation of VOSCs and then their diffusion to the atmosphere. Further characterization of these processes will aid in improving estimate of the atmospheric sulfur budget in present and Recent times.

4 SUMMARY AND OUTLOOK

Over the past four decades, applications of CSIA have vastly expanded into multiple paleoenvironmental applications using an extended range of isotopes and ever more sophisticated analytical techniques. The study of carbon and hydrogen isotopes of hydrocarbons such as *n*-alkanes is by now well-established as they are non-functionalized, of well-understood origin and straightforward to analyse. However, there remain a number of challenges, and particularly so for compounds where the biosynthetic pathway is not fully understood, the source varies, or where there are analytical constraints.

4.1 General problems

i) Biosynthesis

It has been observed that compounds produced through different biosynthetic pathways can differ in their carbon isotope value by up to 20% within an individual organism (e.g., Summons et al., 1994; Schouten et al., 1998; van der Meer et al., 1998). However, the exact mechanisms leading to these isotopic differences are often not well-constrained (Hayes, 2001), which may lead to ambiguous results unless biochemical studies improve our understanding of differentiated fractionation within source organisms of biomarkers targeted by CSIA.

ii) Ecological factors

A key factor imposing carbon and hydrogen isotopic variation in land plants is water-use efficiency, as observed in C3, C4 and CAM plants (Ehleringer et al., 1993), which is controlled by local hydrology. In case of aquatic organisms, a range of ecological factors has been found to inflict isotopic variation, including the partial pressure of $CO_{2[aq]}$ ($pCO_{2[aq]}$), cell size and geometry (Goericke et al., 1994; Popp et al., 1998), virus interactions and the growth rate of phytoplanktonic cells (Laws et al., 1995; Bidigare et al., 1997; Chivall et al., 2014). These findings highlight the need of culture studies, in particular, of lacustrine primary producers since most of such investigations so far, like the ones cited above, have been aimed at marine or coastal species.

iii) Source uncertainties

In-situ microbial biomass may add to and bias CSI data of supposedly aquatic or terrestrial sources, and the distinction between genuine change in the isotopic composition of sedimentary compounds and changing proportions of *in-situ* biomass often poses a challenge. In this context, combining biomarker CSI and rDNA analyses in order to pin down the source of specific microbial compounds appears highly promising (e.g., Coolen et al., 2004b).

We have already pointed out some of the more specific challenges associated to isotope analyses of the various compound classes discussed in Section 3. However, challenges typically come along with opportunities, in this case, of further paleolimnological information gained through extended approaches to CSIA, which we expand on in the following.

4.2 Targeting the C and H of alkyl lipids – the easy, the tricky, and the prospective

Applications of CSIA of alkyl lipids as presented in Section 3.1 illustrate the great potential of such measurements for the development of paleohydrological proxies in Quaternary paleolimnology on a range of different time-scales, from the early Pleistocene to the Holocene. However, these examples, as well as recent reviews (e.g., Eglinton and Eglinton, 2008; Sachse et al., 2012; Reiffarth et al., 2016; Sessions, 2016; Diefendorf and Freimuth, 2017), also indicate some gaps in our understanding of alkyl lipid stable isotopes. The fractionation pathways of stable carbon isotopes and stable hydrogen isotopes, in particular, need to be better understood in order to be able to arrive at robust reconstructions of paleohydrological changes. Changes in species distribution in response to ecosystem adaption to environmental change alone may be responsible for significant change in the δ^2H values of non-species-specific aquatic biomarkers (e.g., Rach et al., 2017). Laboratory-based growth experiments as well as studies of isotope fractionation in modern ecosystems continue to expand the knowledge of the biogeochemical fingerprint of the various OM sources and our understanding of the origins and functions of alkyl lipids through time. Despite the many influences on the δ^2H or δ^{13}C values of alkyl lipids in environmental archives, much of the variability that results, e.g., from seasonality or the patchiness of organic matter sources in the catchment of the studied archive is averaged out due to intermediate storage of the compounds over extended time intervals in soils and/or along transport across the catchment (e.g., Oakes and Hren, 2016). Still, the effects of changes in the source vegetation on CSI records are often understudied and cannot be determined by isotope analysis alone (e.g., Rach et al., 2017). Studies combining independent indicators of vegetation change, such as pollen or macrofossil analysis, and compound-specific stable isotope analyses can highlight where factors other than climate played a role. Such information is especially needed when, e.g., δ^2H-records of long-chain *n*-alkyl lipids are used to calculate terrestrial evaporation (e.g., Sachse et al., 2004; Rach et al., 2014) as this has been problematic in cases where vegetation was diverse and showed spatiotemporal variability (e.g., Berke et al., 2012; Rao et al., 2014; Rach et al., 2017; van den Bos et al., 2018).

Furthermore, the importance of the soil organic matter pool as a source of biomarkers in sedimentary records is increasingly recognised. Systematically changing offsets, for example, in $\delta^{13}C$ values between suberin-derived mid-chain (C_{22}) and cuticular long-chain lipids ($>C_{26}$) have been reported (Holtvoeth et al., 2017). However, despite the apparent environmental control, they cannot be interpreted unless the mechanisms behind the mismatch between cuticular and suberin alkyl lipid CSI are understood. In this context, the transport pathways of biomarkers from their source to the sediment archive are currently understudied. Specific organic matter fractions are likely associated to certain grain size fraction in soils as well as sediments (Baldock and Skjemstad, 2000; Gentsch et al. 2015; Wakeham and Canuel, 2016). Therefore, the combination of paleohydrological and mineralogical data with source-sensitive CSI data is advisable. Where possible, alkyl lipids and their isotope values from extant sources should be investigated in order to reduce the uncertainty in the interpretation of CSI data from environmental archives (e.g., Eley et al., 2016). Studies that use multiple *n*-alkyl compounds (e.g., *n*-alkanes, *n*-alkanoic acids) or combine $\delta^{13}C$ and $\delta^{2}H$ measurements are still few but will likely enhance our understanding of how alkyl lipids are ultimately preserved in geological records (Sachse et al., 2012; Sessions, 2016; Diefendorf and Freimuth, 2017).

Long-chain alkenones remain a challenge for CSI studies in lakes due to the biodiversity of their source organisms and, therefore, the uncertainty associated to the ecological drivers of lacustrine alkenone production and isotope fractionation during biosynthesis. Similar to the marine biome, salinity appears to be a major factor affecting the $\delta^{2}H$ value of lacustrine alkenones, in addition to assumed effects of growth rate (e.g., Chivall et al., 2014). Thus, $\delta^{2}H$ values of lacustrine alkenones may potentially be applied to lake systems that experienced large climatically controlled changes in salinity throughout their evolution once the sources of the alkenones have been ascertained. As phylogenetic shifts among the alkenone producers are also likely to correlate with environmental changes, it appears advisable to combine CSI with DNA studies of alkenone producers in both modern and ancient contexts, in particular, with regard to alkenone producers in freshwater systems that are currently under-investigated.

4.3 Propping up steroids and hopanoids

The $\delta^{13}C$ and $\delta^{2}H$ of algal sterols and steranes offers great potential for the reconstruction of Quaternary ecosystems and environments. This includes changes in organic matter sources, shifts in algal communities and productivity, as well as variations in the isotopic composition of DIC and meteoric water, and salinity. However, the need for multiple purification steps prior to analysis and for correction of the determined isotope ratio for derivatised carbon and hydrogen atoms currently precludes a more routine use of sterols in high-resolution paleoenvironmental studies. Dinosterol has become the most commonly used sterol for CSI analysis, particularly for δ^2H, due to its biological specificity compared to other sterols. Several new preparatory protocols using high performance liquid chromatography (HPLC) have been developed for its purification from complex sterol/alcohol mixtures (e.g., Smittenberg and Sachs, 2007; Atwood and Sachs; 2012; Nelson and Sachs, 2013).

CSIA determined from hopanes will have continued utility in deconvolving modern and ancient carbon cycling. Whereas bacterial inputs, especially with respect to inputs of methanotroph-derived material (c.f. Talbot et al 2014; Raghoebarsing et al., 2005), as such do not demonstrate that methanotrophy was actually taking place, significantly ^{13}C-depleted hopanoids are difficult to explain otherwise. Stable isotope probing and “pulse-chase” experiments are likely to offer substantial advances in understanding the applications and limitations of compound-specific isotope analysis of hopanoids (Crossman et al., 2001). CSIA of derivatized BHPs improves our ability to analyze compounds with potentially greater source/metabolic specificity; this will certainly fuel new and broader applications. For instance, further work on applications of the BHT isomer as a potential biomarker for anammox activity will greatly expand our knowledge of the complexity of nitrogen fixation processes in lacustrine ecosystems. A better understanding of the drivers of hopanoid synthesis will improve application of all hopanoid-based proxies. Coupling hopanoid CSIA with archaeal lipids is a powerful approach to reconstructing prokaryotic roles in past ecosystems and response to environmental change.

4.4 Shedding light on pigments

Research into disentangling the complex array of factors that affect the synthesis, transformation and sedimentation of pigment transformation products in the modern environment is required to facilitate a more rigorous approach to interpreting isotope ratios in pigments extracted from sediments. For example, we can anticipate that further work on phaeopigments, such as limnic phaeophytin and pyrophaeophytin (Tyler et al., 2010), especially in redox-stratified basins (Fulton et al., 2018), will improve paleoenvironmental interpretations of chlorin-specific isotopic data. In addition, studies focused on environmental conditions, including the impact of oxygen (particularly in the case of maleimides, c.f. Naeher et al. 2013) can assist the development of novel proxies for estimating the degree of organic matter degradation on a variety of timescales.

4.5 Buttressing cellulose

Interpretation of sedimentary cellulose $\delta^{18}O$ values for reconstructions of lake-water ^{18}O (Section 3.6.2) has to consider that variable contributions of terrestrial cellulose can modify the aquatic isotope signal. The choice of adequate sites with scarcely vegetated catchment is one option to overcome this potential bias. Methodological difficulties may have also biased previous results (Beuning et al. 2002). The development of the CUAM method for cellulose extraction (Wissel et al., 2008) therefore was a milestone for gaining pure cellulose from sediments albeit its potential is not yet fully explored due to the scarcity of comparative studies. The applicability of the method is sometimes limited by low content of cellulose in lacustrine sediments, which is typically in the order of 0.1 wt% in productive lakes (Heyng et al., 2014). Uncertainties still exist regarding the exact oxygen-isotope fractionation factors between source water and cellulose, possibly due to methodological challenges. Reported fractionation values vary between 25 ‰ and 32 ‰ according to different studies and preparation methods (Wolfe, et al. 2001; Mayr et al. 2013, 2015). The occurrence of a temperature effect on oxygen-isotope fractionation during cellulose formation is still discussed (Sternberg and Ellsworth, 2011; Mayr et al., 2013). A potential methodological extension is the recent development of an analytical procedure for $\delta^{18}O$ analyses on hemicellulose-derived sugar biomarkers (Zech et al., 2014; Hepp et al., 2015).

4.6 Sulfur on the horizon

Compound-specific $\delta^{34}S$ analysis will help to illuminate the operation of organic sulfur cycles of the past and present. A rapid transition is anticipated from the current practice of measuring the bulk $\delta^{34}S$ isotopic value of whole sediments or major organic fractions to measuring the $\delta^{34}S$ composition of individual molecular species – similar to the uptake of compound specific $\delta^{13}C$ and $\delta^{2}H$ technologies. Further maturity of the technology for CSIA of sulfur-containing compunds should lead to greater improvements in analytical performance (i.e., precision and reproducibility <±0.5 ‰) and further targeted application leading to a better understanding of the properties, interactions and fate of organic sulfur in lake basins.

4.7 Stones unturned

Although the understanding of the various fractionation factors associated to amino acid biosynthesis and metabolism is constantly improving, the fact that they also have a low preservation potential in lacustrine sediments may limit their applicability for paleoenvironmental studies. Still, as demonstrated by Carstens et al. (2013) for shallow sediments (6 cm) of an oligotrophic and a eutrophic lake, $\delta^{15}N$ values of amino acids did preserve the different trophic status of the two lakes. Thus, for studies that aim to investigate recent anthropogenic ecosystem change, e.g., in the context of industrialization or urbanization, amino acid $\delta^{15}N$ values may hold promising information on changes in nutrient loading, while the limit of such an approach going back in time remains to be tested.

Some compounds have been frequently observed but appear notoriously understudied. One such example is loliolide and its epimer, iso-loliolide. They represent the end pieces of the carotenoid pigment fucoxanthine (Fig. 10) and are formed in equal quantities during the anaerobic degradation of the compound (Repeta, 1989), which is the main pigment in diatoms but also occurs in dinoflagellates and haptophytes (Repeta and Gagosian, 1982; Klok et al., 1984). Loliolide and iso-loliolide are frequently detected in marine sediments (Repeta and Gagosian, 1982; ten Haven et al., 1987; Repeta, 1989; Hinrichs et al., 1999b; Menzel et al., 2003) but have also been found in significant amounts in sediments of Lake Kivu (Al-Mutlaq et al., 2008), Lake Malawi (Castañeda et al., 2009, 2011), Lake Challa (van Bree et al., 2018) and Lake Ohrid (J. Holtvoeth, unpublished data). While they have been used as biomarkers for diatoms for reconstructing changes in the marine (Hinrichs et al., 1999b) and limnic phytoplankton community (Castañeda et al., 2009, 2011; van Bree et al., 2018), only Menzel et al. (2003) determined the $\delta^{13}C$ values of loliolide/iso-loliolide in eastern Mediterranean sediments in order to find evidence for productivity changes during sapropel deposition. We are not aware of any CSI study of these biomarkers in a lacustrine context where, e.g., changes in salinity, CO_2 limitation or productivity could potentially be targeted through CSIA of these algal compounds. The $\delta^{13}C$ of the planktonic iGDGTs has also been reported to contain some information about pCO_2 in marine environments (Kuypers et al., 2002; Pearson et al., 2016). As iGDGTs are also common in lake environments (Powers et al., 2004), they could be exploited for this purpose.

Finally, there is much scope for extending CSIA in future analytical technologies. These include further applications of the relatively new analytical capability of compound-specific $\delta^{34}S$ (Amrani et al., 2012), high-temperature GC-IRMS analysis of GDGTs (Lengger et al., 2018), and the possible expansion of a variety of preparatory LC–MS techniques for purification of steranes and hopanes. Also, the revolutionary ability to measure stable carbon and hydrogen isotopes at specific molecular positions (Eiler et al., 2017) radically enhances the details of the complex processes involved in the biosynthesis of molecules and usefulness as unique environmental informants.

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REFERENCES

Abella, C., Montesinos, E., Guerrero, R., 1980. Field studies on the competition between purple and green sulfur bacteria for available light (Lake Siso, Spain). In: Dokulil, M., Metz, D., Jewson, D. (eds.), Developments in Hydrobiology, 3. Junk, The Hague, pp. 173–181.

Aichner, B., Herzschuh, U., Wilkes, H., Vieth, A., Böhner, J., 2010a. δD values of *n*-alkanes in Tibetan lake sediments and aquatic macrophytes - A surface sediment study and application to a 16ka record from Lake Koucha. Org. Geochem. 41, 779-790. doi: 10.1016/j.orggeochem.2010.05.010

Aichner, B., Wilkes, H., Herzschuh, U., Mischke, S., Zhang, C., 2010b. Biomarker and compound-specific $\delta^{13}C$ evidence for changing environmental conditions and carbon limitation at Lake Koucha, eastern Tibetan Plateau. J. Paleolimnol. 43, 873–899. DOI 10.1007/s10933-009-9375-y

Aizenshtat Z. and Amrani, A., 2004. Significance of $\delta^{34}S$ and evaluation of its imprint on sedimentary organic matter I. The role of reduced sulfur species in the diagenetic stage: a conceptual review. Geochem. Soc. Spec. Pub. 9, 15-33. doi:10.1016/S1873-9881(04)80004-X

Alewell, C., Birkholz, A., Meusburger, K., Schindler Wildhaber, Y., Mabit, L., 2016. Quantitative sediment source attribution with compound-specific isotope analysis in a C3 plant-dominated catchment (central Switzerland). Biogeosci. 13, 1587-1596. doi:10.5194/bg-13-1587-2016

Amrani, A. and Aizenshtat, Z., 2004. Mechanisms of sulfur introduction chemically controlled: $\delta^{34}S$ imprint. Org. Geochem. 35, 1319-1336. doi:10.1016/j.orggeochem.2004.06.019

Amrani, A, Sessions, A.L., Adkins, J.F., 2009. Compound-specific $\delta^{34}S$ analysis of volatile organics by coupled GC/multicollector-ICPMS. Anal. Chem. 81, 9027-9034. doi:10.1021/ac9016538

Amrani, A, Sessions, A.L., Tang, Y., Adkins, J.F., Hills, R.J., Moldowan, M.J., Wei, Z., 2012. The sulfur-isotopic compositions of benzothiophenes and dibenzothiophenes as a proxy for thermochemical sulfate reduction. Geochim. Cosmochim. Acta 84, 152-164.

doi:10.1016/j.gca.2012.01.023

Andreae, M.O., 1990. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. Mar. Chem. 30, 1-29. doi:10.1016/0304-4203(90)90059-L

Atwood, A.R. and Sachs, J.P., 2012. Purification of dinosterol from complex mixtures of sedimentary lipids for hydrogen isotope analysis. Org. Geochem. 48, 37-46. doi:10.1016/j.orggeochem.2012.04.006

Atwood, A.R. and Sachs, J.P., 2014. Separating ITCZ- and ENSO-related rainfall changes in the Galápagos over the last 3 kyr using D/H ratios of multiple lipid biomarkers. Earth Planet. Sci. Lett. 404, 408-419. doi:10.1016/j.epsl.2014.07.038

Aristegui, J., Montero, M.F., Ballesteros, S., Basterretxea, G., van Lenning, K., 1996. Planktonic primary production and microbial respiration measured by C-14 assimilation and dissolved oxygen changes in coastal waters of the Antarctic Peninsula during austral summer: implications for carbon flux studies. Mar. Ecol. Progr. Series 132, 191-201. doi:10.3354/meps132191

Baldock, J.A. and Skjemstad, J.O., 2000. Role of the soil matrix and minerals in protecting natural organic materials against biological attack. Org. Geochem. 31, 697-710. doi:10.1016/S0146-6380(00)00049-8

Barber, C.N., Grice, K., Bastow, T.P., Alexander, R. Kagi, R.I., 2001. The identification of crocetane in Australian crude oils. Org. Geochem. 32, 943-947. doi:10.1016/S0146-6380(01)00057-2

Berg, J.M., Tymoczko, J.L., Gatto, G.J., Stryrer, L., 2015. Biochemistry - 8th edition, W.H. Freeman, New York, pp.1120.

Berke, M.A., Johnson, T.C., Werne, J.P., Grice, K., Schouten, S., Sinninghe Damsté, J.S., 2012. Molecular records of climate variability and vegetation response since the Late Pleistocene in the Lake Victoria basin, East Africa. Quat. Sci. Rev 55, 59-74. doi: 10.1016/j.quascirev.2012.08.014

Beuning, K.R.M., Kelts, K., Russell, J., Wolfe, B.B., 2002. Reassessment of Lake Victoria–Upper Nile River paleohydrology from oxygen isotope records of lake-sediment cellulose. Geology 30, 559-562. doi:10.1130/0091-7613(2002)030<0559:ROLVUN>2.0.CO;2

Bidigare, R.R., Fluegge, A., Freeman, K.H., Hanson, K.L., Hayes, J.M., Hollander, D., Jasper, J.P., King, L.L., Laws, E.A., Milder, J., Millero, F.J., Pancost, R., Popp, B.N., Steinberg, P.A., Wakeham, S.G., 1997. Consistent fractionation of ^{13}C in nature and in the laboratory: Growth-rate effects in some haptophyte algae. Glob. Biogeochem. Cycles 11, 279-292. doi:10.1029/96GB03939

Blaga, C.I., Reichart, G.-J., Schouten, S., Lotter, A.F., Werne, J.P., Kosten, S., Mazzeo, N., Lacerot, G., Sinninghe Damsté, J.S., 2010. Branched glycerol dialkyl glycerol tetraethers in lake sediments: Can they be used as temperature and pH proxies? Org. Geochem. 41, 1225-1234. doi:10.1016/j.orggeochem.2010.07.002

Bloch, K., 1991. Cholesterol: evolution of structure and function. New Compr. Biochem. 20, 363-381. doi:10.1016/S0167-7306(08)60340-3

Blumenberg, M., Hoppert, M., Krüger, M., Dreier, A.,Thiel, V., 2012. Novel findings on hopanoid occurrences among sulfate reducing bacteria: Is there a direct link to nitrogen fixation? Org. Geochem. 49, 1-5. doi:10.1016/j.orggeochem.2012.05.003

Boreham, C.J., Summons, R.E., Roksandic, Z., Dowling, L.M., Hutton, A.C., 1994. Chemical, molecular and isotopic differentiation of organic facies in the Tertiary lacustrine Duaringa oil shale deposit, Queensland, Australia. Org. Geochem. 21, 685-712. doi:10.1016/0146-6380(94)90013-2

Boschker, H.T.S., Moerdijk-Poortvliet, T.C.W., van Breugel, P., Houtekamer, M., Middelburg, J.J., 2008. A versatile method for stable carbon isotope analysis of carbohydrates by high-performance liquid chromatography/isotope ratio mass spectrometry. Rapid Commun. Mass Spectrom. 22, 3902-3908. doi:10.1002/rcm.3804

Böttcher, M.E., Ferdelman, T.G., Jørgensen, B.B., Blake, R.E., Surkov, A.V., Claypool, G.E., 2006. Sulfur isotope fractionation by the deep biosphere within sediments of the eastern equatorial Pacific and Peru margin. In: Jørgensen, B.B., D'Hondt, S.L., Miller, D.J. (eds.), Proc. ODP, Sci. Res. 201, pp. 1-21.

Bouchard, F., Turner, K.W., MacDonald, L.A., Deakin, C., White, H., Farquharson, N., Medeiros, A.S., Wolfe, B.B., Hall, R.I., Pienitz, R., Edwards, T.W.D., 2013. Vulnerability of shallow subarctic lakes to evaporate and desiccate when snowmelt runoff is low. Geophys. Res. Lett. 40, 6112-6117. doi:10.1002/2013GL058635

Bradley, A.S., Pearson, A., Sáenz, J.P., Marx C.J., 2010. Adenosylhopane: The first intermediate in hopanoid side chain biosynthesis. Org Geochem 41: 1075-1081. doi:10.1016/j.orggeochem.2010.07.003

Brocks, J.J. and Summons, R.E., 2005. Sedimentary hydrocarbons - Biomarkers for early life. In: Schlesinger, W.H. (ed.), Treatise on Biogeochemistry 8, Elsevier, Amsterdam, pp. 63-115.

Brocks, J.J. and Hope, J.M., 2013. Tailing of chromatographic peaks in GC-MS caused by interaction of halogenated solvents with the ion source. J. Chrom. Sci. 52, 471-475. doi:10.1093/chromsci/bmt068.

Brocks, J.J., Grosjean, E., Logan, G.A., 2008. Assessing biomarker syngeneity using branched alkanes with quaternary carbon (BAQCs) and other plastic contaminants. Geochim. Cosmochim. Acta, 72, 871-888. doi:10.1016/j.gca.2007.11.028

Brocks, J.J., Jarrett, A.J., Sirantoine, E., Hallmann, C., Hoshino, Y., Liyanage, T., 2017. The rise of algae in Cryogenian oceans and the emergence of animals. Nature. 548, 578-581. doi:10.1038/nature23457

Brown, S.B., Smith, K.M., Bisset, G.M.F., Troxler, R.F. 1980. Mechanism of photo-oxidation of bacteriochlorophyll *c* derivatives – a possible model for natural chlorophyll breakdown. J. Biol. Chem. 255, 8063-8068.

Bush, R.T. and McInerney, F.A., 2013. Leaf wax *n*-alkane distributions in and across modern plants: Implications for paleoecology and chemotaxonomy. Geochim. Cosmochim. Acta 117, 161-179. doi:10.1016/j.gca.2013.04.016

Callot, H.J., Ocampo, R., Albrecht, P., 1990. Sedimentary porphyrins: correlations with biological precursors. Energ. Fuels 4, 635-639. doi: 10.1021/ef00024a002

Callot, H.J. and Ocampo, R., 2000. Geochemistry of porphyrins. In: Kadish, K.M., Smith, K.M., Guilard, R. (eds.), The Porphyrin Handbook: Volume 1. Acad. Press, Burlington., pp. 349-398.

Calvin, M. and Benson, A.A., 1948. The path of carbon in photosynthesis. Science 107, 476-480. doi:10.1126/science.107.2784.476

Canfield, D.E. and Thamdrup, B., 1994. The production of ^{34}S-depleted sulfide during bacterial disproportionation of elemental sulfur. Science 266, 1973-1975. doi:10.1126/science.11540246

Canfield, D.E., Boudreau, B.P., Mucci, A., Gundersen, J.K. 1998. The early diagenetic formation of organic sulfur in the sediments of Mangrove Lake, Bermuda. Geochim. Cosmochim. Acta 62, 767-781.

Canfield, D.E., Stewart, F.J., Thamdrup, B., De Brabandere, L., Dalsgaard, T., Delong, E.F., Revsbech, N.P., Ulloa, O., 2010. A cryptic sulfur cycle in oxygen-minimum–zone waters off the Chilean coast. Science, 330,1375-1378. doi:10.1126/science.1196889

Canuel, E.A., Freeman, K.H., Wakeham, S.G., 1997. Isotopic compositions of lipid biomarker compounds in estuarine plants and surface sediments. Limnol. Oceanogr. 42, 1570-1583. doi:10.4319/lo.1997.42.7.1570

Carstens, D., Lehmann, M.F., Hofstetter, T.B., Schubert, C.J., 2013. Amino acid nitrogen isotopic composition patterns in lacustrine sedimenting matter. Geochim. Cosmochim. Acta 121, 328-338. doi:10.1016/j.gca.2013.07.020

Castañeda, I.S., Werne, J.P., Johnson, T.C., 2007. Wet and arid phases in the southeast African tropics since the Last Glacial Maximum. Geology 35, 823-826. doi:10.1130/G23916A.1

Castañeda, I.S., Mulitza, S., Schefuβ, E., Lopes dos Santos, R.A., Sinninghe Damsté, J.S., Schouten, S., 2009. Wet phases in the Sahara/Sahel region and human migration patterns in North Africa. Proc. Nat. Acad. Sci. 106, 20159-20163. doi:10.1073/pnas.0905771106

Castañeda, I.S. and Schouten, S., 2011. A review of molecular organic proxies for examining modern and ancient lacustrine environments. Quat. Sci. Rev. 30, 2851-2891. doi:10.1016/j.quascirev.2011.07.009

Castañeda, I.S., Werne, J.P., Johnson, T.C., 2009. Influence of climate change on algal community structure and primary productivity of Lake Malawi (East Africa) from the Last Glacial Maximum to the present. Limnol. Oceanogr. 54, 2431-2447. doi:10.4319/lo.2009.54.6_part_2.2431

Castañeda, I.S., Werne, J.P., Johnson, T.C., Powers, L.A., 2011. Organic geochemical records from Lake Malawi (East Africa) of the last 700 years, part II: Biomarker evidence for recent changes in primary productivity. Palaeogeogr., Palaeoclim., Palaeoecol. 303, 140-154. doi:10.1016/j.palaeo.2010.01.006

Castoreno, A.B., Wang, Y., Stockinger, W., Jarzylo, L.A., Du, H., Pagnon, J.C., Shieh, E.C., Nohturfft, A., 2005. Transcriptional regulation of phagocytosis-induced membrane biogenesis by sterol regulatory element binding proteins. Proc. Nat. Acad. Sci. 102, 13129-13134. doi:10.1073/pnas.0506716102

Cernusak, L.A., Ubierna, N., Winter, K., Holtum, J.A.M., Marshall, J.D., Farquhar, G.D., 2013. Environmental and physiological determinants of carbon isotope discrimination in terrestrial plants. New Phytol. 200, 950-965. doi:10.1111/nph.12423

Chikaraishi, Y., Naraoka, H., Poulson, S.R., 2004. Hydrogen and carbon isotopic fractionations of lipid biosynthesis among terrestrial (C3, C4 and CAM) and aquatic plants. Phytochem. 65, 1369-1381. doi:10.1016/j.phytochem.2004.03.036

Chikaraishi, Y., Yamada, Y., Naraoka, H., 2005. Carbon and hydrogen isotopic compositions of sterols from riverine and marine sediments. Limnol. Oceanogr., 50, 1763-1770. doi:10.4319/lo.2005.50.6.1763

Chikaraishi, Y. and Naraoka, H., 2005. $\delta^{13}C$ and δD identification of sources of lipid biomarkers in sediments of Lake Haruna (Japan). Geochim. Cosmochim. Acta, 69, 3285-3297. doi:10.1016/j.gca.2005.02.023

Chikaraishi, Y. and Naraoka, H., 2006. Carbon and hydrogen isotope variation of plant biomarkers in a plant–soil system. Chem. Geol., 231, 190-202. doi:10.1016/j.chemgeo.2006.01.026

Chikaraishi, Y., Kashiyama, Y., Ogawa, N.O., Kitazato, H., Ohkouchi, N., 2007. Metabolic control of nitrogen isotope composition of amino acids in macroalgae and gastropods: implications for aquatic food web studies. Mar. Ecol. Prog. Ser. 342, 85-90. doi: 10.3354/meps342085

Chikaraishi, Y., Ogawa, N.O., Kashiyama, Y., Takano, Y., Suga, H., Tomitani, A., Miyashita, H., Kitazato, H., Ohkouchi, N., 2009. Determination of aquatic food-web structure based on compound-specific nitrogen isotopic composition of amino acids. Limnol. Oceanogr. Methods 7, 740-750. doi:10.4319/lom.2009.7.740

Chikaraishi, Y., Ogawa, N.O., Ohkouchi, N., 2010. Further evaluation of the trophic level estimation based on nitrogen isotopic composition of amino acids. In: Ohkouchi, N., Tayasu, I., Koba, K. (eds.), Earth, Life and Isotopes. Kyoto University Press, Kyoto, pp. 37-51.

Chivall, D., M'Boule, D., Sinke-Schoen, D., Sinninghe Damsté, J.S., Schouten, S., van der Meer, M.T.J., 2014. The effects of growth phase and salinity on the hydrogen isotopic composition of alkenones produced by coastal haptophyte algae. Geochim. Cosmochim. Acta 140, 381-390. doi:10.1016/j.gca.2014.05.043

Cisneros-Dozal, L.M., Huang, Y., Heikoop, J.M., Fawcett, P.J., Fessenden, J., Anderson, R.S., Meyers, P.A., Larson, T., Perkins, G., Toney, J., Werne, J.P., Goff, F., WoldeGabriel, G., Allen, C.D., Berke, M.A., 2014. Assessing the strength of the monsoon during the late Pleistocene in southwestern United States. Quat. Sci. Rev. 103, 81-90. doi:10.1016/j.quascirev.2014.08.022

Cole, J.J. and Prairie, Y.T., 2009. Dissolved CO_2. In: Likens, G.E. (ed.), Encyclopedia of Inland Waters, vol. 2. Elsevier, Oxford, pp. 30-34.

Collister, J.W. and Hayes, J., 1991. A preliminary study of the carbon and nitrogen isotopic biogeochemistry of lacustrine sedimentary rocks from the Green River Formation. In: Tuttle, M. (ed.), Geochemical, Biogeochemical, and Sedimentological Studies of the Green River Formation, Wyoming, Utah and Colorado.U.S. Geol. Surv. Bull. 1973, pp. C1-C16.

Collister, J.W., Summons, R.E., Lichtfouse, E., Hayes, J.M., 1992. An isotopic biogeochemical study of the Green River oil-shale. Org. Geochem. 19, 265-276. doi:10.1016/0146-6380(92)90042-V

Collister, J.W., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific $\delta^{13}C$ analyses of leaf lipids from plants with differing carbon dioxide metabolisms. Org. Geochem. 21, 619-627. doi:10.1016/0146-6380(94)90008-6

Coolen, M.J.L., Muyzer, G., Rijpstra, W.I.C., Schouten, S., Volkman, J.K., Sinninghe Damsté, J.S., 2004a. Combined DNA and lipid analyses of sediments reveal changes in Holocene haptophyte and diatom populations in an Antarctic lake. Earth Planet. Sci. Lett. 223, 225-239. doi:10.1016/j.epsl.2004.04.014

Coolen, M.J.L., Hopmans, E.C., Rijpstra, W.I.C., Muyzer, G., Schouten, S., Volkman, J.K., Sinninghe Damsté, J.S., 2004b. Evolution of the methane cycle in Ace Lake (Antarctica) during the Holocene: response of methanogens and methanotrophs to environmental change. Org. Geochem. 35, 1151-1167. doi:10.1016/j.orggeochem.2004.06.009

Coolen, M.J.L., Talbot, H.M., Abbas, B.A., Ward, C., Schouten, S., Volkman, J.K., Sinninghe Damsté, J.S., 2008. Sources for sedimentary bacteriohopanepolyols as revealed by 16S rDNA stratigraphy. Env. MIcrobiol. 10, 1783-1803. doi:10.1111/j.1462-2920.2008.01601.x

Coursolle, D., Lian, J., Shanklin, J., Zhao, H., 2015. Production of long chain alcohols and alkanes upon coexpression of an acyl-ACP reductase and aldehyde-deformylating oxygenase with a bacterial type-I fatty acid synthase in *E. coli*. Mol. BioSyst.11, 2464. doi:10.1039/c5mb00268k

Craig, H. 1961. Isotopic variations in meteoric waters. Science 133, 1702-1703. doi:10.1126/science.133.3465.1702

Cranwell, P.A., 1981. Diagenesis of free and bound lipids in terrestrial detritus deposited in a lacustrine sediment. Org. Geochem. 3, 79-89. doi:10.1016/0146-6380(81)90002-4

Cranwell, P.A., 1985. Long-chain unsaturated ketones in recent lacustrine sediments. Geochim. Cosmochim. Acta 49, 1545-1551. doi:10.1016/0016-7037(85)90259-5

Cross, M.M., Manning, D.A.C., Bottrell, S.H., Worden, R.H., 2004. Thermochemicalsulfate reduction (TSR): experimental determination of reaction kinetics and implications of the observed reaction rates for petroleum reservoirs. Org. Geochem. 35, 393-404. doi:10.1016/j.orggeochem.2004.01.005

Crossman, Z.M., McNamara, N., Parekh, N., Ineson, P., Evershed, R.P., 2001. A new method for identifying the origins of simple and complex hopanoids in sedimentary materials using stable isotope labeling with ^{13}(CH^{4}) and compound specific stable isotope analyses. Org. Geochem. 32, 359-364. doi:10.1016/S0146-6380(00)00178-9

D'Andrea, W.J. and Huang, Y., 2005. Long chain alkenones in Greenland lake sediments: low δ^{13}C values and exceptional abundance. Org. Geochem. 36, 1234-1241. doi:10.1016/j.orggeochem.2005.05.001

D'Andrea, W.J., Lage, M., Martiny, J.B.H., Laatsch, A.D., Amaral-Zettler, L.A., Sogin, M.L., Huang, Y.S., 2006. Alkenone producers inferred from well-preserved 18S rDNA in Greenland lake sediments. J. Geophys. Res. Biogeosci. 111. doi:10.1029/2005JG000121.

Darling, W.G., Bath, A.H., Gibson, J.J., Rozanski, K., 2005. Isotopes in water, in: Leng, M.J. (ed.), Isotopes in Palaeoenvironmental Research. Springer, Dordrecht, pp. 1-66.

Davies, K.L., Pancost, R.D., Edwards, M.E., Walter Anthony, K.M., Langdon, P.G., Chaves Torres, L., 2016. Diploptene δ^{13}C values from contemporary thermokarst lake sediments show complex spatial variation. Biogeosci. 13, 2611-2621. doi:10.5194/bg-13-2611-2016.

Dawson, D., Grice, K., Wang, S.X., Alexander, R., Radke, J., 2004. Stable hydrogen isotopic composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited under various climatic conditions. Org. Geochem. 35, 189-197. doi:10.1016/j.orggeochem.2003.09.004

De Jonge, C., Stadnitskaia, A., Hopmans, E.C., Cherkashov, G., Fedotov, A., Sinninghe Damsté, J.S., 2014. In situ produced branched glycerol dialkyl glycerol tetraethers in suspended particulate matter from the Yenisei River, Eastern Siberia. Geochim. Cosmochim. Acta 125, 476-491. doi:10.1016/j.gca.2013.10.031

de Kluijver, A., Schoon, P.L., Downing, J.A., Schouten, S., Middelburg, J.J., 2014. Stable carbon isotope biogeochemistry of lakes along a trophic gradient. Biogeosci. 11, 6265-6276. doi:10.5194/bg-11-6265-2014

DeLong, E.F., 1992. Archaea in coastal marine environments. Proc. Natl. Acad. Sci. 89, 5685-5689. doi:10.1073/pnas.89.12.5685

DeNiro, M.J. and Epstein, S., 1978. Influence of diet on the distribution of carbon isotopes in animals. Geochim. Cosmochim. Acta 42, 495-506. doi.org/10.1016/0016-7037(78)90199-0

Diefendorf, A. F. and Freimuth, E. J., 2017. Extracting the most from terrestrial plant-derived *n*-alkyl lipids and their carbon isotopes from the sedimentary record: A review. Org. Geochem. 103, 1-21. doi:10.1016/j.orggeochem.2016.10.016

Diefendorf, A.F., Freeman, K.H., Wing, S.L., Graham, H.V., 2011. Production of *n*-alkyl lipids in living plants and implications for the geologic past. Geochim. Cosmochim. Acta 75, 7472-7485. doi:10.1016/j.gca.2011.09.028

Edwards, T.W.D. and McAndrews, J.H. (1989). Paleohydrology of a Canadian Shield lake inferred from ^{18}O in sediment cellulose. Can. J. Earth Sc. 26, 1850-185. doi:10.1139/e89-158

Eglinton, G. and Hamilton, R.J., 1967. Leaf epicuticular waxes. Science 156, 1322-1335. doi: 10.1126/science.156.3780.1322

Eglinton, T.I. and Eglinton, G., 2008. Molecular proxies for paleoclimatology. Earth Planet. Sci. Lett. 275, 1-16. doi:10.1016/j.epsl.2008.07.012

Ehleringer, J.R., Hall, A.E., Farquhar, G.D., 1993. Stable isotopes and plant carbon/water relations. Academic Press, San Diego, California, USA.

Eickhoff, M., Birgel, D., Talbot, H.M., Peckmann, J., Kappler, A., 2013. Bacteriohopanoid inventory of *Geobacter sulfurreducens* and *Geobacter metallireducens*. Org. Geochem. 58, 107-114. doi:10.1016/j.orggeochem.2013.02.013

Eley, Y., Dawson, L., Pedentchouk, N., 2016. Investigating the carbon isotope composition and leaf wax *n*-alkane concentration of C3 and C4 plants in Stiffkey saltmarsh, Norfolk, UK. Org. Geochem. 96, 28-42. doi:10.1016/j.orggeochem.2016.03.005

Eltgroth, M.L., Watwood, R.L., Wolfe, G.V., 2005. Production and cellular localization of neutral long-chain lipids in the haptophyte algae *Isochrysis galbana* and *Emiliania huxleyi*. J. Phycol. 41, 1000-1009. doi:10.1111/j.1529-8817.2005.00128.

Elvert, M., Pohlman, J.W., Becker, K.W., Gaglioti, B., Henrichs, K.-U., Wooler, M.J., 2016. Methane turnover and environmental change from Holocene lipid biomarker records in a thermokarst lake in Arctic Alaska. Holocene 26, 1766-1777.

Englebrecht, A.C. and Sachs, J.P., 2005. Determination of sediment provenance at drift sites using hydrogen isotopes and unsaturation ratios in alkenones. Geochim. Cosmochim. Acta 69, 4253-4265. doi:10.1016/j.gca.2005.04.011

Engels, S., Bakker, M.A.J., Bohncke, S.J.P., Cerli, C., Hoek, W.Z., Jansen, B., Peters, T., Renssen, H., Sachse, D., van Aken, J.M., van den Bos, V., van Geel, B., van Oostrom, R., Winkels, T., Wolma, M., 2016. Centennial-scale lake level lowstand at Lake Uddelermeer (The Netherlands) indicates changes in moisture source region prior to the 2.8-kyr event. Holocene 26, 1075-7091. doi:10.1177/0959683616632890

Farquhar, J., Bao, H., Thiemens, M., 2000. Atmospheric influence of Earth's earliest sulfur cycle. Science 289, 756-758. doi:10.1126/science.289.5480.756

Farquhar, J., Johnston, D.T., Wing, B.A., Habicht, K.S., Canfield, D.E., Airieau, S., Thiemens, M.H., 2003. Multiple sulphur isotopic interpretations of biosynthetic pathways: implications for biological signatures in the sulphur isotope record. Geobiol. 1, 27-36. doi:10.1046/j.1472-4669.2003.00007.x

Farquhar, J., Johnston, D.T., Wing, B.A., 2007. Implications of conservation of mass effects on mass-dependent isotope fractionations: influence of network structure on sulfur isotope phase space of dissimilatory sulfate reduction. Geochim. Cosmochim. Acta 71, 5862–5875. doi:10.1016/j.gca.2007.08.028

Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. Org. Geochem. 31, 745-749. doi:10.1016/S0146-6380(00)00081-4

Freeman, K.H., Hayes, J.M., Trendel, J.-M., Albrecht, P., 1990. Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. Nature 343, 254-256. doi:10.1038/343254a0

Freeman, K.H. and Pancost, R.D., 2014. Biomarkers for terrestrial plants. In: Holland, H.D. and Turekian, K.K. (eds.), Treatise on Geochemistry, 2nd edition, vol. 12. Elsevier, Amsterdam, pp. 395-416. doi:10.1016/B978-0-08-095975-7.01028-7

Freitas, F.S., Pancost, R.D., Arndt, S., 2017. The impact of alkenone degradation on $U_{37}^{K'}$ paleothermometry: a model-derived assessment. Paleoceanogr. 32, 648-672. doi:10.1002/2016PA003043

Fry, B., Cox, J., Gest, H., Hayes, J., 1986. Discrimination between ^{34}S and ^{32}S during bacterial metabolism of inorganic sulfur compounds. J. Bacteriol. 165, 328-330.

Fry, B., 1986. Sources of carbon and sulfur nutrition for consumers in three meromictic lakes of New York State. Limnol. Oceanogr., 31, 79-88. doi: doi.org/10.4319/lo.1986.31.1.0079

Fuhrman, J. and Davis, A., 1997. Widespread archaea and novel bacteria from the deep sea as shown by 16S rRNA gene sequences. Mar. Ecol. Prog. Ser. 150, 275-285. doi:10.3354/meps150275

Fulton, J.M., Arthur, M.A., Thomas, B. Freeman, K.H., 2018. Pigment carbon and nitrogen isotopic signatures in euxinic basins. Geobiol. 16, 429-445. doi:10.1111/gbi.12285

Gaebler, O.H., Vitti, T.G., Vukmirovich, R., 1966. Isotope effects in metabolism of ^{14}N and ^{15}N from unlabeled dietary proteins. Can J Biochem 44, 1249-1257. doi:10.1139/o66-142

Galimov, E.M.,1985. The Biological Fractionation of Isotopes. Academic Press, Orlando, pp. 261.

Gamarra, B. and Kahmen, A., 2015. Concentrations and δ^2H values of cuticular *n*-alkanes vary significantly among plant organs, species and habitats in grasses from an alpine and a temperate European grassland. Oecologia 178, 981-998. doi:10.1007/s00442-015-3278-6

Gamarra, B., Sachse, D., Kahmen, A., 2016. Effects of leaf water evaporative ^2H-enrichment and biosynthetic fractionation on leaf wax *n*-alkane δ^2H values in C3 and C4 grasses. Plant, Cell, Env. 39, 2390-2403. doi: 10.1111/pce.12789

Garcin, Y., Schefuß, E., Schwab, V.F., Garreta, V., Gleixner, G., Vincens, A., Todou, G., Séné, O., Onana, J.-M., Achoundong, G., Sachse, D., 2014. Reconstructing C_3 and C_4 vegetation cover using *n*-alkane carbon isotope ratios in recent lake sediments from Cameroon, Western Central Africa. Geochim. Cosmochim. Acta 142, 482-500. doi:10.1016/j.gca.2014.07.004

Gelpi, E., Schneider, H., Mann, J., Oro, J., 1970. Hydrocarbons of geochemical significance in microscopic algae. Phytochem. 9, 603-612. doi:10.1016/S0031-9422(00)85700-3

Glazer, A.N., Apell, G.S., Hixson, C.S., Bryant, D.A., Rimon, S., Brown, D.M. 1976. Biliproteins of cyanobacteria and Rhodophyta: homologous family of photosynthetic accessory pigments. Proc. Natl. Acad. Sci. USA 73, 428-431. doi:10.1073/pnas.73.2.428

Glibert, P.M., Wilkerson, F.P., Dugdale, R.C., Raven, J.A., Dupont, C.L., Leavitt, P.R., Parker, A.E., Burkholder, J.M., Kana, T.M., 2016. Pluses and minuses of ammonium and nitrate uptake and assimilation by phytoplankton and implications for productivity and community composition, with emphasis on nitrogen-enriched conditions. Limnol. Oceanogr. 61, 165-197. doi:10.1002/lno.10203

Goericke, R., Montoya, J.P., Fry, B., 1994. Physiology of isotope fractionation in algae and cyanobacteria. In: Lajtha, K. and Michener, B. (eds.), Stable Isotopes in Ecology. Blackwell Scientific, Boston, pp. 187-221.

Goldhaber, M.B. and Kaplan, I.R., 1980. Mechanisms of sulfur incorporation and isotope fractionation during early diagenesis in sediments of the Gulf of California. Mar. Chem. 9, 95-143. doi:10.1016/0304-4203(80)90063-8

Goodwin, T.W., 1976. Distribution of Carotenoids. In: Goodwin, T.W. (ed.), Chemistry and Biochemistry of Plant Pigments, vol. 1, pp. 225-261. Academic Press, London.

Goossens H., de Leeuw, J.W., Schenck, P.A., Brassell, S.C., 1984. Tocopherols as likely precursors of pristane in ancient sediments and crude oils. Nature 312, 440-442. doi:10.1038/312440a0

Grantham, P.J. and Wakefield, L.L., 1988. Variations in the sterane carbon number distributions of marine source rock derived crude oils through geological time. Org. Geochem. 12, 61-73. doi:10.1016/0146-6380(88)90115-5

Greenwood, P.F. and Summons, R.E., 2003. GC–MS detection and significance of crocetane and pentamethylicosane in sediments and crude oils. Org. Geochem. 34, 1211-1222. doi:10.1016/S0146-6380(03)00062-7

Greenwood, P.F., Mohammed, L., Grice, K., McCulloch, M.T., Schwark, L, 2018. The application of compound-specific sulfur isotopes to the oil-source rock correlation of Kurdistan petroleum. Org. Geochem. 117, 22-30. doi:10.1016/j.orggeochem.2017.11.016

Grice, K., Gibbison, R., Atkinson, J.E., Schwark, L., Eckardt, C.B., Maxwell, J.R., 1996a. Maleimides (1**H**-pyrrole-2,5-diones) as molecular indicators of anoxygenic photosynthesis in ancient water columns. Geochim. Cosmochim. Acta 60, 3913-3924. doi:10.1016/0016-7037(96)00199-8

Grice, K., Schaeffer, P., Schwark, L, Maxwell, J.R., 1996b. Molecular indicators of palaeoenvironmental conditions in an immature Permian shale (Kupferschiefer, Lower Rhine Basin, north-west Germany) from free and S-bound lipids. Org. Geochem. 25,131-147. doi:10.1016/S0146-6380(96)00130-1

Grice, K., Schaeffer, P., Schwark, L., Maxwell, J.R., 1997. Changes in palaeoenvironmental conditions during deposition of the Permian Kupferschiefer (Lower Rhine Basin, northwest Germany) inferred from molecular and isotopic compositions of biomarker components. Org. Geochem. 26, 677-690. doi:10.1016/S0146-6380(97)00036-3

Grice, K., Schouten, S., Nissenbaum, A., Charrach, J., Sinninghe Damsté J.S., 1998. Isotopically heavy carbon in the C_{21} to C_{25} regular isoprenoids in halite-rich deposits from the Sdom Formation, Dead Sea Basin, Israel. Org. Geochem. 28, 349–359. doi:10.1016/S0146-6380(98)00006-0

Grice K., Twitchett R.J., Alexander R., Foster C.B., Looy C., 2005. A potential biomarker for the Permian-Triassic ecological crisis. Earth Planet. Sci. Lett. 236, 315-321. doi:10.1016/j.epsl.2005.05.008

Griffiths, M., 1978. Specific blue-green algal carotenoids in sediments of Esthwaite Water. Limnol. Oceanogr. 23, 777-784. doi:10.4319/lo.1978.23.4.0777

Guilizzoni, P., Lami, A., Marchetto, A., 1992. Plant pigment ratios from lake sediments as indicators of recent acidification in alpine lakes. Limnol. Oceanogr. 37, 1565-1569. doi:10.4319/lo.1992.37.7.1565

Habicht, K.S. and Canfield, D.E., 1997. Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments. Geochim. Cosmochim. Acta 61, 5351-5361. doi:10.1016/S0016-7037(97)00311-6

Habicht, K.S. and Canfield, D.E., 2001. Isotope fractionation by sulfate-reducing natural populations and the isotopic composition of sulfide in marine sediments. Geology 29, 555-558. doi:10.1130/0091-7613(2001)029<0555:IFBSRN>2.0.CO;2

Habicht, K.S., Canfield, D.E., and Rethmeier, J., 1998. Sulfur isotope fractionation during bacterial reduction and disproportionation of thiosulfate and sulfite. Geochim. Cosmochim. Acta 62, 2585-2595. doi:10.1016/50016- 7037(98)00167-7.

Hartgers, W.A., Koopmans, M.P., Sinninghe Damsté, J.S., De Leeuw, J.W., 1993. Sedimentary evidence for a diaromatic carotenoid with an unprecedented aromatic substitution pattern. J. Chem. Soc. Chem. Comm. 23, 1715-1716. doi: 10.1039/C39930001715

Harvey, H.W., 1940. Nitrogen and phosphorus required for the growth of phytoplankton. J. Mar. Biol. Assoc. 24, 115-123. doi:10.1017/S0025315400054485

Harvey, H.W., 1953. Synthesis of organic nitrogen and chlorophyll by *Nitzschia closterium*. J. Mar. Biol. Assoc. 31, 477-487. doi:10.1017/S0025315400011632

Hayes, J.M., 2001. Fractionation of carbon and hydrogen isotopes in biosynthetic processes. Rev. Mineral. Geochem. 43, 225-277. doi:10.2138/gsrmg.43.1.225

Hayes, J.M., Takigiku, R., Ocampo, R., Callot, H.J., Albrecht, P., 1987. Isotopic compositions and probable origins of organic molecules in the Eocene Messel shale. Nature 329, 48-51. doi:10.1038/329048a0

Hayes, J.M., Popp, B.N., Takigiku, R., Johnson, M.W., 1989. An isotopic study of biogeochemical relationships between carbonates and organic carbon in the Greenhorn Formation. Geochim. Cosmochim. Acta 53, 2961-2972. doi:10.1016/0016-7037(89)90172-

5

Hayes, J.M., Strauss, H., Kaufman, A.J., 1999. The abundance of ^{13}C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. Chem. Geol. 161, 103-125. doi:10.1016/S0009-2541(99)00083-2

Hedges, J.I., 1992. Global biogeochemical cycles - Progress and problems. Mar. Chem. 39, 67-93. doi:10.1016/0304-4203(92)90096-S

Hedges, J.I. and Keil, R.G., 1995. Sedimentary organic matter preservation - An assessment and speculative synthesis. Mar. Chem. 49, 81-115. doi:10.1016/0304-4203(95)00008-F

Hepp, J., Tuthorn, M., Zech, R., Mügler, I., Schlütz, F., Zech, W., Zech, M., 2015. Reconstructing lake evaporation history and the isotopic composition of precipitation by a coupled δ^{18}O– δ^{2}H biomarker approach. J. Hydrol. 529, 622-631.

Hershberger, K.L., Barns, S.M., Reysenbach, A.-L., Dawson, S.C., Pace, N.R., 1996. Wide diversity of Crenarchaeota. Nature 384, 420-420. doi:10.1038/384420a0

Heyng, A.M., Mayr, C., Lücke, A., Wissel, H., Striewski, B., 2014. Late Holocene hydrologic changes in northern New Zealand inferred from stable isotope values of aquatic cellulose in sediments from Lake Pupuke. J. Paleolim. 51, 485-497. doi:10.1007/s10933-014-9769-3

Heyng, A.M., Mayr, C., Lücke, A., Moschen, R., Wissel, H., Striewski, B., Bauersachs, T., 2015. Middle and Late Holocene paleotemperatures reconstructed from oxygen isotopes and GDGTs of sediments from Lake Pupuke, New Zealand. Quat. Int. 374, 3-14. doi:10.1016/j.quaint.2014.12.040

Higgins, M.B., Robinson, R.S., Carter, S.J., Pearson, A., 2010. Evidence from chlorin nitrogen isotopes for alternating nutrient regimes in the Eastern Mediterranean Sea: Earth Planet. Sci. Let. 290, no. 1–2, p. 102-107, doi: 10.1016/j.epsl.2009.12.009.

Hilkert, A.W., Douthitt, C.B., Schlüter, H.J., Brand, W.A., 1999. Isotope ratio monitoring gas chromatography/mass spectrometry of D/H by high temperature conversion isotope ratio mass spectrometry. Rapid Commun. Mass Spectrom. 13, 1226-1230. doi:10.1002/(SICI)1097-0231(19990715)13:13<1226::AID-RCM575>3.0.CO;2-9

Hinrichs, K.U., Hayes, J.M., Sylva, S.P., Brewer, P.G., DeLong, E.F., 1999. Methane-consuming archaebacteria in marine sediments. Nature 398, 802-805. doi:10.1038/19751

Hinrichs, K.U., Schneider, R.R., Müller, P.J., Rullkötter, J., 1999. A biomarker perspective on paleoproductivity variations in two Late Quaternary sediment sections from the Southeast Atlantic Ocean. Org. Geochem. 30, 341-366. doi:10.1016/S0146-6380(99)00007-8

Hinrichs, K.-U., Summons, R.E., Orphan, V., Sylva, S.P., Hayes, J.M., 2000. Molecular and isotopic analysis of anaerobic methane-oxidizing communities in marine sediments. Org. Geochem. 31, 1685-1701. doi:10.1016/S0146-6380(00)00106-6

Hoefs, J., 2004. Stable Isotope Geochemistry, 5th edition. Springer, Berlin, pp. 244.

Hoefs, M., Schouten, S., De Leeuw, J.W., King, L.L., Wakeham, S.G., Sinninghe Damsté, J.S., 1997. Ether lipids of planktonic archaea in the marine water column. Appl. Environ. Microbiol. 63, 3090-3095.

Hoering, T.C. and Ford, H.T., 1960. The isotope effect in the fixation of nitrogen by *Azotobacter*. J. Am. Chem. Soc., 82, 376-8. doi:10.1021/ja01487a031

Hollander, D.J. and Smith, M.E., 2001. Microbially mediated carbon cycling as a control on the $\delta^{13}C$ of sedimentary carbon in eutrophic Lake Mendota (USA): New models for interpreting isotopic excursions in the sedimentary record. Geochim. Cosmochim. Acta 65, 4321-4337. doi:10.1016/S0016-7037(00)00506-8

Hollander, D.J., Sinninghe Damsté, J.S., Hayes, J.M., De Leeuw, J.W., Huc, A.Y., 1993. Molecular and bulk isotopic analyses of organic matter in marls of the Mulhouse Basin (Tertiary, Alsace, France). Org. Geochem. 20, 1253-1263. doi:10.1016/0146-6380(93)90013-2

Holtvoeth, J. Rushworth, D., Imeri, A., Cara, M., Vogel, H., Wagner, T., Wolff, G.A., 2016. Improved end-member characterisation of modern organic matter pools in the Ohrid Basin (Albania, Macedonia) and evaluation of new palaeoenvironmental proxies. Biogeosci. 13, 795-816. doi:10.5194/bg-13-795-2016

Holtvoeth, J., Vogel, H., Valsecchi, V., Lindhorst, K., Schouten, S., Wagner, B., Wolff, G.A., 2017. Linear and non-linear responses of vegetation and soils to glacial-interglacial climate change in a Mediterranean refuge. Sci. Rep. 7, 8121. doi:10.1038/s41598-017-08101-y

Hou, J., D'Andrea, W.J., MacDonald, D., Huang, Y., 2007. Hydrogen isotopic variability in leaf waxes among terrestrial and aquatic plants around Blood Pond, Massachusetts (USA). Org. Geochem. 38, 977-984. doi:10.1016/j.orggeochem.2006.12.009

Huang, X., Pancost, R.D., Xue, J., Gu, Y., Evershed, R.P., Xie, S., 2018. Response of carbon cycle to drier conditions in the mid-Holocene in central China. Nature Communications 9:1369. DOI: 10.1038/s41467-018-03804-w.

Huang, Y., Murray, M., Eglinton, G., 1995. Sacredicene, a novel monocyclic C_{33} hydrocarbon from sediment of Sacred Lake, a tropical freshwater lake, Mount Kenya. Tetrahedron

Letters 36, 5973-5976. doi:10.1016/0040-4039(95)01156-C

Huang, Y., Lockheart, M.J., Logan, G.A., Eglinton, G., 1996. Isotope and molecular evidence for the diverse origins of carboxylic acids in leaf fossils and sediments from the Miocene Lake Clarkia deposit, Idaho, U.S.A.. Org. Geochem. 24, 289-299. doi:10.1016/0146-6380(96)00030-7

Huang, Y.S., Street-Perrott, F.A., Perrot, R.A., Metzger, P., Eglinton, G., 1999. Glacial-interglacial environmental changes inferred from molecular and compound-specific δ^{13}C analyses of sediments from Sacred Lake, Mt. Kenya. Geochim. Cosmochim. Acta 63, 1383-1404. doi:10.1016/S0016-7037(99)00074-5

Huang, Y., Street-Perrott, F.A., Metcalfe, S.E., Brenner, M., Moreland, M., Freeman, K.H., 2001. Climate change as the dominant control on glacial-interglacial variations in C_3 and C_4 plant abundance. Science 293, 1647-1651. doi:10.1126/science.1060143

Huang, Y., Shuman, B., Wang, Y., Webb III, T., 2004. Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. J. Paleolim. 31, 363-375. doi:10.1023/B:JOPL.0000021855.80535.13

Huang, Y., Shuman, B., Wang, Y., Webb III, T., Grimm, E.C., Jacobson, G.L. Jr., 2006. Climatic and environmental controls on the variation of C3 and C4 plant abundances in central Florida for the past 62,000 years. Palaeogeogr., Palaeoclim., Palaeoecol. 237, 428-435. doi:10.1016/j.palaeo.2005.12.014

Jaeschke, A., Ziegler, M., Hopmans, E.C., Reichart, G.J., Lourens, L.J., Schouten, S., Sinninghe Damsté, J.S., 2009. Molecular fossil evidence for anaerobic ammonium oxidation in the Arabian Sea over the last glacial cycle. Paleoceanogr. 24, PA2202-1-PA2202-11. doi:10.1029/2008PA001712

Jaffé, R., Cabrera, A., Najje, N., Carvajal-Chitty, H., 1996. Organic biogeochemistry of a hypereutrophic tropical, freshwater lake – Part 1: particle associated and dissolved lipids. Org. Geochem. 25, 227-240. doi:10.1016/S0146-6380(96)00114-3

Jahnke, L.L., Summons, R.E., Hope, J.M., Des Marais, D.J., 1999. Carbon isotopic fractionation in lipids from methanotrophic bacteria II: The effects of physiology and environmental parameters on the biosynthesis and isotopic signatures of biomarkers. Geochim. Cosmochim. Acta 63, 79-93. doi:10.1016/S0016-7037(98)00270-1

Jetter, R., Schaffer, S., Riederer, M., 2000. Leaf cuticular waxes are arranged in chemically and mechanically distinct layers: evidence from *Prunus laurocerasus* L. Plant Cell Env. 23, 619-628. doi:10.1046/j.1365-3040.2000.00581.x

Jochmann, M.A. and Schmidt, T.C., 2012. Compounds-specific Stable Isotope Analysis. The Royal Society of Chemistry, Cambridge, pp. 250.

Johnson, T.C., Werne, J.P., Brown, E.T., Abbott, A., Berke, M., Steinman, B.A., Halbur, J., Contreras, S., Grosshuesch, S., Deino, A., Lyons, R.P., Scholz, C.A., Schouten, S., Sinninghe Damsté, J.S., 2016, A progressively wetter climate in southern East Africa over the past 1.3 million years. Nature 537, 220-224. doi:10.1038/nature19065

Johnston, D.T., Farquhar, J., Wing, B.A., Kaufman, A., Canfield, D.E., Habicht, K.S., 2005. Multiple sulfur isotope fractionations in biological systems: a case study with sulfate reducers and sulfur disproportionators. Am. J. Sci. 305, 645-660. doi:10.2475/ajs.305.6-8.645

Johnston, D.T., Farquhar, J., Canfield, D.E. 2007. Sulfur isotope insights into microbial sulfate reduction: when microbes meet models. Geochim. Cosmochim. Acta 71, 3929-3947. doi:10.1016/j.gca.2007.05.008

Johnston, D.T., Farquhar, J., Habicht, K., Canfield, D.E. 2008. Sulphur isotopes and the search for life: strategies for identifying sulphur metabolisms in the rock record and beyond. Geobiol. 6, 425–435. doi:10.1111/j.1472-4669.2008.00171.x

Jones, D.M., Carter, J.F., Eglinton, G., Jumeau, E.J., Fenwick, C.S., 1991. Determination of $\delta^{13}C$ values of sedimentary straight chain and cyclic alcohols by gas chromatography/isotope ratio mass spectrometry. Biol. Mass Spectr. 20, 641-646. doi:10.1002/bms.1200201009

Jones G.J., Nichols P.D., Shaw P.M., 1994. Analysis of microbial sterols and hopanoids. In: Goodfellow M. and O'Donnell A.G (eds.), Chemical Methods in Prokaryotic Systematics. Wiley, Chichester, pp.163-195

Jørgensen, B.B. (1978). A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. Geomicrobiol. J. 1, 29-47. doi:1080/01490457809377722

Jørgensen, B.B., Böttcher, M.E., Lüschen, H., Neretin, L.N., Volkov, I.I., 2004. Anaerobic methane oxidation and a deep H_2S sink generate isotopically heavy sulfides in Black Sea sediments. Geochim. Cosmochim. Acta, 68, 2095-2118. doi:10.1016/j.gca.2003.07.017

Kahmen, A., Schefuß, E., Sachse, D., 2013a. Leaf water deuterium enrichment shapes leaf wax *n*-alkane δD values of angiosperm plants I: Experimental evidence and mechanistic insights. Geochim. Cosmochim. Acta 111, 39-49. doi:10.10 16/j.gca.2012.09 .003.

Kahmen, A., Hoffmann, B., Schefuß, E., Arndt, S.K., Cernusak, L.A., West, J.B., Sachse, D., 2013b. Leaf water deuterium enrichment shapes leaf wax *n*-alkane δD values of angiosperm plants II: Observational evidence and global implications. Geochim. Cosmochim. Acta 111, 50-63. doi:10.1016/j.gca.2012.09.004

Kaneko, M., Kitajima, F., Naraoka, H., 2011. Stable hydrogen isotope measurement of archaeal ether-bound hydrocarbons. Org. Geochem. 42, 166-172. doi:10.1016/j.orggeochem.2010.11.002

Kaplan, I. and Rittenberg, S., 1964. Microbiological fractionation of sulphur isotopes. J. Gen. Microbiol. 34, 195-212. doi:10.1099/00221287-34-2-195

Kaplan, I.R., Emery, K.O., Rittenberg, S.C., 1963. The distribution and isotopic abundance of sulphur in recent marine sediments off southern California. Geochim. Cosmochim. Acta 27, 297-331. doi:10.1016/0016-7037(63)90074-7

Karner, M.B., DeLong, E.F., Karl, D.M., 2001. Archaeal dominance in the mesopelagic zone of the Pacific Ocean. Nature 409, 507-510. doi:10.1038/35054051

Kasprak, A.H., Sepúlveda, J., Price-Waldman, R., Williford, K.H., Schoepfer, S.D., Haggart, J.W., Ward, P.D., Summons, R.E., Whiteside, J.H., 2015. Episodic photic zone euxinia in the northeastern Panthalassic Ocean during the end-Triassic extinction. Geology 43, 307-310. doi:10.1130/G36371.1

Kharasch, N., (ed.) 2013. Organic Sulfur Compounds. Elsevier.

Khezami, L., Chetouani, B., Tauk, B., Capart, R., 2005. Production and characterisation of activated carbon from wood components in powder: Cellulose, lignin, xylan. Powder Tech. 157, 48-56. doi:10.1016/j.powtec.2005.05.009

Kimble, B.J., Maxwell, J.R., Philp, R.P. Eglinton, G., Albrecht, P., Ensminger, A., Arpino, P., Ourisson, G., 1974. Tri- and tetraterpenoid hydrocarbons in the Messel oil shale. Geochim. Cosmochim. Acta 38, 1165-1181. doi:10.1016/0016-7037(74)90011-8

Kitamura, E., Kotajima, T., Sawada, K., Suzuki, I., Shiraiwa, Y., 2018. Cold-induced metabolic conversion of haptophyte di- to tri-unsaturated C_{37} alkenones used as palaeothermometer molecules. Sci. Rep. 8, 2196. doi:10.1038/s41598-018-20741-2

Knoll, A.H., Summons, R.E., Waldbauer, J.R., Zumberge, J.E., 2007. The geological succession of primary producers in the oceans. In: Falkowski, P.D. and Knoll, A.H. (eds.), Evolution of Primary Producers in the Sea, Elsevier, Oxford, pp.133-163.

Kodner, R.B., Pearson, A., Summons, R.E., Knoll, A.H., 2008. Sterols in red and green algae: quantification, phylogeny, and relevance for the interpretation of geologic steranes. Geobiol. 6, 411-420. doi:10.1111/j.1472-4669.2008.00167.x

Kohn, M.J., 2010. Carbon isotope compositions of terrestrial C3 plants as indicators of (paleo)ecology and (paleo)climate. Proc. Nat. Acad. Sci. 101, 19691–19695. doi:10.1073/pnas.1004933107

Konecky, B.L., Russell, J.M., Johnson, T.C., Brown, E.T., Berke, M.A., Werne, J.P., Huang, Y., 2011. Atmospheric circulation patterns during late Pleistocene climate changes at Lake Malawi, Africa. Earth Planet. Sci. Lett. 312, 318-326. doi:10.1016/j.epsl.2011.10.020

Könneke, M., Lipp, J.S., Hinrichs, K.-U., 2012. Carbon isotope fractionation by the marine ammonia-oxidizing archaeon *Nitrosopumilus maritimus*. Org. Geochem. 48, 21-24. doi:10.1016/j.orggeochem.2012.04.007

Kool, D.M., Talbot, H.M., Rush, D., Ettwig, K., Sinninghe Damsté, J.S., 2014. Rare bacteriohopanepolyols as markers for an autotrophic, intra-aerobic methanotroph. Geochim. Cosmochim. Acta 136, 114-125. doi:10.1016/j.gca.2014.04.002

Koopmans, M.P., Köster, J., van Kaam-Peters, H.M.E., Kenig, F., Schouten, S., Hartgers, W.A., de Leeuw, J.W., Sinninghe Damsté, J.S., 1996. Diagenetic and catagenetic products of isorenieratene: Molecular indicators for photic zone anoxia. Geochim. Cosmochim. Acta 60, 4467-4496. doi:10.1016/S0016-7037(96)00238-4

Körner, C. H., Farquhar, G. D., Wong, S. C., 1991. Carbon isotope discrimination by plants follows latitudinal and altitudinal trends. Oecologia 88, 30-40. doi:10.1007/BF00328400

Koyama, M., Sugiyama, J., Itoh, T., 1997. Systematic survey on crystalline features of algal celluloses. Cellulose 4, 147-160. doi:10.1023/A:101842760

Kraal, P., Burton, E.D., Bush, R.T., 2013. Iron monosulfide accumulation and pyrite formation in eutrophic estuarine sediments. Geochim. Cosmochim. Acta, 122, 75-88. doi:10.1016/j.gca.2013.08.013

Krouse, H.R., Viau, C.A., Eliuk, L.S. (1988) Chemical and isotopic evidence of thermo-chemical sulfate reduction by light hydrocarbon gases in deep carbonate reservoirs. Nature 333, 415-419. doi:10.1038/333415a0

Kümmel, S., Starke, R., Chen, G., Musat, F., Richnow, H.H., Vogt, C., 2016. Hydrogen isotope fractionation as a tool to identify aerobic and anaerobic PAH biodegradation. Environ. Sci. Technol. 50, 3091-3100. doi:10.1021/acs.est.5b04819

Kuypers, M.M.M., Blokker, P., Erbacher, J., Kinkel, H., Pancost, R.D., Schouten, S., Sinninghe Damsté, J.S., 2001. Massive expansion of marine archaea during a mid-Cretaceous oceanic anoxic event. Science 293, 92–95. doi:10.1126/science.1058424

Kuypers, M.M.M., Blokker, P., Hopmans, E.C., Kinkel, H., Pancost, R.D., Schouten, S., Sinninghe Damsté, J.S., 2002. Archaeal remains dominate marine organic matter from the early Albian oceanic anoxic event 1b. Palaeogeogr., Palaeoclim., Palaeoecol. 185, 211-234. doi:10.1016/S0031-0182(02)00301-2

Ladd, S.N., Dubois, N., Schubert C.J., 2017. Interplay of community dynamics, temperature, and productivity on the hydrogen isotope signatures of lipid biomarkers. Biogeosci. 14, 3979-3994. doi:10.5194/bg-14-3979-2017.

Lamb, A.L., Wilson, G.P., Leng, M.J., 2006. A review of coastal palaeoclimate and relative sea-level reconstructions using $\delta^{13}C$ and C/N ratios in organic material. Earth-Sci. Rev. 75 29-57. doi:10.1016/j.earscirev.2005.10.003

Langworthy, T.A., 1977. Long-chain diglycerol tetraethers from *Thermoplasma acidophilum*. Biochim. Biophys. Acta BBA - Lipids Lipid Metab. 487, 37-50. doi:10.1016/0005-2760(77)90042-X

Langworthy, T.A., 1982. Lipids of *Thermoplasma*. Meth. Enzym., 88, 396-406. doi:10.1016/0076-6879(82)88055-5

Langworthy, T.A., Smith, P.F., Mayberry, W.R., 1972. Lipids of *Thermoplasma acidophilum*. J. Bacteriol. 112, 1193-1200.

Larsen, T., Bach, L.T., Salvatteci, R., Wang, Y.V., Andersen, N., Ventura, M., McCarthy, M.D., 2015. Assessing the potential of amino acid ^{13}C patterns as a carbon source tracer in marine sediments: effects of algal growth conditions and sedimentary diagenesis. Biogeosci. 12, 4979-4992. doi: 10.5194/bg-12-4979-2015

Laws, E.A., Popp, B.N., Bidigare, R.R., Kennicutt, M.C., Macko, S.A., 1995. Dependence of phytoplankton carbon isotopic composition on growth rate and $[CO_2]_{aq}$: Theoretical considerations and experimental results. Geochim. Cosmochim. Acta 59, 1131-1138. doi:10.1016/0016-7037(95)00030-4

De Leeuw, J.W., Rijpstra, W.I.C., Schenck, P.A., Volkman, J.K., 1983. Free, esterified and residual bound sterols in Black Sea Unit I sediments. Geochim. Cosmochim. Acta 47, 455-465. doi:10.1016/0016-7037(83)90268-5

Leininger, S., Urich, T., Schloter, M., Schwark, L., Qi, J., Nicol, G.W., Prosser, J.I., Schuster, S.C., Schleper, C., 2006. Archaea predominate among ammonia-oxidizing prokaryotes in soils. Nature 442, 806-809. doi:10.1038/nature04983

Lengeler, J.W., Drew, G., Schlegel, H.G., 1999. Biology of the Prokaryotes. Blackwell Science, New York, pp. 984.

Lengger, S.K., Lipsewers, Y.A., de Haas, H., Sinninghe Damsté, J.S., Schouten, S., 2014. Lack of ^{13}C-label incorporation suggests low turnover rates of thaumarchaeal intact polar tetraether lipids in sediments from the Iceland shelf. Biogeosci. 11, 201-216. doi:10.5194/bg-11-201-2014

Lengger, S.K., Sutton, P.A., Rowland, S.J., Hurley, S.J., Pearson, A., Naafs, B.D.A., Dang, X., Inglis, G.N., Pancost, R.D., 2018. Archaeal and bacterial glycerol dialkyl glycerol tetraether (GDGT) lipids in environmental samples by high temperature-gas chromatography with flame ionisation and time-of-flight mass spectrometry detection. Org. Geochem. 121, 10-21. doi:10.1016/j.orggeochem.2018.03.012

Li, J. Philp, R.P., Pu, F., Allen, J., 1996. Long-chain alkenones in Qinghai Lake sediments. Geochim. Cosmochim. Acta 60, 235-241. doi:10.1016/0016-7037(95)00389-4

Li, C., Sessions, A.L., Kinnaman, F.S., Valentine, D.L., 2009. Hydrogen-isotopic variability in lipids from Santa Barbara Basin sediments. Geochim. Cosmochim. Acta 73, 4803-4823. doi:10.1016/j.gca.2009.05.056

Liaaen-Jensens, S., 1979. Marine carotenoids. In: Scheuer, P. (ed.), Marine Natural Productions, Chemical and Biological Perspectives, vol. 2, pp. 2-73, Academic Press, London.

Lucas, W.J., 1983. Photosynthetic assimilation of exogenous HCO_3^- by aquatic plants. Annu. Rev. Plant Physiol. 34, 71-104. doi:10.1146/annurev.pp.34.060183.000443

Luo, Y.-H., Sternberg, L., Suda, S., Kumazawa, S., Mitsui, A., 1991. Extremely low D/H ratios of photoproduced hydrogen by cyanobacteria. Plant Cell Physiol. 32, 897-900.

MacGregor, B.J., Moser, D.P., Alm, E.W., Nealson, K.H., Stahl, D.A., 1997. Crenarchaeota in Lake Michigan sediment. Appl. Environ. Microbiol. 63, 1178-1181.

Mackenzie, A.S., Brassell, S.C., Eglinton, G., Maxwell, J.R., 1982. Chemical fossils: the geological fate of steroids. Science 217, 491-504. doi:10.1126/science.217.4559.491

Magill, C.R., Ashley, G.M., Freeman, K.H., 2013. Ecosystem variability and early human habitats in eastern Africa, Proc. Nat. Acad. Sci. 110, 1167-1174. doi:10.1073/pnas.1206276110

Mansour, M.P., Volkman, J.K., Jackson, A.E., Blackburn, S.I., 1999. The fatty acid and sterol composition of five marine dinoflagellates. J. Phycol. 35, 710-720. doi:10.1046/j.1529-8817.1999.3540710.x

Marlowe, I.T., Brassell, S.C., Eglinton, G., Green, J.C., 1984. Long chain unsaturated ketones and esters in living algae and marine sediments. Org. Geochem. 6, 135-141. doi:10.1016/0146-6380(84)90034-2

Maslen, E., Grice, K., Gale, J.D., Hallmann, C., Horsfield, B., 2009. Crocetane: A potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age. Org. Geochem. 40, 1-11. doi:10.1016/j.orggeochem.2008.10.005

Maslen, E., Grice, K., Dawson, D., Wang, S., Horsfield, B., 2012. Stable hydrogen isotopes of isoprenoids and *n*-alkanes as a proxy for estimating the thermal history of sediments through geological time. In: Harris, N.B. and Peters, K.E (eds.) Analyzing the Thermal History of Sedimentary Basins: Methods and Case Studies. SEPM Spec. Publ. 103, SEPM, Tulsa, pp. 29-44. doi:10.2110/sepmsp.103

Matsumoto, G., Torii, T., Hanya, T., 1982. High abundance of algal 24-ethylcholesterol in Antarctic lake sediment. Nature 299, 52-54. doi:10.1038/299052a0

Matsumoto, G.I., Fujimura, C., Minoura, K., Takamatsu, N., Takemura, T., Hayashi, S., Shichi, K., Kawai, T., 2003. Paleoenvironmental changes in the Eurasian continental interior during the last 12 million years derived from organic components in sediment cores (BDP-96 and BDP-98) from Lake Baikal. In: Kashiwaya, K. (ed.), Long Continental Records from Lake Baikal, Springer, Tokyo, pp. 75-94.

Matthews, D.E. and Hayes, J.M., 1978. Isotope-ratio-monitoring gas chromatography-mass spectrometry. Anal. Chem. 50, 1465-1473. doi: 10.1021/ac50033a022

Matys, E.D., Sepulveda, J., Pantoja, S., Lange, C.B., Caniupan, M., Lamy, F., Summons, R.E., 2017. Bacteriohopaneopolyols along redox gradients in the Humbodlt Current System off northern Chile. Geobiol. 15, 844-857. doi:10.1111/gbi.12250

Maxwell, J.R., Douglas, A.G., Eglinton, G., McCormick, A., 1968. The Botryococcenes—hydrocarbons of novel structure from the alga Botryococcus braunii, Kützing. Phytochem. 7, 2157-2171. doi:10.1016/S0031-9422(00)85672-1

Mayr, C., Lücke, A., Wagner, S., Wissel, H., Ohlendorf, C., Haberzettl, T., Oehlerich, M., Schäbitz, F., Wille, M., Zhu, J., Zolitschka, B., 2013. Intensified southern hemisphere westerlies regulated atmospheric CO_2 during the last deglaciation. Geology 41, 831-834. doi:10.1130/G34335.1

Mayr, C., Laprida, C., Lücke, A., Martín, R.S., Massaferro, J., Ramón-Mercau, J., Wissel, H., 2015. Oxygen isotope ratios of chironomids, aquatic macrophytes and ostracods for lake-water isotopic reconstructions - Results of a calibration study in Patagonia. J. Hydrol. 529, 600-607. doi:10.1016/j.jhydrol.2014.11.001

M'boule, D., Chivall, D., Sinke-Schoen, D., Sinninghe Damsté, J.S., Schouten, S., van der Meer, M.T.J., 2014. Salinity dependent hydrogen isotope fractionation in alkenones produced by coastal and open ocean haptophyte algae. Geochim. Cosmochim. Acta 130, 126-135. doi:10.1016/j.gca.2014.01.029

McCarthy, M.D., Benner, R., Lee, C., Fogel, M.L., 2007. Amino acid nitrogen isotopic fractionation patterns as indicators of heterotrophy in plankton, particulate, and dissolved organic matter. Geochim. Cosmochim. Acta 71, 4727-4744. doi:10.1016/j.gca.2007.06.061

McClelland, J.W. and Montoya, J.P., 2002. Trophic relationships and the nitrogen isotopic composition of amino acids in plankton. Ecology 83, 2173-2180. doi:10.1890/0012-9658(2002)083[2173:TRATNI]2.0.CO;2

Mendez-Millan, M, Dignac, M.-F., Rumpel, C, Derenne, S., 2010. Can cutin and suberin biomarkers be used to trace shoot and root-derived organic matter? A molecular and isotopic approach. Biogeochem. 106, 23-38. doi:10.1007/s10533-010-9407.

Menzel, D., van Bergen, P.F., Schouten, S., 2003. Reconstruction of changes in export productivity during Pliocene sapropel deposition: a biomarker approach. Palaeogeogr., Palaeoclim., Palaeoecol. 190, 273-287. doi:10.1016/S0031-0182(02)00610-7

Metzger, P. and Largenau, C., 1999. Chemicals of *Botryococcus braunii*. In: Cohen Z (ed.) Chemicals from Microalgae. London: Taylor and Francis.

Metzger, P., Casadevall, E., Pouet, M.J., Pouet, Y., 1985. Structures of some botryococcenes - branched hydrocarbons from the B race of the green-alga Botryococcus braunii. Phytochem. 24, 2995-3002. doi:10.1016/0031-9422(85)80043-1

Meyers, P.A. and Ishiwatari, R., 1993. Lacustrine organic geochemistry - an overview of indicators of organic matter sources and diagenesis in lake sediments. Org. Geochem. 20, 867-900. doi:10.1016/0146-6380(93)90100-P

Meyers, P.A. and Ishiwatari, R., 1995. Organic matter accumulation records in lake sediments. In: Lerman, A., Imboden, D.M., Gat, J.R. (eds.), Physics and Chemistry of Lakes. Springer, Berlin, Heidelberg, pp. 279-328.

Meyers, P.A. and Teranes, J.L., 2001. Sediment Organic Matter. In: Last, W.M. and Smol, J.P. (eds.), Tracking Environmental Change Using Lake sediments, vol. 2, Physical and Geochemical Methods. Kluwer Academic Publishers, Dordrecht, pp. 239-270.

Millar, A.M. and Kunst, L., 1997. Very-long-chain fatty acid biosynthesis is controlled through the expression and specificity of the condensing enzyme. Plant Journal 12, 121-131. doi:10.1046/j.1365-313X.1997.12010121.x

Minagawa, M. and Wada, E., 1984. Stepwise enrichment of ^{15}N along food chains: Further evidence and the relation between δ^{15}N and animal age. Geochim. Cosmochim. Acta 48, 1135-1140. doi:10.1016/0016-7037(84)90204-7

Moldowan, J.M., 1984. C_{30}-steranes, novel markers for marine petroleums and sedimentary rocks. Geochim. Cosmochim. Acta, 48, 2767-2768. doi:10.1016/0016-7037(84)90321-1

Molina, I., Bonaventure, G., Ohlrogge, J., Pollard, M., 2006. The lipid polyester composition of *Arabidopsis thaliana* and *Brassica napus* seeds. Phytochem. 67, 2597-2610. doi: 10.1016/j.phytochem.2006.09.011

Morana, C., Borges, A.V., Roland, F.A.E., Darchambeau, F., Descy, J.-P., Bouillon, S., 2015. Methanotrophy within the water column of a large meromictic tropical lake (Lake Kivu, East Africa). Biogeosci. 12, 2077-2088. doi:10.5194/bg-12-2077-2015

Mügler, I., Sachse, D., Werner, M., Xu, B., Wu, G., Yao, T., Gleixner, G., 2008. Effect of lake evaporation on δD values of lacustrine *n*-alkanes: A comparison of Nam Co (Tibetan Plateau) and Holzmaar (Germany). Org. Geochem. 39, 711-729. doi:10.1016/j.orggeochem.2008.02.008

Naeher, S., Smittenberg, R.H., Gilli, A., Kirilova, E.P., Lotter, A.F., Schubert, C.M., 2012. Impact of recent lake eutrophication on microbial community changes as revealed by high resolution lipid biomarkers in Rotsee (Switzerland). Org. Geochem. 49, 86-95. doi:10.1016/j.orggeochem.2012.05.014

Naeher, S., Schaeffer, P., Adam, P., Schubert, C.J., 2013. Maleimides in recent sediments – Using chlorophyll degradation products for palaeoenvironmental reconstructions. Geochim. Cosmochim. Acta 119, 248-263. doi:10.1016/j.gca.2013.06.004

Naeher, S., Niemann, H., Peterse, F., Smittenberg, R.H., Zigah, P.K., Schubert, C.M., 2014. Tracing the methane cycle with lipid biomarkers in Lake Rotsee (Switzerland). Org. Geochem. 66, 174-181. doi:10.1016/j.orggeochem.2013.11.002

Nelson, D.B. and Sachs, J.P., 2013. Concurrent purification of sterols, triterpenols and alkenones from sediments for hydrogen isotope analysis using high performance liquid chromatography. Org. Geochem. 64, 19-28. doi:10.1016/j.orggeochem.2013.09.005

Nelson, D.B. and Sachs, J.P., 2014. The influence of salinity on D/H fractionation in alkenones from saline and hypersaline lakes in continental North America. Org. Geochem. 66, 38-47. doi:10.1016/j.orggeochem.2013.10.013

Nelson, D.B. and Sachs, J.P., 2016. Galápagos hydroclimate of the Common Era from paired microalgal and mangrove biomarker $^2H/^1H$ values. Proc. Nat. Acad. Sci., 113, 3476-3481. doi:10.1073/pnas.1516271113

Neunlist, S. and Rohmner, M., 1985. Novel hopanoids from the methylotrophic bacteria *Methylococcus capsulatus* and *Methylomonas methanica* (22S)-35-aminobacteriohopane-30,31,32,33,34-pentol and (22S)-35-amino-3β-methylbacteriohopane-30,31,32,33,34-pentol. Biochem. J. 231, 635-639.

Neunlist, S., Rodier, C., Llopiz, P., 2002. Isotopic biogeochemistry of the lipids in recent sediments of Lake Bled (Slovenia) and Baldeggersee (Switzerland). Org. Geochem. 33, 1183-1195. doi:10.1016/S0146-6380(02)00085-2

Nichols, J.E., Walcott, M., Bradley, R., Pilcher, J., Huang, Y., 2009. Quantitative assessment of precipitation seasonality and summer surface wetness using ombrotrophic sediments from an Arctic Norwegian peatland. Quat. Res. 72, 443-451. doi: 10.1016/j.yqres.2009.07.007

Niemann, H. and Elvert, M., 2008. Diagnostic lipid biomarker and stable carbon isotope signatures of microbial communities mediating the anaerobic oxidation of methane with sulphate. Org. Geochem. 39, 1668-1677. doi:10.1016/j.orggeochem.2007.11.003

Nieto-Moreno, V., Rohrmann, A., van der Meer, M.T.J., Sinninghe Damsté, J.S., Sachse, D., Tofelde, S., Niedermeyer, E.M., Strecker, M.R., Mulch, A., 2016. Elevation-dependent changes in *n*-alkane δD and soil GDGTs across the South Central Andes. Earth Planet. Sci. Lett. 453, 234-242. doi:10.1016/j.epsl.2016.07.049

Oakes, A.M. and Hren, M.T., 2016. Temporal variations in the δD of leaf *n*-alkanes from four riparian plant species. Org. Geochem. 97, 122-130. doi:10.1016/j.orggeochem.2016.03.010

Ocampo, R., Callot, H.J., Albrecht, P., 1985. Occurrence of bacteriopetroporphyrins in oil shale. J. Chem. Soc., Chem. Commun., 200-201. doi:10.1039/C39850000200

O'Connell, T.C., 2017. 'Trophic' and 'source' amino acids in trophic estimation: a likely metabolic explanation. Oecologia 184, 317-326. doi:10.1007/s00442-017-3881-9

Oduro, H., Kamyshny, A., Guo, W., Farquhar, J., 2011. Multiple sulfur isotope analysis of volatile organic sulfur compounds and their sulfonium precursors in coastal marine environments. Mar. Chem. 124, 78-89. doi:10.1016/j.marchem.2010.12.004

Oduro, H., Van Alstyne, K.L., Farquhar, J., 2012. Sulfur isotope variability of oceanic DMSP generation and its contributions to marine biogenic sulfur emissions. PNAS 109, 9012-9016. doi:10.1073/pnas.1117691109

Oduro, H., Kamyshny Jr, A., Zerkle, A.L., Li, Y., Farquhar, J., 2013. Quadruple sulfur isotope constraints on the origin and cycling of volatile organic sulfur compounds in a stratified sulfidic lake. Geochim. Cosmochim. Acta 120, 251-262. doi:10.1016/j.gca.2013.06.039

Ohkouchi, N., Kahiyama, Y., Chikaraishi, Y., Ogawa, N.O., Tada, R., Kitazato, H., 2006. Nitrogen isotopic composition of chlorophylls and porphyrins in geological samples as tools for reconstructing paleoenvironment. Geochim. Cosmochim. Acta 70, A452, doi:10.1016/j.gca.2006.06.911.

Ohkouchi, N., Chikaraishi, Y., Close, H.G., Fry, B., Larsen, T., Madigan, D.J., McCarthy, M.D., McMahon, K.W., Nagata, T., Naito, Y.I., Ogawa, N.O., Popp, B.N., Steffan, S., Takano, Y., Tayasu, I., Wyatt, A.S.J., Yamaguchi, Y.T., Yokoyama, Y., 2017. Advances in the application of amino acid nitrogen isotopic analysis in ecological and biogeochemical studies, Org. Geochem. 113, 150-174. doi:10.1016/j.orggeochem.2017.07.009

O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. BioSci. 38, 328-336. doi:10.2307/1310735

Ono, S., Wing, B., Johnston, D., Farquhar, J., Rumble, D., 2006. Mass-dependent fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles. Geochim. Cosmochim. Acta 70, 2238-2252. doi:10.1016/j.gca.2006.01.022

Orphan, V.J., Hinrichs, K.-U., Ussler, III, W., Paull, C.K., Taylor, L.T., Sylva, S.P., Hayes, J.M., Delong, E.F., 2001. Comparative analysis of methane-oxidizing Archaea and sulfate-reducing bacteira in anoxic marine sediments. Appl. Environ. Microbiol. 67, 1922-1934. doi:10.1128/AEM.67.4.1922-1934.2001

Osborne, K. A., Gray, N.D., Sherry, A., Leary, P., Mejeha, O., Bischoff, J., Rush, D., Sidgwick, F.R., Birgel, D., Kalyuzhnaya, M.G., Talbot, H.M., 2017. Methanotroph-derived bacteriohopanepolyol signatures as a function of temperature related growth, survival, cell death and preservation in the geological record. Env. Microbiol. Rep. 9, 492–500. doi:10.1111/1758-2229.12570

Osburn, M.R., Dawson, K.S., Fogel, M.L., Sessions, A.L., 2016. Fractionation of hydrogen isotopes by sulfate- and nitrate-reducing bacteria. Front. Microbiol. 7, 1166. doi:10.3389/fmicb.2016.01166

Otto, A. and Simpson, M.J., 2005. Degradation and preservation of vascular plant-derived biomarkers in grassland and forest soils from Western Canada. Biogeochem. 74, 377-409. doi:10.1007/s10533-004-5834-8

Pancost, R.D. and Sinninghe Damsté, J.S., 2003. Carbon isotopic compositions of prokaryotic lipids as tracers of carbon cycling in diverse settings. Chem. Geol. 195, 29-58. doi:10.1016/S0009-2541(02)00387-X

Pancost, R.D. and Pagani, M., 2006. Controls on the carbon isotopic compositions of lipids in marine environments. In: Marine Organic Matter: Biomarkers, Isotopes and DNA, Springer, Berlin, pp. 209-249.

Pancost, R.D., Freeman, K.H., Wakeham, S.G., 1999. Controls on the carbon-isotope compositions of compounds in Peru surface waters. Org. Geochem. 30, 319-340. doi:10.1016/S0146-6380(99)00004-2

Pancost, R.D, Crawford, N., Maxwell, J.R., 2002. Molecular evidence for basin-scale photic zone euxinia in the Permian Zechstein Sea. Chem. Geol. 188, 217-227. doi:10.1016/S0009-2541(02)00104-3

Pancost, R.D., Sinninghe Damsté, J.S., de Lint, S., van der Maarel, M.J.E.C., Gottschal, J.C., The Medinaut Shipboard Scientific Party, 2000. Biomarker evidence for widespread anaerobic methane oxidation in mediterranean sediments by a consortium of methanogenic archaea and bacteria. Appl. Environ. Microbiol. 66, 1126–1132. doi:10.1128/AEM.66.3.1126-1132.2000

Paoli, M., Marles-Wright, J., Smith, A., 2002. Structure-function relationships in heme-proteins. DNA Cell Biol. 21, 271-280. doi:10.1089/104454902753759690

Parkin, T.B. and Brock, T.D., 1980. The effects of light quality on the growth of phototrophic bacteria in lakes. Archives Microbiol. 125, 19-27. doi:10.1007/BF00403193

Pärn, J., Affolter, S., Ivask, J., Johnson, S.C., Kirsimäe, K., Leuenberger, M., Martma, T., Raidla, V., Schloemer, S., Sepp, H., Vaikmäe, R., Walraevens, K., 2018. Redox zonation and organic matter oxidation in palaeogroundwater of glacial origin from the Baltic Artesian Basin. Chem. Geol. 488, 149-161. doi:10.1016/j.chemgeo.2018.04.027

Passier, H.F. Böttcher, M.E., De Lange, G.J. 1999. Sulphur enrichment in organic matter of

Eastern Mediterranean sapropels: A study of sulphur isotope partitioning. Aq. Geochem. 5, 99-118. doi:10.1023/A:1009676107330

Pearson, A., Budin, M., Brocks, J.J., 2003. Phylogenetic and biochemical evidence for sterol synthesis in the bacterium Gemmata obscuriglobus. Proc. Nat. Acad. Sci. 100, 15352-15357. doi:10.1073/pnas.2536559100

Pearson A., Flood Page, S.R., Jorgenson, T.L., Fischer, W.W., Higgins, M.B., 2007. Novel hopanoid cyclases in the environment. Environm. Microbiol. 9, 2175-2188. doi:10.1111/j.1462-2920.2007.01331.x

Pearson, A., Hurley, S.J., Walter, S.R.S., Kusch, S., Lichtin, S., Zhang, Y.G., 2016. Stable carbon isotope ratios of intact GDGTs indicate heterogeneous sources to marine sediments. Geochim. Cosmochim. Acta 181, 18-35. doi:10.1016/j.gca.2016.02.034

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide. Cambridge University Press.

Peterson, B.J. and Fry, B., 1987. Stable isotopes in ecosystem studies. Ann. Rev. Ecol. Syst. 18, 293-320. doi:10.1146/annurev.es.18.110187.001453

Pfenning, 1978. General physiology and ecology of photosynthetic bacteria. In: Clayton, R.K. and Sistrom, W.R. (eds.) Photosynthetic Bacteria, Plenum Press, pp. 3-16.

Pickering M.D. and Keely, B.J., 2011. Low temperature abiotic formation of mesopyrophaeophorbide *a* from pyrophaeophorbide a under conditions simulating anoxic natural environments. Geochim. Cosmochim. Acta 75, 533-540. doi:10.1016/j.gca.2010.10.020

Pollard, M., Beisson, F., Li, Y., Ohlrogge, J., 2008. Building lipid barriers: biosynthesis of cutin and suberin. Trends Plant Sci. 13, 236-246. doi: 10.1016/j.tplants.2008.03.003

Popp, B.N., Takigiku, R., Hayes, J.M., Louda, J.W., Baker, E.W., 1989. The post-Paleozoic chronology and mechanism of ^{13}C depletion in primary marine organic matter. Am. J. Sci., 289, 436-454. doi:10.2475/ajs.289.4.436

Popp, B.N., Kenig, F., Wakeham, S.G., Laws, E.A., Bidigare, R.R., 1998. Does growth rate affect ketone unsaturation and intracellular carbon isotopic variability in *Emiliania huxleyi*? Paleoceanogr. 13, 35-41. doi:10.1029/97PA02594

Popp, B.N., Trull, T., Kenig, F., Wakeham, S.G., Rust, T.M., Tilbrook, B., Griffiths, B., Wright, S.W., Marchant, H.J., Bidigare, R.R., Laws, E.A., 1999. Controls on the carbon isotopic composition of Southern Ocean phytoplankton. Global Biogeochem. Cycles 13, 827-843.

doi:10.1029/1999GB900041

Popper, Z.A., Michel, G., Hervé, C., Domozych, D.S., Willats, W.G.T., Tuohy, M.G., Kloareg, B., Stengel, D.B., 2011. Evolution and diversity of plant cell walls: from algae to flowering plants. Ann Rev Plant Biol 62, 567-590. doi:10.1146/annurev-arplant-042110-103809

Poralla, K., Härtner, T., Kannenberg, E., 1984. Effect of temperature and pH on the hopanoid content of *Bacillus acidocaldarius*. FEMS Microbiol. Let. 23, 253-256. doi:10.1111/j.1574-6968.1984.tb01073.x

Post, W.M., Emanuel, W.R., Zinke, P.J., Stangenberger, A.G., 1977. Soil carbon pools and world life zones. Nature 298, 156-159. doi:10.1038/298156a0

Powers, L.A., Werne, J.P., Johnson, T.C., Hopmans, E.C., Sinninghe Damsté, J.S., Schouten, S., 2004. Crenarchaeotal membrane lipids in lake sediments: A new paleotemperature proxy for continental paleoclimate reconstruction? Geology 32, 613. doi:10.1130/G20434.1

Prahl, F., Herbert, T., Brassell, S.C., Ohkouchi, N., Pagani, M., Repeta, D., Rosell-Melé, A., Sikes, E., 2000. Status of alkenone paleothermometer calibration: Report from Working Group 3. Geochem. Geophys. Geosyst. 1, paper no. 2000GC000058. doi:10.1029/2000GC000058

Prahl, F.G., Cowie, G.L., De Lange, G.J., Sparrow, M.A., 2003. Selective organic matter preservation in “burn-down” turbidites on the Madeira Abyssal Plain. Paleoceanogr. 18. doi:10.1029/2002PA000853

Prins, H.B.A. and Elzenga, J.T.M., 1989. Bicarbonate utilization: Function and mechanism. Aquatic Bot. 34, 59-83. doi:10.1016/0304-3770(89)90050-8

Quandt, L., Gottschalk, G., Ziegler, H., Stichler, W., 1977. Isotope discrimination by photosynthetic bacteria. FEMS Microbiology Letters 1, 125-128, doi:10.1111/j.1574-6968.1977.tb00596.x

Rach, O., Brauer, A., Wilkes, H., Sachse, D., 2014. Delayed hydrological response to Greenland cooling at the onset of the Younger Dryas in western Europe. Nat. Geosci. 7, 109-113. doi:10.1038/ngeo2053

Rach O., Engels, S., Kahmen, A., Brauer, A., Martín-Puertas, C., van Geel, B., Sachse D., 2017. Hydrological and ecological changes in western Europe between 3200 and 2000 cal years BP derived from lipid biomarker δD values in Lake Meerfelder Maar sediments. Quatern. Sci. Rev. 172, 44-54. doi:10.1016/j.quascirev.2017.07.019

Raghoebarsing, A.A, Smolders, A.J., Schmid, M.C., Ripstra, I.C., 2005. Methanotrophic symbionts provide carbon for phososynthesis. Nature 436; doi:10.1038/nature03802

Rampen, S.W., Schouten, S., Abbas, B., Panoto, F.E., Muyzer, G., Campbell, C.N., Fehling, J., Sinninghe Damsté, J.S., 2007. On the origin of 24-norcholestanes and their use as age-diagnostic biomarkers. Geology 35, 419-422. doi:10.1130/G23358A.1

Rampen, S.W., Abbas, B.A., Schouten, S., Sinninghe Damsté, J.S., 2010. A comprehensive study of sterols in marine diatoms (Bacillariophyta): implications for their use as tracers for diatom productivity. Limnol. Oceanogr. 55, 91-105. doi:10.4319/lo.2010.55.1.0091

Rao, Z., Jia, G., Qiang, M., Zhao, Y., 2014. Assessment of the difference between mid- and long chain compound specific $\delta D_{n\text{-alkanes}}$ values in lacustrine sediments as a paleoclimatic indicator. Org. Geochem. 76, 104-117. doi:10.1016/j.orggeochem.2014.07.015

Raven, M.R., Adkins, J.F., Werne, J.P., Lyons, T.W., Sessions, A.L., 2015. Sulfur isotopic composition of individual organic compounds from Cariaco Basin sediments. Org. Geochem. 80, 53-59. doi:10.1016/j.orggeochem.2015.01.002

Redfield, A.C., 1958. The biological control of chemical factors in the environment. Am. Sci., 46, 205-211.

Rees, C.E., Jenkins, W.J., Monster, J., 1978. The sulfur isotope geochemistry of ocean water sulfate. Geochim. Cosmochim. Acta 42, 377-381. doi:10.1016/0016-7037(78)90268-5

Reiffarth, D.G., Petticrew, E.L., Lobb, D.A., 2016. Sources of variability in fatty acid (FA) biomarkers in the application of compound-specific stable isotopes (CSSIs) to soil and sediment fingerprinting and tracing: A review. Sci. Total Environ. 565, 8-27. doi:10.1016/j.scitotenv.2016.04.137

Rho, J. and Litsky, W., 1979. Cellulose production by planktonic algae in lacustrine environments. Hydrobiologia 66, 249-258. doi:10.1007/BF00020907

Ricci, J.N., Coleman, M.L., Welander, P.V., Sessions, A.L., Summons, R.E., Spear, J.R., Newman, D.K., 2014. Diverse capacity for 2-methylhopanoid production correlates with a specific ecological niche. ISME J 8:675-684. doi:10.1038/ismej.2013.191

Ricci, J.N., Morton, R., Kulkarni, G., Summers, M.L., Newman, D.K. 2017. Hopanoids play a role in stress tolerance and nutrient storage in the cyanobacterium *Nostoc punctiforme*. Geobiol. 15, 173-183. doi:10.1111/gbi.12204

Richey, J.N. and Sachs, J.P., 2016. Precipitation changes in the western tropical Pacific over the past millennium. Geology 44, 671-674. doi:10.1130/G37822.1

Riedinger, N., Brunner, B., Krastel, S., Arnold, G.L., Wehrmann, L.M., Formolo, M.J., Beck, A., Bates, S.M., Henkel, S., Kasten, S., Lyons, T.W., 2017. Sulfur cycling in an iron oxide-dominated, dynamic marine depositional system: The Argentine continental margin. Front. Earth Sci. 5, 33. doi:10.3389/feart.2017.00033

Roden, J.S, Lin, G., Ehleringer, J.R, 2000. A mechanistic model for interpretation of hydrogen and oxygen isotope ratios in tree-ring cellulose. Geochim. Cosmochim. Acta 64, 21-35. doi:10.1016/S0016-7037(99)00195-7

Rodrigo, M.A., Vicente, E., Miracle, M.R., 2000. The role of light and concentration gradients in the vertical stratification and seasonal development of phototrophic bacteria in a meromictic lake. Archives Hydrobiol. 148, 533-548. doi:10.1127/archiv-hydrobiol/148/2000/533

Rohmer, M., Knani, M., Simonin, P., Sutter, B., Sahm, H., 1993. Isoprenoid biosynthesis in bacteria: a novel pathway for the early steps leading to isopentenyl diphosphate. Biochem. J. 295, 517-524. doi:10.1042/bj2950517

Rohmer, M., Bouvier, P., Ourisson, G., 1979. Molecular evolution of biomembranes: structural equivalents and phylogenetic precursors of sterols. Proc. Nat. Acad. Sci., 76, 847-851. doi:10.1073/pnas.76.2.847

Rohmer M., Bouvier-Nave, P., Ourisson G., 1984. Distribution of hopanoid triterpenes in prokaryotes. J. Gen. Microbiol. 130,1137-1150. doi:10.1099/00221287-130-5-1137

Romero-Viana, L., Kienel, U., Wilkes, H., Sachse, D., 2013. Growth-dependent hydrogen isotopic fractionation of algal lipid biomarkers in hypersaline Isabel Lake (México). Geochim. Cosmochim. Acta 106, 490-500. doi:10.1016/j.gca.2012.12.017

Ronkainen, T., McClymont, E.L., Väliranta, M., Tuittila, E.-S., 2013. The *n*-alkane and sterol composition of living fen plants as a potential tool for palaeoecological studies. Org. Geochem. 59, 1-9. doi:10.1016/j.orggeochem.2013.03.005

Rontani, J.-F., Prahl, F.G., Volkman, J.K., 2006. Re-examination of the double bond position in alkenones and derivatives: biosynthetic implications. J. Phycol. 42, 800-813. doi:10.1111/j.1529-8817.2006.00251.x

Ross, P., Mayer, R., Benziman, M., 1991. Cellulose biosynthesis and function in bacteria. Microbiol. Rev. 55, 35-58.

Rozanski, K., Klisch, M. A., Wachniew, P., Gorczyca, Z., Goslar, T., Edwards, T. W. D., Shemesh, A., 2010. Oxygen-isotope geothermometers in lacustrine sediments: New insights through combined $\delta^{18}O$ analyses of aquatic cellulose, authigenic calcite and biogenic silica in Lake Gosciaz, central Poland. Geochim. Cosmochim. Acta 74, 2957-2969. doi:10.1016/j.gca.2010.02.026

Rush, D., Sinninghe Damsté, J.S., Poulton, S.W., Thamdrup, B., Garside, A.L., González, J.A., Schouten, S., Jetten, M.S.M., Talbot, H.M., 2014. Anaerobic ammonium-oxidising bacteria: A biological source of the bacteriohopanetetrol stereoisomer in marine sediments. Geochim. Cosmochim. Acta. 140, 50-64. doi:10.1016/j.gca.2014.05.014

Rush, D., Osborne, K.A., Birgel, D., Kappler, A., Hirayama, H., Peckmann, J., Poulton, S.W., Nickel, J.C., Mangelsdorf, K., Kalyuzhnaya, M., Sidgwick, F.R., Talbot, H.M., 2016. The bacteriohopanepolyol inventory of novel aerobic methane oxidising bacteria reveals new biomarker signatures of aerobic methanotrophy in marine systems. PLoS One 11, e0165635. doi:10.1371/journal.pone.0165635

Sachs, J.P. and Repeta, D.J., 1999. Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events: Science 286, 2485-2488, doi:10.1126/science.286.5449.2485.

Sachs, J.P. and Repeta, D.J., 2000. The purification of chlorins from marine particles and sediments for nitrogen and carbon isotopic analysis. Org. Geochem. 31, 317-329, doi:10.1016/S0146-6380(99)00149-7.

Sachs, J.P., Sachse, D., Smittenberg, R.H., Zhang, Z., Battisti, D.S., Golubic, S., 2009. Southward movement of the Pacific intertropical convergence zone AD 1400-1850. Nature Geosci. 2, 519-525. doi:10.1038/NGEO554

Sachse, D. and Sachs, J.P., 2008. Inverse relationship between D/H fractionation in cyanobacterial lipids and salinity in Christmas Island saline ponds. Geochim. Cosmochim. Acta 72, 793-806. doi: 10.1016/j.gca.2007.11.022

Sachse, D., Radke, J., Gleixner, G., 2004. Hydrogen isotope ratios of recent lacustrine sedimentary *n*-alkanes record modern climate variability. Geochim Cosmochim. Acta 68, 4877-4889. doi:10.1016/j.gca.2004.06.004

Sachse, D., Billault, I., Bowen, G.J., Chikaraishi, Y., Dawson, T.E., Feakins, S.J., Freeman, K.H., Magill, C.R., McInerney, F.A., van der Meer, M.T.J., Polissar, P., 10 Robins, R.J., Sachs, J.P., Schmidt, H.-L., Sessions, A.L., White, J.W.C., West, J.B., Kahmen, A., 2012. Molecular paleohydrology: Interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. Annu. Rev. Earth Planet. Sci. 40, 221-49.

doi:10.1146/annurev-earth-042711-105535

Sáenz, J.P., Wakeham, S.G., Eglinton, T.I., Summons, R.E., 2011. New constraints on the provenance of hopanoids in the marine geologic record: Bacteriohopanepolyols in marine suboxic and anoxic environments. Org. Geochem. 42, 1351-1362, doi:10.1016/j.orggeochem.2011.08.016

Sakata, S., Hayes, J.M., Rohmer, M., Hooper, A.B., Seeman, M., 2008. Stable carbon-isotopic compositions of lipids isolated from the ammonia-oxidizing chemoautotroph *Nitrosomonas europaea.* Org. Geochem. 39, 1725-1734. doi:10.1016/j.orggeochem.2008.08.005

Sarkar, S., Wilkes, H., Prasad, S., Brauer, A., Riedel, N., Stebich, M., Basavaiah, N., Sachse, D., 2014. Spatial heterogeneity in lipid biomarker distributions in the catchment and sediments of a crater lake in central India. Org. Geochem. 66, 125-136. doi:10.1016/j.orggeochem.2013.11.009

Sanger, J.E., 1988. Fossil pigments in paleoecology and paleolimnology. Palaeogeogr., Palaeoclim., Palaeoecol. 62, 343-359. doi:10.1016/0031-0182(88)90061-2

Sauer, P.E., Miller, G.H., Overpeck, J.T., 2001a. Oxygen isotope ratios of organic matter in Arctic lakes as a paleoclimate proxy: field and laboratory investigations. J. Paleolim. 25, 43-64. doi: 10.1023/A:1008133523139

Sauer, P.E., Eglinton, T.I., Hayes, J.M., Schimmelmann, A., Sessions, A.L., 2001b. Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions. Geochim. Cosmochim. Acta 65, 213-222. doi:10.1016/S0016-7037(00)00520-2

Schaeffer, P., Adam, P., Werung, P., Bernasconi, S., Albrecht, P., 1997. Molecular and isotopic investigation of free and S-bound lipids from an actual meromictic lake (Lake Cadagno, Switzerland). In: Proceedings of the 18th International Meeting on Organic Geochemistry, September 22-26, 1997, Maastricht, The Netherlands, Forschungszentrum Jülich, Jülich, Germany, pp. 57–58.

Schefuß, E., Schouten, S., Schneider, R.R., 2005. Climatic controls on central African hydrology during the past 20,000 years. Nature 437, 1003-1006. doi:10.1038/nature03945

Schefuß, E., Kuhlmann, H., Mollenhauer, G., Prange, M., Pätzold, J., 2011. Forcing of wet phases in southeast Africa over the past 17,000 years. Nature 480, 509-512. doi:10.1038/nature10685

Schoell, M., Simoneit, B.R.T., Wang, T.G., 1994. Organic geochemistry and coal petrology of Tertiary brown coal in the Zhoujing mine, Baise Basin, South China. Biomarker sources inferred from stable carbon isotope compositions of individual compounds. Org. Geochem. 21, 713-719. doi:10.1016/0146-6380(94)90014-0

Schouten, S., van der Maarel, M.J.E.C., Huber, R., Sinninghe Damsté, J.S., 1997. 2,6,10,15,19-Pentamethylicosenes in *Methanolobus bombayensis*, a marine methanogenic archaeon, and in *Methanosarcina mazei*. Org. Geochem. 26, 409-414. doi:10.1016/S0146-6380(97)00011-9

Schouten, S., Hoefs, M.J.L., Koopmans, M.P., Bosch, H.-J., Sinninghe Damsté, J.S., 1998a. Structural characterization, occurrence and fate of archaeal ether-bound acyclic and cyclic biphytanes and corresponding diols in sediments. Org. Geochem. 29, 1305-1319. doi:10.1016/S0146-6380(98)00131-4

Schouten, S., Breteler, W.C.K., Blokker, P., Schogt, N., Rijpstra, W.I.C., Grice, K., Baas, M., Sinninghe Damsté, J.S., 1998b. Biosynthetic effects on the stable carbon isotopic compositions of algal lipids: Implications for deciphering the carbon isotopic biomarker record. Geochim. Cosmochim. Acta 62, 1397-1406. doi:10.1016/S0016-7037(98)00076-3

Schouten, S., Rijpstra, W.I.C., Kok, M.., Hopmans, E.C., Summons, R.E., Volkman, J.K., Sinninghe Damsté, J.S., 2001. Molecular organic tracers of biogeochemical processes in a saline meromictic lake (Ace Lake). Geochim. Cosmochim. Acta 65, 1629-1640. doi:10.1016/S0016-7037(00)00627-X

Schouten, S., Ossebaar, J., Schreiber, K., Kienhuis, M.V.M., Langer, G., Benthien, A., Bijma, J., 2006. The effect of temperature, salinity and growth rate on the stable hydrogen isotopic composition of long chain alkenones produced by *Emiliania huxleyi* and *Gephyrocapsa oceanica*. Biogeosci. 3, 113–119. doi:10.5194/bg-3-113-2006

Schouten, S., Hopmans, E.C., Sinninghe Damsté, J.S., 2013. The organic geochemistry of glycerol dialkyl glycerol tetraether lipids: A review. Org. Geochem. 54, 19-61. doi:10.1016/j.orggeochem.2012.09.006

Schwab, V.F. and Sachs, J.P., 2011. Hydrogen isotopes in individual alkenones from the Chesapeake Bay estuary. Geochim. Cosmochim. Acta 75, 7552-7565. doi:10.1016/j.gca.2011.09.031

Schwab, V.F. and Sachs, J.P., 2009. The measurement of D/H ratio in alkenones and their isotopic heterogeneity. Org. Geochem. 40, 111-118. doi:10.1016/j.orggeochem.2008.09.013

Segarra, K.E.A., Schubotz, F., Samarkin, V., Yoshinaga, M.Y., Hinrichs, K.-U., Joye, S.B., 2015. High rates of anaerobic methane oxidation in freshwater wetlands reduce potential atmospheric methane emissions. Nature Comm. 6, 7477. doi:10.1038/ncomms8477

Sessions, A.L. and Burgoyne, T.W., Schimmelmann, A., Hayes, J.M., 1999. Fractionation of hydrogen isotopes in lipid biosynthesis. Org. Geochem. 30, 1193-200. doi:10.1016/S0146-6380(99)00094-7

Sessions, A.L., 2016. Factors controlling the deuterium contents of sedimentary hydrocarbons. Org. Geochem. 96, 43-64. doi:10.1016/j.orggeochem.2016.02.012

Showalter, A.M., 1993. Structure and function of plant cell wall proteins. Plant Cell 5, 9-23. doi:10.1105/tpc.5.1.9

Sikes, E., Farrington, J.W., Keigwin, L.D., 1991. Use of the alkenone unsaturation ratio U_{37}^{k} to determine past sea surface temperatures: core-top SST calibrations and methodology considerations. Earth Planet. Sci. Lett. 104, 36-47. doi:10.1016/0012-821X(91)90235-A

Sinninghe Damsté, J.S., Rampen, S., Irene, W., Rijpstra, C., Abbas, B., Muyzer, G., 2003. A diatomaceous origin for long-chain diols and mid-chain hydroxy methyl alkanoates widely occurring in Quaternary marine sediments: Indicators for high-nutrient conditions. Geochim. Cosmochim. Acta 67, 1339-1348. doi:10.1016/S0016-7037(02)01225-5

Sinninghe Damsté, J.S., Verschuren D., Ossebaar J., Blokker J., van Houten R., van der Meer M.T.J., Plessen B., Schouten S., 2011a. A 25,000-year record of climate-induced changes in lowland vegetation of eastern equatorial Africa revealed by the stable carbon-isotopic composition of fossil plant leaf waxes. Earth Planet. Sci. Lett. 302, 236-246. doi:10.1016/j.epsl.2010.12.025

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopmans, E.C., Weijers, J.W.H., Foesel, B.U., Overmann, J., Dedysh, S.N., 2011b. 13,16-Dimethyl octacosanedioic acid (iso-diabolic acid), a common membrane-spanning lipid of *Acidobacteria* subdivisions 1 and 3. Appl. Environ. Microbiol. 77, 4147-4154. doi:10.1128/AEM.00466-11

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopmans, E.C., Foesel, B.U., Wust, P.K., Overmann, J., Tank, M., Bryant, D.A., Dunfield, P.F., Houghton, K., Stott, M.B., 2014. Ether- and ester-bound iso-diabolic acid and other lipids in members of *Acidobacteria* subdivision 4. Appl. Environ. Microbiol. 80, 5207-5218. doi:10.1128/AEM.01066-14

Smith, B.N. and Epstein, S., 1970. Biogeochemistry of the stable isotopes of hydrogen and carbon in salt marsh biota. Plant Physiol. 46, 738-742.

Smittenberg, R.H. and Sachs, J.P., 2007. Purification of dinosterol for hydrogen isotopic analysis using high-performance liquid chromatography–mass spectrometry. J. Chromatogr. A 1169, 70-76. doi:10.1016/j.chroma.2007.09.018

Spaak, G., Edwards, D.S., Allen, H.J., Grotheer, H., Summons, R.E., Coolen, M.J.L., Grice, K. 2018. Extent and persistence of photic zone euxinia in Middle-Late Devonian seas - Insights from the Canning Basin and implications for petroleum source rock formation. Mar. Petrol. Geol. 93, 33-56. doi:10.1016/j.marpetgeo.2018.02.033

Stal, L.J., 2015. Nitrogen fixation in cyanobacteria. In: eLS. John Wiley & Sons Ltd., Chichester. doi:10.1002/9780470015902.a0021159.pub2

Sternberg, L.D.L., 1988. D/H ratios of environmental water recorded by D/H ratios of plant lipids. Nature 333, 59-61. doi:10.1038/333059a0

Sternberg, L. and Ellsworth, P.F.V., 2011. Divergent biochemical fractionation, not convergent temperature, explains cellulose oxygen isotope enrichment across latitudes. PLoS ONE 6, e28040. doi:10.1371/journal.pone.0028040

Sternberg, L.D.S.L., Pinzon, M-C., Vendramini, P.F., Anderson, W.T., Jahren, A.H., Beuning, K., 2007. Oxygen isotope ratios of cellulose-derived phenylglucosazone: An improved paleoclimate indicator of environmental water and relative humidity. Geochim. Cosmochim. Acta 71, 2463-2473. doi:10.1016/j.gca.2007.03.004

Stötter, T., Bastviken, D., Bodelier, P.L.E., van Hardenbroek, M., Rinta, P., Schilder, J., Schubert, C.J., Heiri, O., 2018. Abundance and d^{13}C values of fatty acids in lacustrine surface sediments: Relationships with in-lake methane concentrations. Quat. Sci. Rev. 191, 337-347. doi:10.1016/j.quascirev.2018.04.029

Strauss, H., 1997. The isotopic composition of sedimentary sulfur through time. Palaeogeogr., Palaeoclim., Palaeoecol. 132, 97-118. doi:10.1016/S0031-0182(97)00067-9

Street, J.H., Anderson, R.S., Paytan, A., 2012. An organic geochemical record of Sierra Nevada climate since the LGM from Swamp Lake, Yosemite. Quat. Sci. Rev. 40, 89-106. doi:10.1016/j.quascirev.2012.02.017

Summons, R.E. and Powell, T.G.,1987. Identification of aryl isoprenoids in source rocks and crude oils: Biological markers for the green sulphur bacteria. Geochim. Cosmochim. Acta 51, 557-566. doi:10.1016/0016-7037(87)90069-X

Summons, R.E., Volkman, J.K., Boreham, C.J., 1987. Dinosterane and other steroidal hydrocarbons of dinoflagellate origin in sediments and petroleum. Geochim. Cosmochim.

Acta 51, 3075-3082. doi:10.1016/0016-7037(87)90381-4

Summons, R.E., Jahnke, L.L., Roksandic, Z., 1994. Carbon isotopic fractionation in lipids from methanotrophic bacteria: Relevance for interpretation of the geochemical record of biomarkers. Geochim. Cosmochim. Acta 58, 2853-2863. doi:10.1016/0016-7037(94)90119-8

Summons, R.E., Hope, J.M., Dowling, L.M., Jahnke, L.L., Largeau, C., Metzger, P., 1996. Carbon isotope fractionation in lipid biosynthesis by algae and cyanobacteria. In: Grimalt, J. O. and Dorronsoro, C. (eds.), Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History. San Sebastian, Spain: A.I.G.O.A., pp. 6-7.

Summons, R.E., Jahnke, L.L., Hope, J.M., Logan, G.A., 1999. 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. Nature 400, 554-557. doi:10.1038/23005

Summons, R.E., Metzger, P., Largeau, C., Murray, A.P., Hope, J.M., 2002. Polymethylsqualanes from *Botryococcus braunii* in lacustrine sediments and crude oils. Org. Geochem. 33, 99-109. doi:10.1016/S0146-6380(01)00147-4

Summons, R.E., Bradley, A.S., Jahnke, L.J., Waldbauer, J.R., 2006. Steroids, triterpenoids and molecular oxygen. Philos. Trans. R. Soc. Lond. B, Biol. Sci. 361, 951-968. doi:10.1098/rstb.2006.1837

Sun, Q., Chu, G.Q., Liu, G.X., Li, S., Wang, X.H., 2007. Calibration of alkenone unsaturation index with growth temperature for a lacustrine species, *Chrysotila lamellosa* (Haptophyceae). Org. Geochem. 38, 1226-1234. doi:10.1016/j.orggeochem.2007.04.007

Swain, E.B., 1985. Measurement and interpretation of sedimentary pigments. Freshw. Biol. 15, 53-75. doi:10.1111/j.1365-2427.1985.tb00696.x

Talbot, H.M., Watson, D.F., Pearson, E.J., Farrimond, P., 2003. Diverse biohopanoid compositions of non-marine sediments. Org. Geochem. 34, 1353-1371. doi:10.1016/S0146-6380(03)00159-1

Talbot, H.M., Handley, L., Spencer-Jones, C., Dinga, B.J., Schefuß, E., Mann, P.J., Poulsen, J.R., Spencer, R.G.M., Wabakanghanzi, J.N., 2014. Variability in aerobic methane oxidation over the past 1.2 Myrs recorded in microbial biomarker signatures from Congo fan sediments. Geochim. Cosmochim. Acta 133, 387-401. doi:10.1016/j.gca.2014.02.035

Talbot, M.R., 2001. Nitrogen isotopes in paleolimnology. In: Last, W.M. and Smol, J.P.

(eds.), Tracking Environmental Change Using Lake Sediments, vol. 2: Physical and Geochemical Methods, Kluwer, Dordrecht, pp. 401-439.

Tani, Y., Nara, F., Soma, Y., Soma, M., Itoh, N., Matsumoto, G.I., Tanaka, A., Kawai, T., 2009. Phytoplankton assemblage in the Plio-Pleistocene record of Lake Baikal as indicated by sedimentary steryl chlorin esters. Quat. Int. 205, 126-136. doi:10.1016/j.quaint.2009.02.004

Theroux, S., D'Andrea, W.J., Toney, J., Amaral-Zettler, L., Huang, Y., 2010. Phylogenetic diversity and evolutionary relatedness of alkenone-producing haptophyte algae in lakes: Implications for continental paleotemperature reconstructions. Earth Planet. Sci. Lett. 300, 311-320. doi:10.1016/j.epsl.2010.10.009

Thiel, V., Jenisch, A., Landmann, G., Reimer, A., Michaelis, W., 1997. Unusual distributions of long-chain alkenones and tetrahymanol from the highly alkaline Lake Van, Turkey. Geochim. Cosmochim. Acta 61, 2053-2064. doi:10.1016/S0016-7037(97)00038-0

Thiel, V., Peckmann, J., Seifert, R., Wehrung, P., Reitner, J., Michaelis, W., 1999. Highly isotopically depleted isoprenoids: Molecular markers for ancient methane venting. Geochim. Cosmochim. Acta 63, 3959-3966. doi:10.1016/S0016-7037(99)00177-5

Tierney, J.E. and Russell, J.M., 2009. Distributions of branched GDGTs in a tropical lake system: Implications for lacustrine application of the MBT/CBT paleoproxy. Org. Geochem. 40, 1032-1036. doi:10.1016/j.orggeochem.2009.04.014

Tierney, J.E., Russell, J.M., Huang, Y.S., Sinninghe Damsté, J.S., Hopmans, E.C., Cohen, A.S., 2008. Northern hemisphere controls on tropical southeast African climate during the past 60,000 years. Science 322, 252-255. doi:10.1126/science.1160485

Tierney, J.E., Russell, J.M, Huang, Y., 2010. A molecular perspective on Late Quaternary climate and vegetation change in the Lake Tanganyika basin, East Africa. Quat. Sci. Rev. 29, 787-800. doi:10.1016/j.quascirev.2009.11.030

Tierney, J.E., Russell, J.M., Sinninghe Damsté, J.S., Huang, Y., Verschuren, D., 2011. Late Quaternary behavior of the East African monsoon and the importance of the Congo Air Boundary. Quat. Sci. Rev. 30, 798-807. doi:10.1016/j.quascirev.2011.01.017

Tipple, B.J. and Pagani, M., 2013. Environmental control on eastern broadleaf forest species’ leaf wax distributions and D/H ratios. Geochim. Cosmochim. Acta 111, 64-77. doi:10.10 16/j.gca.2012.10 .042

Toney, J.L., Leavitt, P.R., Huang, Y., 2011. Alkenones are common in prairie lakes of interior

Canada. Org. Geochem. 42, 707-712. doi:10.1016/j.orggeochem.2011.06.014

Treibs, A., 1936, Chlorophyll- und Häminderivate in organischen Mineralstoffen: Angew. Chemie 49, 682-686, doi:10.1002/ange.19360493803.

Tulipani, S., Grice, K., Greenwood, P., Schwark, L., Böttcher, M.E., Summons, R.E., Foster, C., 2015. Molecular proxies as indicators of freshwater incursion-driven salinity stratification. Chem. Geol. 409, 61-68. doi:10.1016/j.chemgeo.2015.05.009

Tyler, J., Kashiyama, Y., Ohkouchi, N., Ogawa, N., Yokoyama, Y., Chikaraishi, Y., Staff, R.A., Ikehara, M., Bronk Ramsey, C., Bryant, C., Brock, F., Gotanda, K., Haraguchi, T., Yonenobu, H., Nakagawa, T., 2010. Tracking aquatic change using chlorin-specific carbon and nitrogen isotopes: The last glacial-interglacial transition at Lake Suigetsu, Japan. Geochim. Geophys. Geosyst. 11, Q09010, doi:10.1029/2010GC003186

Uhle, M.E., Macko, S.A., Spero, H.J., Engel, M.H., Lea, D.W., 1997. Sources of carbon and nitrogen in modern planktonic foraminifera: the role of algal symbionts as determined by bulk compound specific stable isotopic analyses. Org. Geochem. 27, 103-113. doi:10.1016/S0146-6380(97)00075-2

Urban, N.R., Ernst, K., Bernasconi, S.,1999. Addition of sulfur to organic matter during early diagenesis of lake sediments. Geochim. Cosmochim. Acta 63, 837-853. doi:10.1016/S0016-7037(98)00306-8

van Bree, L.G.J., Rijpstra, W.I.C., Cocquyt, C., Al-Dhabi, N.A., Verschuren, D., Sinninghe Damsté, J.S., de Leeuw, J.W., 2014. Origin and palaeoenvironmental significance of C_{25} and C_{27} *n*-alk-1-enes in a 25,000-year lake-sedimentary record from equatorial East Africa. Geochim. Cosmochim. Acta 145, 89-102. doi:10.1016/j.gca.2014.08.035

van Bree, L.G.J., Peterse, F., van der Meer, M.T.J., Middleburg, J.J., Negash, A.M.D., De Crop, W., Cocquyt, C., Wieringa, J.J., Verschuren, D., Sinninghe Damsté, J.S., 2018. Seasonal variability in the abundance and stable carbon-isotopic composition of lipid biomarkers in suspended particulate matter from a stratified equatorial lake (Lake Chala, Kenya/Tanzania): Implications for the sedimentary record. Quat. Sci. Rev. 192, 208-224. doi:10.1016/j.quascirev.2018.05.023

van den Bos, V., Engels, S., Bohncke, S.J.P., Cerli, C., Jansen, B., Kalbitz, K., Peterse, F., Renssen, H., Sachse, D., 2018. Late Holocene changes in vegetation and atmospheric circulation at Lake Uddelermeer (The Netherlands) reconstructed using lipid biomarkers and compound specific δD analysis. J. Quatern. Sci. 33, 100-111. doi:10.1002/jqs.3006

van der Meer, M.T.J., Schouten, S., Sinninghe Damsté, J.S., 1998. The effect of the reversed tricarboxylic acid cycle on the ^{13}C contents of bacterial lipids. Org. Geochem. 28, 527-533. doi:10.1016/S0146-6380(98)00024-2

van der Meer, M.T.J, Schouten, S., Rijpstra, W.I.C., Fuchs, G., Sinninghe Damsté, J.S., 2001. Stable carbon isotope fractionations of the hyperthermophilic crenarchaeon *Metallosphaera sedula*. FEMS Microbiol. Lett. 196, 67-70. doi:10.1111/j.1574-6968.2001.tb10542.x

van der Meer, M.T.J., Baas, M., Rijpstra, W.I.C., Marino, G., Rohling, E.J., Sinninghe Damsté, J.S., Schouten, S., 2007. Hydrogen isotopic compositions of long-chain alkenones record freshwater flooding of the Eastern Mediterranean at the onset of sapropel deposition. Earth Planet. Sci. Lett. 262, 594-600. doi:10.1016/j.epsl.2007.08.014

van Soelen, E.E., Lammers, J.M., Eglinton, T.I., Sinninghe Damsté, J.S., Reichart, G.J., 2014. Unusual C_{35} to C_{38} alkenones in mid-Holocene sediments from a restricted estuary (Charlotte Harbor, Florida). Org. Geochem. 70, 20-28. doi:10.1016/j.orggeochem.2014.01.021

van Winden, J.F., Kip, N., Reichart, G-J., Jetten, M.S.M., Huub, M.S., Op den Camp, J.M., Sinninghe Damsté, J.S., 2010. Lipids of symbiotic methane-oxidizing bacteria in peat moss studied using stable carbon isotopic labeling. Org. Geochem. 41, 1040-1044. doi:10.1016/j.orggeochem.2010.04.015

van Winden, J.F., Talbot, H.M., De Vleeschouwerr, F., Reichart, G-J., Sinninghe Damsté, J.S., 2012. Variation in methanotroph-related proxies in peat deposits from Misten Bog, Hautes-Fagnes, Belgium. Org. Geochem. 53, 73-79. doi:10.1016/j.orggeochem.2012.07.001

Vetriani, C., Reysenbach, A.-L., Doré, J., 1998. Recovery and phylogenetic analysis of archaeal rRNA sequences from continental shelf sediments. FEMS Microbiol. Lett. 161, 83-88. doi:10.1111/j.1574-6968.1998.tb12932.x

Vila, X. and Abella, C.A., 1994. Effects of light quality on the physiology and the ecology of planktonic green sulfur bacteria in lakes. Photosy. Res. 41, 53-65. doi:10.1007/BF02184145

Villinski, J.C., Hayes, J.M., Brassell, S.C., Riggert, V.L., 2008. Sedimentary sterols as biogeochemical indicators in the Southern Ocean. Org. Geochem. 39, 567-588. doi:10.1016/j.orggeochem.2008.01.009

Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. Org. Geochem. 9, 83-99. doi:10.1016/0146-6380(86)90089-6

Volkman, J.K., Eglinton, G., Corner, E.D.S., Forsberg, T.E.V., 1980a. Long-chain alkenes and alkenones in the marine coccolithophorid Emiliania huxleyi. Phytochem. 19, 2619-2622. doi:10.1016/S0031-9422(00)83930-8

Volkman, J.K., Eglinton, G., Corner, E.D.S., Sargent, J.R., 1980b. Novel unsaturated straight-chain C_{37}-C_{39} methyl and ethyl ketones in marine sediments and a coccolithophore Emiliania huxleyi. Phys. Chem. Earth 12, 219–227. doi:10.1016/0079-1946(79)90106-X

Volkman, J.K., Barrett, S.M., Dunstan, G.A., 1994. C_{25} and C_{30} highly branched isoprenoid alkenes in laboratory cultures of two marine diatoms. Org. Geochem. 21, 407-413. doi:10.1016/0146-6380(94)90202-X

Volkman, J.K., Barrett, S.M., Blackburn, S.I., Mansour, M.P., Sikes, E.L., Gelin, F., 1998. Microalgal biomarkers: a review of recent research developments. Org. Geochem. 29, 1163-1179. doi:10.1016/S0146-6380(98)00062-X

Volkman, J.K., 2003. Sterols in microorganisms. Appl. Microbiol. Biotech. 60, 495-506. doi:10.1007/s00253-002-1172-8

Volkman, J.K., 2005. Sterols and other triterpenoids: source specificity and evolution of biosynthetic pathways. Org. Geochem. 36, 139-159. doi:10.1016/j.orggeochem.2004.06.013

Wakeham, S.G., Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2004. Archaeal lipids and anaerobic oxidation of methane in euxinic water columns: a comparative study of the Black Sea and Cariaco Basin. Chem. Geol. 205, 427-442. doi:10.1016/j.chemgeo.2003.12.024

Wakeham, S. G. and Canuel, E. A., 2016. The nature of organic carbon in density-fractionated sediments in the Sacramento-San Joaquin River Delta (California). Biogeosci. 13, 567-582. doi:10.5194/bg-13-567-2016

Weber, Y., De Jonge, C., Rijpstra, W.I.C., Hopmans, E.C., Stadnitskaia, A., Schubert, C.J., Lehmann, M.F., Sinninghe Damsté, J.S., Niemann, H., 2015. Identification and carbon isotope composition of a novel branched GDGT isomer in lake sediments: Evidence for lacustrine branched GDGT production. Geochim. Cosmochim. Acta 154, 118-129. doi:10.1016/j.gca.2015.01.032

Weber, Y., Sinninghe Damsté, J.S., Zopfi, J., De Jonge, C., Gilli, A., Schubert, C.J., Lepori, F., Lehmann, M.F., Niemann, H., 2018. Redox-dependent niche differentiation provides evidence for multiple bacterial sources of glycerol tetraether lipids in lakes. Proc. Nat. Acad. Sci. 115, 10926-10931. doi:10.1073/pnas.1805186115

Wei, J.H., Yin, X., Welander, P.V., 2016. Sterol synthesis in diverse bacteria. Front. Microbiol. 7, article no. 990. doi:10.3389/fmicb.2016.00990

Weijers, J.W.H., Schouten, S., Hopmans, E.C., Geenevasen, J.A.J., David, O.R.P., Coleman, J.M., Pancost, R.D., Sinninghe Damsté, J.S., 2006. Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits. Env. Microbiol. 8, 648-657. doi:10.1111/j.1462-2920.2005.00941.x

Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., Sinninghe Damsté, J.S., 2007. Environmental controls on bacterial tetraether membrane lipid distribution in soils. Geochim. Cosmochim. Acta 71, 703-713. doi:10.1016/j.gca.2006.10.003

Weijers, J.W.H., Wiesenberg, G.L.B., Bol, R., Hopmans, E.C., Pancost, R.D., 2010. Carbon isotopic composition of branched tetraether membrane lipids in soils suggest a rapid turnover and a heterotrophic life style of their source organism(s). Biogeosci. 7, 2959-2973. doi:10.5194/bg-7-2959-2010

Weiss, G.M., Pfannerstill, E.Y., Schouten, S., Sinninghe Damsté, J.S., van der Meer, M.T.J., 2017. Effects of alkalinity and salinity at low and high light intensity on hydrogen isotope fractionation of long-chain alkenones produced by *Emiliania huxleyi*. Biogeosci. 14, 5693-5704. doi:10.5194/bg-14-5693-2017

Welander, P.V., Hunter, R.C., Zhang, L., Sessions, A.L., Summons, R.E., Newman, D.K. 2009. Hopanoids Play a Role in Membrane Integrity and pH Homeostasis in *Rhodospeudomonas* TIE-1. J. Bacteriol. 191, 6145-6156. https://doi.org/10.1128/JB.00460-09

Werne, J.P., Lyons, T.W., Hollander, D.J., Formolo, M., Sinninghe Damsté, J.S. 2003. Reduced sulfur in euxinic sediments of the Cariaco Basin: Sulfur isotope constraints on organic sulfur formation. Chem. Geol. 195, 159-179. doi:10.1016/S0009-2541(02)00393-5

Werne, J.P., Lyons, T.W., Hollander, D.J., Schouten, S., Hopmans, E.C, Sinninghe Damsté, J.S., 2008. Investigating pathways of diagenetic organic matter sulfurization using compound-specific sulfur isotope analysis. Geochim. Cosmochim. Acta 72, 3489-3502. doi:10.1016/j.gca.2008.04.033

Whiteside, J.H. and Grice, K. 2016. Biomarker records associated with mass extinction events. Annu. Rev. Earth Planet. Sci. 44. doi:10.1146/annurev-earth-060115-012501

Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chem. Geol. 161, 291-314. doi:10.1016/S0009-2541(99)00092-3

Wilson, M.A., Hodgson, D.A., Keely, B.J., 2004. Structural variations in derivatives of the bacteriochlorophylls of Chlorobiaceae: impact of stratigraphic resolution on depth profiles as revealed by methanolysis. Organic Geochemistry, Advances in Organic Geochemistry 2003. Proceedings of the 21st International Meeting on Organic Geochemistry 35, 1299-1307.

Wirth, S.B. and Sessions, A.L., 2016. Plant-wax D/H ratios in the southern European alps record multiple aspects of climate variability. Quat. Sci. Rev. 148, 176-191. 10.1016/j.quascirev.2016.07.020

Wissel, H., Mayr, C., Lücke, A., 2008. A new approach for the isolation of cellulose from aquatic plant tissue and freshwater sediments for stable isotope analysis. Org. Geochem. 39, 1545-1561. doi:10.1016/j.orggeochem.2008.07.014

Withers, N.W., 1987. Dinoflagellate sterols. In: Taylor, F.J.R. (ed.), The Biology of Dinoflagellates, vol. 21. Blackwell Scientific, Oxford, pp.316-59.

Wolfe, B.B., Edwards, T.W.D., Elgood, R.J., Beuning, K.R.M., 2001. Carbon and oxygen isotope analysis of lake sediment cellulose: methods and applications. In: Last, W.M. and Smol, J.P. (eds.), Tracking Environmental Change Using Lake Sediments, vol. 2: Physical and Geochemical Methods, Kluwer, Dordrecht, pp. 373-400.

Wolfe, B.B., Falcone, M.D., Clogg-Wright, K.P., Mongeon, C.L., Yi, Y., Brock, B.E., St. Amour, N.A., Mark, W.A., Edwards, T.W.D., 2007. Progress in isotope paleohydrology using lake sediment cellulose. J. Paleolimnol. 37, 221-231. doi:10.1007/s10933-006-9015-8

Wuchter, C., Schouten, S., Boschker, H.T.S., Sinninghe Damsté, J.S., 2003. Bicarbonate uptake by marine Crenarchaeota. FEMS Microbiol. Lett. 219, 203–207. doi:10.1016/S0378-1097(03)00060-0

Wuchter, C., Schouten, S., Coolen, M., Sinninghe Damsté, J.S., 2004. Temperature-dependent variation in the distribution of tetraether membrane lipids of marine Crenarchaeota: Implications for TEX_{86} paleothermometry. Paleoceanogr. 19, PA4028, doi:10.1029/2004PA00104.

Yamaguchi, Y.T., Chikaraishi, Y., Takano, Y., Ogawa, N.O., Imachi, H., Yokoyama, Y., Ohkouchi, N., 2017. Fractionation of nitrogen isotopes during amino acid metabolism in heterotrophic and chemolithoautotrophic microbes across Eukarya, Bacteria, and Archaea: Effects of nitrogen sources and metabolic pathways. Org. Geochem. 111, 101-112. doi:10.1016/j.orggeochem.2017.04.004

Yamoah, K.K.A., Chabangborn, A., Chawchai, S., Väliranta, M., Wohlfarth, B., Smittenberg, R.H., 2016. Large variability in *n*-alkane $\delta^{13}C$ values in Lake Pa Kho (Thailand) driven by wetland wetness and aquatic productivity. Org. Geochem. 97, 53-60. doi:10.1016/j.orggeochem.2016.04.008

Yapp, C.J. and Epstein, S., 1982. A reexamination of cellulose carbon-bound hydrogen δD measurements and some factors affecting plant-water D/H relationships. Geochim. Cosmochim. Acta. 46, 955-965. doi:10.1016/0016-7037(82)90051-5

York, J.K., Tomasky, G., Valiela, I., Repeta, D.J, 2007. Stable isotopic detection of ammonium and nitrate assimilation by phytoplankton in the Waquoit Bay estuarine system. Limnol. Oceanogr., 52, 144-155. doi:10.4319/lo.2007.52.1.0144

Zech, M., Mayr, C., Tuthorn, M., Leiber-Sauheitl, K., Glaser, B., 2014. Oxygen isotope ratios ($^{18}O/^{16}O$) of hemicellulose-derived sugar biomarkers in plants, soils and sediments as paleoclimate proxy I: Insight from a climate chamber experiment. Geochim. Cosmochim. Acta 126, 614-623. doi:10.1016/j.gca.2013.10.048

Zerkle, A.L., Kamyshny Jr, A., Kump, L.R., Farquhar, J., Oduro, H., Arthur, M.A., 2010. Sulfur cycling in a stratified euxinic lake with moderately high sulfate: constraints from quadruple S isotopes. Geochim. Cosmochim. Acta 74, 4953-4970. doi:10.1016/j.gca.2010.06.015

Zhang, X., Gillespie, A.L., Sessions, A.L., 2009. Large D/H variations in bacterial lipids reflect central metabolic pathways. Proc. Nat. Acad. Sci. 106, 1-7. doi:10.1073/pnas.0903030106

Zhang, Z. and Sachs, J.P., 2007. Hydrogen isotope fractionation in freshwater algae: I. Variations among lipids and species. Org. Geochem. 38, 582-608. doi: 10.1016/j.orggeochem.2006.12.004

Zhang, Z., Sachs, J.P., Marchetti, A., 2009. Hydrogen isotope fractionation in freshwater and marine algae: II. Temperature and nitrogen limited growth rate effects. Org. Geochem., 40, 428-439. doi:10.1016/j.orggeochem.2008.11.002

Zheng, Y., Singarayer, J.S., Cheng, P.C., Yu, Xuefeng, Liu, Z., Valdes, P.J., Pancost, R.D., 2014. Holocene variations in peatland methane cycling associated with the Asian summer monsoon system. Nature Comm. 5, 4631. doi:10.1038/ncomms5631.

Zhu, J., Lücke, A., Wissel, H., Mayr, C., Ohlendorf, C., Zolitschka, B., 2014a. Characterizing oxygen isotope variability and host water relation of modern and subfossil aquatic mosses from Laguna Potrok Aike, Southern Patagonia, Argentina. Geochim. Cosmochim. Acta

130, 212-228. doi:10.1016/j.gca.2014.01.013

Zhu, J., Lücke, A., Wissel, H., Mayr, C., Enters, D., Kim, K.J., Ohlendorf, C., Schäbitz, F., Zolitschka, B., 2014b. Climate history of the Southern Hemisphere Westerlies belt during the last glacial-interglacial transition revealed from lake water oxygen isotope reconstruction of Laguna Potrok Aike (52°S, Argentina). Clim. Past 10, 2153-2169. doi:10.5194/cp-10-2153-2014

Zink, K.-G., Leythaeuser, D., Melkonian, M., Schwark, L., 2001. Temperature dependency of long-chain alkenone distributions in Recent to fossil limnic sediments and in lake waters. Geochim. Cosmochim. Acta 65, 253-265.