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Lipid compound classes display diverging hydrogen isotope responses in lakes along a nutrient gradient

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Abstract

Compound specific hydrogen isotope ratios ($^2H/^1H$) of lipid biomarkers preserved in sediments are used as paleohydrologic proxies. However, several variables, including contributions from different source organisms and their growth rates, can influence $^2H/^1H$ fractionation between lipids and source water. Significant uncertainties remain about how these factors combine to produce the net $^2H/^1H$ signal exported to sediments.

To assess the influence of phosphorus availability on $^2H/^1H$ ratios of lipids accumulating in lake sediments, we analyzed surface sediments and sediment traps from ten central Swiss lakes representing a wide range of trophic states. In agreement with results from laboratory cultures, $^2H/^1H$ fractionation for the diatom biomarker brassicasterol (24-methyl cholest-5,22-dien-3β-ol) increased in more productive lakes ($0.6 \pm 0.1‰$ per μg/L total P in sediment traps and surface sediments). In contrast, $^2H/^1H$ fractionation for phytol, the isoprenoid side-chain moiety of chlorophyll, decreased with increasing total P ($-0.4 \pm 0.1‰$ per μg/L total P in sediment traps), suggesting that different biochemical mechanisms are responsible for changes in $^2H/^1H$ fractionation for each type of isoprenoidal lipid. Opposing changes in ^2H-fractionation for sterols and phytol cause their $^2H/^1H$ ratios to converge as total P increases. This response may be a new tracer for phytoplankton growth conditions and is not influenced by the source water isotope value.

Interpreting the $^2H/^1H$ ratios of short to long chain (C_{14}–C_{30}) *n*-alkanoic acids and *n*-alkanols is complicated by likely contributions from heterotrophs and/or vascular plants. These values generally did not correlate with lake water isotopes, nor did their fractionation factors correlate with total P. For most lipids there was no significant difference between sediment trap and surface sediment $^2H/^1H$ ratios. However, *n*-C_{14}–*n*-C_{18} fatty acids were ^2H-enriched in the surface sediments, most likely due to degradation in the water column. Our results indicate that interpretations of short-chain fatty acid $^2H/^1H$ ratios as a water isotope signal likely require supporting information about ecological conditions and community structure, but that paired H isotope measurements of phytoplankton-derived sterols and phytol may be developed as a proxy for phytoplankton growth.

Keywords: Hydrogen isotopes; Lipid biomarkers; Eutrophication; Phosphorus; Phytoplankton productivity; Lacustrine sediment

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1. INTRODUCTION

The distributions and stable isotope compositions of lipid biomarkers preserved in lacustrine and marine sediments can provide valuable information about past environmental and climatic conditions (Castañeda and Schouten, 2011; Sachse et al., 2012; Sessions, 2016). In recent years, compound specific hydrogen isotope measurements of leaf waxes have garnered considerable attention as a paleohydrologic proxy, since sedimentary leaf wax δ^2H values ($\delta^2H = \delta D = (({}^2H/{}^1H_{Sample})/({}^2H/{}^1H_{VSMOW}) - 1)$) are well correlated with δ^2H values of local precipitation over large spatial scales (Sachse et al., 2004; Sachse et al., 2012). Precipitation δ^2H values vary by location in response to temperature, amount of precipitation, and atmospheric moisture transport pathways (Dansgaard, 1964; Craig and Gordon, 1965; Gat, 1996). Although there are complications relating to plant type, timing of leaf wax synthesis, and evaporative enrichment of leaf water, extensive studies in modern systems have helped to constrain sources of uncertainty and enhanced the utility of the leaf wax hydrogen isotope proxy (Sachse et al., 2012; Kahmen et al., 2013; Tipple et al., 2013; Ladd and Sachs, 2015; Feakins et al., 2016; Freimuth et al., 2017; Nelson et al., 2018).

Compared to the existing body of work on leaf wax δ^2H values, considerably less has been done to understand the biologic complexity associated with aquatically sourced lipid δ^2H values. Lipids produced by aquatic organisms have δ^2H values that have been observed to correlate with δ^2H_{Water} in a range of natural and laboratory settings (reviewed by Sachse et al., 2012; Sachs, 2014), which has led to the use of aquatic lipid δ^2H values as a proxy for past lake water isotope values (Huang et al., 2002; Sachs et al, 2009; Smittenberg et al., 2011; Nelson and Sachs, 2016; Randlett et al., 2017) and to the pairing of aquatic and leaf wax δ^2H values from the same sediment to reconstruct changes in relative humidity (Rach et al., 2014; Rach et al., 2017).

Previous work has demonstrated that fractionation factors between lipids and source waters (denoted by $\alpha_{Lipid\text{-}Water} = ({}^2H/{}^1H_{Lipid})/({}^2H/{}^1H_{Water})$) are not constant among compounds or among photoautotrophic aquatic species (Sessions et al. 1999; Schouten et al., 2006; Zhang and Sachs, 2007; Chivall et al., 2014; M'Boule et al., 2014; Heinzelmann et al., 2015). Additionally, environmental factors including salinity, temperature, nutrient availability, and light availability can influence the magnitude of $\alpha_{Lipid\text{-}Water}$ values in cyanobacteria and eukaryotic algae (Schouten et al., 2006; Sachs, 2014 and references therein; Nelson and Sachs, 2014; van der Meer et al., 2015; Wolhowe et al., 2015; Maloney et al., 2016; Weiss et al., 2017; Sachs et al., 2017). Furthermore, in the case of short-chained fatty acids that are synthesized by heterotrophs, chemoautotrophs, and photoautotrophs, the central metabolic pathway employed can have a much larger effect on δ^2H_{Lipid} values than any variability observed in response to environmental gradients (Zhang et al., 2009a; Osburn et al., 2011; Heinzelmann et al., 2015). Disentangling the competing influence of different factors on the net δ^2H_{Lipid} value exported to and preserved in sediments is necessary for robust interpretations of down core δ^2H_{Lipid} values.

In particular, the role that lacustrine trophic status might play on sedimentary δ^2H_{Lipid} values warrants more attention (Schwab et al., 2015; Ladd et al., 2017). There are several reasons a lake's trophic status could influence δ^2H_{Lipid} values, the first of which is by facilitating higher algal growth rates. In cultures of eukaryotic marine algae, higher growth rates correlate with a decrease in $\alpha_{Lipid\text{-}Water}$ values for sterols, alkenones, and some fatty acids, indicating more $^2H/^1H$ fractionation (Schouten et al., 2006; Zhang et al., 2009b; Sachs and Kawka, 2015; Wolhowe et al., 2015). Consistent with this result, $\alpha_{Lipid\text{-}Water}$ values from the diatom biomarker brassicasterol (24-methyl cholest-5,22-dien-3β-ol) produced in the surface water of a eutrophic lake in central Switzerland were lower than those of brassicasterol in a nearby oligotrophic lake (Ladd et al., 2017). There was, however, no significant difference in $\alpha_{Lipid\text{-}Water}$ values for short-chain fatty acids and phytol between the two lakes (Ladd et al., 2017).

Another way that trophic status could influence sedimentary δ^2H_{Lipid} values is by changing the algal community. Different nutrient regimes promote the growth of different species of algae (Tilman et al. 1982; Jensen et al., 1994; Watson et al., 1997; Monchamp et al., 2018). This diversity could complicate the δ^2H_{Lipid} signal of compounds common to all photoautotrophs, since $\alpha_{Lipid\text{-}Water}$ values vary significantly for different species of eukaryotic algae grown under identical conditions (Schouten et al., 2006; Zhang and Sachs, 2007; Chivall et al., 2014; M'Boule et al, 2014; Heinzelmann et al., 2015).

Additionally, the trophic status of a lake could affect sedimentary δ^2H_{Lipid} values by changing the sedimentary redox conditions and the activity of different types of heterotrophic microbes. For example, Schwab et al. (2015) demonstrated that δ^2H values of dinosterol (4α,23,24-trimethyl-5α-cholest-22E-en3-ol) accumulating in surface sediments from seven stratified tropical lakes in Cameroon were enriched in ^2H relative to dinosterol in suspended particles, and that this enrichment was greater in more eutrophic lakes, as indicated by the redox potential of the oxic-anoxic interface. ^2H-enrichment of sedimentary dinosterol relative to that in the water column also increased with the ratio of dinostanol to dinosterol, suggesting that hydrogenation of sterols by anaerobic bacteria preferentially reduces molecules that are depleted in ^2H (Schwab et al., 2015).

Finally, heterotrophic microbes can produce some of the same compounds as photoautotrophs, in particular several short-chain fatty acids (Volkman et al., 1980; Heinzelmann et al., 2016). Since $\alpha_{Lipid\text{-}Water}$ values can differ by as much as 0.500 (500 ‰) depending on microbial metabolism (Li et al., 2009; Zhang et al., 2009a; Osburn et al., 2011; Heinzelmann et al., 2015; Osburn et al., 2016), conditions that favor more input of fatty acids or other compounds from heterotrophs could also have a significant effect on the net δ^2H values of fatty acids in sediments. Increased sedimentary contributions of dinosterol from heterotrophic dinoflagellates are thus an alternative explanation for the