EFFECT OF NUTRIENT AVAILABILITY IN FRESHWATER LAKES ON HYDROGEN ISOTOPE FRACTIONATION IN ALGAL LIPID BIOSYNTHESIS

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The stable isotopic composition of lake water is sensitive to important environmental variables including temperature, moisture source, and the balance of precipitation and evaporation. Sedimentary material that records changes in lake water isotope composition is therefore useful for reconstructing past climate change in continental environments. Hydrogen isotope ratios ($^2H/^1H$ or δ^2H) of algal lipids are one such proxy, as they are strongly influenced by the δ^2H value of the water in which the algae grew (*Sachse et al., 2012; Sachs, 2014*). This approach has successfully provided information about past hydroclimate in a variety of marine and lacustrine settings (e.g. *Huang et al., 2002; van der Meer et al., 2007; Sachs et al., 2009; Nelson and Sachs, 2016*).

It has become increasingly apparent that a number of secondary factors can influence hydrogen isotope fractionation in algae, with nutrient availability and growth rate playing a significant role (*Sachse et al., 2012; Sachs, 2014*). Previous investigations into these effects have been conducted with laboratory cultures of marine algae, and in field studies in saline systems. Limited information is available as to how significant these variables are for $^2H/^1H$ fractionation during lipid synthesis by freshwater lacustrine algae, even though lake sediments are a primary archive for paleoclimate studies on land.

We addressed this gap by measuring the δ^2H values of short chain fatty acids, phytol, n-C_{17}-alkane, and algal sterols in surface sediment and sediment traps from ten lakes in the Central Swiss Plateau with different histories of nutrient loading and a range of modern trophic states. We also measured δ^2H values of the same lipids extracted from particulate organic matter at three time points in 20 mesocosms, which were initially stocked with phytoplankton from Lake Greifen and subjected to stepwise additions of phosphate and nitrate.

Our results indicate differing hydrogen isotope responses of different compound classes to nutrient availability. For example, in our sediment trap samples, δ^2H values of the generic n-$C_{16:0}$ fatty acid (palmitic acid) were correlated with water δ^2H values ($R^2 = 0.44$; $p = 0.04$; n = 10), and no correlation was seen between phosphorus concentrations and the fractionation factor, $\alpha_{lipid\text{-}water} = (\delta^2H_{lipid} + 1000)/ (\delta^2H_{water} + 1000)$ ($R^2 = 0.04$) (Fig 1). In marked contrast, δ^2H values of brassicasterol, a sterol primarily produced by diatoms (*Volkman, 2003; Rampen et al., 2010*), were not correlated with those of lake water ($R^2 = 0.08$), and $\alpha_{lipid\text{-}water}$ decreased with total P concentrations ($R^2 = 0.69$; $p = 0.003$; n = 10) (Fig 1).

The differing hydrogen isotope responses to increased nutrient loading between lipids may present an opportunity to develop a new approach to trace past nutrient regimes and/or physiological stress. Brassicasterol and fatty acid δ^2H values increasingly diverge as total phosphorus concentrations increase. This suggests that the offset between δ^2H values of acetogenic and isoprenoidal lipids from the same sedimentary interval might be applicable as an indicator of past nutrient availability and/or productivity. In addition to the utility as an

ecological proxy, this would improve applications of other tracer techniques that may be sensitive to growth rate effects, such as efforts to deduce past hydroclimate changes using algal lipid δ^2H values, or to infer past carbon dioxide concentrations from alkenone $\delta^{13}C$ values.

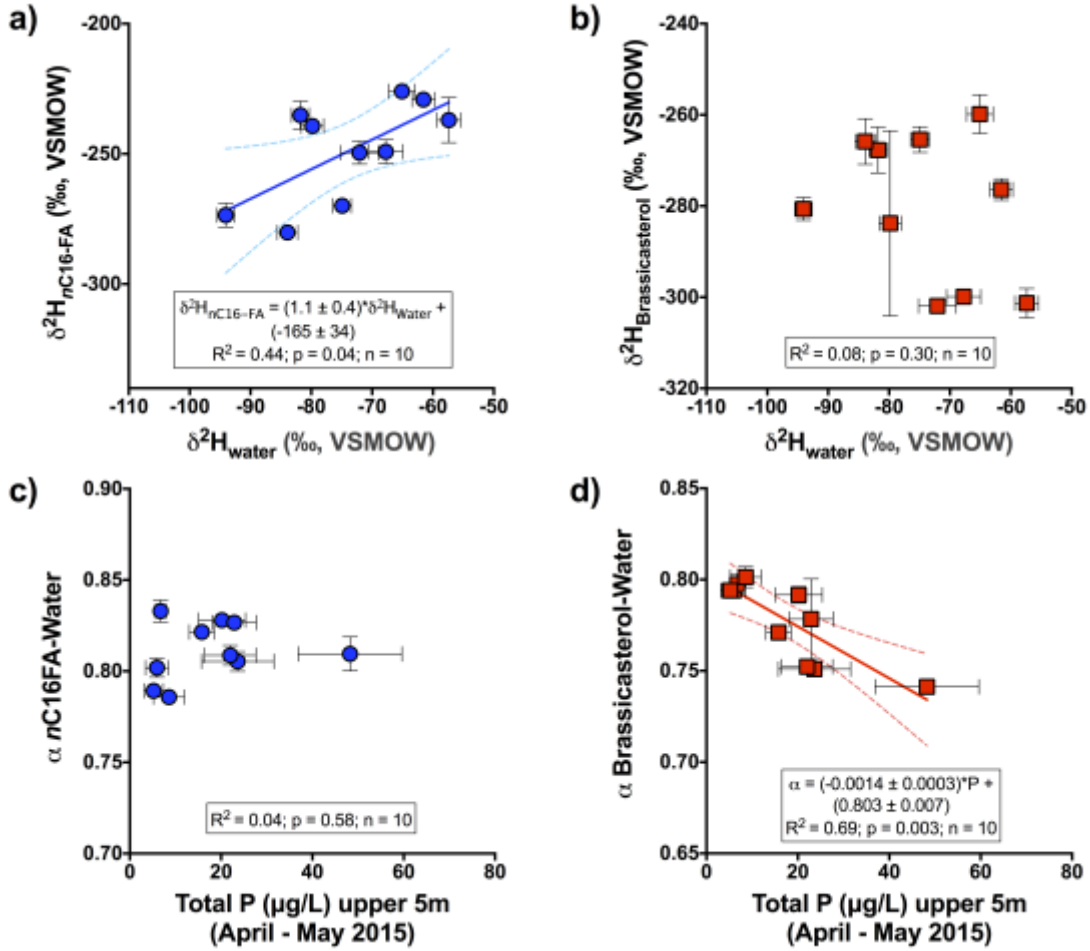

Figure 1 *δ^2H values of (a) palmitic acid and (b) brassicasterol relative to surface water δ^2H values and the fractionation factor $\alpha_{lipid\text{-}water}$ for corresponding to each lipid (c and d).*

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