## Biochemical hydrogen isotope fractionation during *n*-alkanes biosynthesis in higher plants

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Among the biomarkers, long-chain *n*-alkanes (>25 C) are particularly valuable components from the waxy plant cuticles. Their relative abundances of the stable hydrogen isotopes ( $\delta^2$ H) show good correlations with  $\delta^2$ H values of precipitation, making them a promising proxy for paleohydrological conditions. Despite the primary control of leaf wax *n*-alkanes  $\delta^2$ H values by the plant's source water, biochemical hydrogen isotope fractionation during biosynthesis of *n*-alkanes ( $\epsilon_{bio}$ ) account for a large part of the leaf wax *n*-alkanes  $\delta^2$ H values. While  $\epsilon_{bio}$  is frequently assumed to be approximately constant, few studies have directly addressed within species variability in  $\epsilon_{bio}$ .

Here we present the results from a climate-controlled growth chambers experiment where tested the sensitivity of  $\varepsilon_{hio}$ to different light treatments. The different light treatments were applied to induced different metabolic status (autotrophic vs. heterotrophic) in 7 different plant species that we grew from large storage organs (e.g. tubers or roots). The results show a systematic  $\epsilon_{\text{bio}}$  shift (up to 80 ‰) between the different light (i.e. metabolic) treatments. We suggest that this shift is due to the different NADPH pools used by the plants to build up the *n*-alkanes from stored carbohydrates in heterotrophic or autotrophic conditions. Our results have important implications for the calibration and interpretation of sedimentary records of n-alkanes  $\delta^2 H$  values in geological studies. In addition our findings support the idea of n-alkanes as an interesting ecohydrological proxy for ecosystem and plant physiological studies