Understanding D/H systematics of leaf wax *n*-alkanes in C₃ and C₄ plants at Stiffkey saltmarsh, Norfolk, UK

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D/H ratios of *n*-alkyl lipids are becoming increasingly popular as indicators of palaeohydrological regimes. The suitability of these compounds for such applications is dependent upon the precise nature of the information they are conveying. Current interpretations of this proxy are limited by an incomplete understanding of the mechanisms responsible for the variation in *n*-alkyl lipid δD values among plant species at individual locations.

To evaluate the relative importance of environmental, physiological and biochemical factors on the D/H composition of *n*-alkyl lipids, we sampled a range of C_3 and C_4 plants at Stiffkey saltmarsh throughout 2012. The results of δD analysis of soil, xylem, and leaf waters suggest that the bulk of interspecies variation in *n*-alkane δD values (>100%) cannon be explained by environmental and plant physiological factors. Instead, we propose that species-specific D/H fractionation during lipid biosynthesis represents a fundamental control on *n*-alkane δD values of these plants.

Our ongoing work on starch δD will allow us to identify whether variation in carbohydrate recycling may explain the range of lipid δD in key species at our site. Furthermore, we are examining whether seasonal changes in leaf wax composition, including the nature and amount of precursor compounds, affect the *n*-alkyl D/H signal. Finally, our work on chloroplast-bound phytol will allow us to investigate whether the potential existence of different NADPH pools influences the δD of compounds biosynthesized in different plant compartments. Our results indicate an integrated physical and biochemical approach is required to interpret the D/H signals contained in the sedimentary record.

Isotope anomalies of Hf and W in chondrite leachates and residues

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The stepwise dissolution of primitive chondritic meteorites allows to reveal nucleosynthetic anomalies that are otherwise hidden in the bulk rock mix. Leaching experiments for Hf and W have previously been published, but in separate studies that did not include the rare p-process isotopes ¹⁷⁴Hf and ¹⁸⁰W [1, 2]. Here, we present for the first time combined Hf and W isotope data for acid leachates of several chondritic meteorites, including sufficiently precise analyses of p-process ¹⁷⁴Hf and ¹⁸⁰W for some chondrites (EET 96026 (R3), MAC 02839 (EL3) and WSG 95300 (H3.3)).

For leaching experiments, sample powders of the different meteorites were treated with 2M HCl and divided into a leachate and a residue fraction. Tungsten and Hf were separated from the same sample split using anion exchange chromatography. The W fraction was subsequently purified with TODGA resin, and Hf was further purified using Ln-Spec. Measurements were performed on a Neptune MC-ICP-MS. For the collection of the small ion beams, amplifiers with $10^{12}\Omega$ resistors were employed. Interferences from Yb, Lu and W, and Hf, Ta and Os isotopes, respectively, were sufficiently low to allow accurate interference corrections. The external reproducibilities on ¹⁷⁴Hf and ¹⁸⁰W were better than ±60 ppm and ±70 ppm, respectively, but significantly larger for small samples cuts <60 ng Hf and <150 ng W, respectively.

First data reveals that most of the Hf leachates and residues show anomalous s- and r-process patterns that are consistent with the results of [1]. First W isotope s- and r-process patterns are furthermore consistent with data reported by [2]. Neither leachates nor residues exhibit resolvable non-terrestrial ¹⁷⁴Hf, whereas both positive and negative ¹⁸⁰W signatures are resolved for almost all leachates and residues. The origin of the apparent decoupling between ¹⁸⁰W and ¹⁷⁴Hf is presently ambiguous, but possibly point towards different carrier phases for p-process Hf and W.

[1] Qin L. et al. (2011) GCA, 75, 7806-7828. [2] Burkhardt C. et al. (2012) AJL, 753, L6.