The hole story about laser ablation ICP-MS

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Down-hole laser-induced fractionation is one of the largest contributions to the uncertainty budget of LA-ICP-MS measurements of trace elements and isotope ratios. Efforts to improve the accuracy of analyses and to reduce the size of the uncertainty associated with laser-induced fractionation have been divided between developments in laser hardware and data reduction software. Advances in cell design have improved the quantitative transport of material from the ablation site to the ICP and contributed to increased sensitivity and reduced fractionation. Procedures involving rastering the laser or short acquisition times are also commonly adopted to minimize downhole fractionation, but these compromise spatial resolution and depth information. Linear [1], [2] and exponential [3] down-hole models are used in many data reduction software packages and reflect the basic fractionation response for a wide range of laser specifications and operating conditions. In the majority of models the fundamental assumption made is that matrix-matched standards and samples ablate similarly with consistent time-depth relationships [1]. However, further software advances are limited by our current understanding of the fundamental processes of ablation. Here we present the results of a study of the ablation characteristics of zircon using various combinations of laser wavelength, pulse-width, spot size and fluence, in conjunction with laser cell design (New Wave, HelEx) and gas composition and flow. The results are used to identify the optimum set of hardware parameters and operating conditions to maximise spatial resolution, and minimize ablation rate and U-Pb fractionation. A comparison will also be presented between the effects of mass response (instrument mass bias) of a quadrupole (Agilent 7700) and magnetic sector ICP-MS (Nu Attom) on time-dependent fractionation.

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Hydrogen isotope systematics of leaf wax *n*-alkanes in *Betula, Pinus,* and *Salix*: Spatio-temporal investigation

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The use of D/H composition of *n*-alkyl lipids from leaf waxes as a palaeohydrological proxy depends on a thorough understanding of the factors that control D/H fractionation ($\varepsilon_{l/w}$) between these compounds and the source water. The issue becomes particularly important when sedimentary organic compounds are sourced by only a few species with very different $\varepsilon_{l/w}$ values. This project investigates the magnitude and mechanisms that control $\varepsilon_{l/w}$ in several higher plant species that dominate Northern Eurasian forests and thus contribute a significant amount of biomass to soils and sediments in these ecosystems.

First, we measured the δD values of leaf wax *n*-alkanes from *Betula*, *Pinus*, and *Salix* as well as the δD values of tap water in 11 locations from the UK to central Siberia. Second, we measured the δD values of leaf wax *n*-alkanes and leaf water in the same species that were sampled in Norwich, UK throughout the growing season in April, May, July, and September.

The *n*-alkane δD values of the individual genera correlate very strongly with those of tap water along the transect from the UK to central Siberia – the R^2 values calculated for *Betula*, *Pinus*, and *Salix* are 0.95, 0.97, and 0.82, respectively. However, their $\varepsilon_{l/w}$ values are characterized by consistent differences that are inpedendent of the location along the transect: *Betula c*. -85‰, *Pinus c*. -120‰, *Salix c*. -140‰.

Our time-series $\varepsilon_{l/w}$ data calculated from *n*-alkane and leaf water δD values of Norwich trees sampled from April to September show the same pattern among these genera. Even though the magnitudes of the differences among them are not as large as in the transect data, *Betula* $\varepsilon_{l/w}$ values are consistently more positive than those of *Pinus* (by *c*. 5 to 20‰) and *Salix* (by *c*. 20 to 30‰).

Integration of our spatial and temporal δD data provides strong evidence that the processes that lead to the differences in the $\varepsilon_{l/w}$ values are not limited to the physical processes that control source water δD. We hypothesize that D/H fractionation during leaf water photolysis and biosynthesis plays a major role in determining $\varepsilon_{l/w}$ values in these plants. Our results suggest that leaf-wax-based palaeohydrological studies in northern forest ecosystems may require quantitative analysis of the amount of biomass sourced by common plants with very different $\varepsilon_{l/w}$ values.

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