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Position-specific carbon isotope analysis of glucose and tree-ring cellulose by Orbitrap mass spectrometry

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The isotopic compositions of environmentally relevant compounds like glucose and cellulose carry traces of the metabolic processes they have undergone. However, many of the relevant fractionations are imparted at specific atomic positions, whereas most traditional isotope analyses measure the average isotopic composition of the whole molecule. Here, we present the first method for position-specific isotope analysis (PSIA) of glucose and cellulose via Electrospray-Ionization (ESI)-Orbitrap mass spectrometry. Unlike the few existing methods for glucose PSIA, our method enables measurement of natural isotope abundances with the submilligram sensitivity required for most geochemical applications.

Our new method produces carbon isotope ($\delta^{13}C$) measurements of 5 unique intramolecular sites within both reagent-grade and wood cellulose-derived glucose. We have determined optimal preparatory chemistry and instrument conditions, including the oxidation of glucose to gluconate prior to measurement. Our optimized method allows us to achieve precision of 0.7-2.4‰ for replicate measurements of positional $\delta^{13}C$ values. We further show that isotope measurements for each intramolecular fragment are accurate relative to externally verified $\delta^{13}C$ values within 0.1-0.6‰, typically outperforming instrument precision. We have applied this method to glucose standards from C3 and C4 plants, and find that the $\delta^{13}C$ values of intramolecular sites within both glucose standards vary by up to 12‰, but the relative positional trends are similar for both glucose sources. These measurements consume < 30 μg of glucose. We have further demonstrated accurate and precise measurements of cellulose-derived glucose from two tree species grown in climate chambers under varying conditions, with intramolecular $\delta^{13}C$ variability as high as 17‰. Our preliminary analyses, which consume < 1 mg of tree-ring cellulose, suggest that this variability records trees' ecophysiological response to water availability, likely with greater sensitivity than traditional compound-specific measurements. These findings highlight the promise of ^{13}C-PSIA via ESI-Orbitrap for gaining new insights into environmental carbon fluxes.