P-27

Poster Session Day 2

Position-specific Oxygen Isotope Analysis of Vanillin Using Orbitrap Mass Spectrometry

Hao Xie[1,2], Max K. Lloyd[1], Allison A. Baczynski[1], Eric Hasegawa[1], & Katherine H. Freeman[1]*

[1] The Pennsylvania State University

[2] Nanjing University

*Presenting Author Email: hxie@nju.edu.cn

Oxygen isotope ratios of molecular positions in organic compounds have not been much explored but can potentially offer precise constraints on paleo-climatology. Vanillin, a plant-derived biomolecule that has three different oxygen containing functional groups, presents a suitable target for position-specific oxygen isotope analysis. We developed an analytical method for utilizing gas chromatography Orbitrap mass spectrometry (GC-Orbitrap MS) to measure oxygen isotope ratios in the aldehyde, hydroxyl, and methoxyl groups of vanillin. The method can reach around 5 ‰ precision on the oxygen positions using nanomoles of samples. Through isotope exchange experiments using ^{18}O-enriched water, we established that the aldehyde group undergoes rapid oxygen exchange, while the hydroxyl group resists exchange under natural conditions, and the methoxyl group exhibits strong inertness to exchange. These findings helped us identify the oxygen group origination in the molecular fragments. Additionally, the findings highlight the potential of the hydroxyl and methoxyl oxygen isotope compositions as reliable indicators of paleoenvironmental conditions. We also show the necessity of balancing the sample and standard to ensure analytical accuracy. Initial results from commercial and natural vanillin samples reveal distinct oxygen isotope signatures, particularly in the hydroxyl group, suggesting biosynthetic and environmental influences.