

Tracking Carbon Flow within Cells: a View from Biomarker Isotope Patterns

Katherine H. Freeman¹, Youki Sato¹, Julianna Drozd¹, Ophelie M. MacIntosh¹, Paul Volante¹

¹ Dept. of Geosciences, Penn State University, USA

*Presenting Author Email: khf4@psu.edu

Lipid biomarkers and their isotopes capture changes in water, carbon, and life that provide essential insights to ancient climate and Earth history. While metabolisms and carbon fluxes are sensitive to changing environments, only recently have new methods enabled researchers to look more deeply at their isotope fingerprints within lipids.

Lipid isotope patterns are tied to cellular central metabolism via small metabolites, pyruvic acid and acetic acid. Pyruvate dehydrogenase facilitates the conversion of pyruvic acid to acetyl-CoA, which is then directed either to generate energy in the tricarboxylic acid (TCA) cycle or to build lipids. The conversion step is accompanied by carbon isotope fractionation that is enhanced or attenuated by the relative flux of pyruvate to acetate versus other metabolic fates, including amino acids (i.e., Hayes, 2001; Gilbert, 2021). Our approach builds on prior studies of amino acids (Wilkes et al., 2022), small metabolites (Mueller et al., 2022a; Frey et al., 2016), and acetogenic lipids (Julien et al., 2022; Zeichner et al., 2022). Our work seeks to test imprints of metabolite flux on fractionation predicted with models (Mueller et al., 2022b) using GC-EI-HRMS (Orbitrap) methods to evaluate intramolecular signatures of small metabolites, nitrogen isotopes of selected amino acids, and the potential for isotopic patterns in larger biomarker compounds of paleoclimate relevance.

References:

- Frey, A. J., Feldman, D. R., Trefely, S., Worth, A. J., Basu, S. S., & Snyder, N. W. (2016). *Analytical and Bioanalytical Chemistry*, 408(13), 3651–3658.
- Gilbert, A. (2021). *Annual Review of Earth and Planetary Sciences*, 49(1), 435–464.
- Hayes J.M. (2001) In: *Reviews in Mineralogy and Geochemistry* (2001) 43 (1): 225–277.
- Julien, M., Zhao, Y., Ma, R., Zhou, Y., Nakagawa, M., Yamada, K., Yoshida, N., Remaud, G. S., & Gilbert, A. (2022). *Organic Geochemistry*, 174, 104516.
- Mueller, E. P., Sessions, A. L., Sauer, P. E., Weiss, G. M., & Eiler, J. M. (2022a). *Analytical Chemistry*, 94(2), 1092–1100.
- Mueller, E. P., Wu, F., & Sessions, A. L. (2022b). *Chemical Geology*, 610, 121098.
- Wilkes, E. B., Sessions, A. L., Zeichner, S. S., Dallas, B., Schubert, B., Jahren, A. H., & Eiler, J. M. (2022). *Rapid Communications in Mass Spectrometry*, 36(18), e9347.
- Zeichner, S.S., Wilkes, E.B., Hofmann, A.E., Chimiak, L., Sessions, A., Makarov, A. & Eiler, J.M. (2022). *International Journal of Mass Spectrometry* 447, 116848.