



Reconstructing Paleofire-Climate Connections in Speleothems Using Organic Molecules: A Source to Sink Perspective

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Records of past fire frequency and intensity are critical for understanding the links between atmospheric $p\text{CO}_2$, climate and ecosystem change. In terrestrial settings, stalagmites provide one of the most precise, multi-proxy, and high-resolution archives of climate information. Yet, records of past fire occurrence or fire intensity, which are commonly derived from charcoal abundances in sediments, are generally not available within the same archive or at comparable time resolution.

Sedimentary organic molecular biomarkers are increasingly utilized as proxies for past fire, environment and climate, and there is considerable potential for past fire activity to be archived in stalagmites^{1,2,3}. Recent analytical and methodologic advances now allow measurement of molecular markers of climate and fire at trace abundances, and surface-generated, plant-derived biomolecules and fire markers, including polycyclic aromatic hydrocarbons (PAHs), lignin oxidation products (LOPs), and anhydrosugars such as levoglucosan (LG) and its isomers mannosan (MA) and galactosan (GA), have been documented in stalagmites older than 100 ka¹.

Fire markers are preserved in stalagmites at multiple caves across the fire-prone landscape of California, USA, and recent study of LG and LOPs in a California Coast Range stalagmite provides evidence for a strong connection between fire activity and climate whiplash², while measurements of PAHs from a well-studied stalagmite in McLean's Cave located in the central Sierran foothills (ML-1) captures a link between increased fire intensity and climate change during Heinrich Stadial-1³. Despite clear preservation of fire-derived molecules in stalagmites, results from modern California cave systems and surface environments show that fire markers produced from recent fire events have variable mobility through soils and the epikarst system, while plant lipids produced by surface vegetation record significant degradation during transit from the surface to cave drip water.

Here, we discuss the promises and pitfalls of producing organic molecular records of climate and fire from speleothems. Specifically, we present modern surface to cave organic molecular data from several sites in California, USA to review: 1) factors that influence the terrestrial production of organic molecular markers of ecosystem, fire and climate; 2) mobilization of organic markers through the soil, epikarst and cave environment; 3) alteration of surface-generated molecular

signatures due microbial activity or preferential mobilization of different molecular classes; and 4) incorporation of organic markers of fire and climate in stalagmites.

¹Blyth, A.J., Baker, A., Collins, M.J., Penkman, K.E.H., Gilmour, M.A., Moss, J.S., Genty, D. & Drysdale, R.N. (2008) Molecular organic matter in speleothems and its potential as an environmental proxy. *Quat. Sci. Rev.*, 27, 905-921.

²Homann, J., Oster, J. L., de Wet, C. B., Breitenbach, S. F. M., & Hoffmann, T. (2022). Linked fire activity and climate whiplash in California during the early Holocene. *Nature Communications*, 13(1), 7175.

³Smolen, J., Montañez, I., and Hren, M.: Fire, Work with Me: A PAH record from a Southwestern US speleothem , EGU General Assembly 2023, Vienna, Austria, 24–28 Apr 2023, EGU23-16912, <https://doi.org/10.5194/egusphere-egu23-16912>, 2023.