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Using speleothem SO_4 isotopes to elucidate S cycling in a fire prone region

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Wildfires are a global hazard that can have catastrophic impacts on communities and ecosystems. A speleothem-based wildfire record will allow us to determine long-term natural fire regimes and better understand the relationship between wildfires and climate. Recent research has demonstrated the potential of using S as a speleothem paleofire proxy[1] but a full characterisation of S in a fire-prone environment is lacking.

Firstly, we used modern monitoring to quantify the relative contributions of S sources in a cave environment with overlying post-fire forest regrowth. Sulphate concentration and isotopic values (δ^{34}S- SO_4 and δ^{18}O- SO_4) for rainfall (+18.8‰ and +8.1‰ respectively), cave drip water (+20.3‰ and +3.2‰), bedrock (+21.7‰ and +10.6‰) vegetation (δ^{34}S- SO_4 +22.1‰) and soil (δ^{34}S- SO_4 +19.5‰) were characterised. Results showed the SO_4 rainfall input was from a marine source. A 1-2‰ fractionation of drip water δ^{34}S- SO_4 compared to rainfall δ^{34}S- SO_4 revealed there was assimilation of SO_4 into vegetation above the cave. δ^{18}O- SO_4 indicated biogeochemical cycling of S by mineralisation of organic S compounds to sulphate within the soil. These results demonstrate the necessity of dual isotope analysis of δ^{34}S- SO_4 and δ^{18}O- SO_4 to correctly identify S sources and biogeochemical cycling prior to incorporation of SO_4 into a speleothem.

Secondly, the S isotope proxy was applied to a 2-12 ka speleothem record from the same region and forest cover. More than fifty 200 mg samples from a flowstone were analysed for δ^{34}S- SO_4 and δ^{18}O- SO_4.Mean speleothem δ^{34}S- SO_4 was enriched in ^{34}S by $>$2 ‰ compared to modern rainfall, indicative of vegetation fractionation. LGM mean δ^{34}S- SO_4 was more negative than Holocene (+22.1‰ and +23.2‰ respectively). Fast growth periods at $\sim$10 and 7ka provided multi-annual resolution and 1.5‰ variability in δ^{34}S- SO_4 was observed over decadal timescales, indicative of changes in vegetation cycling of S, which we interpret as a possible fire record.

[1]Treble, P.C., Fairchild, I.J., Baker, A., Meredith, K.T., Andersen, M.S., Salmon, S.U., Bradley, C., Wynn, P.M., Hankin, S.I., Wood, A., McGuire, E., 2016. Roles of forest bioproductivity, transpiration and fire in a nine-year record of cave dripwater chemistry from southwest Australia. Geochim. Cosmochim. Acta 184, 132–150. https://doi.org/10.1016/j.gca.2016.04.017