Transport-coupled Sulfur Isotopic Fractionation by Sulfur Oxidizing Microbes as Biosignatures on the Walls of Earth and Martian Caves.

M. Mansor[1,2], K. Harouaka[1,3], M. S. Gonzales[1], J. L. Macalady[1] and M. S. Fantle[1]. [1]Geosciences Dept., Penn State University, University Park, PA 16801, USA. [2]Dept. of Geological Sciences, University of Texas at El Paso, El Paso, TX 79968, USA (mbmansor@utep.edu). [3]Dept. of Civil and Environmental Engineering, Rice University, Houston, TX 77005, USA.

The isotopic composition of minerals formed by microbial processes can be used as biosignatures, but this approach yields notoriously ambiguous results if abiotic processes induce similar isotopic fractionation with microbial processes. A specific example is the sulfur isotopic composition ($\delta^{34}S$) of gypsum ($CaSO_4.2H_2O$) formed in the sulfidic Frasassi caves in Italy, Earth. Even though sulfur-oxidizing microbes such as *Acidithiobacillus sp.* are the primary drivers of sulfide oxidation to sulfate, the $\delta^{34}S$ values of gypsum within a cave room are only depleted by up to 8‰ relative to the H_2S source [1], which also overlaps with the range expected from abiotic H_2S oxidation [2]. Therefore, no strong case can be made for a biosignature signal at first glance.

The viewpoint changes however if we consider isotopic expression in the context of *transport processes* and the faster *kinetics* of microbial H_2S oxidation compared to abiotic reaction [3]. In the caves, the sulfide source is transported as H_2S gas that continuously circulates along the walls. The fast kinetics of microbial sulfur oxidation leads to isotopic distillation of H_2S over a few meters that is reflected in the trend between height (or distance) and gypsum $\delta^{34}S$ along sections of the cave wall (**Fig. 1**). The slower abiotic H_2S oxidation cannot produce the same trend over a few meters, but may eventually produce a similar trend over a few tens to hundreds of meters. Therefore, the *length scale* of sampling is a primary consideration in detecting this biosignature, one that we term as a type of *spatial isotopic biosignatures*.

The processes causing spatial isotopic biosignatures are not limited to caves on Earth. For example, we hypothesize that spatial isotopic biosignatures may also arise from acid mine drainages where Fe(II) is released and continuously oxidized by microbes to Fe(III)-oxides along a stream flow path. On Mars, subsurface life utilizing Fe and S may also result in spatial isotopic biosignatures that are recognizable even in the absence of extant life as we know it.

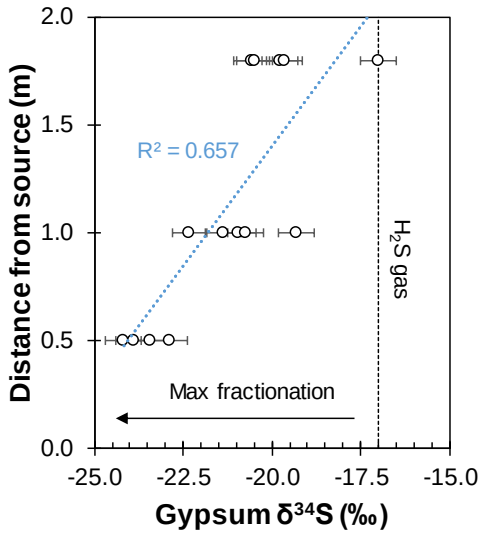

Figure 1: Gypsum $\delta^{34}S$ approaches the isotopic composition of the H_2S gas within a few meters due to fast microbial oxidation.

References: [1] Mansor M. et al. (2018) *Astrobiology, 18,* 59-72. [2] Fry B. et al. (1988) *Chem. Geol., 73,* 205-210. [3] Luther G. W. et al. (2011) *Front. Microb. 2,* 62.