DEVELOPING CAVE AIR AS A BIOSIGNATURE. K. D. Webster[1], [1]Planetary Science Institute, 1700 E. Fort Lowell Rd. Suite # 106, Tucson, AZ 85719

Introduction: Caves are one of the most exciting environments in the search for signs of present and past life on Mars. The composition of air in caves is known to be depleted in methane (CH_4) and enriched in carbon dioxide (CO_2) compared to the background atmosphere. Previous research has shown that these differences are the result of biological metabolism [1-3]. However, these are the two trace gases may represent anomalous cases and together may not be able to consist of a biosignature. To expand the usage of cave air as a biosignature, the concentrations of other trace gases from a number of caves will need to measured.

Methods: To determine the possibility for cave air to serve as a biosignature, the concentration of 25 trace gases in eight caves across the United States were measured. Cave air was measured *in-situ* with a Fourier Transform infrared spectrometer (FTIR, Gasmet DX4030). Cave air was sampled along gradients from the entrance of the cave to the cave interior. The gases measured included but were not limited to CO_2, CH_4, dichloromethane (CCl_2H_2), benzene (C_6H_6), and acetonitrile (C_2H_3N).

Results: FTIR measurements showed that the trace gas composition of cave air was different than the composition of the background atmosphere. For example, benzene, acetonitrile, and dichloromethane were all depleted in cave air compared to the atmosphere. Nitrous oxide (N_2O), which is thought to trace the movement of soil gas, was typically enriched in cave air compared to the background atmosphere. Samples of cave air, regardless of the cave they originated from, were more similar to each other than to samples of the atmosphere (PERMANOVA, $F = 229$, $r^2 = 0.64$, $p = 0.001$).

Discussion: The differences in the composition of cave air and the atmosphere appear to be due to metabolic processes. Benzene and acetonitrile are functionally similar to CH_4 because they are all reduced. This creates an oxidation-reduction potential in the presence of oxygen that cave-dwelling microorganisms may be able to exploit to power their cells. Conversely, N_2O was enriched in cave air, likely as a byproduct of the entrance of soil gas into the cave [4]. Further research is needed to confirm that the consumption of the gases like acetonitrile and benzene is a result of microbial metabolism in caves.

Overall, the tendency of cave-air is to show less free energy than the background atmosphere. This is most likely due to the slow speed at which cave air flows through the subsurface. This allows for the metabolic actions of microorganisms to manifest themselves in a macroscopic way through effectively removing the reactive components of the atmosphere.

When thinking about caves on Mars, a biological signature would appear to be the removal of reactive components of the atmosphere. This should manifest itself in a lower Gibbs Free Energy of cave air compared to the atmosphere. Several candidates for lava tube caves on Mars have been discovered and more continually being discovered. The exploration and the measurement of cave air on Mars may be pursued through either remote or *in-situ* methods.

References: [1] Mattey D. P. et al. (2013) *EPSL, 374,* 71–80. [2] Lennon J. T. et al. (2017) *Geobiology., 15(2),* 254-34. [3] Webster K. D. et al. (2018) *EPSL,* 9–18. [4] Waring C. L. (2017) *Scientific Reports 7 (8314).*