CCG21

Microbial activity in speleothem fluid inclusions from a central Texas cave

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Secondary cave calcite deposits (speleothems) are a well-established terrestrial paleoclimate proxy. Carbon- and oxygen-isotope ratios ($\delta^{13}C$ and $\delta^{18}O$) in precipitated calcite provide commonly studied speleothem records, recording a combination of the drip water composition, temperature of formation, and kinetic isotope fractionation effects during calcite precipitation. $\delta^{13}C$ in the drip water is controlled by a combination of surface vegetation (C_3 versus C_4 photosynthesis), micro-organism respiration in the soil, and the composition of the dissolved carbonate host rock. The $\delta^{18}O$ in the drip water is controlled primarily by the source and amount of meteoric precipitation.

While most studies of speleothems focus on inorganic geochemistry, a nontrivial portion of the deposits is formed from organic material of either allogenic or autochthonous origin. These materials, dissolved in a film of water on the speleothem or growing directly on the speleothem surface, can become incorporated into the growing speleothem, either between crystals or in small water- and air-filled pores (30-150 nm) in the crystal structure.

These inclusions of drip water, cave air, and organic material in actively forming calcite can provide records of changing geochemistry in the cave and overlying soil environments. Analysis of trapped gases in the speleothems by mass spectrometry can inform interpretation of coeval carbonate isotopic records and potentially provide a record of microbial effects within and on the surface of the speleothems (Blamey and Norman, 2002; Norman and Blamey, 2001). We hypothesize that this analysis, applied to speleothems from central Texas caves, will provide evidence of microbial activity occurring in the speleothem inclusions or on the speleothem surface.

We propose to measure fluid and gas inclusions for CH_4, H_2O, N_2, O_2, Ar, and CO_2 in central Texas speleothems and speleothem analogs grown in situ on glass plates. The calcite inclusion measurements will be performed by incremental crushing and heating under a vacuum followed by mass spectrometry. We will collect monthly cave air, drip water, and plate calcite samples from various environments within the cave as well as soil air samples above the cave for analysis and comparison to the values in the speleothem inclusions. The abundance of O_2, CH_4, and CO_2 in the speleothem inclusions and plate calcite samples should reflect the nature of microbial activity in the inclusions, a poorly understood factor in speleogenesis and cave environments. Elevated levels of N_2 above atmospheric N_2 concentrations could indicate breakdown of nitrogenous biomolecules in the speleothem inclusions.

Keywords: Speleothems, Paleoclimate, Biogeochemistry