GEOCHEMICAL ANALYSES AND MODELING TO UNDERSTAND SECONDARY MINERAL FORMATION IN VOLCANIC (LAVA TUBE) CAVES.

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Introduction: Secondary mineral features (speleothems) in volcanic (lava tube) caves are considered to preserve present or extant life signatures and hence could be important terrestrial analogs for lava tubes on Mars and Moon. Lava tubes on Earth host diverse microbial life and liquid water, and associated speleothems are morphologically and chemically distinct. We studied lava tubes at Lava Beds National Monument (California, USA) to elucidate the process of speleothem formation of speleothems.

Methods: Cave water samples were analyzed for their stable isotopic composition (δ¹⁸O and δ²H), concentrations of major ions and trace elements, and dissolved organic matter. Various speleothem morphologies were analyzed for their mineralogical characterization (X-ray diffraction) and elemental composition (X-ray fluorescence), and micro-morphologies were characterized using thin section and electron microprobe analyses. These data were combined in a PHREEQC based forward reaction model to test plausible pathways for precipitation of secondary minerals in speleothems.

Results and Discussion: Our results (Ford, 2020; Kulkarni et al., 2022), as indicated by an isotopic trend determined for cave puddle water (δ²H = 8.3*δ¹⁸O + 9.6), lie parallel to the global meteoric water line (GMWL). From this, we conclude that the source of cave water was primarily regional meteoric precipitation. This is consistent with our observations of water entering caves primarily through cracks in the cave walls and ceiling, presumably percolating from the surface through overburden and fractured basalt. Cave ceiling drip waters were moderately evaporated in comparison, as indicated by an isotopic trend line (δ²H = 3.4*δ¹⁸O – 44.8) that intersects the GMWL. Chemical analyses revealed that waters were enriched in Si (22±7 mg/L) and contained trace levels of Al, Fe, Zn, Li, Sr, Cu, B, V, Ba, Cr and Mn; we interpret this to reflect weathering of silicate materials that were entrained and transported in the water. Characterization of speleothem samples showed that amorphous silica (SiO₂am) and calcite (CaCO₃) were primary components in most of the morphologies. Microstromatolite-like, laminar features identified in speleothem thin sections were composed of alternating SiO₂am and CaCO₃ laminations. Based on saturation index calculations, cave waters were not supersaturated with respect to either SiO₂am or CaCO₃, yet they were the dominant minerals found in the speleothems. This led to a hypothesis that evaporation within the cave environments may play a key role in precipitation of these minerals. Using a forward reaction model, it was shown that evaporative concentration of cave waters could lower the solubility of SiO₂am and CaCO₃ and increase their concentrations above saturation which leads to precipitating and forming observed speleothem morphologies. Exceptionally high concentrations of dissolved organic carbon (DOC, 12 ± 8 mg/L) with a molar C/N ratio ranging from 2 to 22 were found in cave waters. The dissolved organic matter (DOM) was found to be aromatic (SUVA₂₅₄, 1.2–2.9 L/mg/m), terrestrially-derived and humic-like (humification index, 7 – 26), and with a bimodal distribution of molecular weights clustering around 100 Da and 5,000 Da. These results are consistent with our interpretation that terrestrially derived carbonaceous organic matter transported into caves exceeds the amount used by heterotrophic microbial metabolic activity in these subsurface environments. In fact, chemo-litho-autotrophy may be the dominant metabolism in these volcanic cave environments. Finally, our study better constrains the roles of water, evaporation, and microbial activity in the production of secondary mineral formation in lava tubes. We will discuss our data and interpretations in the context of Mars Astrobiology.

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