Geochemistry and Geochemical Models in explaining the formation of Secondary Minerals in Lava Caves - Terrestrial Analog Study towards Martian Environments

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Terrestrial lava caves at Lava Beds National Monument (N. California) exhibit secondary mineral deposits (speleothems) of diverse morphologies and chemistry, and of biologic or abiotic origin. To understand the mechanisms of speleothem formation, detailed geochemical analyses of speleothems and associated drip and pool waters from inside cave was conducted. The samples were collected from seven lava caves of varying ages, flows, temperatures, humidity and light intensity. Inorganic, organic constituents and stable isotopes (δ_2H and δ^2H) were measured in cave waters. Mineralogy and chemical composition of speleothem samples were determined by x-ray diffraction, fluorescence and petrographic analyses. Inverse and forward geochemical models (PHREEQC) were used to identify the possible mechanisms of minerals precipitations. It was demonstrated that the cave waters were enriched in Si, Na, K, Ca, Mg, Cl^-, NO_3^-, organic carbon and appeared more evaporated compared to meteoric waters. The predominant secondary minerals in speleothems were amorphous or cryptocrystalline (opaline) silica (SiO_2, 47–96 wt%), calcite (CaO, 1–25 wt%) and high Mg-calcite (MgO, 0.25–18wt%). Petrographic analysis showed the presence of microstromatolitic-like structures with laminations with alternating bands of opaline silica and calcite. Biomarker elements (Fe, Mn, S, V, As, U) were also found in the concentrations higher than the host basalt. The geochemical model suggests that the precipitation of opaline silica is favored by cave water evaporation whereas co-occurrence of biomarker elements speleothems may indicate biotic influence. The enriched SiO_2 in these speleothems could be biologically turbated. These results support the hypothesis that speleothems in lava caves can preserve the biomarkers over geologic time and could be potential targets. This work contributes to a NASA BRAILLE (Biologic and Resource Analog Investigations in Low Light Environments) studying lava caves as terrestrial analogs for future robotic missions and the search for biosignatures on the Mars and other rocky planets.