

A Proxy for Life Detection on the Other Planetary Bodies: Calcium Carbonate Clumped Isotope Geochemistry from Serpentinizing Environments

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This project aims to analyze the clumped isotopic composition of several carbonate samples recently collected from a serpentinizing hydrothermal system. The project will potentially provide 'first ever' insights into using clumped isotope signatures in carbonates from serpentinizing environments as a proxy for life detection on other planetary bodies, and is specifically designed to provide preliminary data for an upcoming NASA Exobiology or Habitable Worlds proposal. Serpentinization is the hydrous alteration of ultramafic (i.e., iron-rich) rocks, which provides abundant disequilibrium important for sustaining microbial life. Because of their inherent disequilibrium, many researchers suggest these systems played a role in the origin of life on Earth and may have done the same on other planetary bodies. Serpentinizing environments have been detected on Mars, Enceladus, Europa and Titan, all of which are priority targets for upcoming NASA missions (e.g., Mars 2020, Dragonfly). Carbonate minerals that precipitate in serpentinizing environments on Earth are often considered to be the result of rapid precipitation -upon mixing- of calcium-rich hydrothermal fluids with either seawater or atmospheric CO₂; a hypothesis supported by traditional bulk carbon isotope values. Preliminary data from our site, the Prony Hydrothermal Field (PHF), New Caledonia, suggests however that the carbonates may have precipitated as a result of CO₂ production through microbial anaerobic oxidation of methane (AOM). Microbial processes select for the lighter isotope (¹²C), and therefore the CO₂ derived from AOM should impart significant isotopic depletions on the resulting carbonate precipitates. Carbonates on other planetary bodies may have precipitated by this process, and for this reason our Prony samples will provide us with the unique opportunity to evaluate carbonates precipitated from AOM as proxy for life detection. We will use a new isotopic method that combines $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and "multiply substituted isotopologues" – i.e., molecular "species" with more than one heavy isotope substitution, so called 'clumped' isotopes – of CO₂ (e.g., ¹³C¹⁸O¹⁶O). This method can provide information on the temperature, the precipitating fluid composition, and importantly the source of DIC for carbonate formation (e.g., biotic or abiotic). Clumped carbonate measurements on CO₂ by laser spectroscopy, which is suitable for satellite or rover deployment, are now possible, paving the way for this proxy to be used in astrobiology research. Carbonates have been detected on many planetary bodies, including Mars, Enceladus, Europa, Ceres, and associated with meteorites, but their provenance by either biotic or abiotic pathways remains equivocal. As a result, this project is highly relevant to NASA Exobiology program goals "to understand the origin, evolution, distribution, and future of life in the Universe" with implications for understanding the potential of life to adapt to different environments, life elsewhere, and the identification of biosignatures for in situ and remote sensing applications. We want to show, unequivocally, that our samples from PHF are isotopically unique compared to any other samples, and that they can broaden our interpretation for carbonate samples from other environments, particularly those on other planetary bodies.