

THE CHARACTERIZATION OF BIOSIGNATURES IN CAVES USING A SUITE OF INSTRUMENTS.

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Introduction: The search for life and habitable environments on other solar system bodies is a major motivator for planetary exploration. Due to the difficulty and significance of detecting extant or extinct extraterrestrial life *in situ*, several independent measurements from multiple instrument techniques are necessary to support such a claim. We demonstrate the unambiguous detection of biosignatures using a suite of instrument techniques including IR reflectance spectroscopy, laser desorption/ionization time-of-flight mass spectrometry (LD-TOF-MS), laser induced breakdown spectroscopy (LIBS), and scanning electron microscopy (SEM) / energy dispersive X-Ray spectroscopy (EDS). We focus our measurements on subterranean field samples, whose primitive biosignatures are analogous to those expected on high-interest astrobiology targets [1]. In this presentation, we discuss the value of each of the aforementioned instrument techniques for the detection of biosignatures *in situ* and present results on the autonomous characterization of biosignatures using multivariate statistical analysis techniques.

Fort Stanton Cave Calcite Measurements: To characterize the biosignature detection capabilities of the instrument suite described above, we present measurements of a set of calcite samples collected from Fort Stanton Cave, an extensive limestone cavern in central New Mexico with diverse speleothems and cave decorations. Calcite samples were identified in the field and selected to ensure that both abiologic and biologically precipitated minerals were collected based on other characterization methods not detailed here. Carbonate minerals, including calcite (CaCO_3), have been identified at several distinct geologic regions on Mars, and represent some of the most astrobiologically interesting samples to investigate due to their association with aqueous formation conditions [2, 3] and terrestrial biomineralization products [1, 3]. Calcium carbonate speleothems commonly precipitate out of a carbonic acid-rich solution saturated with Ca^{2+} cations [4], however, biologic processes may influence speleothem formation [1, 4]. We present measurements of characteristic biologically precipitated calcite samples with macroscopic morphological features consistent with biologic activity, as shown in Figure 1a.

Results from SEM imaging presented in Figure 1b contain evidence of biologic films coating the carbonate host rock, as well as long (50 μm) filaments approximately 5 μm in diameter, indicative of fungal filaments, perhaps calcified [5, 6]. An EDS spectrum of the region probed by the SEM is presented in Figure 1d. Regions with morphological evidence of biologic activity (blue circle) contain 7% more carbon than abiologic features nearby (red square). Additionally, an increased detection of Ca and O in the biologic features may indicate higher concentrations of calcite or calcium oxalate (CaC_2O_4) in these regions, indicative of biologic precipitation [6].

Figure 1c shows an annotated IR spectrum of the calcite sample measured by the AOTF IR reflectance point spectrometer. We measured two regions of the sample: the host rock, and the coralloid features. Carbonate features ($-\text{CO}_3$) are evident in all sample regions, as is a broad H_2O hydration feature. The carbonate feature appears shifted from 1.9 - 1.95 μm in the coralloid spectrum, most likely indicating higher heavy metal content (Mg or Fe) [7]. The hydroxyl (OH) feature at ~2.75 μm is only present in the spectra of freshly cleaved surfaces, and is diminished in spectra of exposed regions due to water adsorption onto the surface. Broad CH and CO_3 features from 3.35 - 3.5 μm are observed only in the host rock [8].

The inorganic composition of this sample is inferred from the LIBS emission spectrum, presented in Figure 1e. The spectrum is dominated by the detection of calcite with strong carbon and oxygen lines, indicating that the major mineral class observed is likely a calcium carbonate. Trace elements often associated with biomineralization of calcite (including Pb, Ba, Mg and light rare earth elements such as Nd) are detected using LIBS, and are used to strengthen the claim of biogenicity of these samples [9].

A mass spectrum of the calcite coralloid sample measured by a two-step LD-TOF-MS in positive ion mode presented in Figure 1f explores the high-mass composition, while suppressing the dominant low-mass metal peaks. We used an IR desorption laser wavelength of 2.75 μm to exploit the OH vibrational resonance shown in the IR reflectance spectrum to enhance the desorption of analyte. An envelope of

peaks centered around a species at 217 Da is present, in a mass range consistent with terrestrial organics originating from extant or fossilized bioactivity.

Discussion: We demonstrate the detection of bi-signatures within a variety of subterranean samples on Earth using a suite of instruments, many of which are candidates for future landed and roving missions to other planetary surfaces. Measurements of biogenic field samples from each of these instrumentation techniques provide a unique data product useful in identifying the biogenicity of a sample.

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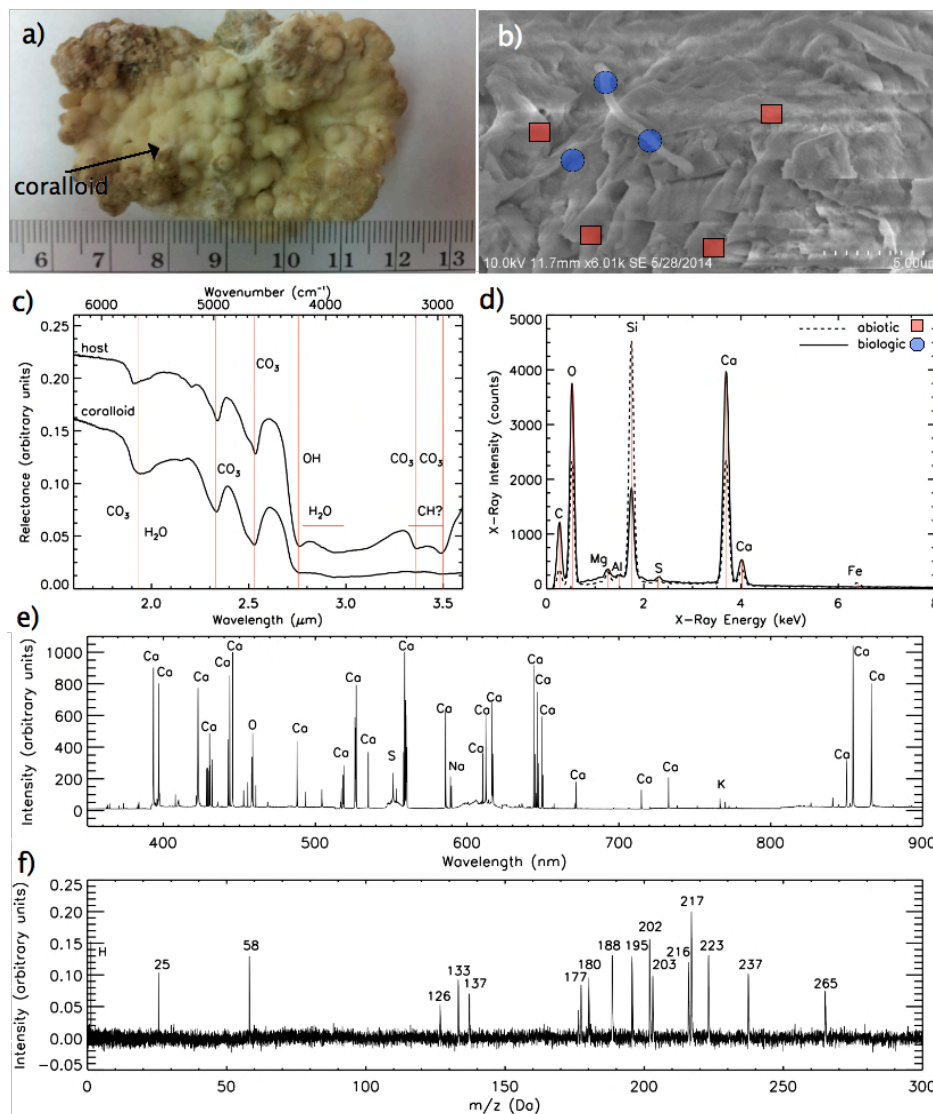


Figure 1: Results of the calcite coralloid sample showing the a) macroscopic coralloid structure; b) SEM micrograph; c) IR spectrum; d) EDS spectrum; e) LIBS spectrum; f) two-step LD-TOF-MS mass spectrum.