

# A MULTI-INSTRUMENT INVESTIGATION OF A UNIQUE LOW-TEMPERATURE, CO<sub>2</sub>-RICH GEYSER RELEVANT TO MARS AND ICY MOONS: CRYSTAL GEYSER, UTAH, USA. Z. U Wolf<sup>1\*</sup>, E. A. Cloutis<sup>1</sup>, N. N. Turenne<sup>1</sup>, D. M. Applin<sup>1</sup>, S. Potter-McIntyre<sup>2</sup>, S. Mertzman<sup>3</sup>. <sup>1</sup>Center for Terrestrial and Planetary Exploration (C-TAPE), University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9;

<sup>2</sup>Department of Geology, Southern Illinois University, Parkinson, Mail Code 4324, Carbondale, IL 62901;

<sup>3</sup>Department of Earth and Environment, Franklin and Marshall College, P.O. Box 3003, Lancaster, PA, USA 17604-3003. \*wolf-z@webmail.uwinnipeg.ca.

**Introduction:** The presence of carbonates on Mars is well-established and they may have formed via different processes. While hydrothermal and lacustrine formation processes are well known, less is known about low-temperature, CO<sub>2</sub>-driven deposits, which may be more relevant for some carbonate deposits on Mars and icy moons. Crystal Geyser is located 14.5 km SE of Green River, UT, USA and is part of a natural spring system along the Little Grand Wash fault in the northern section of the Paradox Basin of the Colorado Plateau [1]. This spring system is a rare example of a man-made low-temperature geyser [2] that was created in 1935 during exploration for oil and gas in the area [3]. Unlike a typical geothermally-activated geyser, this spring system erupts due to large amounts of CO<sub>2</sub> dissolved in water and underlying gas pressure.

The consistent and persistent eruption of the geyser has created a gently-sloping travertine mound a few meters thick consisting of precipitated carbonates, predominately composed of calcite, with aragonite increasing in concentration approaching the spring [4]. The erupted water is rich in dissolved species, resulting in the precipitation of dominantly carbonate minerals.

Carbonates are a type of primary or secondary mineral that record past environmental conditions, as their formation is dependent on prevailing physical and chemical conditions [5] and their ongoing preservation can depend on subsequent environmental conditions [6, 7]. This makes carbonates of particular interest in trying to understand potential habitability and astrobiological potential of Mars and icy moons.

Carbonates can form under different conditions such as temperature, varying ion activity in solution, or CO<sub>2</sub> levels. In the case of calcium carbonate, there are three anhydrous crystalline polymorphs, two of which are stable: aragonite, and calcite [8, 9].

Aragonite, normally a high-pressure polymorph or bioprecipitate, is metastable at low temperatures and ambient pressure [8] and transforms into calcite through a dissolution-reprecipitation mechanism which can allow for sub-micrometer scale preservation of morphologies [10]. Aragonite crystallization is often pre-sent in environments such as limestone caves or biogenically in marine environments [8]. Aragonite's hardness allows it to withstand changes in environmen-

tal conditions [8, 9]. On a smaller scale, there are several species of bacteria that can precipitate aragonite due to their cell surface structures and metabolic activity [11]. Cyanobacteria can enable the formation of aragonite laminations due to their common presence as microbial mats as well as their metabolism [12]. Records of past environmental conditions can be identified from structural features formed in aragonite left behind by living organisms [10].

Aragonite commonly transforms into calcite, the most stable form of calcium carbonate via an endothermic and irreversible reaction [8]. Rate of transformation of aragonite to calcite is dependent on temperature, taking only a few minutes at temperatures over 400°C, or a few days at temperatures between 50 to 100°C [8].

Samples collected from the Crystal Geyser site were obtained at various distances from the vent pipe but are all surficial samples. The samples likely vary in age and the extent of alteration they have undergone because of the temporally changing outflow paths.

**Methods:** Each sample was analyzed as a whole rock, including exterior weathered surfaces, broken fresh surfaces, and polished interior surfaces using a variety of techniques described below. Reflectance spectroscopy of the samples was used to identify the mineralogy of the deposits and any characteristics unique to low-temperature, CO<sub>2</sub>-driven carbonate deposits such as crystal preservation abilities, or trace element composition. Reflectance spectra were collected with an ASD LabSpec4 Hi-Res spectrometer (350-2500 nm), at a viewing geometry of  $i=0^\circ$ ,  $e=30^\circ$ . Raman spectra were collected with the BWTek 532 laser iRaman system (150-4000  $\Delta$  cm<sup>-1</sup>). Subsamples were also crushed to <45  $\mu$ m powders for analysis by X-ray diffractometry (XRD) using a Bruker D8 Advance with a DaVinci automated diffractometer, with an integration time of 1 second per 0.02° step. SEM+EDS with BSE was conducted with the Hitachi FlexSEM 1000 II on carbon-coated samples. Some of these analytical techniques are similar to instruments on current and future Mars rovers.

## Results:

**Reflectance:** Reflectance spectroscopy was able to identify a mixture of calcite and aragonite in each

sample collected from the site, as shown by the adsorption feature at ~2350 nm (Fig. 1). Chlorophyll, ~675 nm (Fig. 1) and quartz, ~2200 nm, was also present in some of the samples in minor quantities.

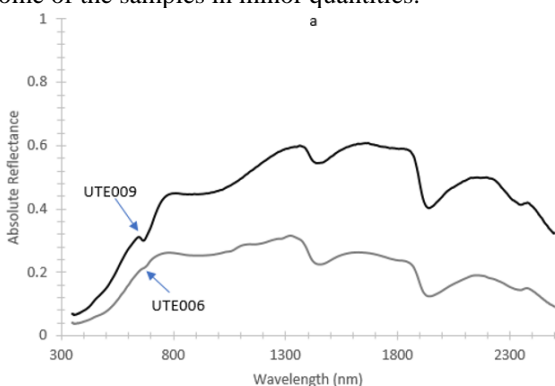


Figure 1: Reflectance spectra of sample UTE006 and UTE009 showing the presence of chlorophyll (675 nm band) and a calcite-aragonite mixture (2350 nm adsorption feature).

**X-ray diffraction:** XRD shows each sample as a mixture of both calcite and aragonite with the presence of quartz in a few samples.

**Raman:** Raman spectra indicated the presence of only calcite in some samples, only aragonite in other samples, and a mixture of both in some samples. This indicates that the sample is not transforming uniformly throughout, as Raman is testing a single spot of a sample. Raman also showed no organic signatures, likely due in part to the strong fluorescence masking the Raman signal (Fig. 2).

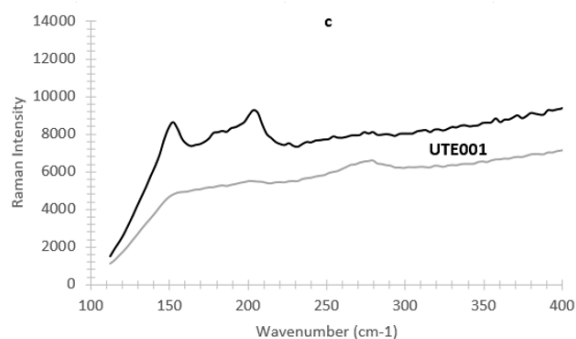


Figure 2: Raman spectra for sample UTE001. The upper band indicates the presence of aragonite and the lower band indicates the presence of calcite in the sample.

**SEM+EDS:** SEM was able to show microscale structures of calcite and aragonite crystals within the samples. SEM also showed the ability of carbonates to preserve and entomb microbes. Fig. 3 shows a perfectly entombed microbe that is ~3  $\mu\text{m}$  in diameter.

**X-ray fluorescence:** XRF results identified major and selected minor elements in each sample. This in-

formation confirmed the presence of silica which was seen in reflectance and some of the Raman spectra.

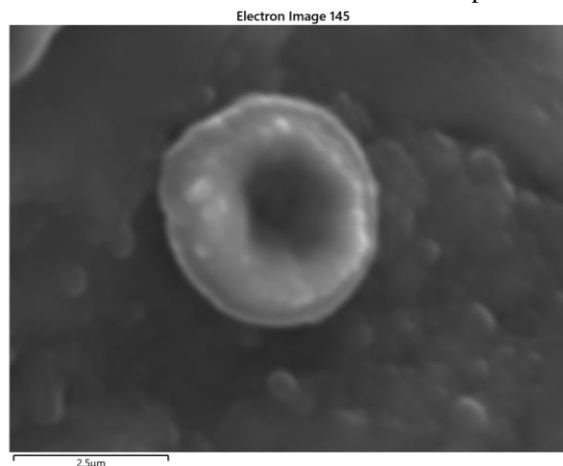


Figure 3: SEM electron image of a microbe entombed within sample UTE008.

**Discussion:** Carbonates are important targets in terms of astrobiology as they can be indicative of extinct or extant life. Carbonates have been identified at several localities on Mars [13] including Jezero Crater, current location of the Perseverance rover [14].

This study suggests that the most effective way to detect calcite and aragonite is through Raman and reflectance spectroscopy. This study also confirms the ability for carbonates to preserve microbes which was detected by the SEM. The SuperCam instrument on the Perseverance rover has relevant instruments that should be able to identify carbonates such as calcite or aragonite.

**Future work:** Further analysis of the Crystal Geyser samples is expected to reveal additional features that allow low-temperature,  $\text{CO}_2$ -driven carbonate precipitates to be distinguished from other types of carbonate deposits.

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**References:** [1] Potter-McIntyre, (2019) *Geosites*, 1, 1–6. [2] Potter-McIntyre; (2017) *Astro.bio.*, 17(3), 216–230. [3] Waltham, (2001) *Geol. Today*, 17(1), 22–24. [4] Barth, (2014) *Sed.*, 62(3), 607–620. [5] Shaheen et al., (2010) *Nat Acad. Sci. USA*, 107(47), 20213–20218. [6] Cloutis et al., (2008) *Icar.*, 197(1), 321–347. [7] Turenne et al., (2021) *Plan. and Space Sci.*, 105377. [8] Parker et al., (2010) *CrystEngComm*, 12(5), 1590. [9] Xu & Sommerdijk, (2018) *Proc. of the Nat. Acad. of Sci.*, 115(34), 8469–8471. [10] Beruto & Giordani, (1993) *J. Chem. Soc.*, 89(14), 2457–2461. [11] Khan et al., (2021) *Geomicrobio. J.*, 38(3), 231–236. [12] Okumura et al., (2012) *Sed. Geol.*, 265–266, 195–209. [13] Boynton et al., (2021) *Min.*, 8(6), 221. [14] Tarnas et al., (2021) *J. of Geophys. Res.: Planets*.