

**Martian Analogue Salts from Billion-Year-Old water** J. T. Poiras<sup>1</sup>, K.T. Tait<sup>2</sup>, E. A. Cloutis<sup>3</sup>, and D. M. Applin<sup>3</sup>. <sup>1</sup>Department of Earth Sciences, University of Toronto, 22 Russell St. Toronto, ON, Canada (jordan.poiras@mail.utoronto.ca), <sup>2</sup>Department of Natural History, Royal Ontario Museum, Toronto, ON, Canada <sup>3</sup>Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, MB, Canada.

**Introduction:** Future missions from both NASA and the ESA aim, in part, to learn about life and habitability on Mars [1]. The Mars 2020 rover from NASA will be tasked with finding and caching samples that have a high probability of containing microbial life. This may be a difficult task considering that life in such low abundances would be difficult to detect. The potential for life to exist on the Martian surface seems unlikely, given the temperature, pressure and UV conditions. However, there is evidence that life may still exist on Mars (example: methane [2,3]) and life has been found to thrive in the most unlikely places on Earth. If life were once abundant on Mars it would have been billions of years ago. One place that allows us to make a comparison is the Kidd Creek mine in Timmins, Ontario, Canada 2.6 km below the surface, a closed hydrological system was found that sustained microbial life [4]. The system also has a proposed residence time between 1.0 to 2.2 Ga [5,6] and has been quiescent for the past 2.6 Ga. The waters are enclosed in mafic to ultramafic rocks, producing a highly saline brine, making the water relevant to Martian analogue studies.

Some work has been done to produce analogous brines assuming for groundwater interaction with igneous rocks. Bullock et al. [7] used Shergottite, Nakhilite, and Chassigny (SNC) martian meteorites to produce a brine with major constituents  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Na}^+$ ,  $\text{C}$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$ . This brine was later desiccated in a present day Martian atmospheric environment and an acidic Noachian (3.6 Ga) environment [8]. The acidic environment was favorable to Mg sulfates and  $\text{Na}_2\text{SO}_4$  while the present day environment produced a calcium sulfate with minor aluminum and magnesium sulfate.

Little is known about the impacts biology has on the precipitation and composition of evaporite minerals. If there are spectral differences in minerals produced alongside microbial life, compared to minerals that are not, then we should be able to measure and quantify these differences. By precipitating salts in different atmospheric environments with different biological loads, this experiment aims to quantify biological spectral signatures.

**Method:** Brine solution was collected from two cased boreholes (studied by Holland et al. and Warr et al. [5,6]), 12299 and 12261, from the Kidd Creek Mine using sterilized 1L Nalgene containers. Water was fed into the containers using a rubber hose attached to the borehole casing taking care to minimize mixing with

ambient air. Containers were closed and sealed with tape and stored at the University of Winnipeg until the time of desiccation. Samples were also sent to Actlabs for anion cation analyses.

For mineral precipitation, water was filtered by 0.22  $\mu\text{m}$  mesh filters and desiccated in a  $\text{CO}_2$  environment and ambient dry air environment. To minimize the impact of microbial contact, evaporation pans, and tools were sterilized with 5.0% hydroxyl bleach as described by Rogers et al. [9] and the glove box was sterilized with methanol. Both closed environments were kept between 10-20% relative humidity. This method was done again with unfiltered water, and without sterilization. The evaporation process took approximately 7 days for each sample, resulting in a coarse salt.

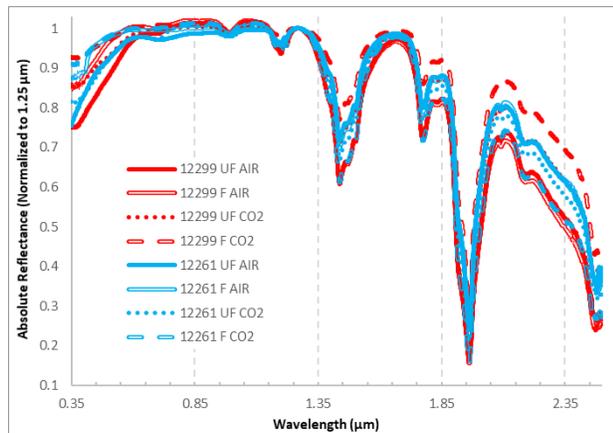
Further handling of the samples was done in a dry  $\text{N}_2$  enclosed environmental glove box to maintain sample stability. Reflectance spectra (350-2500 nm) was acquired inside the  $\text{N}_2$  environment with an Analytical Spectral Devices FieldSpec Pro HR spectrometer. The 150 watt quartz-tungsten-halogen collimated light source was fed into the glove box, as well as the spectrometer detector fiber. Measurements were done relative to a Spectralon 99% diffuse reflectance standard. 500 averages of dark current, standard, and sample were acquired.

**Table 1: Significant anions, cations and salinity**

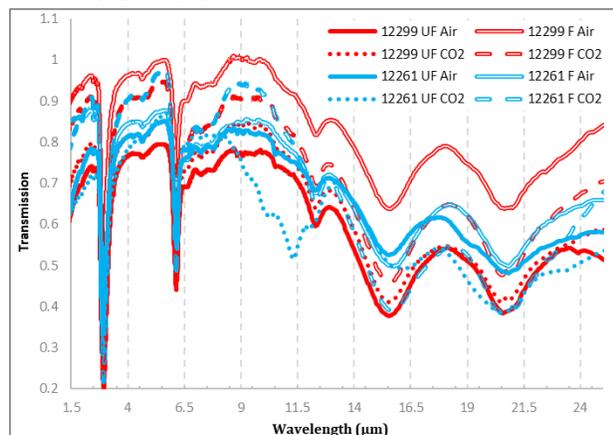
Sample	Salinity (mg/L)			
12261	211458.4			
12299	190849.4			
	Na	Mg	K	Ca
	mg/L	mg/L	mg/L	mg/L
12261	17900	2120	118	68300
12299	17300	2460	123	58200
	Li	B	Mn	Ba
	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$
12261	<500	3450	33900	43300
12299	636	3540	28700	42900
	Cl	Br	Sr	Pb
	mg/L	mg/L	mg/L	$\mu\text{g/L}$
12261	120000	1910	1100	12
12299	110000	1760	997	<5

Airtight sample holders were used to acquire X-ray diffractometry (XRD). The specimens were investigated at continuous scan between  $10^\circ$  to  $80^\circ$   $2\theta$  at  $0.02^\circ$  increments at 1 second per step.

Transmission spectra were collected using a Bruker FTIR. Samples were prepared in a dry environment where 2 mg of sample were hand mixed with KBr using



**Figure 1:** Reflectance spectra from 0.35 to 2.5  $\mu\text{m}$ . Red lines: borehole 12299 Blue Lines: Borehole 12261. Solid lines are unfiltered water and hollowed lines are filtered.



**Figure 2:** Transmittance spectra from 1.5 to 25  $\mu\text{m}$ . Red lines: borehole 12299 Blue Lines: Borehole 12261. Solid lines are unfiltered water and hollowed lines are filtered.

a mortar and pestle for 5 minutes. Transmission pellets were pressed under 3 tonnes of pressure for 5 minutes using a 3 mm die. 1000 measurements were averaged per sample.

**Preliminary Results:** Anion/cation analysis results indicate a diverse saline fluid from both boreholes (**Table 1**). Results from the X-ray diffractograms indicate halite in all samples, as well as the mineral sinjarite, ghiraitite, antarcticite, and tachyhydrite. There are subtle shifts in peak position, but these cannot be quantified due to their low resolution. Reflectance data are also highly similar to sinjarite [10] seen in **Fig. 1**. The intensity of the OH/H<sub>2</sub>O bands located at 1.4 and 1.9  $\mu\text{m}$  varies between sample, indicating varying degrees of hydration between the mineral products. Transmission

spectra presented in **Fig. 2** have absorption features associated with SO<sub>4</sub>, OH, H<sub>2</sub>O, and the sample 12261 UF CO<sub>2</sub>, appears to have been contaminated with some silicates due to the triple feature located between 9 and 12  $\mu\text{m}$ . The features located at ~15  $\mu\text{m}$  and ~20  $\mu\text{m}$  have unique band minimums for each sample. This feature is associated with SO<sub>2</sub> despite no sulfate mineral identification in the XRD patterns. In general the filtered salts appear to be brighter, and the tail end into 25  $\mu\text{m}$  slopes upward, while the unfiltered salts slope downward.

**Discussion and Future Work:** The reflectance and transmittance spectra all have subtle differences that may allow us to characterize what spectral features are or are not associated with microbial activity in mineral precipitation. At this point in time only the relative hydration state can be determined from the reflectance data. Raman spectroscopy and a higher resolution investigation by XRD may be able to provide more pertinent information for addressing the spectral signatures of biology.

The minerals produced through the desiccation process would not be stable on the surface of Earth, but are potentially stable on the surface of Mars. Increasing the diversity of spectral libraries is essential for exploring Mars, especially with minerals that do not form on Earth. Given the dry formation conditions we can expect this deliquescent salt to be dispersed throughout the Martian surface. This analogue product is important since various chloride and perchlorate salts have been identified on the surface of Mars [11,12], which may provide microbial life a transient source of water [13]. This data may allow new remote sensing instruments (Mars 2020 rover) to detect salts that are pertinent in the search for life on Mars.

**References:** [1] Mustard J. (2013) *MEPAG*, 155. [2] Formisano V. (2004) *Science*, 306, 1758. [3] Lefèvre F., and Forget F. (2009) *Nature*, 460, 720. [4] Doig F. *et al.* (1995) *Geomicrobiol. J.* 13, 91. [5] Warr O. *et al.* (2018) *Geochim. Cosmochim. Acta*, 222 340. [6] Holland G. *et al.* (2013) *Nature*, 497, 357. [7] Bullock M. *et al.* (2004) *Icarus*, 70 404. [8] Moore J. *et al.* (2010) *JGR E:Planets*, 115, 1. [9] Rogers D. *et al.* (2005) *Life in Ancient Ice*, 5. [10] Crowley J. (1991) *JGR*, 96, 16231. [11] Hecht M. *et al.* (2009) *Science*, 325, 64. [12] Osterloo M. (2010) *JGR E:Planets*, 115, 1. [13] Davila A. *et al.* (2010) *Astrobiology*, 10, 617.

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