Maëva MILLAN Lewis and Clark Astrobiology Report rcvd. 10.30.18

Detection & preservation of organic molecules in hot spring spicular sinter deposits as analogs for Mars

Project Report

The search for life is the driving goal of Mars exploration. At present, the Sample Analysis at Mars (SAM) instrument is the most sophisticated gas-chromatograph quadrupole mass spectrometer (GCMS) ever sent to Mars. SAM is housed inside NASA's Curiosity Rover of the Mars Science Laboratory (MSL) mission. Curiosity landed in Gale Crater in 2012, and has begun its ascent and exploration of Mount Sharp, a five kilometer high stack of sediments that records much of Martian history. SAM is a pyrolyzer (pyro)-GCMS and has discovered simple organic molecules at Mars' subsurface for the first time in history. When pyrolysis only is not effective to extract and analyze organics of astrobiological interest, SAM performs wet chemistry experiments, called derivatization, on the solid samples collected by Curiosity. One of the two derivatization reagents is called N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA). It is a silylation method that allows the separation, detection, and identification of complex, polar and/or refractory molecules. MTBSTFA reacts with amino acids, carboxylic acids, and sugars while preserving their chemical structure from degradation. To do so, the labile H of the targeted molecule is replaced by the MTBSTFA silyl group, transforming molecules into volatile derivatives easily amenable to GCMS analysis**. The research goals** were to **(1) evaluate in laboratory the efficiency of the MTBSTFA derivatization on Martian analogs to support the pyro-GCMS experiments performed by SAM on Mars, (2) find the precursors of the organic compounds detected by SAM, (3) select the most fruitful samples for SAM to analyze**, as SAM is only designed to run seven experiments with MTBSTFA. To do so, I am conducting laboratory experiments on Martian analogs samples that have similar mineralogies to the sedimentary rocks on Mars. However, hot spring deposits were lacking in our analogs collection but are very important to understand the organics preservation in geothermal terrains on Mars (*e.g.* Columbia Hills).

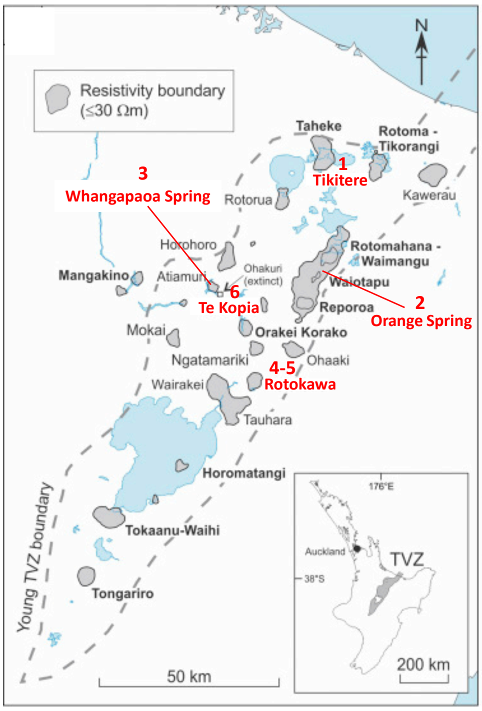

Figure 1. Geographic location of the six geothermal sites visited and from which the samples were collected. They are all located in the Taupo Volcanic Zone in the Northern Island of New-Zealand, about 3 hours driving south of Auckland.

To address the research goals as a Lewis and Clark Fellow, I collected spicular sinters from six active hot springs deposits on five sites near Rotorua. These hot springs have different fluid compositions, from alkali-chloride, acid-sulfate-chloride to acid sultate. The field work took place in late June, 2018. The field expedition team consisted of Kathy Campbell, professor at the University of Auckland, Bruce Damer, researcher at the University of California, Bryan Drake, a professor at the University of Auckland who took care of the daily logistics and of our safety, and Kathy's students Tara Djovic, Jessica Pelser and Yael Heled.

Samples for organic analysis were collected in at least triplicate with spoons and spatulas and deposited in glass jars. All the material used was previously solvent-cleaned and ashed at 550°C for >6 hours to avoid any potential organic contamination. In the field, the samples were placed in a cooler filled with ice and ice packs immediately following sample collection. Back at the hotel, they were stored in a -20°C freezer until shipping. Back in Auckland, the samples were cold shipped to the USA in a cooler. During sampling, the details of each sample and site were logged including GPS coordinates, a site description, the water temperature and pH of the pool and known preliminary elemental mineralogy. Details about each day of field work and the samples I was able to collect are included below.

Day 1

We arrived early in the morning at Rotorua, an area known throughout New Zealand for its geothermal activity. We sampled in the afternoon from 1 to 4:30 pm at the publically accessible geothermal field Hell's gate, at Tikitere, near the "Cooking Pool." This site is an alkali-chloride circumneutral environment mostly constituted of sulfides minerals. The spicules were mostly grey in colors and collected along the channel flow. The water temperature of the pool was ~41°C and the pH: 6.83 where the samples were collected. A mud sample was also collected for GCMS analyses and comparison with the spicules.

Figure 2. (Left) Hell's Gate, Tikitere geothermal field sampling site. The red square represents the exact location on the shallow flow water where the spicules where collected. (Right) Zoom in of the the grey spicular sinter collected. Alkali-chloride circumneutral environments mostly constituted of sulfides.

Day 2

In the morning, we sampled in Orange Spring, near Kerosene Creek, in the middle of a forest that was not publically accessible. The name of the creek is related to its high concentration in "cooked" organic molecules. We had to cross the creek to reach the geothermal site. It took us about an hour and a half to reach the site, and I was able to sample from about 10am to noon. These spicular sinters were mostly acid-sulphates and had a yellowish/brownish, almost gold color. Spicules were quiet friable and easy to collect. They were growing at the edge of the water, at the end of the cooling flow. The water temperature of the pool was ~70°C for a pH of ~ 2.

Figure 3. (Top) Overview of the Orange Spring sampling site with Kerosene Creek in the foreground. (bottom left) Sampling site. Red square is the pool where the spicules where collected. (bottom rigt) Zoom in of the yellow/brown/gold spicules. Hammer is shown for scale. Acid sulfates environment.

In the afternoon, we sampled in Whangapaoa Spring from 1:30 to 5 pm, a terrace with moderate flow from the hot upper pool. The sinters collected were pure alkali-chloride from a circumneutral environment (pH 8.43) and water temperature of ~25°C. The sinters had three different colors layers: black/dark brown, white and then pink. They were particularly hard to collect, and I had to use a hammer and a tiny chisel to remove them from the bedrock.

Figure 4. (Left) Overview of the Whangapaoa Spring sampling site. (Right) Zoom in of the brown/white sinters collected. Pure alkali-chloride circumneutral environment.

Day 3

We sampled all day at the non-publically accessible Rotokawa geothermal site. Permit access was mandatory and delivered to Kathy Campbell to be able to enter the geothermal station. We spent the morning from 9am to 12pm at Rotokawa Lagoon. This is a huge blue/turquoise very streamy lagoon hot spring with several black/grey boiling pools. The elements are mostly arsenic and sulfur. I collected light grey/white spicules at the East of one of the hot spring, from the shoreline, out the water and in the water. The pH of the corresponding pool was ~1.87 with an average temperature of 81°C. I also collected one small vial of darker grey/almost black spicules from a western pool which, because of the dark color of the spicules, may contain more sulfides and therefore could serve as a comparison with the pool where most of the other samples were collected.

Figure 5. Overview of the Rotokawa Lagoon sampling site. Bottom right is a zoom of a white/grey spicular sinter.

We drove about 20 min at the same site to reach the second hot spring field: Parakiri Spring, where we sampled from 1 to 3pm. It was a very streamy tiny creek in a valley with a very light flow from a waterfall on lava bedrock. The water was yellow, green and white in this acid-sulfate-chloride environment. The spicules I collected were white, growing on a green then brown bedrock sinter. Because of their white, almost transparent as crystal color, they are called “the fairy castles.” The water where they were collected was at ~43.6°C for a pH of ~1.65.

Figure 6. Overview of the Parakiri Stream site. Bottom right is a zoom of the "fairy castles" spicules. The green areas is an acidophilic alga, *Cyanidium*, growing at the air-water interace in the shallow pumiceous alluvium. Acide-sulfate-chloride environment.

Day 4

We sampled in the morning from 9 am to 12 pm at the Te Kopia geothermal field site. This hot spring is located at the bottom of a huge mountain and is actually made of several boiling and tiny, very steamy and odory pools. This is a acid sulfate rich environment. I collected pinkish/brown tiny rounded spicules at a first site using a tiny chisel and hammer to remove them from the bedrock. Site 1 was dry but very streamy and the measured temperature was ~80°C. The spicules collected at the second site were brownish/white and much more friable compared to site 1. The water temperature of the pool was 95°C and the corresponding pH ~1.66.

Figure 7. (Left) Overview of the Te Kopia site. The sampling site is located at the bottom right. (Right) Zoom of the tiny salmonish spicules. Acide sulfate environment.

SAM-like pyrolysis and SAM-like MTBSTFA derivatization experiments are now underway to characterize each of these unique samples in laboratory as they represent the best known terrestrial analogs for martian hydrothermal sinters. These new data will complete the set of data we already have on different martian analogs and help understanding the potential for biomarker preservation in different types of Mars analog samples for various martian NASA missions, including Mars 2012 rover, Mars 2020 rover which will select samples for return to Earth, as well as the European Exomars 2020 rover, which will also include a pyro-GCMS, the Mars Organic Molecular Analyzer (MOMA) instrument, and use MTBSTFA as a derivatization reagent.