USING SECONDARY MINERALS IN A HAWAIIAN LAVA TUBE TO INFORM SALT PRECIPITATION ON MARS. P. D. Archer, Jr.[1], R. S. Jakubek[1], J. V. Clark[2], R. V. Patterson[1], and P. D. Casbeer[1], [1]Jacobs, NASA Johnson Space Center, Houston, TX, doug.archer@nasa.gov, [2]Geocontrols Systems –Jacobs JETSII Contract, NASA Johnson Space Center, Houston, TX.

Introduction: Recent data from the Mars Science Laboratory rover *Curiosity* indicates the potential correlation of F and Cl in salts as the rover heads up Mt. Sharp [1]. There is some evidence for the correlation of these two ions in terrestrial environments [2], and we are investigating this potential in a Mars analog environment.

Figure 1 – (top) an image of the entrance to the lava tube on the south (upslope) side. (bottom) looking north from the tube floor near the entrance showing the abundant alteration minerals coating the basalt.

For this study, we collected measurements *in situ* as well as samples for further laboratory analysis from a lava tube on the northern flank of the Mauna Loa volcano on the big island of Hawaii. The lava tube is located on a flow that is ~200-450 years old, next to flows from 1880-1840 (and very close to the flows in December 2022). The lava tube is at an elevation of ~2400m and is a few hundred meters long with two entrances and two skylights along its length. Due to the young age (and therefore less alteration) the location is a good analog for Martian basalt.

Previous work at this site indicated the presence of gypsum as well as thenardite (Na_2SO_4) [3], the former being found pervasively at Gale Crater on Mars, the latter lending credence to the possible presence of halite (NaCl) in the tube.

Methods: This work was done in collaboration with the Goddard Instrument Field Team (GIFT) and, as such, used field instruments to make measurements *in situ* as well as collecting samples for laboratory analysis. In the field, we used a portable Raman instrument (a Metrohm iRaman Plus instrument with a 532 nm laser), an Olympus Vanta handheld X-ray fluorescence (XRF) instrument, and an inXitu (now Olympus) Terra X-ray diffraction (XRD) instrument. The Raman and XRF instruments were carried to the lava tube and the XRD was used to analyze samples in the hotel to inform subsequent field activities. These instruments identified the primary mineralogy of the different types of samples present in the tube to aid in understanding alteration processes and to guide sample collection for further analysis in the lab.

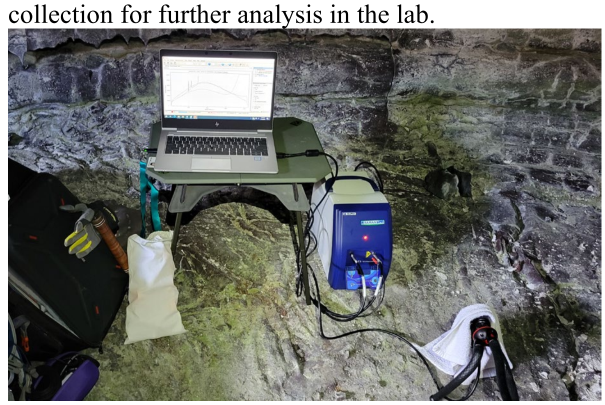
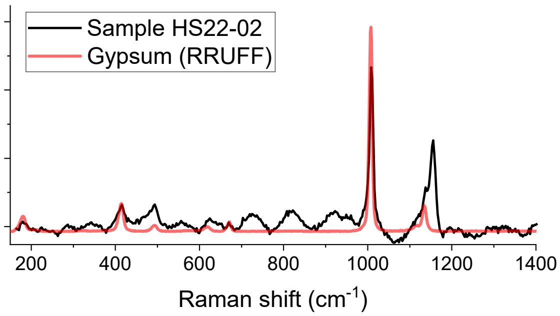


Figure 2 – The iRaman plus instrument setup inside the lava tube with the laser in the lower right connected to the detector in the blue and gray case.

Laboratory Analysis. The samples will be analyzed using the following techniques for further characterization: 1) XRD using a higher resolution instrument (e.g. a Panalytical X'Pert Pro) to identify lower abundance minerals 2) Differential Scanning Calorimetry/Thermal Gravimetry/Evolved Gas Analysis (DSC/TG/EGA) to identify and quantify volatile bearing minerals at levels as low as 10s of ppm 3) ion chromatography (IC) to measure anions and 4) inductively coupled plasma - optical emission spectrometry (ICP-OES) to identify and quantify cations. IC and ICP-OES will be particularly useful because, chlorine-bearing salts, if present at all, are at levels below detection limits for the field XRD/XRF instruments (halite is not detectable with Raman). IC and ICP-OES are highly sensitive techniques that can detect very low levels of ions in solution.

Results: The iRaman instrument proved very useful in identifying different sulfate/carbonate minerals, with each analysis taking 10s of seconds to a few minutes depending on the strength of the Raman bands. The Terra XRD instrument proved invaluable in discriminating between similar minerals (e.g. gypsum and anhydrite) and detecting less abundant minerals, such as carbonates in some samples. The XRF was used to collect geochemical data that will inform alteration models.



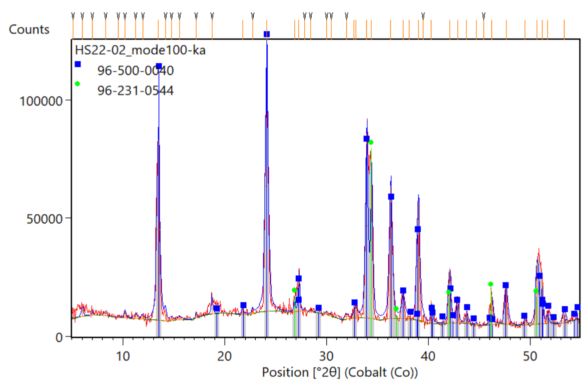


Figure 3 – (top) Raman spectrum of sample HS22-02 (#2 in Table 1) shown with gypsum reference data [4]. (bottom) XRD pattern with gypsum peaks marked in blue squares, calcite with green circles.

Mineralogy/Morphology. We identified 5 different primary types of precipitate morphology in the lava tubes, with some variations within these 5 types. The different types are shown in images below with descriptions and preliminary mineralogy listed in the following table:

Table 1 – Secondary mineral types and mineralogy

#	Description	Mineralogy
1	Flaky coating that covers a large part of cave surfaces	gypsum
2	mushroom-like shape	gypsum + calcite
3	~1 mm thick by ~2-3 mm long spicular material	gypsum + calcite
4	unconsolidated white powder	thenardite
5	cauliflower texture, translucent	thenardite + mirabilite

Interpretation/Relevance to Mars: The relatively young lava tube exhibited a large amount of precipitation of secondary minerals, primarily Ca-sulfates with Na-sulfates concentrated in specific areas. Minor amounts of calcite were also observed. No detectable Cl or F-bearing salts have been detected to date, but laboratory analyses with much higher sensitivity are yet to be conducted. The predominance of Ca-sulfate, similar to what is seen in Gale Crater on Mars, suggests that solubility might be a determining factor, given the low solubility of $CaSO_4$. Future work will determine the presence and potential correlation of Cl and F-bearing minerals.

References: [1] Archer, P. D. Jr., et al (2022) LPS LIII, #2759. [2] Worden R. H. (1996) *Mineralogical Magazine, 60*, 259-274. [3] McAdam, A. C. (2020) LPS LI, #2521. [4] Lafuente B et al (2015) Highlights in Mineralogical Crystallography, https://rruff.info/, gypsum RRUFF ID: R060509.

The primary different precipitate types seen in the lava tube, described in Table 1.