

WEATHERING AND SULFATE FORMATION IN SULFUR SPRINGS ST. LUCIA, A MARS ANALOGUE SITE. B. E. McKeeby, M. S. Gilmore, and J.P. Greenwood, Dept. of Earth and Environmental Sciences, Wesleyan University, 265 Church St., Middletown CT 06438, bmckeeby@wesleyan.edu.

Introduction: The Sulphur Springs region, Soufriere, St. Lucia is a series of collapsed dacitic domes containing phenocrysts of plagioclase, quartz, hornblende, and minor amounts of clay minerals, biotite, and pyrite [3]. Sulphur Springs Park is a collection of acidic geothermal pools fed by meteoric and hydrothermal waters. The park includes several hills containing soft, highly altered material, bubbling pools, mud pots, steam vents, and small springs [4]. Field and laboratory studies in 2004 and 2005 identified jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$, goethite $[\text{FeO}(\text{OH})]$, alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$, gypsum $[\text{CaSO}_4(\text{H}_2\text{O})_2]$, kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ and quartz $[\text{SiO}_2]$ using VNIR, XRD and EDS spectroscopy [4]. Here we expand upon these studies using instrumentation that more closely matches that of the MARS 2020 mission. We seek to better understand the geology of this Mars analogue site and examine any differences between the field instrument and laboratory instrument data and how that may affect geological interpretation.

Methods: Six hand samples collected in 2004 and 2005 were investigated using a combination of scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopic (EDS) mapping, X-ray diffraction (XRD), and μ -Fourier transform infrared spectroscopy (μ FTIR). Samples were placed in epoxy cut in cross section and polished. A JEOL JSM6390LV/LGS SEM with BSE and EDAX Genesis and hyperspectral EDS mapping was used for chemical phase mapping and identification of elemental distribution. Samples were imaged using a Nicolet iN10MX hyperspectral Micro-Imaging FTIR Spectrometer with a spatial scale of $25\mu\text{m}$ and spectral range from 7000 to 715 cm^{-1} . Spectral deconvolution and matching was completed using a combination of ENVI[®] spatial analysis software and the data processing application DAVINCI [5]. Point EDS spectra were collected to relate chemical composition to minerals identified in mid-ir spectra. RAMAN spectroscopy was collected using a Bruker Bravo Handheld Raman spectrometer.

Results and Discussion: We discuss four samples from four environments in the park. Measurements are found in Table 1.

Sample JM18: JM18 was collected at the junction of a dacitic unit underlying a highly altered siliceous unit [4]. Field-collected VNIR spectra show the presence of goethite, hematite, jarosite, and montmorillonite [4]. Raman spectra of the sample also indicate the presence of goethite. At the mm-scale, the sample is layered. FTIR spectroscopy and EDS elemental data

were used together to identify mineralogy of the layers. These data show that the interior layers are composed of aluminosilicates (halloysite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$) and Fe-oxides. The outer edge of JM18 shows layered K-jarosite and aluminum silicates; halloysite and illite $[(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]]$. Pockets of K-jarosite can be seen interfingered with and potentially replacing the Fe-oxides.

The layered mineralogy of JM 18 indicates an initial deposition of aluminosilicates and iron oxides. Goethite formation can occur via weathering of hematite or pyrite, or by oxidation of ferrihydrite [6]. Goethite formation from oxidation of ferrihydrite is favored at a pH 4, while hematite formation is favored at pH 8 [7]. The presence of jarosite, indicating a pH of 1.5-2.5 [8], interfingered with goethite supports the former. The low pH in exterior layers may indicate a low water to rock ratio and formation of evaporite minerals. Precipitation of jarosite may have resulted in a solution rich in aluminum and silica allowing for the continued precipitation of aluminosilicates and sulfate minerals.

Sample ST7A: ST7A was collected near JM-18. VNIR spectra identify jarosite and alunite in this sample. These phases, and gypsum, are also seen in XRD. At the micro-scale, the sample contains large euhedral phenocrysts surrounded by a fine-grained matrix. FTIR measurements of the phenocrysts match opaline silica, which we interpret as weathered quartz grains; EDS confirms the presence of silica and oxygen with trace amounts of aluminum. Infrared spectra of the matrix match that of K-jarosite with a minor alunite contribution; the EDS of the matrix material is rich in K, Fe, Al, Ca and S. BSE images show alunite rhombs rimmed in jarosite. This indicates a change in solution to favor a higher Fe^{3+} activity, higher oxygen fugacity, and lower pH. This may indicate formation of jarosite in the vadose zone where less buffering activity of bedrock is available [9].

Sample GCO: GCO was collected from an area known as Gabriel's Crater, an active mud pot. Alunite and jarosite are seen in VNIR. XRD indicates the presence of kaolinite, K-jarosite, alunite, and quartz. EDS mapping shows a Si-rich center, void of phenocrysts, which FTIR indicates is amorphous or opaline silica. Rimming the sample is a well-defined layer rich in K, Fe, and S, interpreted as K-jarosite based on FTIR, a second layer can be seen exterior to this rich in Al, Fe, Si, S and K.

Opaline silica deposits have been shown to form in acidic hydrothermal systems as a product of leaching,

and deposition, from silicate rich rocks by acid sulfate steam condensate [10]. Acid steam concentrates may precipitate sulfate minerals within these layers.

Sample 20-GC-1: 20GC1 was collected from along a stream bank fed by waters emitting from Gabriel's Crater. Stream banks become inundated during high water events producing evaporite minerals as waters recede [4]. VNIR shows the presence of jarosite, clays, goethite, and alunite. FTIR data show the sample interior is composed of an aluminosilicate, potentially kaolinite, amongst larger quartz phenocrysts. The sample exterior shows alternating jarosite and aluminosilicate layers. The presence of a Na/Fe/S layer we interpret to be natrojarosite $[\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6]$ layer can be observed with EDS mapping but is too fine to be observed spectroscopically. Natrojarosite only forms in solutions limited in K and may occur here as a solid solution with K-jarosite with Na-jarosite precipitating in late stage fluids when K has been previously consumed. The presence of silicates and clay minerals coated in jarosite indicates a drop-in pH due to evaporation or influx of acid K/Na-sulfate rich fluids, or both.

Interpretation: Jarosite formation in these environments indicated the presence of oxidizing sulfate-rich waters with a pH of 1.5-3. While pyrite has been found in drill cores [3], it is not voluminous enough to allow for all the observed sulfate alteration [4]. Therefore, another source of sulfur is required. Jarosite formation may be the result of H_2S degassing in the vadose zone [9]. Organisms or the presence of atmospheric oxygen help to facilitate the oxidation of H_2S to sulfuric acid [11]. Jarosite formation on surfaces and in veins may be derived from hydrothermal waters, meteoric waters or both. However hydrothermal fluids are most commonly the source, due to the production of

waters with higher concentrations of sulfuric acid [11].

Relevance to Mars 2020: This study looked to examine any differences between the field and laboratory instrument data, reflecting on any changes in geological interpretation. VNIR (SUPERCAM), and XRF (PIXL) on Mars 2020 were mimicked using an ASD spectrometer and EDS mapping. μFTIR spectroscopy and XRD analysis can be considered analogous to Raman available on SUPERCAM and SHERLOC. EDS chemical mapping was completed on thin-sections at a comparable spatial scale to PIXL. EDS chemical mapping combined with SEM microscopy revealed finely layered outer edges and alunite rhombs with jarosite coating. Opaline silica was detected by μFTIR spectroscopy, appearing as silica in EDS and QTZ in XRD, and was not detected by other means. Layered aluminosilicate clays, and sulfates were detected throughout indicating a variation in pH. Fine scaled textual information gained through examination by EDS allows for comparison of chemical composition to texture. This is especially important as you consider evidence for potential morphological biosignatures. Biosignature formation and preservation balances on the characteristics of the micro-organism, its environment, and amount of post alteration [13], evidence of which are preserved at fine scales observable by these techniques.

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Sample	XRD (Supercam)	VNIR (Supercam)	UFTIR (Supercam/Sherloc analogue)	EDS (PIXL)	Conclusion
JM18	N/A	Field-Go, Ja, Hem	Ja, Coq, Aln, Go, Il, Hal	Fe,S,K, Al,Si	Field VNIR show Go & Hem. No Hem in FTIR- may be due to spectral range. Microlayers not resolved by other methods.
GCO	Ka, Ja, Aln, Qtz	Ja, Aln	Ja, OpSi, Aln, AlSi	Fe,S,K, Al,Si	No Si seen in VNIR but present in other techniques, AlSi and pure Si detected in all other methods. Detection of OpSi unique to FTIR.
ST7A	Ja, Gyp, Aln	Ja, Aln	Ja, OpSi, AlSi, Aln	Ca,S,K, Fe, Si, Al	Aln rhombs with Ja rims visible in EDS, not in other methods, FTIR identifies silica as opaline. No Si in XRD and VNIR but present in EDS & FTIR.
20GC1	N/A	Field- Ja, Aln, clay, Go, Qtz	Ka, Ja, Qtz, AlSi	Na,K,S, Fe,Al, Si	AlSi seen in All methods. Na phases present in EDS but not resolvable in FTIR or VNIR.

Table 1. Mineralogy and elemental results from study. Field designation represents VNIR data collected from the same unit as the hand sample. Mineral abbreviations: Ja=Jarosite, Gyp=Gypsum, Aln=Alunite, Qtz=Quartz, Go=Goethite, Hem=Hematite, Coq=coquimbite, OpSi=Opaline Silica, AlSi=aluminosilicate, Il=Illite, Hal=Halloysite. Minerals highlighted in red only appear in one spectroscopic technique.