VISIBLE TO NEAR-INFRARED SPECTROSCOPY OF ACID-SULFATE WEATHERING SITE IN NICARAGUAN VOLCANIC SYSTEMS: AN EARLY MARS ANALOG.

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Introduction: Hydrothermal, volcanic acid-sulfate weathering was likely widespread on early Mars. Mineralogy related to this type of weathering identified by the MER rovers at Meridiani Planum and Gusev crater includes Ca-, Mg-, and Fe-sulfates, hematite and goethite, and amorphous silica [1-4]. While the specific formation environment for the Meridiani Planum site is debated (evaporitic vs. volcanic), the Columbia Hills geology in Gusev is generally agreed to be volcanic in origin. This mineralogy was put into a global context with the hyperspectral data from CRISM on MRO and the OMEGA instrument on Mars Express [e.g. 5-7]. The Valles Marineris chasmata and chaos regions contain a number of minerals often found in hydrothermal systems, including gypsum and kieserite, as well as, polyhydrated sulfates [e.g. 5, 7, 9].

To further understand the alteration processes occurring in acid-sulfate hydrothermal systems, we have employed numerous laboratory experiments [14], geochemical modeling, and field campaigns [15, this meeting]. This study focuses on visible and near-infrared spectroscopy collected during our August 2012 field campaign to Nicaragua in an effort to understand the environmental controls on secondary mineral formation in this setting.

Field Sites: We surveyed three young volcanic systems, Cerro Negro (CN), Momotombo (MO), and Telica (TEL), along with the associated San Jacinto Mud Pots (MP), to investigate the utility of hyperspectral data for characterizing acid-sulfate products (Fig. 1). These four locales are part of the subduction-arc volcanic chain in western Nicaragua. Basaltic rock chemistry is similar at each site and characterized by phenocrysts of plagioclase, pyroxene, olivine, and magnetite [10]. The slight variations that do occur are in Al, Ca, and K, which may influence secondary mineralogy. Greater variations exist for the gas chemistries, including a larger range for acid producing gases: H_2S and HCl and minor variations for HF and CO_2 [11].

Methods: Field spectra were collected with the commercially-available TerraSpec4, a high resolution field spectrometer developed by Analytical Spectral Devices, Inc. The instrument measures reflected light in the 0.35-2.50 μm range. The hand probe is put in direct contact with the sample to be measured, thus eliminating atmospheric contributions. Spectra were measured at dozens of sites at each volcano to maximize spatial coverage and a large range of materials. Spectra were imported into the ENVI software package for detailed analysis and mineral identification was based on band matching with the U.S.G.S. mineral library [12] and the sulfate, rock, and oxide CRISM libraries [13].

Figure 1: Images field samples from Cerro Negro (CN) (left) and Momotombo (MO) (right). Spectra in Figure 2.

Results: Alteration mineralogies at the four field sites fall into three classes: sulfates, oxides/hydroxides, and phyllosilicates (Table 1). Hydrated silica is also abundant at all sites, as is elemental sulfur at CN and MO. The minerals were identified using characteristic spectral bands (Figures 1 and 2; Table 1).

Cerro Negro. The major secondary minerals at this site are gypsum ($CaSO_4 \cdot 2H_2O$), hematite (Fe_2O_3), and goethite (FeO(OH)). Less common minerals include hexahydrite ($MgSO_4 \cdot 6H_2O$), jarosite ($KFe_3(OH)_6(SO_4)_2$), and alunite ($KAl_3(SO_4)_2(OH)_6$). Natroalunite, which was detected by SEM/EDS analysis of previous field samples, has a spectra very similar umto alunite, thus the alunite observed may actually be natroalunite. The only example of phyllosilicates present at CN is a kaolinite+smectite mixture found at very limited locations as a crust on rocks. Additional spectra exhibited a broad iron band, but could only be matched to general mineral families, such as ferric oxides and not to a specific mineral. The final sulfate observed at CN shared the 0.43 μm band with jarosite, but lacked similar longer wavelength features. These general ferric oxides and 0.43 μm sulfates occur in trace amounts at CN. Hydrated silica is classified as a major secondary mineral, while sulfur is a minor contributor.

Momotombo. MO shared the highest degree of mineral variability with CN. However, its distribution of mineral abundances is different from CN. The most abundant minerals present are hydrated silica and sulfur. Other minerals occur in much lower abundances.

Gypsum, alunite, hematite, goethite, diaspore (AlO(OH)), and the unknown Fe^{3+} sulfate are all present in minor amounts. Jarosite, pickeringite $(MgAl_2(SO_4)_4 \cdot 22H_2O)$, a general ferric oxide, kaolinite+smectite, and kaolinite occur in trace amounts.

Table 1: Summary table of characteristic spectral bands used in the identified of secondary mineralogy.

Mineral	Characteristic Bands (μm)
Sulfates	
Gypsum	1.4 (triplet), 1.76, 2.2 (doublet)
Hexahydrite	slope at 1.3
Alunite	1.4 (doublet), 1.76, 2.1, 2.3
Jarosite	0.43, 0.7, 1.4, 1.85, 2.2
Pickeringite	0.43, slope at 1.4
unidentified Fe^{3+} sulfate	0.43
Oxides/Hydroxides	
Hematite	0.65 (shoulder), ~0.87
Goethite	0.65 (shoulder), ~0.90
Diaspore	0.75, 0.87
Phyllosilicates	
Kaolinite+Smectite	2.2 (asymmetric)
Kaolinite	2.2 (doublet)
Montmorillonite	2.2 (singlet)
Miscellaneous	
Elemental Sulfur	~0.4 shoulder, flat
Hydrated Silica	1.4, 1.9, ~2.25

Telica. At this site, the mineralogy was the least varied. Alunite, jarosite, and goethite occurred in the greatest number of samples. The unknown Fe^{3+} sulfate and the kaolinite+smectite mixture were also present in minor quantities.

San Jacinto Mud Pots. This area is between CN/MO and TEL in terms of diversity. The only mineral classified in major abundance is goethite. Minor minerals are gypsum, jarosite, hematite, kaolinite+smectite, and montmorillonite. Montmorillonite was only observed here.

Conclusions: While each of the sites studied has representatives from each mineral class (sulfates, oxides/hydroxides, phyllosilicates), they have different diversity within each category. Since basalt composition is similar for all locales, differences can largely be attributed to gas chemistry, temperature, pH, time or sampling bias. Since some of these parameters were not measured during our field campaign or not necessarily at the same location as the spectra sampling, the following are suggested explanations for the trends observed and future work will be needed to investigate these hypotheses.

CN has a large O_2 gas component, which may lead to a higher degree of iron oxidation and formation of iron oxides. CN is also a relatively young volcano resulting in less exposure to atmospheric processes, which would wash away precipitating gypsum. MO volcanic gases contain a greater amount of acid and
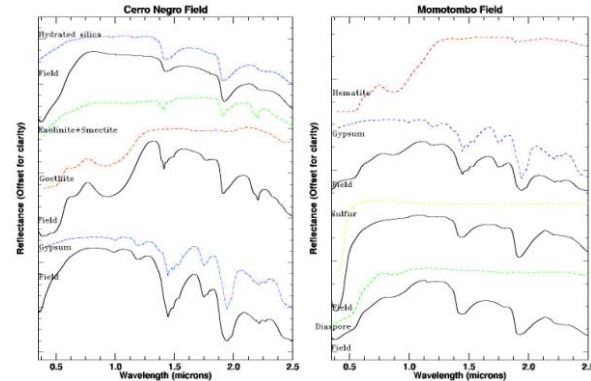

Figure 2: Spectral field examples (solid black), labeled "[site] Field" with library spectra (dashed color) stacked above. Left labels indicate specific library spectra.

sulfur species. Its low pH and concomitant high temperature may account for the dominance of silica deposits. The high sulfur species in gas would contribute to sulfur deposition. Finally MO has also been exposed to precipitation for the longest time due to its age, which would result in removal of alteration minerals. The lack of diversity at TEL may be due to measurements being taken farther away from active vents, lower concentration of H_2S, or the very short time since it erupted in 2011. However, TEL does have the greatest amounts of alunite, which could be related to slightly greater K and Al abundances in the basalt.

The minerals we have observed in the field share mineral classes and specific minerals with those observed and suggested for areas on Mars, many of which are hypothesized to have once hosted hydrothermal systems. Our work suggests that secondary mineralogy is largely controlled by input chemistry, i.e. rock and gas, with secondary controls of duration of weathering, exposure to atmospheric weathering, and environmental parameters, e.g. temperature and pH. However, further systematic sampling at the fieldsites is needed to continue addressing these controls.

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