

CHARACTERIZATION OF HYDROTHERMAL ALTERATION IN COSTA RICA: MINERALOGY, METHODOLOGY, AND IMPLICATIONS FOR MARS. S. R. Black^{1,2}, B. M. Hynek^{1,2}, R. Hoover¹, L. G. Beckerman², and G. E. Alvarado³, ¹Laboratory for Atmospheric and Space Physics & ²Dept. of Geological Sciences, University of Colorado-Boulder, Campus Box 600 UCB, Boulder, CO 80303, ³Instituto Costarricense de Electricidad – ICE, s.black@colorado.edu

Introduction: Many locations on Mars with mineral assemblages consisting of phyllosilicates, sulfates, and hydrated silica have been identified using the Mars Reconnaissance Orbiter’s (MRO) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and the Mars Express’s (MEx) Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) data [1-3]. With our current understanding of hydrothermal alteration and Martian mineralogy, there are some areas on Mars that show putative hydrothermal characteristics, such as Gusev Crater’s Home Plate [4-8], Nili Patera [9], Noctis Labyrinthus [10, 11], and Eastern Coprates Chasma [12].

Proper characterization of mineralogy is an essential part of geologic interpretation. Hydrothermal alteration products often exist in intimate mixtures, and vary widely across a site due to differing pH, temperature, and fluid/gas chemistries. These characteristics require that we develop a detailed understanding regarding the environmental controls on resultant mineral mixtures, and how these various combinations appear in different instrument data sets. Mars rovers carry with them a wide range of analytical tools to aid in the interpretation of Mars’ geologic history. However, many instruments are best suited to detect specific materials, and may miss others. Often, multiple instruments must be utilized to develop a comprehensive understanding of a sample.

If we want to search for signs of ancient life on Mars, one likely target is relict hydrothermal systems. Hydrothermal systems are highly variable on the fine scale, and must be assessed in-situ to provide confident interpretations. Therefore, it is vital that we improve our understanding of alteration processes and products, as well as our interpretative capabilities using instrumentation onboard current and future spacecraft.

Methodology: An initial site survey field campaign for Poás and Turrialba volcanoes (chosen for their compositional similarities to TES surface measurements and Pathfinder APXS data, respectively) was conducted in November 2013. 130 in-situ VNIR samples and 58 hand samples were gathered on Poás and Turrialba volcanoes, focusing on areas with active fumaroles, areas of prior fumarolic activity, and areas in the current acidic steam cloud. Sample collection included all visible mineralogical variations, based on color and texture.

The field-portable VNIR spectrometers utilized in this study are the TerraSpec4 high resolution reflectance spectrometer, and the TerraSpec Halo Gun from Analytical Spectral Devices (ASD), Inc. in Boulder, Colorado. The XRD utilized in this study is the Terra XRD – a field portable analog for the CheMin XRD, developed in 2007. Laboratory Raman analysis will be conducted using the Horiba LabRAM HR Evolution Raman Microscope-Spectrometer via both single point analysis, and DuoScan composition mapping across a field of view. VNIR and XRD data were gathered for each of the returned hand samples and matched to known library samples to determine the mineralogical composition of each specimen. Raman analysis is currently in progress, and will be completed in January 2016.

Results: Instrumentation. As expected, phyllosilicates were more easily identified in VNIR spectra than in XRD patterns due to their often poorly crystalline structure. Conversely, elemental sulfur is easily seen in XRD and Raman spectra due to its crystalline nature and high level of Raman reactivity. The strong sulfur signal may often overpower those of other materials within the same sample.

	Poás	Turrialba
<i>Phyllosilicates</i>		
Kaolinite	Minor	Minor
Montmorillonite	Major	Major
Saponite	Minor	-
Nontronite	Minor	Minor
Smectite/Illite	Minor	Major
Unidentified phyllosilicates	Major	-
<i>Sulfates</i>		
Gypsum/Anhydrite	Major	Major
Alunite/Natroalunite	Major	Major
Fe-rich Alunite/Natroalunite	Major	Major
Jarosite/Natrojarosite	Minor	Major
Hexahydrite	Minor	Minor
Alunogen	Minor	-
<i>Oxides/Hydroxides</i>		
Hematite	Major	Major
Goethite	Minor	Trace
Anatase	Minor	Major
Unidentified Fe-oxides	Minor	Trace
<i>Miscellaneous</i>		
Hydrated silica	Major	Major
Cristobalite	Major	Major
Sulfur	Major	Major

Table 1: Secondary products at Poás and Turrialba, identified through VNIR and XRD. Major: >10%, Minor: 1-10%, Trace: <1% of gathered samples

Mineralogy. A common feature for both sites was the abundance of Al-phyllsilicates and Al-sulfates. Poás has the highest Al enrichment (17.38 wt. %) vs. Turrialba's 16.2 wt % [13] in the parent rocks. The abundance and diversity of Al-bearing alteration products correlates with this trend – both Poás' and Turrialba's spectra indicated numerous detections of alunite, as well as montmorillonite and kaolinite. Similarly, enrichment in Fe in the parent rock appears to correlate to more secondary Fe-oxides/hydroxides in the Poás summit crater. Additionally, both Poás and Turrialba appear to have abundant Fe-rich alunite/natroalunite (appearing in 31% and 19% of sampled spectra, respectively). (table 1; figure 1)

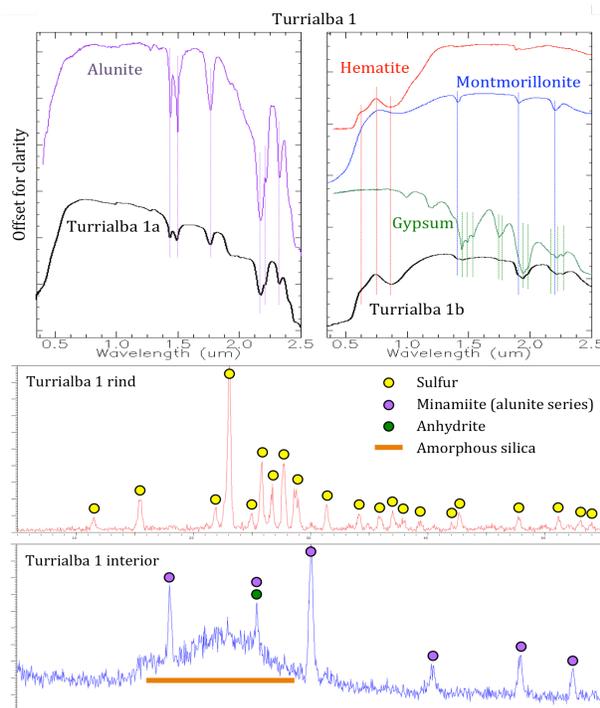


Figure 1: An example of VNIR spectra (top) and XRD patterns (bottom) showing sample "Turrialba 1."

Discussion: Instrumentation. No single method discussed here results in a complete compositional assessment. However, combined analysis via VNIR, XRD, and Raman spectroscopy may result in a fairly complete mineralogical investigation. It is important to note that commonly utilized VNIR spectral libraries such as the USGS and CRISM libraries are missing reference spectra for minerals which regularly appear in both XRD and Raman analysis, such as anatase and cristobalite, and must be supplemented to result in an accurate assessment.

Sulfur's high Raman reactivity poses a problem for comprehensive chemical analysis on sulfur-rich Mars. It is possible to get a quick average composition by combining point analysis at various locations through-

out the sample, and a DuoScan (average) grid analysis to survey a large scene. The combination of these methods gives context as well as detail, and allows for identification of other phases that may be lost in the sulfur signal. DuoScan capability does not appear to be available for the ExoMars or Mars 2020 Raman, but would be beneficial to include in future payloads.

Mineralogy. Alteration mineralogies at Poás and Turrialba continue to support the strong control of parent lithology on secondary mineralogy. Secondary deposits are influenced by the availability of cations in the circulating fluids (due to dissociation of the parent rock) as well as the parent rock itself.

Until Marcucci et al. [14] and McCollom et al. [15] identified naturally occurring Fe-rich natroalunite in Nicaragua, it had only been observed in laboratory settings. However, this appears to be a common alteration product in basalt-hosted hydrothermal systems. The abundance of Fe-rich alunite and natroalunite at these sites suggests there may be abundant Fe-rich alunite/natroalunite in relict hydrothermal systems on Mars.

Identification of jarosite by the Opportunity rover's Mössbauer spectrometer led to interpretations of an extremely low pH environment at some point in the geologic history of Meridiani Planum [16, 17]. However, subsequent work by McCollom et al. [18] showed that jarosite and Fe-rich natroalunite – members of the jarosite-alunite solid solution series – are virtually indistinguishable using Mössbauer spectrometry, and further data, such as VNIR, XRD, and/or Raman, are needed to distinguish between the two. The abundance of Fe-rich alunite/natroalunite in our alteration products suggests that these Mössbauer identifications of jarosite on Mars may not be reliable, and future work should consider Fe-rich alunite/natroalunite as a likely alteration product on Mars.

References: [1] Gendrin et al. (2005) *Science*, 307, 1587-1591; [2] Murchie et al. (2009) *JGR*, 114; [3] Ehlmann et al. (2011) *Clays and Clay Min*, 59, 359-377; [4] Morris et al. (2008) *JGR*, 113; [5] Schmidt et al. (2008) *JGR*, 113; [6] Squyres et al. (2007) *Science*, 316, 738-742; [7] Yen et al. (2008) *JGR*, 113; [8] Ruff, S. W. (2015) *LPSC*, 46; [9] Skok et al. (2010) *Nat. Geosci.*; [10] Thollot et al. (2011) *EPSC-DPS*, 6; [11] Weitz et al. (2011) *Geology*, 39, 899-902; [12] Weitz et al. (2014) *GRL*, 41, 8744-8751; [13] Prosser, J. T. and Carr, M. J. (1987) *JVGR*, 33, 131-146; [14] Marcucci et al. (2013) *JGR: Planets*, 118, 2213-2233; [15] McCollom et al. (2013) *JGR*, 118, 1719-1751; [16] Klingelhöfer et al. (2004) *Science*, 306, 1740-1745; [17] Squyres, S. W. and Knoll, A. H. (2005) *EPSL*, 240, 1-10; [18] McCollom et al. (2014) *Am. Mineralogist*, 99, 948-964.