

SPECTRAL CHARACTERIZATION OF THE SULFATE DEPOSITS AT THE MARS ANALOG SITE OF LA SOLFATARA (ITALY) J. Flahaut¹, J. L. Bishop², I. Daniel¹, S. Silvestro³, D. Tedesco⁴ and C. Quantin¹. LGL, TPE, CNRS/Université Lyon 1, 69622 Villeurbanne Cedex, France (jessica.flahaut@ens-lyon.org). ²SETI Institute/NASA-ARC, Mountain View, CA, 94043. ³INAF- Osservatorio Astronomico di Napoli, Italy. ⁴Second University of Naples, Caserta, Italy.

Introduction: Sulfates were first discovered on the surface of Mars by the spectral imager OMEGA onboard ESA's Mars Express orbiter [1-5]. Sulfates are abundant in the Valles Marineris area, near the northern cap in Utopia Planitia, and locally in the Terra Meridiani plains [1-7]. They have also been observed *in situ* by the two Mars Exploration Rovers in Gusev Crater and Meridiani Planum and the Mars Science Laboratory rover in Gale Crater [8-11].

On Earth, sulfates are produced in a wide range of wet environmental conditions including shallow lakes and deep marine basins, periglacial environments, hydrothermal systems and even acidic rainfalls [12]. On Mars, sulfates are virtually always associated with other minerals including ferric oxides, and are usually found in areas where layered sedimentary deposits have also been observed [e.g., 12-15]. Although this provides strong evidence for the existence of a link between sulfate occurrence, surface water, and climate history on Mars [1], the exact origin of Martian sulfates remains hotly debated [e.g., 3, 7]. For example, sulfate-rich outcrops studied by the Opportunity rover in Meridiani Planum were interpreted as evaporate cementation of pre-existing sediments under the action of a rising water table [8]. Other deposits that lack precise *in situ* analysis, are proposed to originate from the alteration and diagenesis of pre-existing sulfur-bearing rocks [2]. A complicating factor is that the reference spectral libraries used to identify minerals and constrain their composition from remote sensing data are incomplete for sulfates. Not all sulfates have been characterized properly by reflectance spectroscopy, and the effects of matrix minerals and grain size are poorly constrained.

In this study we use field and laboratory morphologic and spectroscopic observations to better constrain the formation processes and mineralogic assemblages of several Mars analog sulfate-rich deposits at la Solfatara, Italy.

Geological context: The Solfatara Crater is a volcanic crater located at the center of the Phlegrean fields caldera, a quaternary volcanic complex located north of the city of Naples, in the town of Pozzuoli, Italy. Volcanic activity in the phlegrean fields is expressed through fumarole emissions that are most active within the Solfatara crater, thermal pools, and seismic activity. Recent studies suggested that bradyseismic events in the Pozzuoli areas could be related to the injection of

magmatic waters in the Solfatara hydrothermal system, resulting in a dual origin for the fumarolic fluids in the craters [16]. Underground temperatures between 200 and 300°C were estimated for the fumarole hot water using geochemical modeling [e.g., 17-18]. Gas emissions include H₂S as a minor specie, supporting the hypothesis that this gas is a precursor of sulfate minerals via oxidation to H₂SO₄, acidic interaction with rocks and crystallization of salts [19]. Sulfate mineral paragenesis previously reported include Al/K sulfates (alunite, mercurite, voltaite), Ca-sulfates (gypsum and anhydrite), ammonium sulfates, ferric sulfates (metavoltine, jarosite) and native sulfur [19,20].



Figure 1: Location of the sampling sites with the Solfatara Crater (DigitalGlobe image).

Field sampling: A field campaign was carried out in September 2015 with the support of the Solfatara site manager and the ENS Lyon Raman team. VNIR and Raman spectra were collected with portable instruments over a total of 7 sites/vents within the crater (Figure 1). VNIR reflectance spectra were collected between 0.35 and 2.5 microns with an ASDinc Field-spec 4. Raman spectra were collected between 100 cm⁻¹ and 4000 cm⁻¹ with a Entspectr RaPort instrument, using a 532 nm green laser. Based on the field observations, a total of about 20 samples were collected to be further characterized in the laboratory.

Mineralogy from VNIR spectroscopy: Local bedrock at Solfatara is comprised of incoherent ignimbrites, often with trachyte occurrences, as exposed in

the crater walls (e.g., at site L3). The bedrock material typically exhibits no spectral signature in the VNIR other than weak hydration bands in some cases. The rather symmetric shape of the 1.9 μm band coupled with the absence of specific Raman signatures suggest the presence of an hydrated amorphous sulfate. Yellow-orange-red surficial coatings on the wall rocks at sites L2 and L6 show additional absorptions at 1.76, 2.16, 2.31 μm (yellow), 1.84, 2.27 μm (orange), sometimes coupled with a broad 0.86 μm absorption (red). These observations were interpreted as mixtures of goldichite, jarosite and hematite (Figure 2). An additional hydrated component is likely present because the H₂O bands in goldichite and hydronium jarosite do not match well with the rounded bands observed for rocks R4 and R5.

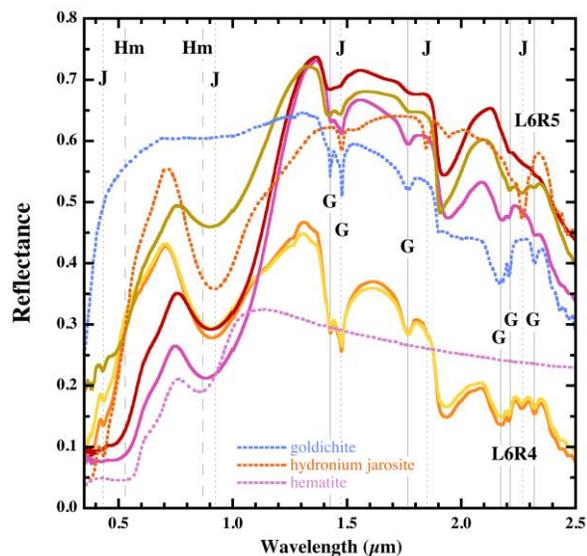


Figure 2: VNIR reflectance spectra taken in the field of rocks R4 and R5 from site L6 compared to lab spectra of minerals.

In a nearby 90°C vent, native sulfur needles grow on a fibrous, massive water-saturated white deposit (R12, 16), possibly an amorphous hydrated sulfate. A white, more powdery material (R13) is surrounding the vent and shows disagnostic absorptions at 1.76 and 1.98 μm , possibly indicative of carnelite or coquimbite. Other iron sulfates are detected in orange-toned deposits (R15, 17, 19).

At site L4 (Bocca Grande), the vent temperature reaches 160°C and arsenic and mercury sulfides are deposited on the rocks located directly above the vent. Realgar (AsS), Cinnabar (HgS) and Orpiment (As₂S₃) can be recognized thanks to their respective burgundy, red and yellow tones; however, these minerals do not exhibit NIR spectral features. They do exhibit progressive shifts in the visible region absorption correspond-

ing to their colors. The strong NIR OH and H₂O bands are characteristic of silica sinter from hot springs (e.g. Octopus Springs, Yellowstone). The presence of additional H₂O bands near 2.03 and 2.16 μm and the lack of Raman features are consistent with the presence of amorphous As₂S₃, and hydrated amorphous FeAs species, which have been observed in other high temperature As-bearing hydrothermal systems [21].

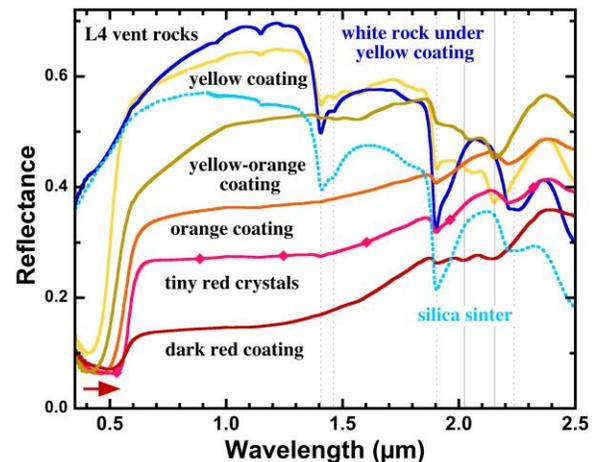


Figure 3: VNIR field spectra of Bocca Grande rocks compared to lab spectra of hot springs sinter.

Discussion and future work: A variety of hydrated minerals, especially sulfates, are observed in the field, as shown by morphological and mineralogical observations derived from VNIR spectroscopy. Different assemblages are observed around the low temperature (L1-L7) pools, the intermediate temperature (L2, L5, L6) and the high temperature (L4) vents. Given the amorphous nature of the bedrock and most of the alteration minerals derived from it, the majority of the Raman analyses made in the field were inconclusive. Ongoing analyses to be performed in the laboratory and presented at the conference include microscopic observations, diffractometry and chemical analyses on selected samples.

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