

HYDROTHERMAL ALTERATION ON MARS COMPARED TO THE ITALIAN SOLFATARA.

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Introduction: Hydrothermal environments have long been assumed for Mars based on orbital observations, terrestrial analogs, and Martian meteorites [e.g., 1 and references therein]. Alteration by hydrothermal circulation in the cooling crust and impact-generated hydrothermal alteration have both been proposed as a plausible formation mechanism for ‘deep’ phyllosilicates on Mars [e.g., 2, 3, 4]. Hydrothermalism is also invoked as a likely source for alteration in localized environment, such as the clays, sulfates and silica-rich deposits identified in Noctis Labyrinthus pits [5] or serpentine and Mg-carbonate detections in Nili Fossae [6]. However, the first definitive evidence for volcanic hydrothermalism on Mars is the *in situ* detection of amorphous silica-rich outcrops (>90% wt opal-A) by the Mars Exploration Rover (MER) Spirit Miniature Thermal Emission Spectrometer (Mini-TES) instrument [7]. These detections were originally compared to observations made at Hawaiian fumarolic sites where silica is produced by acid sulfate leaching [7]. An alternative suggestion was made that the Gusev Home Plate silica could originate from the direct precipitation of silica as observed in hot springs environments [1]. As pointed out in a recent study of terrestrial analogs in the Atacama desert [8], hydrothermal environments may have created suitable environments for life and should be a prime target in the search for biosignatures on Mars. The objective of this study is to characterize the fumarolic environments at the Solfatara Mars analog site (Phlegrean Fields, Italy) and discuss the possibilities and limits of identifying them on Mars.

Geologic setting: The Solfatara volcano is the most active site of the Phlegrean fields caldera. This 4000 year old volcanic crater is located in the Campanian region of Italy, only a few kilometers west of the city of Naples. Current volcanic activity is expressed at the surface through fumarole emissions, thermal pools, and seismic activity [e.g., 9]. Underground water temperatures between 200 and 300°C were estimated for the fumarole dual source using geochemical and thermodynamic modeling [e.g., 10-11]. Gas emissions include H₂O and CO₂ with H₂S as a minor species, supporting the hypothesis that this gas is a precursor of sulfate minerals via oxidation to H₂SO₄, acidic interaction with rocks and crystallization of salts [12]. Alteration at and around the pools (mudpots) and fumaroles was studied with portable instruments (VNIR and Raman

spectrometers) at 7 sites/vents within the crater during a field campaign in September, 2015 [13] (Fig. 1A). Samples were collected for further characterisation by XRD and chemical analyses.

Field and laboratory observations:

Bedrock composition and alteration. Local bedrock at Solfatara is comprised of incoherent ignimbrites as exposed in the crater walls (e.g., at site L3), originating from the latest (third), subaerial, Campanian eruptive period. Previous authors suggested a trachytic composition, which is consistent with our XRD analyses of samples L6R3 and L6R5 (>85% of the alkali feldspar sanidine + X-ray amorphous material). Some ash layers, however, contain mostly amorphous material (>90%) with minor amounts of anatase (TiO₂) and calcite (CaCO₃). No native sulfur was detected in the bedrock samples by XRD. The bedrock material typically exhibits no Raman or VNIR spectral signature, except for weak hydration bands in some cases. The rather symmetric shape of the 1.9 μm band, coupled with the absence of specific Raman signatures, suggests the presence of an hydrated amorphous sulfate. Ongoing chemical analyses will allow us to confirm this assumption.

Locally, the crater walls are covered by yellow to orange coatings, which suggest alteration by fumarolic gases as they reached the surface and condensed over the porous ignimbrites. VNIR spectra are consistent with alunite KAl₃(SO₄)₂(OH)₆, goldichite KFe³⁺(SO₄)₂·4H₂O, jarosite KFe₃³⁺(SO₄)₂(OH)₆ and hematite Fe₂O₃, although XRD analyses do not allow us to detect the hematite but minor quantities of jarosite, alunite, alunogen Al₂(SO₄)₃(H₂O)₁₂·5H₂O and carminite Mg₇(SO₄)₅(OH)₄·H₂O.

Condensation and sublimation at high temperature vents. Highly crystalline (>85%) material of various colors (white, yellow, orange and brown) and textures (fibers, needles, bubbles...) were collected from within a 90°C vent at site L6 (Fig. 1C). VNIR analyses reveal the presence of hydrated material likely mixed with Al and Fe-rich sulfates (various absorptions between 0.86-0.93 and 2.18-2.32 μm are observed). Samples R13 and R18 are consistent with carnelite or coquimbite. XRD analyses reveal the presence of a variety of Al, K and Fe-sulfates (mostly alunogen, K-alum KAl(SO₄)₂·12H₂O, alunite, mercurite KHSO₄,

goldichite, jarosite, coquimbite $\text{Fe}_2^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, plus traces of yavapaiite $\text{KFe}(\text{SO}_4)_2$, millosevichite $\text{Al}_2(\text{SO}_4)_3$, tamarugite $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, mixed with minor Fe-oxides (e.g., ferrihydrite). Unfortunately some of these minerals do not have matches in the existing VNIR spectral libraries. These minerals are deposited in and around the vent within ~1 m. These observations suggest that our samples correspond to fumarolic incrustations and/or sublimated minerals; the former produced by gas condensed and then cooled, while the latter formed directly through vapour deposition processes [14-15].

A distinct variety of minerals were observed at a higher temperature vent at site L4 (gas emissions at 160 C, Fig. 1D). Realgar (AsS), Cinnabar (HgS) and Orpiment (As_2S_3) can be recognized thanks to their respective burgundy, red and yellow colours; however, these minerals do not exhibit NIR spectral features. Strong NIR OH and H_2O bands characteristic of silica sinters from hot springs were observed, as well as bands near 2.03 and 2.16 μm which may indicate the presence of amorphous As_2S_3 , and hydrated amorphous FeAs species [16-17].

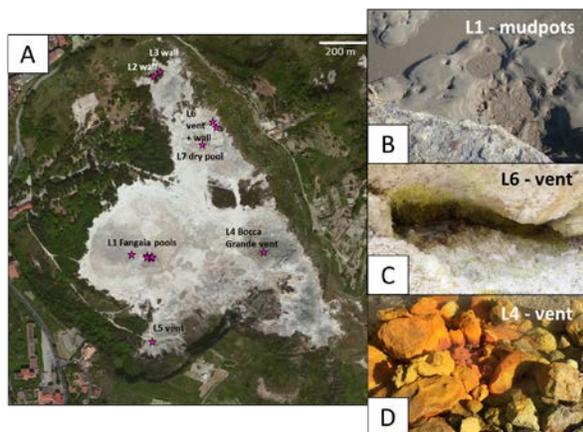


Figure 1: Distribution of sampling sites within the crater (A) and selected views of field sites (B,C,D).

Leaching and/or precipitation at low temperature mudpots. CO_2 bubbles are constantly emitted from low temperature mud pools ($T = 33^\circ\text{C}$, $\text{pH} = 1.5$) at the center of the crater (Fig. 1A, 1B). The pool ramparts are covered in silica coatings whereas polygonal terrains with yellow surficial coatings characterize the dry surroundings. With the exception of one spectrum from the yellow coatings (additional 2.2 doublet consistent with jarosite or gypsum), all NIR spectra exhibit only broad hydration features. XRD analyses reveal that the pool material is comprised of ~50% amorphous material, 25 to 40 % native sulfur, and alunite. The surrounding rocks contain less amorphous material, and the yellow deposits of sample L1R2 are composed of

alunogen + pickeringite ($\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$) mostly, and minor K-alum and alunite. No clay is detected despite carrying out a specific XRD protocol with oriented preparation. This suggests that the muddy, gray material is consistent with amorphous silica. Alunite dominance in samples R3 and R4 could result from the hydrolysis of K-alum in a low pH, wet environment and explain the absence of kaolinite [12].

Relevance to Mars: A variety of hydrated sulfates have been detected at both the Solfatara (this study) and on Mars [e.g., 18], although in the latter case their context is poorly characterized. At the Solfatara site, most sulfates are Al, K, and Fe- rich in accordance with the original bedrock composition, but the Martian crust is expected to be basaltic rather than trachytic. VNIR and XRD analyses are generally in accordance, but VNIR surveys can be swayed by coatings (e.g., hematite at site L6), although they are efficient at characterizing amorphous components, that are difficult to detect with XRD. Additional chemical analyses will help us fully characterize the whole rock composition. A significant proportion of amorphous material might be present on Mars, including hydrated materials such as opaline silica and sulfates, both of which are detected at the Solfatara sites. The CheMin XRD experiment on the Mars Science Laboratory Rover Curiosity reveals the presence of significant amounts of amorphous material in Gale Crater [20], which are not well understood and could represent either primary or secondary phases. Terrestrial analog work as well as combined efforts in comparing multiple techniques [e.g., 16,19] should help address this question in the next years.

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