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2 **The Italian Solfatara as an analog for Mars fumarolic alteration**

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18  
19 **Keywords**

20 Mars analog, hydrothermalism, vents, fumaroles, alteration patterns, Solfatara, VNIR

21 spectroscopy, Raman spectroscopy, XRD

22  
23 **Abstract**

24 The first definitive evidence for continental vents on Mars is the *in situ* detection of amorphous  
25 silica-rich outcrops by the Mars Exploration Rover Spirit. These outcrops have been tentatively  
26 interpreted as the result of either acid sulfate leaching in fumarolic environments or direct  
27 precipitation from hot springs. Such environments represent prime targets for upcoming  
28 astrobiology missions, but remain difficult to identify with certainty, especially from orbit. In  
29 order to contribute to the identification of fumaroles and hot spring deposits on Mars, we  
30 surveyed their characteristics at the analog site of the Solfatara volcanic crater in central Italy.  
31 Several techniques of mineral identification (VNIR spectroscopy, Raman spectroscopy, XRD)  
32 were used both in the field, and in the laboratory on selected samples. The faulted crater walls  
33 showed evidence of acid leaching and alteration into the advanced argillic-alunitic facies, with  
34 colorful deposits containing alunite, jarosite and/or hematite. Sublimates containing a variety of  
35 Al and Fe hydroxyl-sulfates were observed around the active fumarole vents at 90°C. One vent at  
36 160°C was characterized by different sublimates enriched in As and Hb sulfide species.  
37 Amorphous silica and alunite assemblages that are diagnostic of silicic alteration were also  
38 observed at the Fangaia mud pots inside the crater. A wide range of minerals was identified at the  
39 665 m diameter Solfatara crater that is diagnostic of acid-steam heated alteration of a trachytic,  
40 porous bedrock. Importantly, this mineral diversity was captured at each site investigated with at  
41 least one of the techniques used, which lends confidence for the recognition of similar  
42 environments with the next generation Mars rovers.

43

44

## **Introduction**

45 Hydrothermal systems have often been proposed as a possible cradle for early life (e.g., Shock,  
46 1996; Nisbet and Sleep, 2001) and therefore represent a prime astrobiology target. Hydrothermal  
47 environments have long been presumed to exist on Mars based on orbital observations, terrestrial

48 analogs, and martian meteorites (e.g., Farmer et al., 1996; Ruff et al., 2011; Carr and Head,  
49 2010). Evidence for warm and wet environments include the orbital detections by recent VNIR  
50 spectral-imagers of a wide range of hydrated minerals (Bibring et al., 2006; Murchie et al., 2009,  
51 Carter et al., 2013). In particular, the detection of chlorite, prehnite, epidote, serpentine and  
52 carbonates evidences aqueous alteration of Mars basaltic crust at high temperatures (e.g.,  
53 Murchie et al., 2009; Ehlmann et al., 2009; Carter et al., 2013). Alteration by hydrothermal  
54 circulation in the cooling crust and impact-generated hydrothermal alteration have both been  
55 proposed as a plausible formation mechanism (e.g., Abramov and Kring, 2005; Carter et al.,  
56 2010, 2013; Ehlmann et al., 2009, 2011; Carr and Head, 2010). Hydrothermalism is also invoked  
57 as a likely source for alteration in localized surface environments (fumarolic fields or hot  
58 springs), leading to the formation of the clays, sulfates and silica-rich deposits identified in Valles  
59 Marineris Chasma (Milliken et al., 2008; Thollot et al., 2012), the silica detections in the Nili  
60 Patera caldera (Skok et al., 2010) or the serpentine and Mg-carbonate detections in Nili Fossae  
61 (Viviano et al., 2013). However, the first definitive evidence for volcanic hydrothermal activity  
62 (continental vents) on Mars is the *in situ* detection of amorphous silica-rich outcrops (>90% wt  
63 opal-A) by the Mars Exploration Rover (MER) Spirit Miniature Thermal Emission Spectrometer  
64 (Mini-TES) instrument (Squyres et al., 2008). The detection of abundant opaline silica at Home  
65 Plate, combined with high Ti content in local soils, was interpreted as an evidence for the  
66 dissolution of basaltic soils by low pH fluids (Squyres et al., 2008). Iron and phosphate-rich soils  
67 detected nearby, at Paso Robles, were also interpreted as acid-sulfate alteration products in a  
68 hydrothermal (possibly fumarolic) environment of primary phosphate-rich materials (Hausrath et  
69 al., 2013). The nodular aspect of the Home Plate outcrops led to an alternative suggestion that the  
70 Gusev silica could originate from the direct precipitation of sinters as observed in terrestrial hot  
71 springs (Ruff et al., 2011, 2014; Ruff and Farmer, 2016). The objective of this study is to

72 characterize in detail the fumarolic environments (and alteration patterns) at the Solfatara as a  
73 Mars analog site (Campi Flegrei, Italy), and discuss the possibilities and limits of identifying  
74 them on Mars. This specific analog site is used to show how trachytic rocks at the volcanic crater  
75 were hydrothermally altered into sulfate and silica-rich assemblages. Nevertheless, a variety of  
76 alteration assemblages can be produced via fumarolic alteration depending on several factors  
77 (e.g., composition of the bedrock, composition of the fluids). Therefore, the Solfatara site may be  
78 analogous to a some martian hydrothermal environments, which are likely to be more diverse.

79

80

### **Geologic setting**

81 The Solfatara volcano is the most active site of the Campi Flegrei (CF) caldera, a quaternary  
82 volcanic complex located north of the city of Naples, in the Campanian plain graben (Figure 1).

83 Straddling between the Tyrrhenian Sea to the west and the Apennines to the east, the Campanian  
84 plain is thought to originate from the stretching and thinning of the continental crust in an

85 extensional back-arc context. The Campanian plain region is characterized by a general tensional  
86 NE-SW and NW-SE tectonic regime, and upwards migrations of magma that resulted in large

87 ignimbrite eruptions starting from 290,000 years ago (e.g., Torrente et al., 2010). The largest of  
88 the Campanian plain volcano, Campi Flegrei (CF), is a 12km wide, partly submerged depression,

89 inherited from two major collapses during the Campanian Ignimbrite eruption 37,000 years ago  
90 and the Neapolitan Yellow Tuff eruption 12,000 years ago (e.g., Rosi et al., 1983; Piochi et al.,

91 2014 and references therein). The area was later affected by numerous large explosive eruptions  
92 that resulted in the formation of more than 20 craters including the 665 m wide, 4200 year old

93 Solfatara volcanic crater (e.g., Armienti et al., 1983; Rosi and Sbrana, 1987; Di Vito et al., 1999;  
94 Pappalardo et al., 2002; Piochi et al., 2014; Isaia et al., 2015). The CF volcanic complex of

95 potassic alkaline affinity is filled with km-thick pyroclastic deposits, overlapping Miocene flysch

96 facies terrains and Triassic-Paleocene carbonatic outcrops (e.g., Cameli et al., 1975). Previous  
97 analyses at the CF Solfatara reported the presence of incoherent products and ignimbrites of  
98 trachyte to trachyandesite composition, in addition to localized alteration (e.g., Rosi et al., 1983).  
99 Current volcanic activity in the CF is expressed through fumarole emissions, thermal pools and  
100 passive soil degassing that are most active within the Solfatara crater. According to geophysical  
101 measurements, the CF area is underlain by a magma reservoir located at 5 km depth and a Moho  
102 interface at 7 - 25 km depth (Ferrucci et al., 1989; Brandmayr et al., 2010). Combined with recent  
103 eruptive activity, this shallow mantle occurrence results in a local high heat flux of up to 200  
104  $\text{mW}\cdot\text{m}^{-2}$  (Piochi et al., 2014, and references therein). Shallow intrusions and degassing of magma  
105 drive unrest at the Phlegraean fields, and bradyseismic events are frequent in the Pozzuoli area,  
106 where the Solfatara crater is located (Tedesco, 1994; Caliro et al., 2007; Piochi et al., 2014).  
107 Currently the Solfatara area is one of the most active fumarolic manifestations worldwide, with a  
108 diffuse degassing  $\text{CO}_2$  rate  $> 1500 \text{ ton}\cdot\text{day}^{-1}$  (Caliro et al., 2007, 2014 and reference therein). Gas  
109 emissions at the Solfatara include  $\text{H}_2\text{O}$  and  $\text{CO}_2$  with  $\text{H}_2\text{S}$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ , He, Ar, and CO as a  
110 minor species (e.g., Chiodini et al., 2001; Caliro et al., 2007). Fumaroles are distributed along the  
111 crater NE and SE faulted rims, whereas mud pots occupy its central region (Figure 1). Stable  
112 isotope analyses of the water suggested that the Solfatara fumarolic discharge results from a  
113 mixture of  $\text{CO}_2$ -rich fluids degassed from a magma body and the vapor generated at  $360^\circ\text{C}$  from  
114 hydrothermal fluids (Caliro et al., 2007). Underground temperatures between 200 and  $300^\circ\text{C}$   
115 were estimated from the mixed rising plume, using geochemical modeling (e.g., Tedesco and  
116 Sabroux, 1987, Tedesco et al., 1988). Furthermore, S isotopic compositions of  $\text{H}_2\text{S}$  from  
117 fumaroles argue for a typical magmatic origin (Allard et al., 1991), while epithermal minerals  
118 support the formation of sulfur species by acidic interaction of  $\text{H}_2\text{S}$  with the host rock via

119 oxidation to H<sub>2</sub>SO<sub>4</sub>, in a steam-heated environment (e.g., Valentino et al., 1999; Piochi et al.,  
120 2015).

121

## 122 **Sample collection and analyses**

123 Alteration patterns at and around the mud pots (locally named Fangaia) and fumaroles were  
124 studied with portable Visible Near InfraRed (VNIR) and Raman spectrometers at 7 sites within  
125 the crater during a field campaign in September, 2015 (Figure 1c). Rock samples were collected  
126 for laboratory characterization by X-Ray Diffraction (XRD) and chemical analyses (Tables 1-4;  
127 Figures 1c and 2; Flahaut et al., 2017a).

128 VNIR reflectance spectra were measured onsite with an Analytical Spectral Devices (ASDinc)  
129 field spectrometer. The ASDinc Fieldspec 4 Hi-Res instrument collects spectra in the 350 – 2500  
130 nm domain (equivalent to 28000 – 4000 cm<sup>-1</sup>) with a spectral resolution of 3 to 8 nm. All spectra  
131 were acquired in the field with the contact probe (to limit the atmospheric contribution),  
132 converted from radiance to reflectance using the ASDinc software and compared with the VNIR  
133 spectra of reference minerals from the Bishop spectral library, as well as external sources such as  
134 the USGS, RELAB, JPL and CRISM spectral libraries (e.g., Clark et al., 2007; Murchie et al.,  
135 2007; Kokaly et al., 2017).

136 Raman spectra were also measured onsite with a portable Raport instrument from the LGL-TPE  
137 (Lyon, France). Using a 532 nm - 30 mW laser source, the instrument has a sampling resolution  
138 of 4-6 cm<sup>-1</sup> between 100 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>. However, given the large amount of amorphous  
139 material within the crater, few diagnostic signatures were observed *in situ*. Additional Raman  
140 spectra were collected on specific samples or grains at the LGL-TPE laboratory using an Xplora  
141 Raman instrument coupled to an Olympus BX41 microscope and a at 532 nm laser source.

142 Spectra were compared with the reference Raman spectra of minerals in the RUFF libraries and  
143 WURM database (Downs and Hall-Wallace, 2003; Caracas et al., 2011).

144 Semi-quantitative X-Ray diffraction was performed using a Bruker D8 Advance diffractometer  
145 equipped with a Cu X-ray source at the Centre de Diffractométrie of the University Lyon 1,  
146 France. Samples were dried at 70°C for 48 hours, ground in an agate mortar, and dry sieved to  
147 <100 µm prior to measurement. A possible caveat of this preparation in the laboratory is that the  
148 phases detected are those observed in ambient laboratory conditions and may not reflect the  
149 hydration/structural state of these phases *in situ*. Random powder measurements were made over  
150 a 2-theta range of 3° to 70°. Oriented measurements were also performed on selected samples to  
151 enhance the signal originating from the (001) plane of potential clays, but none were detected.  
152 XRD patterns were analyzed and interpreted using the Bruker DIFFRAC. SUITE EVA software,  
153 and the fits were performed by comparing the d-spacing values to those in minerals of the  
154 International Center for Diffraction Data database and the Crystallography Open Database  
155 (Kabekkodu et al., 2002; Grazulis et al., 2009). The identity and relative mineral abundances  
156 were derived from the analyses, using corundum as an external standard. Mineral abundances are  
157 expressed as weight percent (wt. %) of mineral species with ~ 5 % accuracy. The degree of  
158 crystallinity, DOC, is also calculated from the total areas under the defined crystalline and  
159 amorphous components (Table 3).

160 In addition, major element analyses by ICP-OES, selected trace element analyses by ICP-MS,  
161 and S analyses were subcontracted for a selection of rock powder samples (amorphous material  
162 of the mud pots and fresher samples from crater walls) at the SARM facility in Nancy, France  
163 (Tables 2 and 4).

164

165



## Results

166

167 **Nature of the bedrock in the crater walls**

168 The local bedrock at Solfatara is comprised of incoherent ignimbrites (pyroclastic fallout,  
169 pyroclastic density currents, coarse to fine ash beds) as exposed in the crater walls (e.g., at site  
170 L3, Figure 2d), originating from the third and latest subaerial Campanian eruptive period ~ 4500  
171 years ago (Isaia et al., 2015). With a Si content > 80 wt% and total alkali content of ~0.2-0.3 wt%  
172 (Table 2), samples L5R4, L3R1 and L6R1 from the relatively unaltered crater walls plot well in  
173 the field of rhyolite in a TAS (Total Alkali vs Silica) diagram. However, it is difficult to find  
174 pristine bedrock samples; high Si and Ti concentrations and elevated chemical index of alteration  
175 (CIA) indices in these apparently “fresh” ignimbrites suggest that they have been exposed to  
176 several episodes of leaching (Table 2). From a mineralogical point of view, all of samples L5R4,  
177 L3R1 and L6R1 have a more porous / ashy texture, and are mostly dominated by amorphous Si-  
178 rich material (> 90 wt%) with minor amounts of anatase (TiO<sub>2</sub>) and calcite (CaCO<sub>3</sub>) (Table 3).  
179 More rocky wall samples such as L6R3 and L6R5 are composed of > 85 wt% of the alkali  
180 feldspar sanidine (KAlSi<sub>3</sub>O<sub>8</sub>) and correspond to trachytic compositions. Native sulfur was not  
181 detected in the bedrock samples by XRD, but bulk chemical analyses reveal S contents between  
182 0.3 and 1.4 wt%.

183 The bedrock material does not show specific Raman or VNIR spectral signature; weak hydration  
184 bands are observed in some outcrops (Figure 3a, black spectrum; Flahaut et al., 2017a). The  
185 rather symmetric shape of the 1.9 μm band, coupled with the lack of specific Raman signatures,  
186 suggests the presence of a hydrated amorphous sulfate, although hydrated silica could also be a  
187 possible interpretation (Figure 3a). The rounded spectral features near 1.42, 1.91, and 2.23 μm

188 observed for sample L6R1 are strikingly similar to those in opal spectra (C1JB874, McKeown et  
189 al., 2011).

190 Yellow to orange coatings cover the walls locally, which suggests that alteration by sulfur-rich  
191 fumarolic gases occurred as they reached the surface and condensed over the porous ignimbrites  
192 (sites L2, L3, L6; Figure 2c, d, h, k). Limited outcrops also show dark red (e.g., L6R5, L6R10),  
193 grey or turquoise-green colors (e.g., L5R4, L6R6) (Flahaut et al., 2017a). Colorful coatings were  
194 abundant along the NE and SE faulted crater walls, where the fluid circulation might be more  
195 intense. The paucity of vegetation within the crater defines an area of diffuse degassing much  
196 larger than the fumarolic vents and faulted areas. At site L6, a whitish zone delineates a valley  
197 cutting the crater rim and the weathered colored wall, suggesting recent erosion and dissolution  
198 by rainfall and surficial water runoff (Figure 2k). As sites L2 and L3 are similar to L6 but with a  
199 limited extent and a greater vegetation cover, samples from these sites were not analyzed by  
200 XRD and ICP-OES.

201 VNIR spectra of samples from sites L2, L3, L6R1 to R10 are consistent with alunite  
202  $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ , jarosite  $\text{KFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$  and hematite  $\text{Fe}_2\text{O}_3$  (Figure 3a). Alunite is  
203 identified by features near 1.48, 1.76, and 2.16, 2.31  $\mu\text{m}$  and jarosite by features near 0.92, 1.47,  
204 1.85, and 2.26  $\mu\text{m}$  (Bishop and Murad, 2005). The VNIR spectrum of hematite includes a  
205 shoulder near 0.65 and a band near 0.85-0.88  $\mu\text{m}$  that both vary in shape with grain size, but no  
206 bands due to  $\text{H}_2\text{O}$  or  $\text{OH}$  (e.g. Morris et al., 1985, Morris and Lauer, 1990; Bishop and Murad,  
207 2002). XRD analyses detect minor amount of jarosite, alunite, goldichite  $\text{KFe}^{3+}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  
208 alunogen  $\text{Al}_2(\text{SO}_4)_3(\text{H}_2\text{O})_{12} \cdot 5\text{H}_2\text{O}$  and carminite  $\text{Mg}_7(\text{SO}_4)_5(\text{OH})_4 \cdot \text{H}_2\text{O}$  (Figure 3), but no  
209 hematite. This may indicate that the hematite observed by VNIR spectroscopy is poorly

210 crystalline. Raman spectra are consistent with the presence of sanidine remnants, anatase, alunite,  
211 jarosite and amorphous material (Figure 4a).

212

### 213 **Sediments from the mud pots**

214 CO<sub>2</sub> bubbles are continuously released from low temperature mud pools, or mud pots, located at  
215 the center of the crater (Site L1, fig. 1c, fig 2a,b). All three bubbling mud pots have a similar pH  
216 of ~1.5 and temperature of ~33°C (Flahaut et al., 2017a).

217 The shallow pools are filled with greyish, muddy deposits (L1R4). XRD analyses reveal the  
218 presence of ca. 50 % amorphous material consistent with opaline silica in agreement with the  
219 shape and position of the amorphous hump, and with the chemical analyses. Other components  
220 include ~ 25 wt% native sulfur and ~ 25 wt% alunite. Major element analyses confirmed the  
221 presence of a high abundance of volatile elements including sulfur (Table 4).

222 The pool ramparts are covered with silica coatings (L1R3Z1), whereas the muddy soil around the  
223 pool forms polygonal terrains during the dry season (L1R1), sometimes covered with a yellow  
224 coating (L1R2). XRD analyses show that the surrounding rocks contain less amorphous material  
225 than the pool material, and that the yellow deposits of sample L1R2 are primarily composed of  
226 alunogen + pickeringite ( $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ), with minor K-alum and alunite. Clay minerals  
227 were not detected in the XRD patterns. All VNIR spectra are dominated by broad hydration  
228 features, consistent with amorphous silica (Figure 3b). The spectral bands are broadened to 1.41-  
229 1.48 and 2.16-2.21  $\mu\text{m}$  and weak bands are present near 1.76 and 2.31  $\mu\text{m}$ , all of which are  
230 consistent with a minor content of alunite. Raman spectra are consistent with the presence of  
231 native sulfur, sulfates and opal-A (broad bands at 310 and 780  $\text{cm}^{-1}$ ) (Figure 4b).

232

### 233 **Deposits from the fumarolic vents**

234 Material of various colors (white, yellow, orange and brown) and textures (fibers, needles,  
235 bubbles...) with high crystalline contents (> 85% of the total phases) were collected from within  
236 the vents at sites L5 and L6 at 90 °C (Fig. 2g, j; Flahaut et al., 2017a). VNIR analyses reveal the  
237 presence of hydrated materials, likely including Al and Fe-rich sulfates (multiple absorptions  
238 between 0.86-0.93 and 2.18-2.32  $\mu\text{m}$  are observed; Figure 3c). Most spectra contain a strong  
239 water absorption feature that dominates the spectra at wavelengths > 1.8  $\mu\text{m}$ , which may indicate  
240 the presence of highly hydrated sulfates such as alunogen or K-alum. However, no unique  
241 spectral matches could be found in the reference libraries. This is likely also because of the  
242 sensitivity of such hydrated phases to environmental conditions and their ability to adsorb water  
243 near steam vents that is saturating their VNIR spectra. Samples R13 and R18 (site L6) show an  
244 absorption band at 0.77  $\mu\text{m}$  that is, coupled with features at 0.55, 1.48 and 1.97  $\mu\text{m}$ , consistent  
245 with coquimbite  $\text{Fe}_2^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ . Orange-colored samples R15 and R19 have a diagnostic 0.87  
246  $\mu\text{m}$  iron absorption band similar to that of hematite, copiapite or ferricopiapite spectra. XRD  
247 analyses revealed the presence of a variety of Al, K and Fe-sulfates (mostly alunogen, K-alum  
248  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , alunite, mercurite  $\text{KHSO}_4$ , goldichite, jarosite, coquimbite, plus traces of  
249 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  
250 Fe-oxides (e.g., ferryhydrite <2%)). Unfortunately, many of these minerals do not have matches  
251 in the existing VNIR spectral libraries. These minerals are deposited in and around the vent  
252 within ~1 m. These observations suggest that our samples correspond to fumarolic incrustations  
253 and/or sublimated minerals; the former produced by gas cooling and condensation, while the  
254 latter formed directly through vapor deposition processes (e.g., Africano and Bernard, 2000;  
255 Aguilera et al., 2016).

256 A distinct variety of minerals was observed at the higher temperature vent at site L4 (gas  
257 emissions at 160°C, Figure 2e,f; Table 4). Realgar (AsS), Cinnabar (HgS) and Orpiment (As<sub>2</sub>S<sub>3</sub>)  
258 were identified thanks to their respective burgundy, red and yellow colors. These colorful  
259 minerals are only present as thin surficial coatings (sublimates), while the bulk of these rocks  
260 appear to be comprised of the same wall-rock as elsewhere. Spectra of these colorful minerals  
261 contain visible-region electronic absorptions corresponding to their colors, and they should not  
262 exhibit NIR spectral features since their structures do not include either H<sub>2</sub>O, OH, or SO<sub>4</sub> (e.g.,  
263 Cloutis et al., 2016). Cinnabar visible spectra are characterized by a steep absorption edge at 590  
264 nm and no diagnostic absorption features longward of this edge to 2500 nm. Realgar and  
265 orpiment spectra are similar to that of cinnabar, but with absorption edges near shorter  
266 wavelengths, consistent with their more orange to yellow colors. Weak absorptions in the USGS  
267 library spectra of these minerals are attributed to adsorbed water. Strong VNIR OH and H<sub>2</sub>O  
268 bands similar to those of silica sinters from the Yellowstone hot springs were observed in spectra  
269 of the L4 white samples, as well as bands near 2.03 and 2.16 μm in the L4 yellow samples, which  
270 may indicate the presence of amorphous As<sub>2</sub>S<sub>3</sub>, and hydrated amorphous FeAs species (Figure  
271 3d; Bishop et al., 2004a; Henke, 2009). Raman spectra also lack references for comparison but  
272 are consistent with As-bearing species (Figure 4c). XRD or ICP-OES / ICP-MS analyses were  
273 not be performed due to the potential toxicity of the samples.

274

275

## Discussion

### Mineralogical detections and alteration

276 A large variety of minerals have been detected in the Solfatara crater samples, in agreement with  
277 previous studies (e.g., Sgavetti et al., 2009; Valentino et al., 1999). Remnants of sanidine in some  
278 wall samples are consistent with the presumed, original trachytic composition of the rock. Less  
279

280 competent ash layers are consistent with a high proportion of amorphous material. Calcite  
281 detections in the wall samples at L3 and L5 could originate from the underlying sedimentary  
282 rocks, or have precipitated as a secondary mineral. Elevated Si and Ti concentrations suggest  
283 leaching processes and alteration within the entire crater.

284 Silicic alteration around mud pots in the central part of the crater is characterized by the complete  
285 destruction of the original rock/ primary mineral assemblage as evidenced in the XRD patterns of  
286 site L1 samples. The product of this alteration is a porous rock consisting exclusively of residual  
287 amorphous silica associated with sulfur and alunite. Secondary minerals such as K-alum,  
288 alunogen and pickeringite are detected in the dry, surrounding deposits, a few meters away from  
289 the pools (sample L1R2). No phyllosilicates were detected in the L1 (active) mud pots; the low  
290 pH likely hindering the formation of kaolinite (Zimbelman et al., 2005). Muddy gray material in  
291 the pools is consistent with amorphous silica. However, small absorption bands in the VNIR  
292 spectra of L7 (dry, ancient mud pot towards the periphery of the crater) suggest the presence of  
293 minor Al-clays such as kaolinite or montmorillonite (figure 3b). Alunite formation from K –  
294 feldspar hydrolysis has been confirmed by previous SEM and isotopic analyses (Piochi et al.,  
295 2015; Mayer et al., 2016). Alunite dominance in the mud pot samples L1R3 and L1R4 could also  
296 result from the hydrolysis of the K-alum of sample L1R2 in the low pH, wet pool environment  
297 (Valentino et al., 1999).

298 Along the crater rim (sites L2, L3, L6), alteration shifts towards the so-called “advanced argillic  
299 (or alunitic) facies”. The original rocks are replaced by minerals of the alunite group,  
300 natroalunite, alunite and jarosite with a prevalence of alunite. These observations are consistent  
301 with the sequential zoning observed at several volcanoes, and could be explained by progressive  
302 neutralization of the fluid away from the degassing vents (e.g., Fulignati et al., 1998). The spatial  
303 distribution of alunite and jarosite at sites L2, L3 and L6 could be related to the relative

304 availability of Fe and Al within the bedrock. At a temperature close to 100°C (most gas  
305 emissions at Solfatara), alunite and jarosite share a stability boundary at low pH, while at higher  
306 pH alunite is presumably associated with hematite (Zimbelman et al., 2005). We observed both  
307 mineral assemblages in some rocks of site L6. VNIR spectra of the L6 alunite-bearing rock  
308 (L6R4) share common absorption features with K-alunite references at 1.43 and 1.48  $\mu\text{m}$  (rather  
309 than 1.44 and 1.49  $\mu\text{m}$  for Na-alunite), indicating that this sample contains K-alunite (Figure 5a).  
310 The shape of the 2.22/2.26  $\mu\text{m}$  doublet feature in the jarosite spectra from the Solfatara outcrops  
311 are also more consistent with the K-rich endmember, in agreement with the original bedrock  
312 composition (Figure 5b). The spectrum of sample L2R1 includes VNIR features consistent with  
313 the presence of both alunite and jarosite.

314 Jarosite is expected to form at low pH ~2-4 (e.g. Bigham et al., 1996; Elwood Madden et al.,  
315 2004), which would be inconsistent with the preservation of K-feldspar. Still, both are observed  
316 in the same area, suggesting that alteration is concentrated in layers that are more porous, or  
317 fractured and is spatially highly variable. The assemblage silica + alunite  $\pm$  jarosite is diagnostic  
318 of advanced clay alteration as produced by acidic fluids in a steam-heated environment, in the  
319 upper portion of hydrothermal systems (Rye, 2005) such as solfataras (e.g., Bishop et al., 2007).  
320 Previous isotopic measurements of  $^{34}\text{S}$  in sulfate minerals and native sulfur and  $\text{H}_2\text{S}$  in the  
321 fumarolic gases tend to confirm that the sulfates originate from the oxidation of  $\text{H}_2\text{S}$ . While it  
322 seems clear that sulfur and sulfates are mostly derived from the  $\text{H}_2\text{S}$ -gas (Allard et al., 1991), the  
323 debate is still vivid regarding the high versus low sulfidation grade of the CF system, and  
324 especially in the Solfatara area, given that the observed mineralization could be derived from  
325 either one or the other or both processes (e.g., Rye, 2005; Piochi et al., 2015). Recent petrological  
326 and isotopic surveys concluded that the CF is consistent with a low sulfidation system that may

327 transition towards a high sulfidation system in the most active centers (e.g., Solfatarra) (Piochi et  
328 al., 2015).

329 A wide variety of sulfate minerals is also detected in the direct vicinity of active fumarole vents.  
330 Crystalline Al and Fe hydroxysulfates are detected in areas where the bedrock lacks indication of  
331 primary sulfides, suggesting the influence of fumarole deposits and consistent with a steam-  
332 heated environment. Sublimates include alunite, alunogen, alum K, mercallite, goldichite,  
333 coquimbite, ferrihydrite, millosevichite and tamarugite, which are highly soluble minerals not  
334 often preserved. At the highest temperature vent (site L4), sublimates form coatings bearing  
335 various arsenic and mercury species, generally found in epithermal systems. Orpiment and other  
336 arsenic sulfide minerals are likely derived from the oxidation of realgar.

337

### 338 **Coordination of measurement techniques**

339 VNIR, Raman and XRD analyses were carried out to determine the mineralogy of the samples.  
340 The results of these techniques are generally in good agreement (Table 5), but VNIR and Raman  
341 surveys can be swayed by coatings (e.g., hematite at site L6, arsenic bearing species) as their  
342 sensitivity is limited to the first few top  $\mu\text{m}$  of the surface. VNIR and Raman techniques are  
343 advantageous in that they are fast, non-destructive, and do not require sample preparation. XRD  
344 analyses are however useful in gaining insights into minerals that are easily masked or have no  
345 signatures in the VNIR (e.g., feldspars, quartz), and mandatory for deriving quantitative  
346 information. The XRD technique is also the sole one to provide access to the full mineral  
347 assemblage in the case of complex mixtures, whilst VNIR and Raman measurements often reveal  
348 only a few phases.

349 Most sulfates could easily be identified with all of these individual techniques, although Raman  
350 and VNIR reference libraries do not necessarily contain all of the minerals identified by XRD.



351 Some anhydrous sulfates such as yavapaiite do not exhibit spectral features in the NIR (e.g. Lane  
352 et al., 2015). Some sulfate species (e.g., tamarugite) could only be recognized thanks to the vast,  
353 historical XRD standard database. Similarly, the existing VNIR and Raman databases lacked  
354 exact matches for all the arsenic sulfides and iron-bearing species that seemed to be derived from,  
355 or associated with realgar. Amorphous silica detection is not as straightforward as sulfate  
356 detection, but its presence could be inferred in the VNIR data, that are in general more efficient at  
357 characterizing hydrated amorphous components than Raman and XRD. Alternatively, the  
358 presence of amorphous silica can be inferred from the combined chemical analyses and XRD  
359 results. A suite of complementary techniques, such as the one described above, presents the most  
360 effective procedure to derive the most comprehensive information on hydrothermal samples in  
361 the field.

362

363 Both VNIR and Raman spectrometers will be carried onboard the next generation Mars rovers  
364 (e.g., MicrOmega on ExoMars (Bibring et al., 2017), ISEM on ExoMars (Korablev et al., 2017),  
365 RLS on ExoMars (Rull et al., 2017), SuperCam on Mars2020 (Wiens et al., 2016), SHERLOC on  
366 Mars2020 (e.g., Beegle et al., 2014)). A key advantage of both techniques is their efficiency, as  
367 they can easily be deployed *in situ*, without requiring any sample preparation. A possible caveat  
368 will be the potential difference in the scale of analysis between the various instruments, at the  
369 grain scale for Raman, typically larger for VNIR spectrometers (with the exception of  
370 MicrOmega), as noted in previous analog studies (e.g., Flahaut et al., 2017b). Raman  
371 spectroscopy will, however, enable the possibility to identify minerals such as feldspar,  
372 anhydrous silicates or sulfates, and organic molecules, that are difficult to investigate in the  
373 VNIR domain (e.g. Bishop et al., 2003; Bishop and Murad, 2004; Lopez-Reyes et al., 2013;  
374 Sobron et al., 2014; Wiens et al., 2016; Flahaut et al., 2017b). VNIR spectroscopy will obviously

375 present great advantages to infer the presence of hydrated components, those containing Fe, OH,  
376 CO<sub>3</sub>, SO<sub>4</sub>, ClO<sub>4</sub>, PO<sub>4</sub> etc., and distinguish between minerals of the same family (e.g., sulfates, see  
377 figure 4c). Together, these instruments will have a better chance to identify the key minerals at  
378 the selected landing sites. In the absence of XRD however, assessing the full petrologic  
379 assemblage of the outcrops or rock samples will only be possible through a combination of  
380 observations, e.g., elemental abundances from SuperCam, rock textures from ExoMars Close-UP  
381 Imager (CLUPI)... (e.g., Wiens et al., 2016, Josset et al., 2017).

382

383

### **Implications**

384 VNIR spectroscopy is currently used on Mars as a remote sensing technique with instruments  
385 onboard spacecraft that map the planet's surface composition from a distance (e.g., the  
386 Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) instrument onboard  
387 Mars Express (Bibring et al., 2004), the Compact Reconnaissance Imaging Spectrometer for  
388 Mars (CRISM) instrument onboard Mars Reconnaissance Orbiter (Murchie et al., 2007)). Those  
389 instruments have the capacity to detect iron and hydrated minerals such as those described at the  
390 Solfatara analog site and should therefore be able to identify and map areas of silicic alteration  
391 (opaline silica + alunite, as seen in the Solfatara mud pots) and the sequential zoning into argillic-  
392 alunitic alteration (jarosite-alunite-hematite in the crater walls). Presumably, fumarolic  
393 sublimates and condensates (e.g., Al/Fe hydroxyl-sulfates) are also detectable with VNIR  
394 spectroscopy techniques, but the main issue of Mars orbital instruments is their limited spatial  
395 resolution (18 m/pixel at best from CRISM). Mars VNIR hyperspectral imagers on lander/rover-  
396 based missions would have a greater chance of identifying active or former vents than orbital  
397 instruments that might only detect extended areas of alteration, e.g. large fumarolic fields or  
398 geothermal areas. A number of hydrated species, including amorphous hydrated silica and related

399 materials (e.g., Bishop et al., 2008; Milliken et al., 2008, Mustard et al., 2008; Skok et al., 2010;  
400 McKeown et al., 2011; Wray et al., 2011; Weitz et al., 2013, 2014; Sun and Milliken, 2018) and  
401 sporadic jarosite and alunite-rich outcrops (Swayze et al., 2008; Ehlmann et al., 2009, 2016;  
402 Klingelhöfer et al., 2004; Morris et al., 2006; Farrand et al., 2009, 2014; Weitz et al., 2011;  
403 Thollot et al., 2012; Michalski et al., 2013; Bishop et al., 2018), which could be of hydrothermal  
404 origin, have been reported previously on Mars from orbital observations (Figure 6). Ongoing  
405 efforts to understand the context of formation of those minerals, catalog their occurrences, and  
406 recognize key alteration facies/assemblages are supported by analog studies.

407 More limited *in situ* observations already demonstrated the occurrence of hydrothermal processes  
408 on Mars, although previous rovers were not equipped with VNIR or Raman spectrometers.  
409 Amorphous silica was detected by the MER rover Spirit, at Home Plate, thanks to its mini-TES  
410 thermal IR spectrometer. APXS chemistry indicated elevated Ti and P contents in nearby soils  
411 that were interpreted as evidence for acid leaching; this process may have left behind some  
412 alteration minerals. The presence of sulfates may be inferred in the TES wavelength range,  
413 although hydrated minerals are most easily identified in the VNIR domain (e.g., Bibring et al.,  
414 2006; Ehlmann et al., 2012) and are expected to be more readily observed by future rovers such  
415 as ExoMars that include VNIR spectrometers. The presence of a VNIR or Raman spectrometer at  
416 Gusev crater could help to further assess the presence of alteration minerals and possibly of  
417 organics in areas where hydrothermal silica was detected by Spirit (Ruff et al., 2011; Ruff and  
418 Farmer, 2016). Sending an XRD instrument to Gusev crater could bring additional information  
419 on the nature and relative amount of crystalline phases in these unique silica-rich materials near  
420 Home Plate (Ruff et al., 2011). The mini-TES instrument range was however well-suited for  
421 capturing the mafic rock diversity in Gusev crater (e.g., Christensen et al., 2004). A significant  
422 proportion of amorphous material has been detected at another Mars location, in the soils of Gale

423 Crater, by the CheMin XRD instrument on the Mars Science Laboratory rover. The nature and  
424 origin of this amorphous material could not be determined with certainty, but at least part of it  
425 seems to be hydrated (Bish et al., 2013; Dehouck et al., 2014; Achilles et al., 2017; Ehlmann et  
426 al., 2017; Yen et al., 2017; Rampe et al., 2018; Gabriel et al., 2018). As demonstrated above,  
427 VNIR spectroscopy was efficient as detected hydrated amorphous components such as opal, even  
428 in the pumice / ash component of the bedrock, and could assist in characterizing of the alteration  
429 phases identified by CheMin at Gale crater (e.g., Bish et al., 2013) if sent on future missions.

430  
431 In the present study, we have shown an example of how trachytic rocks at the Solfatara crater  
432 were hydrothermally altered into sulfate and silica-rich assemblages. At the Solfatara site, steam-  
433 heated fumarolic alteration due to the presence of acidic sulfate-rich fluids resulted in an  
434 increased rock porosity and permeability, and the crater is currently primarily composed of  
435 incoherent rocks. The most abundant sulfates are Al, K, and Fe-rich in agreement with the  
436 original bedrock composition. Unlike the Solfatara site, the martian crust is more basaltic than  
437 trachytic (e.g., Mc Sween et al., 2003), even though trachytes and trachy-andesites have been  
438 found locally (e.g., Sautter et al., 2015; Cousin et al., 2017). Different alteration assemblages may  
439 be produced based on a number of factors that control hydrothermal alteration such as the rock  
440 type, but also the temperature, pressure, permeability, fluid composition and event duration (e.g.,  
441 Browne, 1978). Previous Mars analog studies of andesitic basalt alteration in Nicaragua reported  
442 the presence of mixed phyllosilicates, oxides/hydroxides and sulfates (gypsum + alunite) in the  
443 active acidic volcanic systems of Cerro Negro, Momotombo, and Telica (Hynek et al., 2013;  
444 Marcucci et al., 2013). Acid-fog weathered basalts at the top of the Hawaiian Kilauea volcano  
445 were found to be dominated by jarosite/natrojarosite sulfates, iron oxides and amorphous silica  
446 (e.g., Schiffman et al., 2006; Seelos et al., 2010). Icelandic expeditions have found abundant Al

447 and Fe/Mg smectites, hematite and hydrous silica, formed from the alteration of basalts by S-poor  
448 fluids (Ehlmann et al., 2012). All of these locations have presumed basaltic composition but show  
449 various assemblages due to varying external factors. Therefore, it is key to catalog in detail  
450 alteration patterns in these various environments and understand the geochemical pathways  
451 involved in those transformations on Earth, in order to shed light on past Mars environments.  
452 A crucial aspect of hydrothermal systems is that on Earth, continental vents are known to be  
453 favorable to the development of life and the preservation of biosignatures. Therefore, they  
454 represent prime targets for the search of Life on Mars (e.g., Damer et al., 2017; Campbell et al.,  
455 2017). The Solfatara crater is home to several thermophilic, thermo-tolerant and acidophilic  
456 Bacteria, algae (e.g., *Cyanidium caldarium*) and Archea, such as *Sulfolobus solfataricus* (named  
457 after our study area, the Italian Solfatara), *Acidianus*, *Pyrobaculum* and *Metallosphaera sp* (e.g.,  
458 DeRosa et al., 1974, 1975; Zillig et al., 1980; Huber et al., 2000a, b). Most of these micro-  
459 organisms are chemolithotrophs and rely on S, Fe oxides and metal sulfides for energy supply  
460 (e.g., Huber et al., 2000a, b). Finding such a biodiversity adapted to this extreme environment is  
461 promising for investigation of potential life elsewhere in the Solar System, and especially on  
462 Mars.

463

464

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## Figure captions

966  
967 Figure 1: a) Location of the study area in Italy. b) View of the Campanian plain and the three  
968 volcanoes from the bay of Naples: Vesuvio (V), Campi Flegrei (CF) and Ischia (I). c) Close-up  
969 view on the Solfatara volcanic crater. Sampling sites are indicated by green stars. Faults and ring  
970 faults from Isaia et al. (2015) are overlain in transparency, and represented by black and red lines  
971 respectively (Background: ArcGIS world imagery maps, Sources: Esri, DigitalGlobe, GeoEye,  
972 Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User  
973 Community).

974  
975 Figure 2: Field impressions at the different sampling sites (See locations on figure 1).

976  
977 Figure 3: VNIR reflectance spectra of selected samples that represent the types of spectral  
978 features observed (thick lines). a) Altered walls at L2 and L6, b) mudpot sediments from L1,  
979 c) deposits from the L6 90°C vent, d) deposits from the L4 160°C vent. Reflectance spectra of  
980 minerals likely present, from the Bishop collection and the USGS spectral library, are given for  
981 comparison (dotted lines). Vertical bars were placed at key wavelengths to facilitate comparison  
982 of the absorption features.

983  
984 Figure 4: Raman spectra of selected samples that represent the types of spectral features  
985 observed. a) Altered walls at L6, b) mudpots sediments from L1, c) deposits at the L4 160°C  
986 vent). RUFF reference library spectra of the minerals commonly identified in the samples are  
987 given for comparison (dotted lines). Vertical bars were placed at key wavelengths to facilitate  
988 comparison of the Raman peaks.

989

990 Figure 5: VNIR field spectra of alunite and jarosite in rock coatings, which are occurring within  
991 the same outcrops at the Solfatara crater, are compared with the spectra of terrestrial references  
992 and Mawrth Vallis (MW) Mars locations from the Bishop collection (Bishop et al., 2004b, 2018;  
993 Bishop and Murad, 2005) and the Viviano-Beck et al. (2014) type spectra marked by V.

994  
995 Figure 6: Mars examples of alunite, jarosite and silica detections. a) Silica-rich deposits (magenta  
996 arrows) identified around the Nili Patera volcanic cone by Skok et al. (2010). The opal\_index  
997 parameters map (in rainbow, stretched values 0.001-0.1) using the index of Thollot et al. (2012)  
998 on CRISM FRT00010628 is overlain in transparency over CTX image  
999 B05\_011459\_1891\_XI\_09N292W. b) Sporadic alunite (yellow arrows) and jarosite (orange  
1000 arrows) detections were made within the clay-rich units of Mawrth Vallis (locations from  
1001 Danielson and Bishop, 2018; Bishop et al., 2018; Sessa et al., 2018). CRISM observation  
1002 FRT00003BFB is displayed in false color (default RGB, R=2.5361  $\mu\text{m}$ , G=1.3358  $\mu\text{m}$ , B=  
1003 0.7749  $\mu\text{m}$ ) over CTX image P03\_002074\_2027\_XI\_22N018W. c) Alunite is detected together  
1004 with kaolinite along the walls of the 65 km diameter Cross Crater (Ehlmann et al., 2018). RGB  
1005 composite of CRISM observations FRT000137C2, FRT0000D24B, FRT0000CC44,  
1006 FRT0000B252, FRT0000987B are overlain over CTX images  
1007 D16\_033383\_1496\_XN\_30S157W, P16\_007446\_1477\_XN\_32S157W,  
1008 P19\_008448\_1493\_XN\_30S158W, P20\_009028\_1495\_XI\_30S157W,  
1009 P15\_006945\_1494\_XN\_30S158W. This RGB composite with the summary parameters  
1010 R=BD2200 (Thollot et al., 2012), G=Kaol-index (Thollot et al., 2012), B= SINDEXT2 (Viviano-  
1011 Beck et al., 2014) was chosen to highlight putative alunite detections in purple, and kaolinite  
1012 detections in yellow (mixed detections appear in white). d) CRISM VNIR spectra of selected  
1013 Mars mineral detections are compared with library references (Mars spectra: CRISM alunite and

1014 jarosite spectra from Viviano-Beck et al. (2014, 2015) and Bishop et al. (2018), Silica spectra  
 1015 from CRISM FRT00010628 (average of 3x3 pixels). Reference spectra: Alunite GDS83, Jarosite  
 1016 GDS99 and Opal TM8896 from the USGS spectral library).

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## Tables

1021 Table 1: List of sampling sites and collected samples.

site	Latitude	Longitude	Type	Description of samples
L1	40.8270	14.1393	mudpot at 33°C, pH = 1.5	R1: white/brown deposits outside the pool. Polygons on a 20 cm scale R2: yellowish/brown deposits outside the pool R3: hard cemented deposits on the pool ramparts (Z1= at surface, Z2 = at a 5cm depth) R4: Light gray, wet sediments from the pool
L2	40.8303	14.1393	weathered wall	R1: Yellow coatings R2: Orange coatings R3 : Red coatings
L3	40.8304	14.1395	weathered wall	R1: white ignimbrite / ashy layer from the crater wall R2: white ignimbrite / pumice from the crater wall R3: yellowish ignimbrite / ashy layer from the crater wall
L4	40.8271	14.1420	fumarolic vent at 160°C	R1: colorful rock lying on the vent (white, yellow, orange, dark and burgundy coatings) R2: colorful rock lying on the vent (yellow and orange coatings)
L5	40.8255	14.1393	fumarolic vent at 90°C	R1 : white material within the vent R2: yellow material (sulfur needles) within the vent R3: friable/ altered, white/beige rocks around the vent R4: friable/ altered rocks with subtle turquoise tones around the vent
L6	40.8295	14.1407	fumarolic vent	R1: White pyroclastic deposits in the crater wall

			at 90°C + weathered wall	R2: Beige pyroclastic deposits in the crater wall R3: Orange/Brown coatings on the crater wall R4: Yellow coatings on the crater wall R5: Dark red coatings on the crater wall R6: Sea green/turquoise coatings on the crater wall R7: Biology - green layer of algae, possibly Cyanidium caldarium R8: White coatings R9: Yellow sulfur crystals R10: Rock with colorful coatings R11: Yellow sulfur crystals from within a vent R12: White fibrous deposits from within a vent R13: White nodular material from within a vent R14: Orange nodular material from within a vent R15: Orange/brown puffy material from within/around a vent R16: White puffy material from within/around a vent R17: White/beige nodular material around the vent R18: White nodular material around the vent R19: Orange/brown ridged/puffy material around the vent R20: White/orange deposits from within a second vent R21: Orange/dark brown deposits from within a second vent
L7	40.8290	14.1405	dry mudpot	R1: brown deposits, polygons on a 10 cm scale.

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 1025 Table 2: Bulk composition of selected crater wall samples that appeared relatively unaltered. All  
 1026 values are given in wt%; D. L.= Detection Limit. Major oxides have been renormalized to 100%  
 1027 to exclude the loss on ignition. This Ignition loss (as measured by ICP-OES, including S) and the  
 1028 S content (as measured separately, by a C-S analyzer) are given for information. The Chemical  
 1029 Index of Alteration (CIA) is calculated using the equation of Nesbitt and Young (1982):  $CIA =$   
 1030  $(Al_2O_3) \times 100 \times (Al_2O_3 + CaO + Na_2O + K_2O)^{-1}$ . CIA values fall within the same range (60-80)  
 1031 of Mayer et al. (2016) who noticed that the Solfatara sample density decreases (porosity  
 1032 increases) with increasing degree of alteration.

Sample ID	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Total major oxides	Ignition loss	S	CIA
<b>L5R4</b>	97.56	0.72	0.08	<D.L.	<D.L.	0.05	0.09	0.22	1.27	<D.L.	100	<b>16.52</b>	<b>1.36</b>	66.30
<b>L3R1</b>	97.03	1.19	0.14	<D.L.	0.06	0.08	0.14	0.11	1.26	<D.L.	100	<b>6.41</b>	<b>0.35</b>	78.37
<b>L6R1</b>	97.16	1.54	0.13	<D.L.	0.05	0.05	0.12	0.10	0.86	<D.L.	100	<b>12.37</b>	<b>0.46</b>	84.95

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1037 Table 3: Summary of XRD detections for selected samples. For the DOC (degree of crystallinity)

1038 values, the -, +, ++ and +++ symbols indicate the following ranges of values, respectively :

1039 <30%, >30%, >50%, >70%. For mineral abundances within the crystalline phases, the -, +, ++

1040 and +++ symbols indicate the following ranges of values, respectively : present but <10%, >10%,

1041 >40%, >70%. Gray lines indicate samples with a lower amount of crystalline phases (<60%).

1042 Sulf= Sulfur, Cal = calcite, Ana = Anatase, San= sanidine, Al= alunite, Jar = jarosite, Alg =

1043 alunogen, Alum = alum-K, Mer = mercurite, Gol =Goldichite, Coq = coquimbite, Pick =

1044 pickeringite, Mag =magnesite, Cam= caminite, Fer = ferrhydrite, Yav = Yavapaiite, Mil =

1045 millosevichite, Mic= mica, Tam = tamarugite.

Sample ID	DOC	Sulf	Cal	Ana	San	Al	Jar	Alg	Alum	Mer	Gol	Coq	Pick	Mag	Cam	Fer	Yav	Mil	Mic	Tam
L5R1	-	+++	-	-										-						
L5R3	++	+++	-																	
L5R4	-		+	++																
L3R1	-		+	+++																
L6R1	-		++	++																
L6R3	+++				+++	-	-												-	
L6R4	++					+++	-	-							-					
L6R5	+++				+++		-												-	
L1R2Z1	+++					-		++	+				+							
L1R3Z1	++	++				+														
L1R3Z2	+	+++		-		+														
L1R4	++	++				++														
L6R11	+++	+++						-	-											
L6R12	+++							++	+	-									-	
L6R13	+++							++	+		+									
L6R14	++					+++		+	+		-									
L6R15	+++					-		++	+		-	-								-
L6R16	+++	-				+		++	+											
L6R17	+++					-		+++	+		-								-	
L6R18	+++					-		+++	-	-										
L6R19	+++					+		++			+	-								





Figure 1

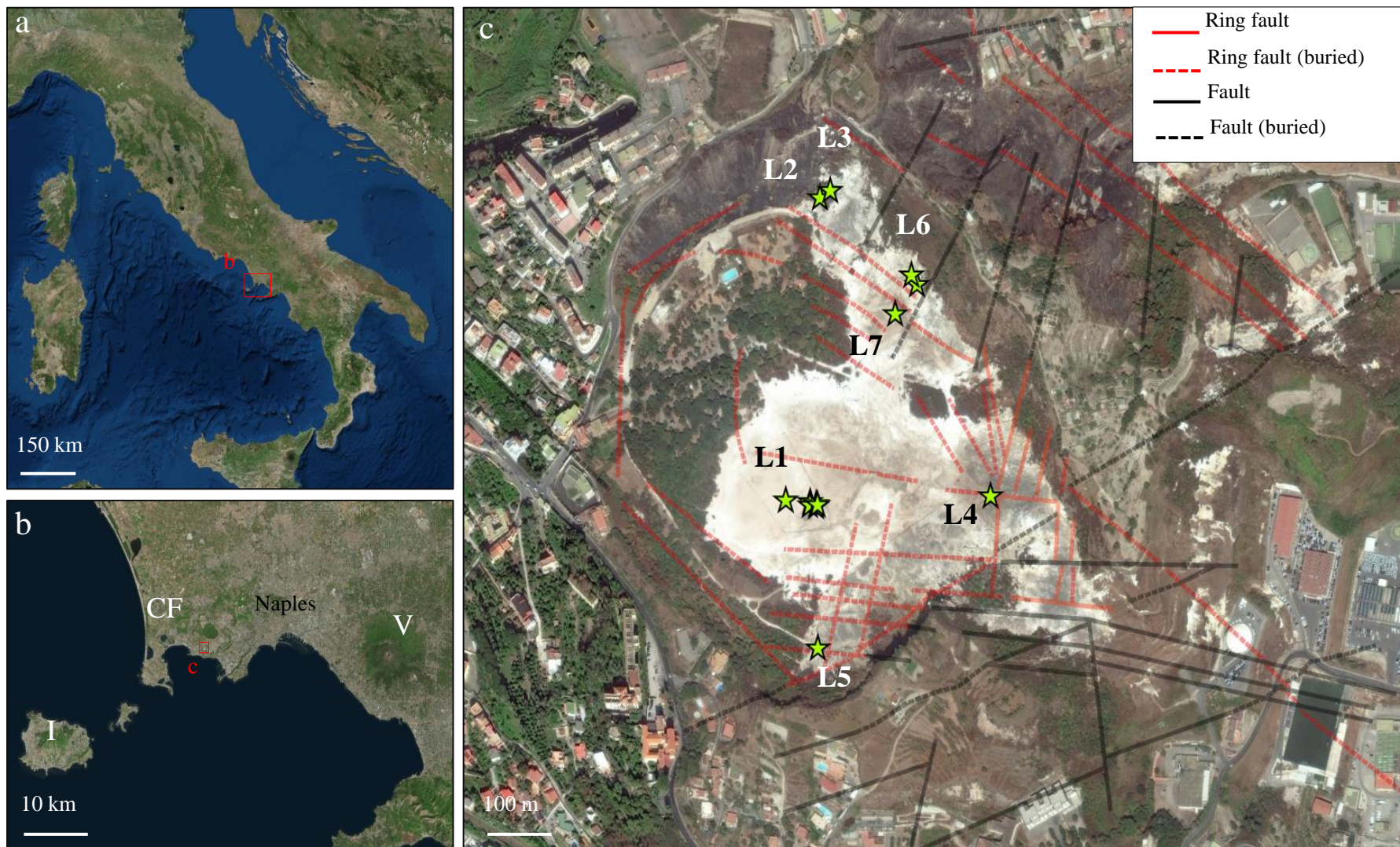


Figure 2

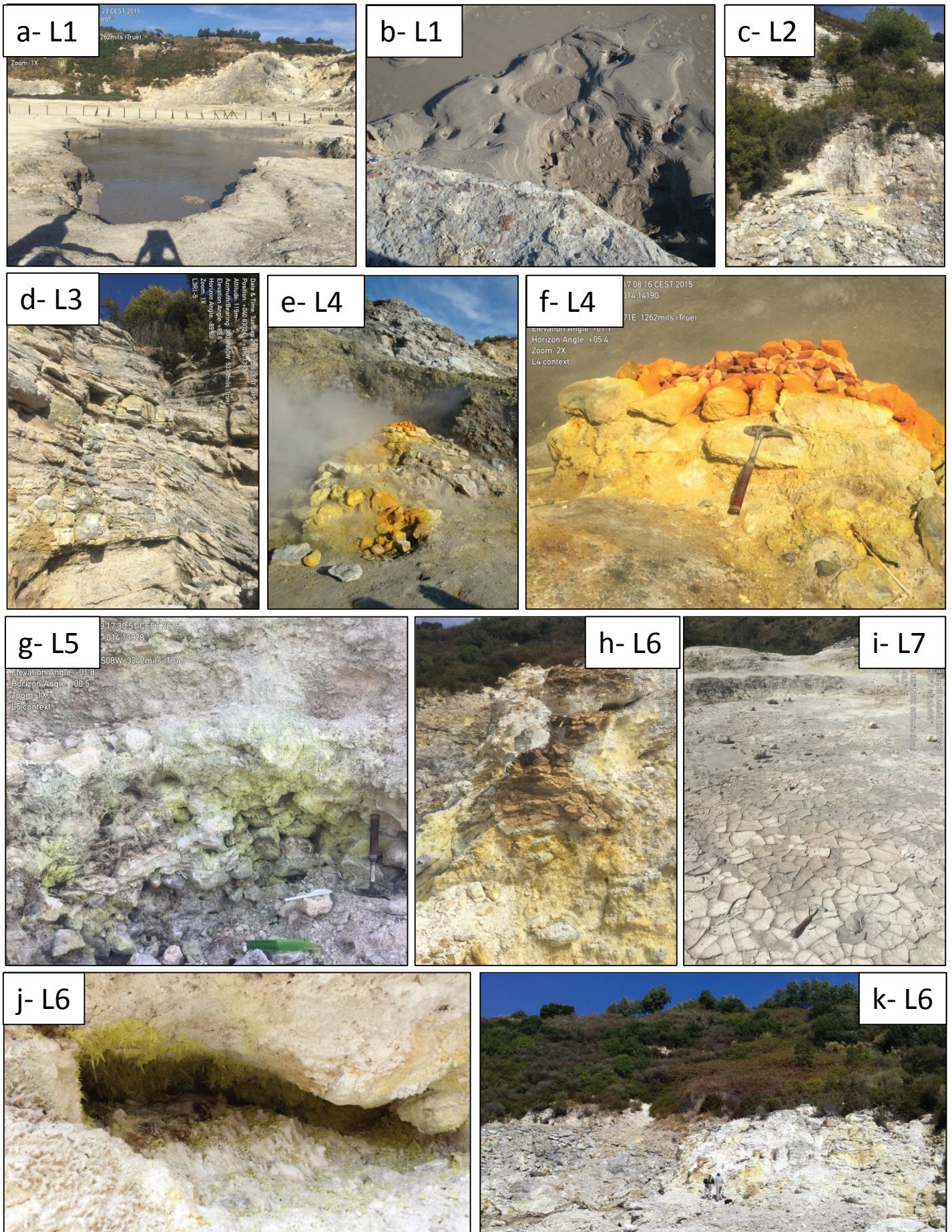


Figure 3

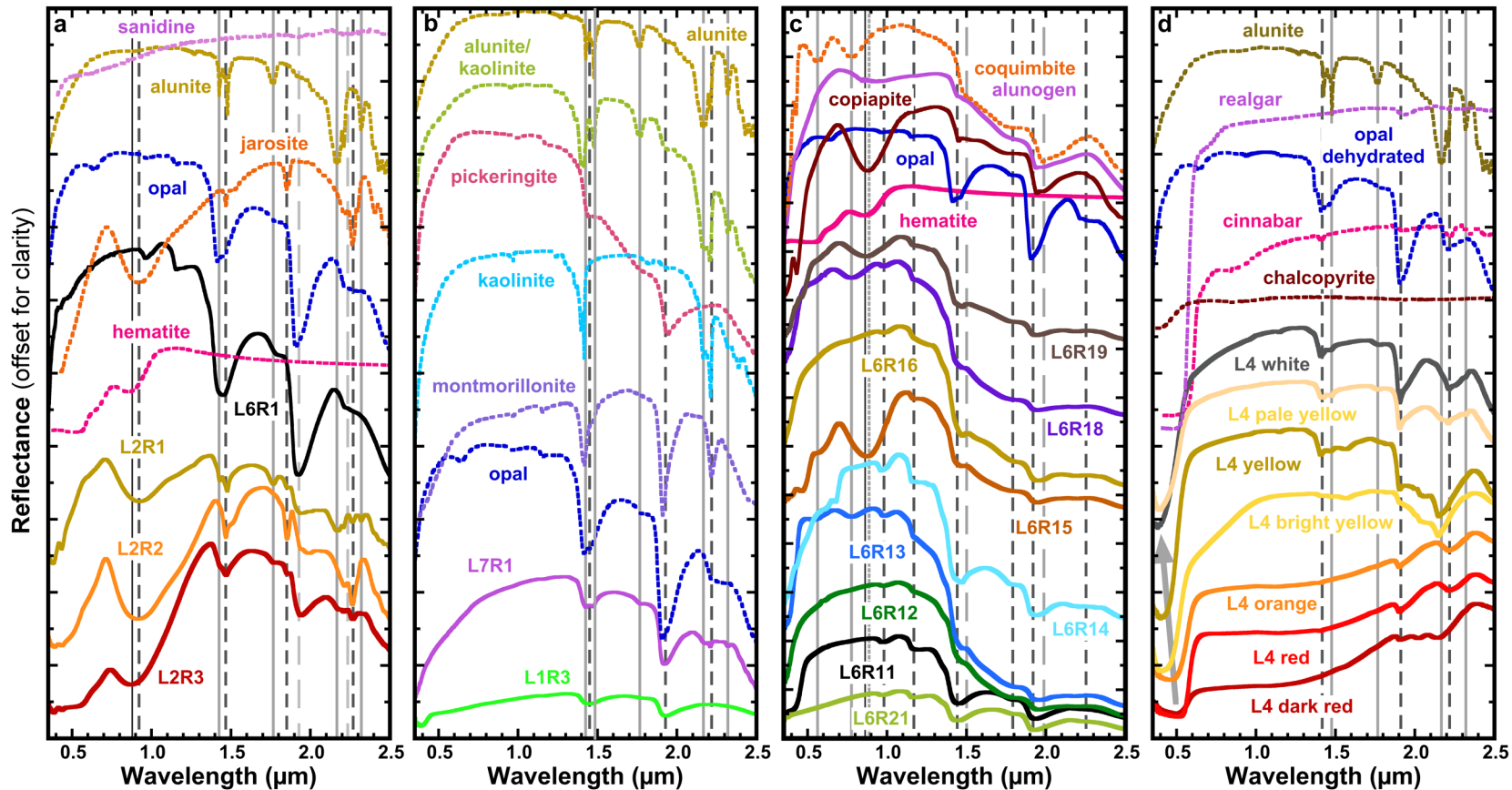


Figure 4

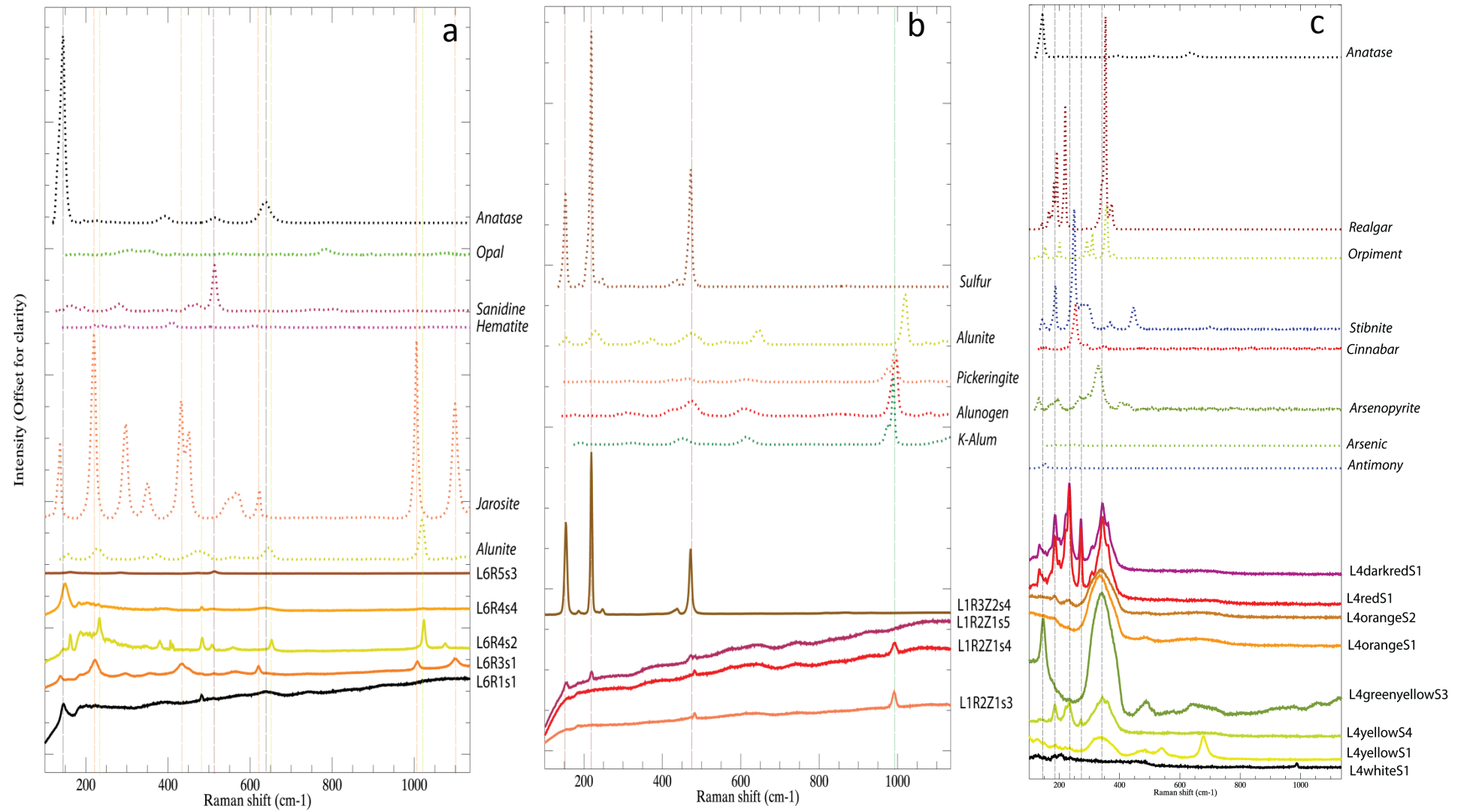


Figure 5

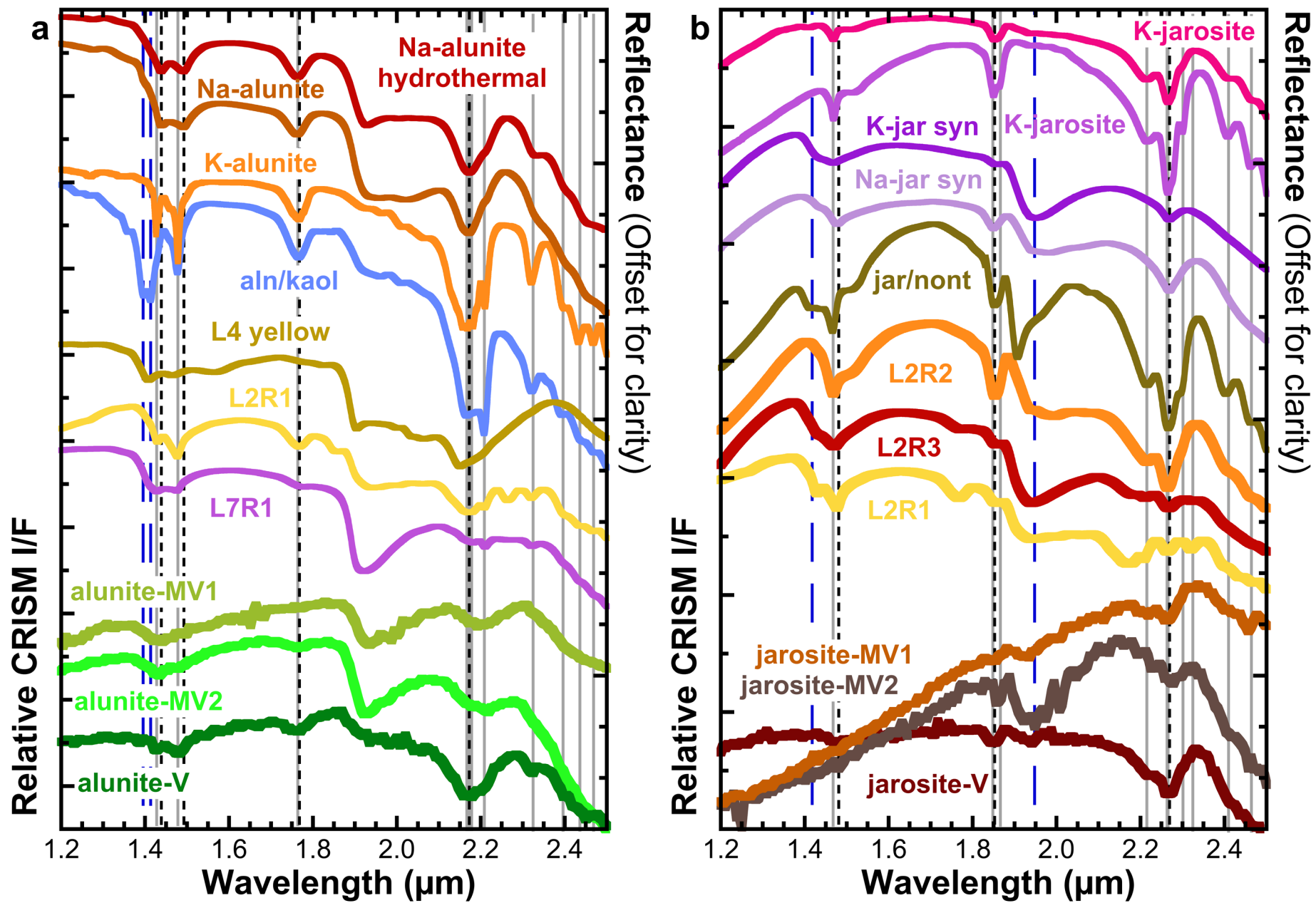


Figure 6

