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# Aqueous alteration processes in Jezero crater, Mars - implications for organic geochemistry

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69 **Abstract:** The Perseverance rover landed in Jezero crater, Mars in February 2021. We used the  
70 Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals  
71 (SHERLOC) instrument to perform deep ultraviolet Raman and fluorescence spectroscopy of  
72 three rocks within the crater. We identify evidence for two ancient aqueous environments. Liquid  
73 water formed carbonates in an olivine-rich igneous rock. A sulfate-perchlorate mixture is present  
74 in the rocks, probably formed by later modifications of the rocks by brine. Fluorescence  
75 signatures consistent with aromatic organic compounds occur throughout these rocks, preserved  
76 in minerals related to both aqueous environments.

77

78

79 **Main text:**

80 The Perseverance rover landed in Jezero crater, Mars to investigate the geology of the crater,  
81 identify habitable environments, assess whether life ever existed on Mars, and to collect samples  
82 for potential return to Earth (1). Jezero hosted an open-basin lake during the Noachian (~3.7 Ga)  
83 (1-2), units associated with the largest carbonate deposit identified on Mars (2-4), and a well-  
84 preserved delta with clay and carbonate-bearing sediments, well-suited to preservation of  
85 organics (1). Organics have previously been detected on Mars (5,6), and here we resolve the  
86 spatial and mineralogical context of organics in Jezero crater with the rover's SHERLOC  
87 instrument (Scanning Habitable Environments with Raman and Luminescence for Organics and  
88 Chemicals), a deep-ultraviolet fluorescence and Raman spectrometer capable of mapping organic  
89 and mineral composition with a spatial resolution of 100  $\mu\text{m}$  (7). Complementary elemental  
90 chemistry analyses are performed by the PIXL (Planetary Instrument for X-ray Lithochemistry)  
91 and SuperCam instruments (8-11).

92

93 We report the presence of organics and aqueously formed minerals at Jezero crater in three rock  
94 targets [8] analyzed during the first 208 sols of the mission (Fig. 1) located in two different  
95 orbitally and rover-identified geological units within the floor of Jezero crater (9,12). The Garde  
96 target is from the altered ultramafic Séítah Formation (Fm), orbitally mapped as the Crater Floor  
97 Fractured 1 unit (CF-f1) (Fig. 1) (9,12). The Guillaumes and Bellegarde targets are from the  
98 overlying and therefore younger basaltic Máaz Fm, orbitally mapped as the ~2.3-2.6 Ga (13)  
99 Crater Floor Fractured Rough unit (CF-fr) (9,12). The Perseverance rover drilled four rock  
100 samples from the Séítah Fm. Montdenier and Montagnac rock samples were obtained from the  
101 Bellegarde rock, while the Guillaumes rock sample attempt, Roubion, failed (12). These rock  
102 samples are planned to be returned to Earth.

103 All three Raman spectral scans (8) from Garde exhibit strong peaks that have a peak position  
104 range of 1080 to 1090  $\text{cm}^{-1}$  (n=38) attributed to carbonate (spectrum 1 and ROI 1-4 in Fig. 2H),  
105 and peaks with a peak position range of 820 to 840  $\text{cm}^{-1}$  (n=60) attributed to olivine (ROI 1 and  
106 4 in Fig. 2H) (8,13-14). Olivines were found to be more Fe-rich than laboratory measured  
107 olivines of Fo# 80-90, while carbonates are likely mixed Fe- and Mg-species based on 1080-  
108 1087  $\text{cm}^{-1}$  peak positions (8) and Ca-dominated species are excluded based on PIXL data (11).  
109 These spectral detections were overlaid on Wide-Angle Topographic Sensor for Operations and  
110 eNginering (WATSON) camera images to correlate spectral position with textures (8). Olivine  
111 and carbonate are associated with  $\mu\text{m}$ - to mm-sized light-toned tan, reddish-brown, and dark-  
112 toned sub-angular grains as well as light-toned intergranular spaces (Fig. 2.B,E). Spectral  
113 features of olivines and carbonates often co-occur in a single spectrum; however, there are also  
114 areas where either olivine or carbonate occur independently. Spectral observations of a weak,  
115 broad Raman peak centered ~1060  $\text{cm}^{-1}$  (FWHM ~200  $\text{cm}^{-1}$ ) may indicate a disordered phase

116 consistent with amorphous silicates, often difficult to detect given their low intensity (Fig. 2). A  
117 peak at  $960\pm 5\text{ cm}^{-1}$  is likely phosphate, although perchlorates cannot be excluded (Fig. 2).

118 Garde detail scans (8) exhibit strong fluorescence signatures, centralized at  $\sim 340\text{ nm}$ , that  
119 spatially correlate with carbonate, probable phosphate, and amorphous silicate spectra localized  
120 within narrow intergranular spaces (Fig. 2.E-F). A less intense fluorescence band centered at  $285\text{ nm}$   
121 typically accompanies the  $340\text{ nm}$  fluorescence. Other areas exhibit no fluorescence (Fig.  
122 2.C).

123

124 Guillaumes features white and reddish brown, anhedral patches, 1-2 mm across (Fig. 3.A, S1).  
125 These are secondary materials within a basaltic igneous rock (9) interpreted as void fills and  
126 correlate with sulfate and perchlorate spectra. Spectra with high intensity  $950\text{-}955\text{ cm}^{-1}$  peaks  
127 and minor  $1090\text{-}1095\text{ cm}^{-1}$  and  $1150\text{-}1155\text{ cm}^{-1}$  peaks match laboratory measurements of  
128 anhydrous Na-perchlorate (8) (Fig. 3.G, S4). Two strong Na-perchlorate detections correlate  
129 with centers of the brightest material within the anhedral patches (8). Guillaumes spectra  
130 commonly contain a single low-intensity peak positioned at  $950\text{-}955\text{ cm}^{-1}$ . We interpret these as  
131 low intensity Na-perchlorate peaks, although the cation species is uncertain due to a lack of  
132 resolvable minor peaks (8) (Fig. 3.G). Other spectra exhibit both  $950\text{-}955\text{ cm}^{-1}$  peaks and  
133 equally strong  $1010\text{-}1020\text{ cm}^{-1}$  peaks, with low intensity broad features at  $1120\pm 5\text{ cm}^{-1}$ , and  
134 occasional broad  $3450\pm 5\text{ cm}^{-1}$  hydration features, consistent with a mixture of sulfate and  
135 perchlorate that is minimally hydrated (Fig. 3.G). A Ca-sulfate species best explains these  
136 spectra when coupled with elemental chemistry data from PIXL and SuperCam (8). Last, two  
137 detected  $965\text{ cm}^{-1}$  peaks are likely phosphates, although perchlorates cannot be excluded.

138

139 Bellegarde contains white 0.5-1 mm anhedral to sub-euhedral secondary crystals that have a  
140 reddish brown semi-isopachous rim interpreted as void fills within a basaltic igneous rock (8)  
141 (Fig. S2). These crystals exhibit  $1010\text{-}1020\text{ cm}^{-1}$  peaks, similarly attributed to Ca-sulfate when  
142 coupled with elemental chemistry data (8). Several of the sulfate peaks are also associated with a  
143 narrow low-intensity hydration feature at  $3560\pm 5\text{ cm}^{-1}$ , consistent with hydrated Ca-sulfates  
144 (Fig. S3). The Bellegarde target contains a single  $1080\pm 5\text{ cm}^{-1}$  peak of possible Ca-carbonate  
145 (Fig. 4, S2). Narrow peaks at  $975\text{ cm}^{-1}$  peak could not definitively be identified and could be  
146 phosphate or perchlorate (8). The SHERLOC mineral detections within the Bellegarde and  
147 Guillaumes targets are consistent with the results from other Perseverance instruments (8-9, 11)  
148 (Fig. S5-S6).

149

150 Guillaumes and Bellegarde targets commonly exhibit a weak, broad fluorescence feature with a  
151 maximum at  $\sim 340\text{ nm}$  (Fig. 3D, 4D) that appears to be widely distributed across each surface and  
152 is occasionally correlated with reddish-brown materials. Although this feature sometimes co-  
153 occurs with perchlorate, sulfate, and possibly phosphate, it occurs equally often in areas with  
154 unidentified mineralogy. Bellegarde has two other signatures at  $\sim 275$  and  $\sim 305\text{ nm}$  (blue and

155 green respectively in Fig. 4D), which are strong and localized on specific, light-toned features.  
156 The ~305 nm signature is associated with detected sulfate (Fig. 4.D-F, S2). In Guillaumes, a  
157 second fluorescence signature at ~275 nm (Fig. 3D) is observed in two locations, approximately  
158 300  $\mu\text{m}$  in diameter, coincident with previous SuperCam laser spots (8).  
159

160 Observation of olivine and carbonate mixtures within the Garde target of the Séítah Fm is  
161 consistent with orbital infrared observations (2-4) and substantiated by multiple lines of evidence  
162 (9-11). Previously proposed hypotheses for the precipitation of these carbonates include low-  
163 temperature and high-temperature aqueous alteration of an olivine-rich protolith (3,15-17) or  
164 authigenic precipitation from lake or groundwater (4,15-17). Our 10-100  $\mu\text{m}$ -scale textural and  
165 spectroscopic evidence supports carbonate formation through aqueous alteration of an ultramafic  
166 protolith, known as carbonation. The supporting evidence includes: (i) Carbonate cation  
167 compositions consistent with those of olivines, suggesting mixed Fe- and Mg-olivine gave rise to  
168 mixed Fe- and Mg-carbonates, similar to on Earth and within Martian meteorites (16,18-19). (ii)  
169 The observed carbonates co-occur with hydrated materials (9) and potentially aqueously formed  
170 amorphous silicates and phosphate. (iii) The spectral and textural variation of olivine and  
171 carbonate dominated zones within both primary grains and intergranular spaces are expected for  
172 carbonated ultramafic protoliths on Earth (reviewed in (16)) and within Martian meteorites (18-  
173 19).

174 These observations suggest that the degree of aqueous alteration to the ultramafic protolith was  
175 relatively low since large olivine-rich domains remain intact, although the alteration is pervasive  
176 and occurs throughout the primary lithology rather than in specific spatial domains, e.g.,  
177 fractures. In ultramafic alteration environments on Earth (16) and in Martian meteorites (18-19),  
178 carbonation can be associated with the formation of oxides, hydroxides, and/or Fe/Mg-rich  
179 phyllosilicates, which have not been observed (9). Carbonation can occur in a wide range of  
180 temperatures from low to ambient to hydrothermal/metamorphic (15-17). Other alteration  
181 minerals, such as serpentine, have not been definitively observed in the Séítah Fm to date, which  
182 may suggest time limited interactions, low water rock ratios, or ambient fluid temperatures  
183 during carbonation (3,15-17).

184 The similarity between the mineralogy of the Garde target in the Séítah Fm to the surrounding  
185 widespread, regional olivine-carbonate-bearing unit with a similar orbital spectroscopic signature  
186 and geomorphological texture (3-4,15-16) suggests that carbonation of olivine may have  
187 occurred throughout this extensive region on ancient Mars (~2.7-3.8 Ga). These observations  
188 parallel those made by the Spirit rover in Gusev Crater (20) and within (1.3-4 Ga) Martian  
189 meteorites (18-19). Previous modeling efforts have suggested that carbonate deposition could  
190 have played a role in the evolution of Mars' atmosphere (3,17,22), but the geological nature of  
191 such a depositional mechanism had remained unexplained. Taken together, micron-scale

192 SHERLOC observations of this phenomenon bridges previous orbital and meteorite observations  
193 and demonstrates ultramafic alteration resulting in geological deposition of carbonates.

194

195 Jezero crater perchlorate detections, like the initial Phoenix observations (23), are substantiated  
196 by three independent instruments (9). Previous evidence for Martian perchlorates includes  
197 observations by the Curiosity rover (24), proposed but later disputed orbital detections within  
198 recurring slope lineae (25), and detection within the Tissint meteorite (26). The SHERLOC  
199 perchlorate detections differ from previous mission observations because they are observed  
200 within the interior of a rock and not on the surface, are related to aqueous processes, and are  
201 likely Na-perchlorate as compared to previously detected Ca-, Fe- or Mg-perchlorates (24).

202 Previous hypotheses for perchlorate formation on Mars are (i) irradiation of chlorine-bearing  
203 parent minerals (37), (ii) atmospheric oxidation of chlorine species (28), or (iii) formation from  
204 brines (26). Perchlorates may also be mobilized in thin films of fluid (24). The Jezero  
205 perchlorates form white void-fills within rock interiors, and did not form directly on the surface  
206 as expected from materials formed by cosmic irradiation or atmospheric oxidation, indicating  
207 either formation or mobilization through briny fluids after basalt formation. The concomitant  
208 detection of sulfates and perchlorates within the Guillaumes target suggests that sulfate formed  
209 together with perchlorate or parent chlorine-bearing species, such as halite, within percolating  
210 briny waters that were then subsequently oxidized to perchlorate. Bellegarde exhibited sulfate  
211 without perchlorate, suggesting these brines did not precipitate chlorine-bearing parent species,  
212 that perchlorate formation was not pervasive, or that perchlorates were since dissolved.  
213 Perchlorates are easily dissolved, and therefore perchlorates likely formed when these rocks were  
214 last exposed to liquid water. Perchlorate and sulfate detections within the stratigraphically  
215 younger Máaz Fm (9) substantiates an aqueous environment on Mars that occurred separately  
216 from the stratigraphically older (9) Séítah Fm carbonation environment.

217

218 Deep ultraviolet (DUV) fluorescence is particularly sensitive to aromatic organic compounds,  
219 and the fluorescence signatures observed in all three targets are consistent with emission from  
220 aromatic organic compounds containing 1 or 2 fused aromatic rings and/or aromatic heterocycles  
221 (7-8,29) (Fig. S7). Although assignment of fluorescence signatures to specific organic  
222 compounds is non-specific, ~340 nm fluorescence is consistent with a base structure of 2-ring  
223 aromatic organics like naphthalene, whereas ~275-285 nm fluorescence is more consistent with  
224 1-ring aromatic organics like benzene (8,29). The ~305 nm fluorescence may indicate either 1-  
225 or 2-ring aromatics, depending on functional groups. We interpret ~305 nm and ~275 nm  
226 fluorescence as organics that occurred with sulfates within the Bellegarde target (Fig. 4.D-F),  
227 while we interpret ~285 nm fluorescence as organics that occurred with carbonate-phosphate-  
228 amorphous silicate brown microcrystalline alteration zones within the Garde target (Fig. 2) (8).  
229 The ~340 nm fluorescence co-occurs with carbonate-phosphate-amorphous silicate alteration

230 zones in Garde but is not associated with particular phases in Guillaumes and Bellegarde (8).  
231 Both organics in phosphate-containing alteration zones and/or inorganic Ce-containing  
232 phosphate can explain 340 nm fluorescence in Garde (8). In Guillaumes and Bellegarde, 340 nm  
233 fluorescence is predominantly uncoupled from phosphate detections, suggesting part of this  
234 signal is best assigned to organics (8). However, that some or all of the ~340 nm fluorescence  
235 signal is from Ce cannot be excluded (8).

236 When taken into context with Curiosity observations of organic material in mudstones (21), this  
237 study's confirmation of organic material in igneous rocks implies a diverse relationship between  
238 geological processes and organic compounds on Mars. Several explanations for the presence of  
239 Martian organics are possible, e.g., infall of meteoritic material (6), *in situ* synthesis mechanisms  
240 (18-19,26), or a putative relic Martian biosphere. The association between organics and sulfate-,  
241 phosphate-, perchlorate-, carbonate-, and amorphous silicate-bearing mineralogy as well as  
242 alteration textures suggests that aqueous alteration of igneous rocks may have played a role in  
243 the preservation or even synthesis of these particular organics, as seen for similar organics-  
244 mineral correlations in Martian meteorites (18-19,26). However, potentially organic, widespread  
245 ~340 nm fluorescence could suggest other processes, such as dust, contributed to detections. We  
246 note that some mineral phase associations may not be apparent due to instrument limitations (8),  
247 and higher spatial resolution analyses upon return of these samples to Earth are necessary to  
248 conclusively establish the origins of the detected organics.

249

250 We did not detect Raman peaks consistent with aromatic organic compounds, such as the C=C  
251 stretching mode (or G band) around ~1600 cm<sup>-1</sup>. However, Raman scattered light is several  
252 orders of magnitude weaker than fluorescence (8,29). Organic concentrations were likely  
253 insufficient to produce detectable Raman scattering, either due to low original concentration or  
254 subsequent degradation. Conservative estimates of quantification suggest a range from 5 x 10<sup>-11</sup>  
255 to 3 x 10<sup>-10</sup> grams of aromatic organics in localized points in the scan (8). Estimates from the  
256 average fluorescence maps suggest a bulk concentration of 0.1 to 10 ppm, with higher  
257 concentrations associated with more aqueously altered surfaces (8), consistent with known bulk  
258 concentrations of organics, containing one and two ring aromatic species, indigenous to Martian  
259 meteorites (11.2 ± 6.9 ppm (18)) and Curiosity rover detections in mudstones (~70 ppbw to 10.6  
260 ± 8.9 ppm (6,21)). The SHERLOC observations cement these previous detections of Martian  
261 organics (18-19,21) and reveal that the type, distribution, and material-associations are highly  
262 complex and are vital to understand in order to determine evidence of potential past life and  
263 provide key insights into the organic chemistry of terrestrial planets.

264

265 Collectively, the data show the six drilled samples collected by Perseverance are  
266 astrobiologically significant. The evidence for carbonation, formation of sulfates and  
267 perchlorates, and fluorescence signatures consistent with organics present within these materials  
268 indicates an interplay between igneous rocks, aqueous alteration, and organic material on Mars.

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489 **Fig. 1: Rover images of the three abraded targets and their orbital context.** (A) Map of  
490 orbitally defined geological units within Jezero crater from (12), including the Crater Floor  
491 Fractured Rough unit (CF-fr) equivalent to the Máaz Fm and the Crater Floor Fractured 1 (CF-  
492 fl) unit equivalent to the Séítah Fm. Star shows the landing site, while white circles show the  
493 position of the three abraded targets. The locations of panels B and C are outlined in black  
494 rectangles. (B) Orbital infrared spectroscopy map showing the location of pyroxene- or olivine-  
495 bearing materials in the study area from (4). Labels on white circles correspond to panel G. (C)  
496 HiRISE view of study area. (D) Mastcam-Z image showing the Garde patch on the Bastide  
497 outcrop. (E) Hazcam image showing the Bellegarde patch on the Rochette rock. (F) Navcam  
498 image showing the Guillaumes patch on the Roubion outcrop. (G) WATSON images of abraded  
499 targets analyzed in this study. Greyscale images for the colorblind are available in Fig. S9-S11  
500 (8).

501

502 **Fig. 2: SHERLOC Raman and fluorescence results for the Garde abraded patch.** (A)  
503 WATSON image. (B) Context image and scan outlines. (C-G) Grey-scale version of context  
504 image with data superimposed. (C) Fluorescence map showing the intensity of three main  
505 features centralized at 340 nm, 305 nm, and 285 nm in red, green, and blue respectively. (D)  
506 Raman mineral maps showing the location of detected olivine, carbonate, phosphate, and weak  
507 amorphous silicate features. White numbers as well as purple and green region of interest  
508 outlines (ROIs 1-2) were used for spectra shown in panel H. (E) Zoom in on panel B shows  
509 fluorescence correlation with intergranular spaces (outlined in white lines). (F) Fluorescence map  
510 from detail scan. (G) Raman map from detail scan and ROI 3-4 outlines intergranular and  
511 mineral domain textures (same legend as panel D) used in panel H. (H) Average ROI and single  
512 point (1-2) SHERLOC spectra (positions in panel D and G) compared with laboratory  
513 measurements. Greyscale images for the colorblind are available in Fig. S12-S15 (8).

514

515 **Fig. 3: SHERLOC Raman and fluorescence results for the Guillaumes abraded patch.** (A)  
516 WATSON image. Two SHERLOC scans (yellow outlines) and one PIXL scan (black outline)  
517 shown. (B) Context image and scan outlines. (C) Average Raman spectrum compared with  
518 laboratory measurements of amorphous silicate, Na-perchlorate, and anhydrite. Laboratory  
519 spectral features at 1500-1600  $\text{cm}^{-1}$  are  $\text{O}_2$  (vertical, dotted line) and organic contaminants. (D-F)  
520 Grey-scale version of context image with data superposed. (D) Fluorescence map showing the  
521 intensity of three main features centralized at 340 nm, 305 nm, and 275 nm in red, green, and  
522 blue respectively. White circles indicate locations exposed to LIBS shots (8). (E-F) Low and  
523 high SNR [8] Raman mineral maps showing the locations of detected perchlorate, Ca-sulfate  
524 with and without hydration, and 965  $\text{cm}^{-1}$  peaks. (G) Raman spectra (positions indicated with  
525 numbers in panel E-F) from SHERLOC (1-4) compared with laboratory measurements.  
526 Greyscale images for the colorblind are available in Fig. S16-S19 (8).

527

528 **Fig. 4: SHERLOC Raman and fluorescence results for the Bellegarde abraded patch.** (A)  
529 WATSON image. (B) Context image and scan outlines (C) Average Raman spectrum compared  
530 with laboratory measurements of amorphous silicate and obsidian. Laboratory spectral features at  
531  $1500\text{-}1600\text{ cm}^{-1}$  are  $\text{O}_2$  (vertical, dotted line) and trace organic contaminants. (D-F) Grey-scale  
532 version of context image with data superposed. (D) Fluorescence map showing the intensity of  
533 three main features centralized at 340 nm, 305 nm, and 275 nm in red, green, and blue  
534 respectively. (E-F) Low and high SNR (8) Raman mineral maps showing the location of detected  
535 Ca-sulfate with and without hydration, carbonate, and  $975\text{ cm}^{-1}$  peaks. (G) Raman spectra  
536 (positions indicated with numbers in panel E-F) from SHERLOC (1-3) compared with laboratory  
537 measurements (full hydrated sulfate spectrum in Fig. S3 (8)). Greyscale images for the  
538 colorblind are available in Fig. S20-S23 (8).

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## Supplementary Materials for

### **Aqueous alteration processes and implications for organic geochemistry in Jezero crater, Mars**

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## Materials and Methods

### S1. SHERLOC operation

SHERLOC is a deep-ultraviolet Raman and fluorescence spectrometer (29) mounted on the turret at the end of *Perseverance*'s robotic arm, alongside a high-resolution camera named WATSON (Wide-Angle Topographic Sensor for Operations and eNginEering) (7). SHERLOC operates by scanning the target surface with a 110  $\mu\text{m}$  diameter, 248.5794 nm pulsed laser, collecting any back-scattered Raman scattering and fluorescence emissions produced by illuminated material in the near-subsurface, which are detected by a 512x2048 pixel e2v 42-10 CCD kept at  $-28\text{ }^{\circ}\text{C}$  by a phase change material. The laser spot is moved from point to point in a grid by an internal scanning mirror, acquiring a combined Raman and fluorescence spectrum for each point. Spectra are measured between 250 and 354 nm, at a spectral resolution of 0.269 nm ( $\sim 40\text{ cm}^{-1}$  in the Raman region) and 0.071 nm/pixel ( $\sim 10\text{ cm}^{-1}$ /pixel). By using deep-ultraviolet excitation, the Raman spectrum is compressed into a narrow spectral range (250–275 nm) that is relatively free of fluorescence signal, allowing for spectral separation of the two phenomena in a single measurement. SHERLOC scans can be up to 1296 points, and cover an area of up to 7x7 mm. The hollow cathode NeCu laser spot is annular in shape, with an outer diameter of  $\sim 110\text{ }\mu\text{m}$ , and is fired in 40  $\mu\text{s}$  pulses at 80 Hz, with an estimated pulse energy of  $\sim 9\text{ }\mu\text{J}$  at the start of mission. The instrument has a working distance of 48 mm, and focusing is achieved using an autofocus context imager (ACI), which also acquires a high-resolution, grayscale image of the target surface at  $\sim 10.1\text{ }\mu\text{m}/\text{pixel}$ . SHERLOC typically operates after local sunset, to maximize the time that the phase change material (PCM) can maintain the detector's ideal operating temperature of  $-28\text{ }^{\circ}\text{C}$  (7).

### Arm placement accuracy

Based on pre-launch assessments of arm placement accuracy under terrestrial gravity, *Perseverance*'s robotic arm is capable of placing SHERLOC within 12 mm of a targeted location. Lateral arm drift during operation is expected to be  $<100\text{ }\mu\text{m}/\text{min}$  (7). The SHERLOC scanning mirror itself has a positioning error of  $<22\text{ }\mu\text{m}$  at the target.

### Spectral calibration, resolution and accuracy

The SHERLOC spectral calibration during surface operations on Mars has an estimated uncertainty of  $\pm 5\text{ cm}^{-1}$  ( $\pm 0.004\text{ nm}$ ) in the 700–1800  $\text{cm}^{-1}$  region (253.0–260.2 nm). The uncertainty was estimated by analyzing observed Raman peak positions for the ten SHERLOC calibration target materials mounted to the front of the rover, which were measured on sols 59 and 181, and comparing them to pre-launch values obtained on a laboratory instrument (30). This comparison was done to evaluate any potential changes in calibration that may have occurred during launch, cruise, or landing, and determined that a small linear correction was needed, as described by (30). The stated spectral uncertainty reflects the updated calibration, which was applied to all spectra reported in this article.

### Target selection and sampling

Once selected, each target presented here was abraded by *Perseverance*'s abrasion tool prior to characterization by SHERLOC (1). The abraded patch is circular, approximately 45 mm in diameter, and 8–10 mm deep (Fig. 1). The abraded patch was then cleaned of dust/tailings using a jet of compressed gas from the gas Dust Removal Tool (gDRT), providing a clean, flat rock surface for proximity science analysis (1). SHERLOC operates by scanning the target surface in a grid in order to construct Raman mineral and fluorescence maps, and analyses generate three different types of scans, referred to as survey (coverage: 5x5 mm, resolution: 140  $\mu\text{m}$ ), high-dynamic range (HDR) (coverage: 7x7 mm, resolution: 740  $\mu\text{m}$ ), and detail scans (coverage: 1x1 mm, resolution: 100  $\mu\text{m}$ ). In addition, survey scans are shot with 15 pulses per point (ppp), HDR scans are shot with between 250-500 ppp, and detail scans are shot with 500 ppp. This means survey scans will have low SNR Raman spectra compared with Raman spectra from HDR and detail scans. Hence, fluorescence and low SNR Raman mineral maps in Fig. 3-4 were created from survey scan results. High SNR Raman mineral maps were created from HDR scans in Fig. 2-4. Both fluorescence detail and Raman detail maps were created from detail scans in Fig. 2. Further detail for the scans performed on each target can be read below.

**Guillaumes:** The Guillaumes abraded target was characterized over sols 161–162. On sol 161, SHERLOC conducted one survey scan of 36x36 points in a 5x5 mm area at 15 pulses per point (ppp), and three co-located high dynamic range (HDR) scans of 10x10 points in a 7x7 mm area at 100, 100, and 300 ppp respectively. On sol 162, SHERLOC was positioned over a second area of the abraded target (Fig. 3) and conducted one survey scan of 36x36 points in a 5x5 mm area at 15 ppp and two co-located HDR scans of 10x10 points in a 7x7 mm area, both at 250 ppp. The results of the sol 162 survey and HDR #2 scans are shown in Fig. 3.

**Bellegarde:** The Bellegarde abraded target was characterized on sol 186 using one survey scan of 36x36 points in a 5x5 mm area at 15 ppp, and two HDR scans of 10x10 points in a 7x7 mm area, both at 250 ppp. The results of the survey and HDR #2 scans are shown in Fig. 4.

**Garde:** The Garde abraded target was characterized over sols 207–208. On sol 207, SHERLOC conducted one survey scan of 36x36 points in a 5x5 mm area at 15 ppp, and two HDR scans of 10x10 points in a 7x7 mm area, both at 500 ppp. On Sol 208, SHERLOC conducted three detail scans of 10x10 points in three different 1x1 mm areas that overlapped with the survey area, all at 500 ppp. The results of the fluorescence survey, HDR #2 scans, and the central detail scan are shown in Fig. 2.

### S2. Spectral Processing

Due to the curved projection of the DUV spectrum onto SHERLOC's detector, the CCD is divided into three vertical binning regions that are read out separately in order to minimize noise. For each region in each spectrum, an active frame is acquired while the laser is firing and a dark frame is acquired with the same duration without triggering the laser, which is then subtracted from the active frame. The full 250–354 nm spectrum can be obtained by recombining the three

regions, but this introduces additional noise in the Raman region that may obscure weak Raman signals. To avoid this when generating Raman data products, Region 1 (250–284 nm) is processed separately without recombination. Large positive (active frame) and negative (dark frame) spikes in the spectral data that were typically <3 pixels wide were due to cosmic rays impacting the detector during an acquisition.

Initial data processing was done using NASA internal software produced at the Jet Propulsion Laboratory by K. Uckert, named Loupe. Full processing includes dark frame subtraction, normalization to measured laser output, and cosmic ray removal using the method described in (31). Loupe also provides functionality for correlating individual spectra to specific points on the ACI image based on scanning mirror positioning. Further data processing was done using custom Python scripts, following methods described in (13). This includes polynomial baseline subtraction, automatic peak detection, and determining peak positions via Gaussian fitting. The requirements for automatic peak detection are local maxima that are at least  $50 \text{ cm}^{-1}$  apart, >5% of the spectrum's maximum intensity (after baseline subtraction), and >2 times the background noise (estimated as the standard deviation of baselined intensity in the peak-free region between 2000 and  $2100 \text{ cm}^{-1}$ ). Furthermore, peak identification was also performed semi-quantitatively and subsequently compared to automated detections. Semi-quantitative detections were performed by identifying peaks with intensity >2 times the noise and a full-width half maximum that is >3 pixels ( $> \sim 30 \text{ cm}^{-1}$ ) wide. In all cases, peak fitting was performed by assigning a Gaussian function to each peak, and freely fitting the sum Gaussian curve to the data via either linear least square regression using the LMFIT python package (32) or the Levenberg-Marquardt method using the Scipy python package (33).

### Mineral identification

Mineralogical assignments were done by comparing baselined SHERLOC spectra and fitted peak positions to the SHERLOC spectral library, a database of spectral standards for minerals and organic compounds measured on Earth using the Brassboard instrument, an optical analog of the SHERLOC flight model that was adapted to function under terrestrial ambient conditions (13). The mineral standard spectra shown in Figs. 2-4 are taken from the database and described in detail by (13) with the exception of perchlorate spectra obtained later, which are detailed below. Following mineral identification of each automated and semi-quantitatively defined peak through above-described methods, we constructed mineral maps of each obtained grid point within Figs. 2-4. Deriving quantitative concentrations of minerals from the Raman spectra is not currently possible (34). Details outlining different Mars-relevant minerals and rocks ability to attenuate UV radiation and thus the SHERLOC DUV laser are detailed in (35). As different minerals have different Raman scattering cross sections and peak intensities, not all points scanned exhibit peaks above the level of detection for a mineral phase, and will therefore appear unclassified.

### Raman and fluorescence intensity maps

Spectral intensity maps of both Raman and fluorescence spectra were generated using three pre-defined spectral bands, and assigning the summed intensities of each band in each spectrum to the R, G, B values of the corresponding pixel, normalized to the 2% and 98% percentiles for all three bands across the entire map. For fluorescence maps, R, G, B values represent the 330–350 nm, 295–315 nm, and 265–285 nm bands, respectively, of the full composition spectrum; for Raman maps, R, G, B values represent the 1075–1125  $\text{cm}^{-1}$ , 995–1045  $\text{cm}^{-1}$ , and 945–995  $\text{cm}^{-1}$  bands of the baselined Region 1 spectrum. The Raman spectral intensity maps were compared to the mineral identification maps for secondary validation, and the resulting product is the presented mineral maps in Figs. 2-4.

### Olivine doublet peak convolution

SHERLOC detection of olivine in Garde was based on the appearance of a single Raman peak at 820–840  $\text{cm}^{-1}$ , rather than the doublet at  $\sim 820$  and  $\sim 850$   $\text{cm}^{-1}$  that has been widely reported for olivines in the literature (36-37). The convolution of the olivine doublet into a single peak was also observed in laboratory measurements of olivines using the Brassboard, SHERLOC's terrestrial analog instrument, and is due to the 40–50  $\text{cm}^{-1}$  spectral resolution of both instruments, as described in (13). It may still be possible to quantitatively derive olivine Fo# compositions from the convoluted peak position, based on the shifting doublet positions reported in (36-37), but current analysis is limited to qualitatively associating lower Raman shifts to lower Fo#.

### S3. Image processing

SHERLOC includes two imaging subsystems, each equipped with a CCD camera: the Wide Angle Topographic Sensor for Operations and eNginEering (WATSON) and the Autofocus Context Imager (ACI) (7,38). WATSON provides color imaging (1600 x 1200-pixel) of analysis targets from 2.5-40cm standoff distances. WATSON is able to contextualize the SHERLOC and PIXL instrument data, acquire stand-alone observations of rock surfaces, and image rover components and calibration targets to maintain the instruments onboard. The ACI acquires high-resolution grayscale images (1600 x 1200-pixel,  $\sim 10.1$   $\mu\text{m}/\text{pixel}$  spatial scale) at a working distance of 4.5-5 cm to focus SHERLOC's laser and provide context for spectroscopic measurements (7). Both of these imaging subsystems' camera heads are mounted atop a rotatable turret on the robotic arm of the Perseverance rover, and can be independently positioned on a chosen target to provide complementary information, though they are not co-boresighted (7).

The ACI focus merge products used here were created on Earth and flat-fielded using "sky flat" images acquired by ACI of the Martian sky on Sol 77. ACI focus stacks consist of 31 images obtained at different focus positions that capture the scene in increments of  $\sim 0.2$  mm focus range (e.g., 45.0 mm to 50.4 mm in 31 steps). Images outside the below ranges were not in focus and

thus not used in the creation of the focus merge products. The images used in each focus merge product were as follows:

Guillaumes\_161 - sol 161 - images 16-26 of 31

Guillaumes\_162 - sol 162 - images 13-31 of 31

Bellegarde\_186 - sol 186 - images 15-20 of 31

Garde\_207 - sol 207 - images 15-19 of 31

Dourbes\_257 - sol 257 - images 14-21 of 31

Dourbes\_269 - sol 269 - images 14-20 of 31

Image registration and processing was performed using a custom Python script that utilized corresponding ACI (non-focus merged) and WATSON (onboard focus merge) images for a target to create an overlay. Keypoint detection was performed using the Binary Robust Invariant Scalable Keypoints (BRISK) method (39) and subsequently matched using the Fast Library for Approximate Nearest Neighbors (FLANN) based matcher utilizing the OpenCV python package (40). Colors from the two images were blended in hue, saturation, value (HSV) space to create a “colorized” ACI. Each colorized ACI was then overlaid with a map of laser points targeted by SHERLOC and generated in Loupe for each scan type (see S2).

#### S4. Assessment of carbonate and olivine compositions

The carbonate peak positions observed within interstitial materials and surrounding grains are observed to be within  $\pm 5 \text{ cm}^{-1}$  uncertainty of each other (Fig. 2.H). Laboratory data show that Mg-rich carbonates, such as dolomite and magnesite, have peak positions of 1095-1100  $\text{cm}^{-1}$ , while Ca-rich and Fe-rich carbonates have peak positions at 1080-1087  $\text{cm}^{-1}$  (13-14). Although some of our carbonate measurements fall within the uncertainty of these ranges, wavenumber peak positions mostly between them suggest solid solutions of either Fe-Mg or Ca-Mg carbonate, similar to carbonates in Martian meteorites (18-19). Other Perseverance instrument observations found mixed Fe- and Mg-carbonates consistent with SHERLOC observations (9,11). The position of the olivine peak appears shifted compared to our reference spectra, which were acquired for Mg-rich olivines with Fo# 80-90 (13); lower frequency indicates that the olivines present in Garde are relatively Fe-rich by comparison (10,36-37).

#### S5. Perchlorate laboratory measurements

The measurement of reference DUV Raman spectra for synthetic perchlorate salts was done using the SHERLOC brassboard instrument, an optical analog of the flight model that was designed to work under terrestrial ambient conditions (13). The salts and their sources were as follows: sodium perchlorate monohydrate (Sigma Aldrich 310514), potassium perchlorate (Alfa Aesar A11296), magnesium perchlorate (Sigma Aldrich 63102), and calcium perchlorate hydrate (Alfa Aesar 11655), all of which had reported purities of >95%. Each salt was characterized as a powder on a clean Aluminum wafer and all measurements were done under ambient conditions;

the calcium perchlorate hydrate deliquesced during measurement. Spectra were collected and processed using the method described in (13).

#### S6. Assessment of perchlorate species

Detailed consideration of multiple different chemical compounds were considered for assignment of Guillaumes perchlorate spectra. Fig. S4 demonstrates several potential minerals that were assessed as an alternative to a perchlorate origin, including carbonate, phosphates, and sulfates. We compared our strongest SHERLOC spectra to a number of different perchlorate salts, including anhydrous and hydrated species, that were obtained through laboratory measurements with the SHERLOC Brassboard, an analog DUV Raman and fluorescence instrument at the NASA Jet Propulsion Laboratory with similar sensitivity and spectral resolution to SHERLOC. The position of the major 950–955  $\text{cm}^{-1}$  peak observed on Mars places it between the observed major peak positions of Na-perchlorate and fluorapatite. However, the observation of two minor peaks at 1090–1095  $\text{cm}^{-1}$  and 1150–1155  $\text{cm}^{-1}$  are both consistent with Na-perchlorate rather than fluorapatite, which only has a single secondary mode at 1050  $\text{cm}^{-1}$  (Fig. S4). Of the perchlorates we measured in the laboratory, only Na-perchlorate exhibits the two minor peaks we observe, the others exhibit a single minor peak at 1095–1115  $\text{cm}^{-1}$ . Therefore, despite the ~5–10  $\text{cm}^{-1}$  difference in major peak position compared to our Na-perchlorate reference, we are confident that we have observed Na-perchlorate on Mars. When comparing SHERLOC spectra to hydrous and anhydrous versions of Na-perchlorate from (41), we find that there is no conclusive difference in match to minor peaks. However, the only spectral evidence we have for hydration (the O–H stretching mode around 3300  $\text{cm}^{-1}$ ) was observed in locations that exhibited sulfate peaks, indicating a hydrated sulfate species rather than a hydrated perchlorate species. Last, we compared our spectra to those obtained for other oxygen chloride and chlorate species by a previous study (41). Higher oxidative states will systematically shift the peak position upwards and will also alter the position of minor peaks. No examined alternative Na oxygen chlorides or chlorate yielded a match with either major or minor peaks of the SHERLOC spectra. It is possible that – yet unexamined – down-shifting of peaks related to other cation oxygen chlorides or chlorates, such as Ca and Mg species, could explain the major 950–955  $\text{cm}^{-1}$  peaks. However, these would not be able to explain the position and shape of the two minor peaks that appeared in our strongest spectra.

#### S7. Assessment of fluorescence correlation with SuperCam LIBS shots

The two bright ~275 nm spots in Guillaumes, which are co-located with previous LIBS shots, are likely fluorescence emission from 1-ring aromatics either created by the LIBS plasma, or exposed by ablation of surface material. Given that this was done on an already abraded surface, it seems unlikely that we are examining pristine 1-ring aromatics in the sub-surface, instead we suspect that we are seeing the 1-ring aromatics produced by LIBS-induced photochemical breakdown of MMC (macromolecular carbons) present within the rock. However, we cannot

currently rule out the possibility that LIBS-induced crystal defects within the exposed rock may be producing the observed luminescence.

#### S8. Comparison between SHERLOC mineral identifications and other instruments

SHERLOC Raman detections of sulfates within the Bellegarde target correlate directly with Ca-sulfate detections and minor Mg-sulfate components by the PIXL elemental maps, cementing the interpretation of secondary mm-scale Ca/Mg-sulfate crystals (Fig. S5). The PIXL elemental maps also reveal closely spaced Ca-sulfate and Na-Cl phases correlating with white, anhedral patches within the Guillaumes target, but the maps were not measured over the same area as the SHERLOC Raman map (Fig. S6). Lastly, SuperCam LIBS and Raman observations also confirm the presence of mixed Na-Mg-Cl phases, Na-perchlorate, and Ca/Mg-sulfates within partially overlapping measurements compared to SHERLOC in Guillaumes and Bellegarde (9).

In the remaining measured spots that cover the primary texture within the Guillaumes and Bellegarde targets, we did not detect definitive mineral Raman peaks. However, the average spectra for each scan of Guillaumes and Bellegarde reveal the presence of a broad peak centered at  $1060\text{ cm}^{-1}$  with a full width half maximum (FWHM) of  $160\text{ cm}^{-1}$  and low intensity, consistent with amorphous silicate. This spectrum was similar to the single-point detection of amorphous silicate found within Garde. PIXL observations of Bellegarde and Guillaumes indicate primary phases consist of pyroxene, plagioclase, and olivine, which were not observed in the SHERLOC data (Fig. S5-S6) (9). SHERLOC cannot report on the presence of plagioclases, as the dominant Raman peak of plagioclase (around  $500\text{ cm}^{-1}$ ) falls within the spectral range of SHERLOC's edge filter, which significantly attenuates signal below  $700\text{ cm}^{-1}$  and makes peaks in this range harder to detect (13). Fe-rich pyroxenes and olivines may not have been detected for a number of reasons, for example low abundance, crystallographic orientation, or attenuation of the DUV signal due to Fe or opaqueness (13,35,42). Alternatively, some of these phases may also be significantly disordered giving rise to broader, weaker Raman peaks similar to amorphous silicate signatures. Modeling of orbital data from the Thermal Emission Spectrometer predicted ~24% and ~15% amorphous silicate components within the Máaz and Seitah formations (43). The Curiosity rover also detected 15-70 wt% X-ray amorphous components within samples of sedimentary rocks in Gale crater, suggesting the presence of amorphous silicates may be a common phenomenon on Mars (44). While the SHERLOC Raman detections of amorphous silicates at present cannot distinguish between the proposed origin as volcanic glass, impact glass, or aqueous alteration of previously crystalline silicate phases, the amorphous silicates within Gale crater have been found to be more consistent with aqueous alteration of previously crystalline silicate phases (44).

#### S9. Fluorescence assignment and laboratory measurements of phosphates

SHERLOC is capable of detecting organic material via DUV fluorescence emission and Raman scattering, and is most sensitive to compounds containing 1- and 2-ring aromatic units and/or aromatic heterocycles, which typically fluoresce within SHERLOC's spectral range (29,45-47)

(Fig. S7). Aromatic organic compounds typically dominate SHERLOC spectra, due to strong fluorescence emission and molecular resonance enhancement of Raman scattering (29,45-47) (Fig. S7). The only currently known inorganic material that causes fluorescence at the wavelengths relevant to the SHERLOC instrument is Ce (48-51). All other known inorganic materials in context with the measured mineralogy fluoresce at wavelengths higher than 350 nm (47,50). Hence, fluorescence signals centered at 275 nm, 285 nm, and 305 nm within the Bellegarde and Garde targets can be assigned to aromatic organic compounds with no interference from rare earth element fluorescence.

Some inorganic complexes, specifically Ce-containing phosphates such as merrillite or apatite, are known to fluoresce with maxima between 340 and 350 nm (47,49-50) (Fig. S8). A series of laboratory experiments were conducted on the Analogue Complimentary Raman for Operations on Mars (ACRONM) SHERLOC analogue instrument at NASA Johnson Space Center. The ACRONM instrument build was modeled after the MOBIUS instrument, described in (13). Incident excitation is produced using a PhotonSystems NeCu70-248 hollow cathode laser producing 248.5794 nm excitation with a  $\sim 100$   $\mu\text{m}$  beam spot. The Raman scattered light is dispersed using a Horiba Scientific iHR 320 spectrometer equipped with a 300 g/mm grating. Fluorescence spectra of apatites with measured Ce concentrations (Table S1) were collected using a 20 Hz laser pulse rate with a 40  $\mu\text{s}$  pulse width and  $\sim 4.7$   $\mu\text{J}$ /pulse laser energy at the sample. For collection of a single spectrum, we averaged 30 spectra collected at the same point on the sample, each with an accumulation time of 0.01 seconds. For each apatite sample in Table S1, ten single spectra were collected at different sample locations to account for any heterogeneity of the fluorescence signal. For all samples, the fluorescence band positions and shapes were consistent for all ten points. The ten spectra were averaged for each sample, producing a single fluorescence spectrum representative of each sample, which are presented in Figure S8. Spectra were baselined using a linear function. The average spectra were then used to extract the band parameters presented in Table S1. It can be observed that even 100 ppm of Ce present in phosphates can result in fluorescence features centered at 340-350 nm, which overlaps with the fluorescence signal of 2-ring aromatics such as naphthalene (Fig. S8). Notably, no fluorescence signals centered at 275 nm, 285 nm, and 305 nm occur within the phosphate samples.

Within Bellegarde, one peak at  $975\text{ cm}^{-1}$ , designated as a possible phosphate detection, also exhibited a 340 nm fluorescence response. However, the 340 nm fluorescence signal was more widespread within this target and predominantly occurred without  $975\text{ cm}^{-1}$  peaks. Furthermore,  $975\text{ cm}^{-1}$  peaks were detected without the 340 nm fluorescence response. In Guillaumes, the 340 nm fluorescence did not correlate with any particular mineral phase, occurred throughout the target, and phosphate-designated  $965\text{ cm}^{-1}$  peaks occurred without the presence of 340 nm fluorescence. Fluorescence signals are stronger in intensity than Raman detections. Hence, it could be possible that 340 nm fluorescence from Ce-containing phosphate is detected, while the Raman signature of phosphates are not. It is also possible that other Ce-containing phases could

cause 340 nm fluorescence. However, we note that in general Ce-concentrations in phosphates are higher compared to those in other phases known to be present in the target, as Ce preferentially substitutes into phosphates. All of the laboratory measurements of other relevant phases for the Martian targets performed to this date on SHERLOC analogue instruments (*e.g.* 13-14) did not exhibit fluorescence signatures, except for the mentioned phosphates. As such, it is expected that phosphate would be the prime producer of Ce-associated 340 nm fluorescence. Several phosphate-designated  $965\text{-}975\text{ cm}^{-1}$  peaks occurred in both Bellegarde and Guillaumes targets without the presence of 340 nm fluorescence, suggesting that these materials did not produce an inorganic 340 nm fluorescence peak related to their Ce-content. While Ce-containing phosphate may explain part of the 340 nm fluorescence signatures in Bellegarde, the 340 nm fluorescence is predominantly uncoupled to phosphate detections in both Bellegarde and Guillaumes. This suggests that part of 340 nm features are presently best explained as two ring aromatic compounds.

Within the Garde target, several measurement points, specifically within detail scans (Fig. 2.F-G), showed correlation between fluorescence signals centered at 340 and 285 nm and phosphate-designated Raman peaks positioned at  $955\text{-}965\text{ cm}^{-1}$ . In this case, the intensity of the probable phosphate detections were observed to co-vary with the intensity of the 340 nm fluorescence as examined with a linear regression that resulted in  $R^2=0.95$ . However, we note that phosphate-designated  $955\text{-}965\text{ cm}^{-1}$  detections within the scan of Fig. 2.D did not exhibit 340 nm fluorescence, similar to observations of Bellegarde and Guillaumes. Two hypotheses are possible for the origin of the phosphate and 340 nm fluorescence correlation in Garde. (1) 340 nm fluorescence is the result of Ce-bearing phosphate, which would explain the covarying intensity, while 285 nm fluorescence is the result of aromatic organics. (2) Aromatic organics that give rise to both 340 nm and 285 nm fluorescence preferentially occur within alteration/weathering zones that happen to be phosphate-containing. SHERLOC-WATSON characterized the 340 nm and 285 nm fluorescence features to occur in brown, microcrystalline interstitial zones affiliated with phosphate, carbonate, and amorphous silicates. Thus, these materials, including phosphates, appear to have been influenced by secondary alteration processes that occurred after protolith formation and were likely to preserve or even synthesize organic compounds.

#### S10. Quantification of organics

Fluorescence provides an exceptionally strong signal, enabling detection of fluorescent compounds even at very low concentrations (7), while Raman is generally multiple orders of magnitude weaker than fluorescence but provides a spectrum highly specific to chemical structure, enabling identification of particular compounds. Measured Raman and fluorescence intensities are determined by laser energy at the target, the size of the illuminated volume within the target, the concentration and scattering cross-section/quantum yield of the organic molecule, and optical attenuation by surrounding material (34). The presence of certain metals that have strong absorptions in the DUV, such as Fe (35,42,48) or Ce (49), may attenuate measured signals from any organic molecules within the same sample. Because of such dependencies,

quantification of organic concentrations from either Raman or fluorescence signal yields is limited to estimations that utilize a set of assumptions and known instrument performance characteristics, and provide upper/lower bounds for concentration rather than specific values. To estimate the localized concentration and bulk concentrations observed, we utilized the optical performance model that was used to design and verify the performance of the SHERLOC instrument (9,56). The model incorporates all the primary SHERLOC instrument parameters such as the laser energy at the target, the collection performance, the noise as a function of CCD operation temperature, CCD gain, background subtraction effects to noise, dark noise, and read noise to generate an expected analog to digital count for both signal and noise. This value is dependent on the interrogation volume, the quantum yield of the compound, and its concentration within the interrogation volume. The interrogation volume is approximated by the product of the illumination area and the depth of penetration. We assume that the instrument is focused (within  $\pm 500 \mu\text{m}$  of the optimal focus) and generates a  $106 \mu\text{m}$  diameter annular beam (34). The depth of penetration into a Mars simulate with similar Fe concentrations was shown to be up to  $150 \mu\text{m}$  (35). The current estimation in the model conservatively assumes a  $75 \mu\text{m}$  depth of penetration. Using an average density of an igneous rock of  $2.7 \text{ g/cm}^3$ , the total mass analyzed in a single point measurement is  $0.6 \mu\text{g}$ . Over a 1296 point map, this equates to a total mass of  $\sim 800 \mu\text{g}$ .

To determine the concentration of organics in a single point in the map, we use a highly conservative fluorescence cross-section for benzene ( $1.5 \times 10^{-24} \text{ cm}^2 \text{ sr}^{-1} \text{ nm}^{-1} \text{ molecule}^{-1}$ ) (57) at the SHERLOC excitation wavelength,  $248.5794 \text{ nm}$ . Based on these values, the model adjusts the concentration within a single spot to achieve the detected CCD counts (Fig. S7). The mass of organics is determined for a single point. To assess bulk concentration for comparison the average fluorescence spectrum of the map is used to determine the total mass of organics detected (Fig. S7). This is then divided by the total mass in the scanned volume to derive a concentration in terms of ppm. These values are used to bound the concentration for comparison to previous analyses on Mars and of Martian meteorites and provide a means to compare the difference as we traverse through Jezero crater.

### S11. Data Sources

All SHERLOC spectral and WATSON image data used for this study is available through the NASA PDS SHERLOC data bundle (58).

Reference spectra for perchlorates, phosphates, obsidian, and organic compounds used in Fig. 2-4, Fig. S4, Fig. S7, and Fig. S8 measured in the laboratory for this study are archived (59). All other mineral laboratory spectra used in Fig. 2-4 and Fig. S4 are already published and available in (13).

Below is additional information about how to find specific datasets used for each figure.

Fig. 1: HiRISE images are available in (60).

Mastcam-Z images are available through the NASA PDS Mastcam-Z bundle (61).

Image IDs for Garde image (panel D):

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ZR0\_0207\_0685316330\_331RAD\_N0071836ZCAM08235\_1100LMA02  
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ZR0\_0207\_0685316217\_348RAD\_N0071836ZCAM08235\_1100LMA03

NavCam and Hazcam images are available through the NASA PDS ECAM bundle (62).

Specific Hazcam image link for Bellegarde (panel E):

<https://mars.nasa.gov/resources/26227/abrasion-patch-on-rochette/>

Image ID for Guillaumes (panel F):

NRF\_0160\_0681144352\_237ECM\_N0060000NCAM00314\_07\_195J.IMG

WATSON images are available from SHERLOC data bundle, Mars 2020 SHERLOC WATSON Data Collection (58). WATSON image of the Garde target (same as Fig. 2A) can be found under sol 206. WATSON image of the Bellegarde target can be found under sol 185. WATSON image of the Guillaumes target can be found under sol 160.

Fig. 2: Spectroscopic data from SHERLOC data bundle (58), Processed Spectroscopy data collection, sol 207 and sol 208 (Garde). Image data from SHERLOC data bundle, Mars 2020 SHERLOC ACI Data Collection, sol 207 and 208. Colorized by using image data from SHERLOC data bundle, Mars 2020 SHERLOC WATSON Data Collection, sol 206.

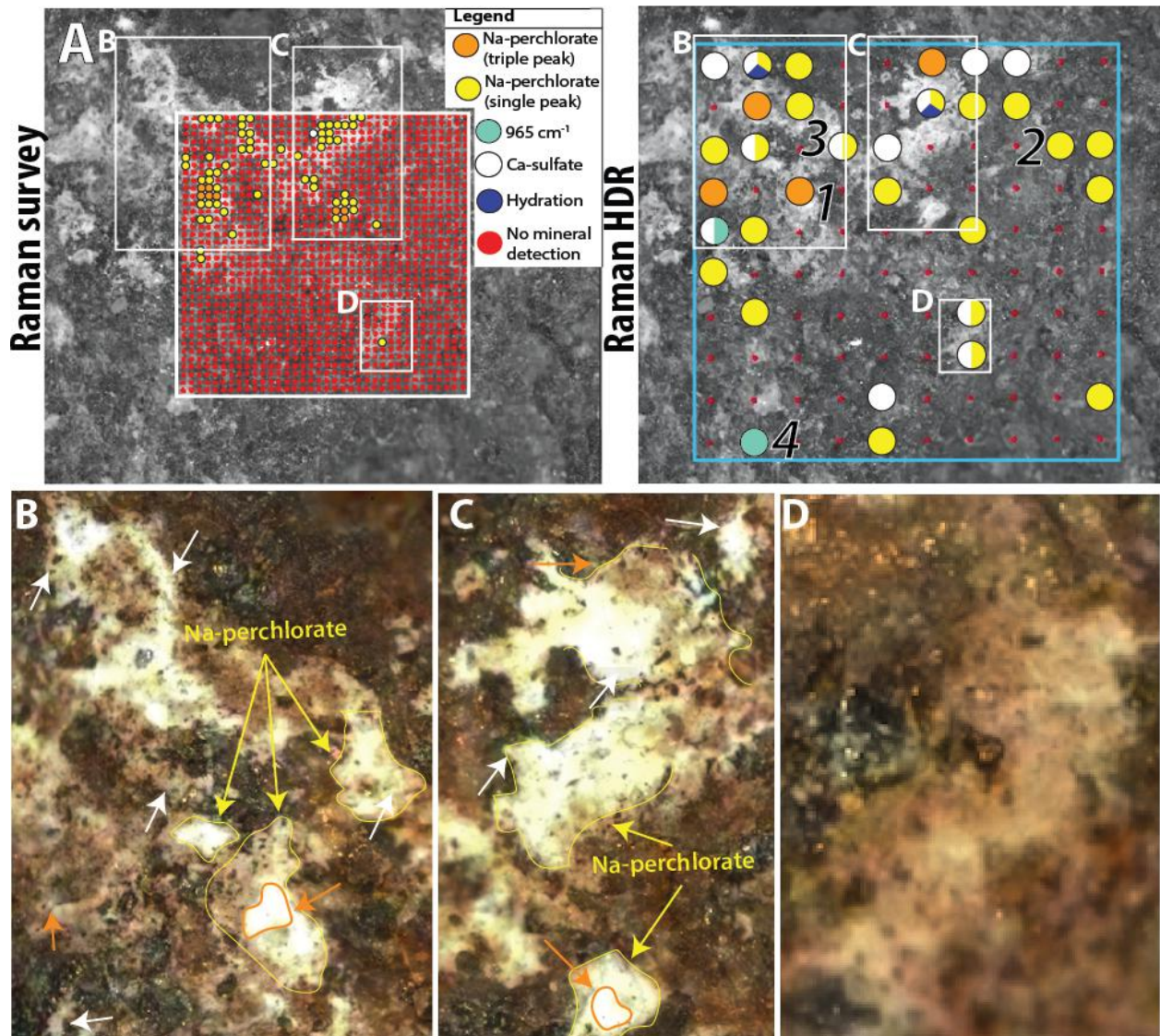
Fig. 3, Fig. S1, Fig. S4: SHERLOC data bundle (58), Processed Spectroscopy data collection, sol 162 (Guillaumes). Image data from SHERLOC data bundle, Mars 2020 SHERLOC ACI Data Collection, Mars 2020 SHERLOC ACI Data Collection, sol 162. Colorized by using image data from Mars 2020 SHERLOC WATSON Data Collection, sol 160.

Fig. 4, Fig. S3: SHERLOC data bundle (58), Processed Spectroscopy data collection, sol 186 (Bellegarde). Image data from SHERLOC data bundle, Mars 2020 SHERLOC ACI Data Collection, sol 186. Colorized by using image data from Mars 2020 SHERLOC WATSON Data Collection, sol 185.

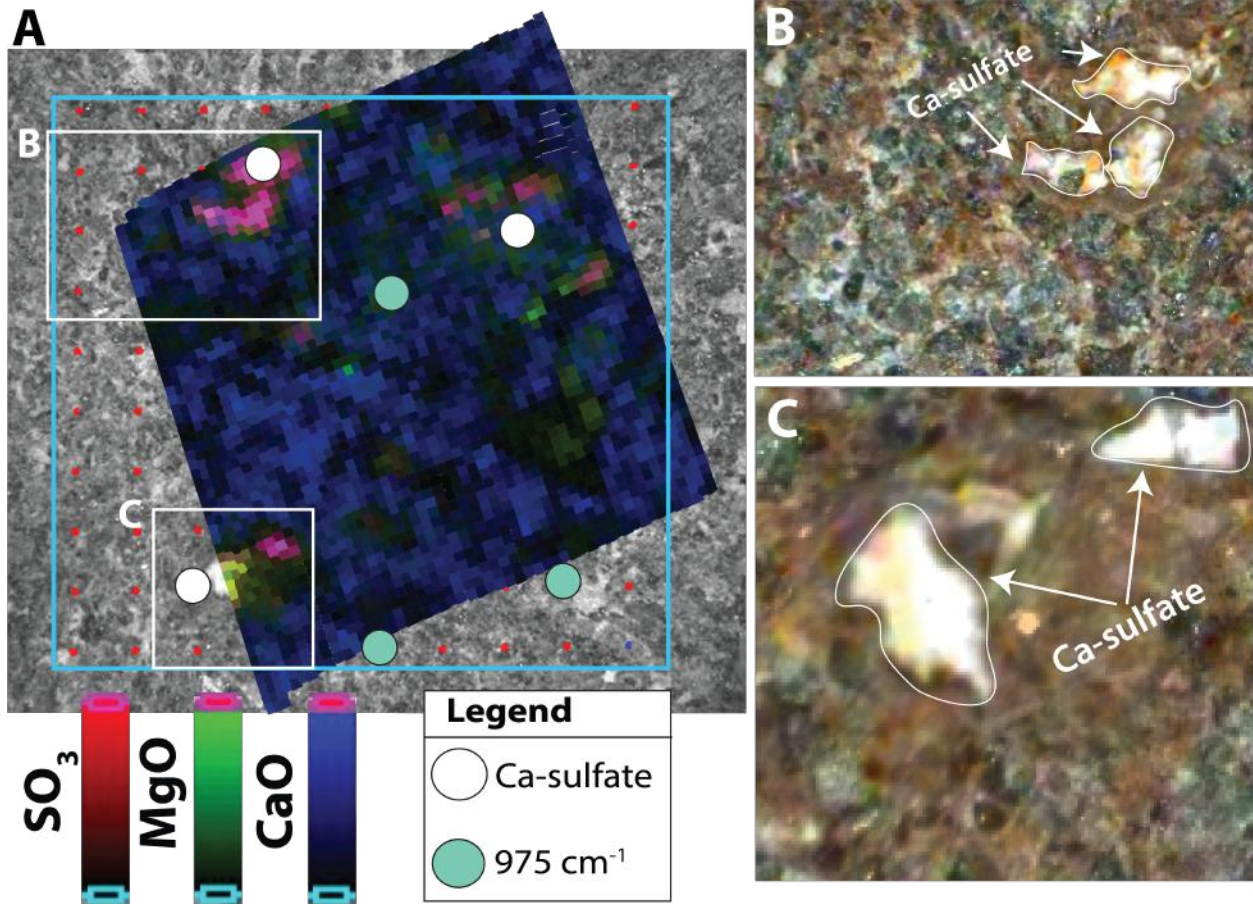
Fig. S2, Fig. S5, Fig. S6: PIXL data sets are available through the NASA PDS PIXL bundle (63). Guillaumes and Bellegarde abrasion patch data are listed under Processed data collection, sols 167 and 187, respectively. SHERLOC Bellegarde datasets are the same as for Fig. 4.

Fig. 7: Same datasets as in Fig. 2-4.

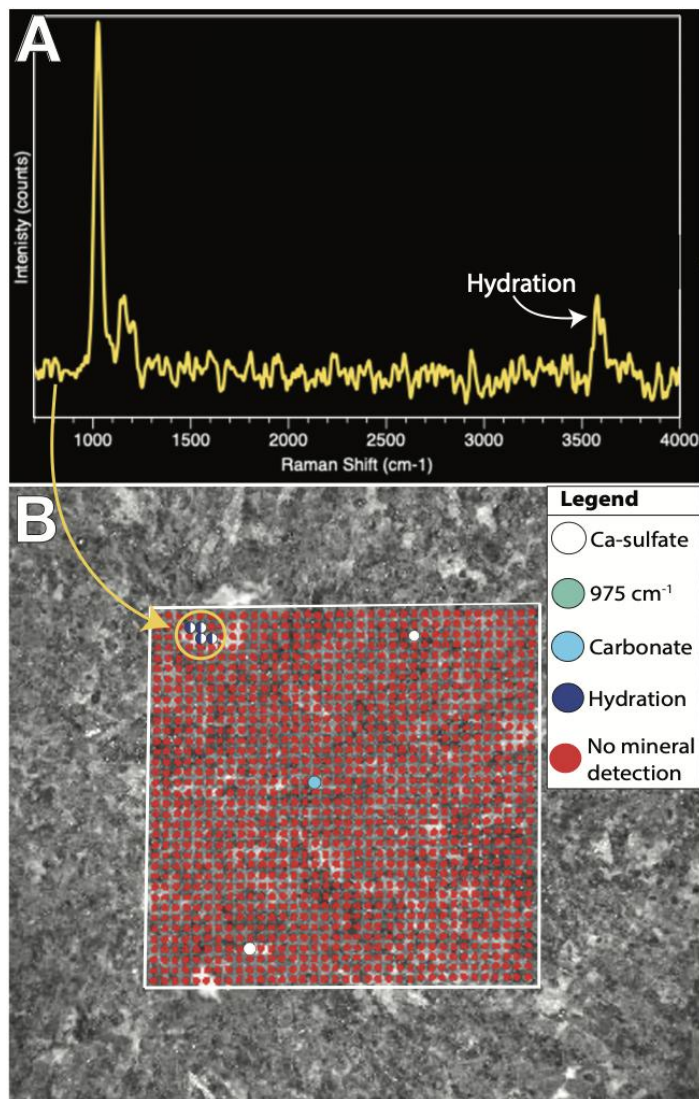
**Fig. S1. SHERLOC context and WATSON image merge showing the textures of mineral assemblages within the Guillaumes target.** (A) Mineral detections within survey and HDR scans of the Guillaumes target from Fig. 3. (B-D) Texture of high intensity Na-perchlorate detections (orange outline and arrows), low intensity less certain Na-perchlorate detections (yellow outlines and arrows) as well as occasional Ca-sulfate detections (white arrows). The mineral detections are mixed within anhedral, white, tan to reddish brown patches of material that are secondary to the primary lithology of the Guillaumes target.



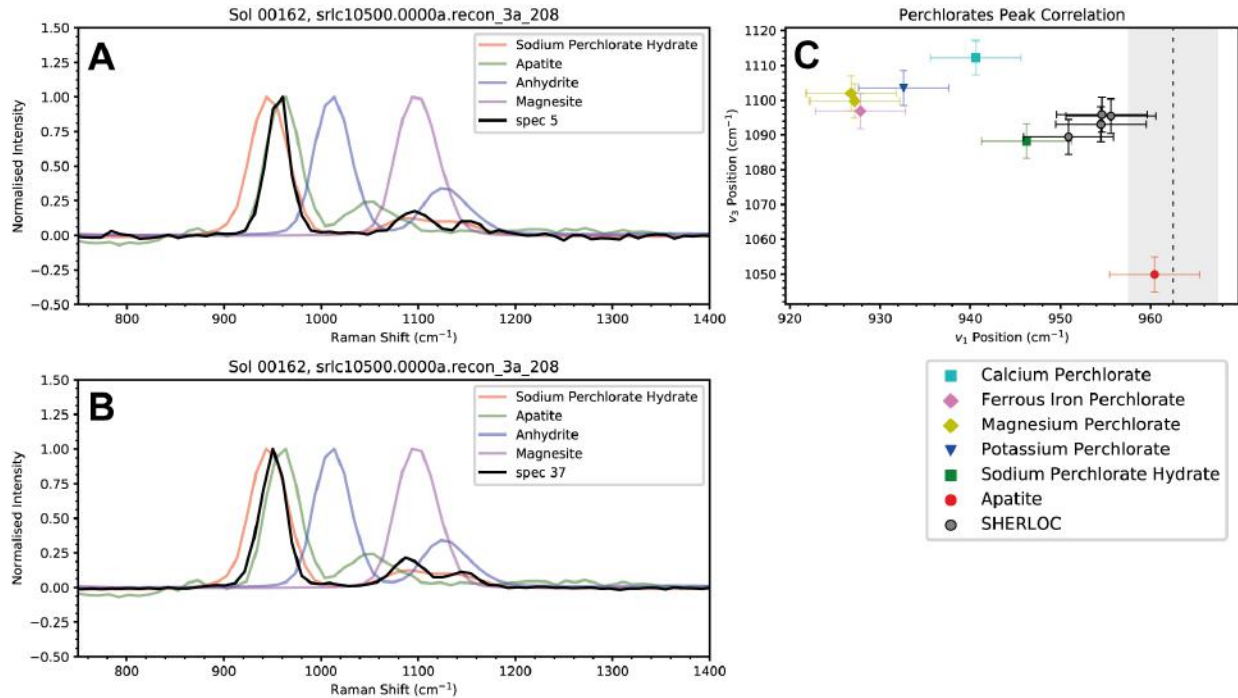
**Fig. S2. SHERLOC context and WATSON image merge showing the textures of mineral assemblages within the Bellegarde target.** (A) Mineral detections within HDR scans of the Bellegarde target overlain on the PIXL elemental chemistry map of  $\text{SO}_3$ , MgO, and CaO from Fig. S5. (B-C) Texture of Ca-sulfate detections (white arrows). Ca-sulfates are detected within white anhedral to sub-euhedral crystals that have a reddish rim around them that appear secondary to the primary lithology. Textures of possible phosphate minerals are more nebulous.



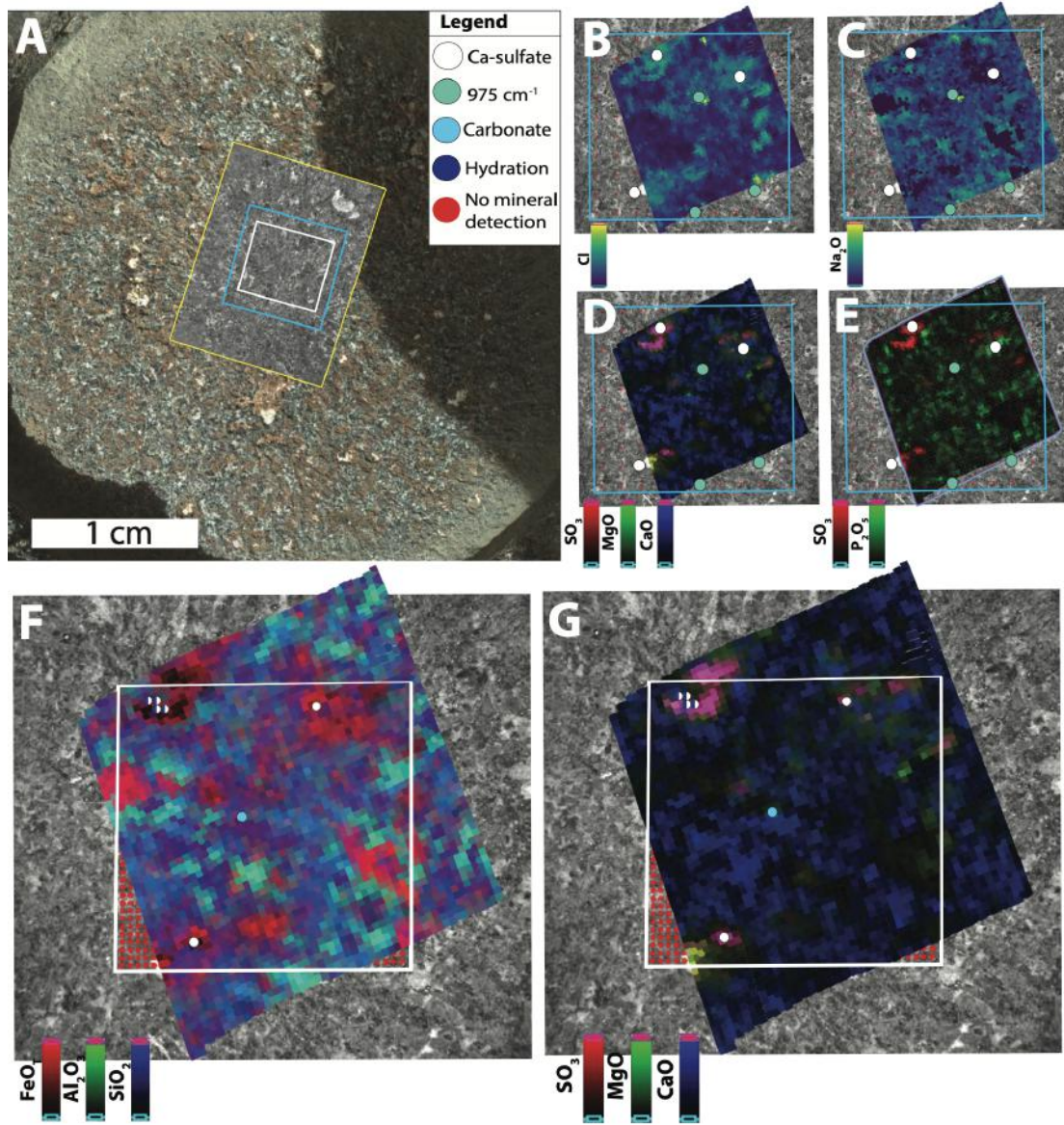
**Fig. S3. Hydration feature recorded within Bellegarde sulfates.** (A) Average SHERLOC spectrum of the sulfate material within the yellow ROI in panel B showing weak hydration feature at  $3560\text{ cm}^{-1}$ . Same spectrum as spectrum no. 1 in Fig. 4. (B) Low SNR Raman map from Fig. 4.E.



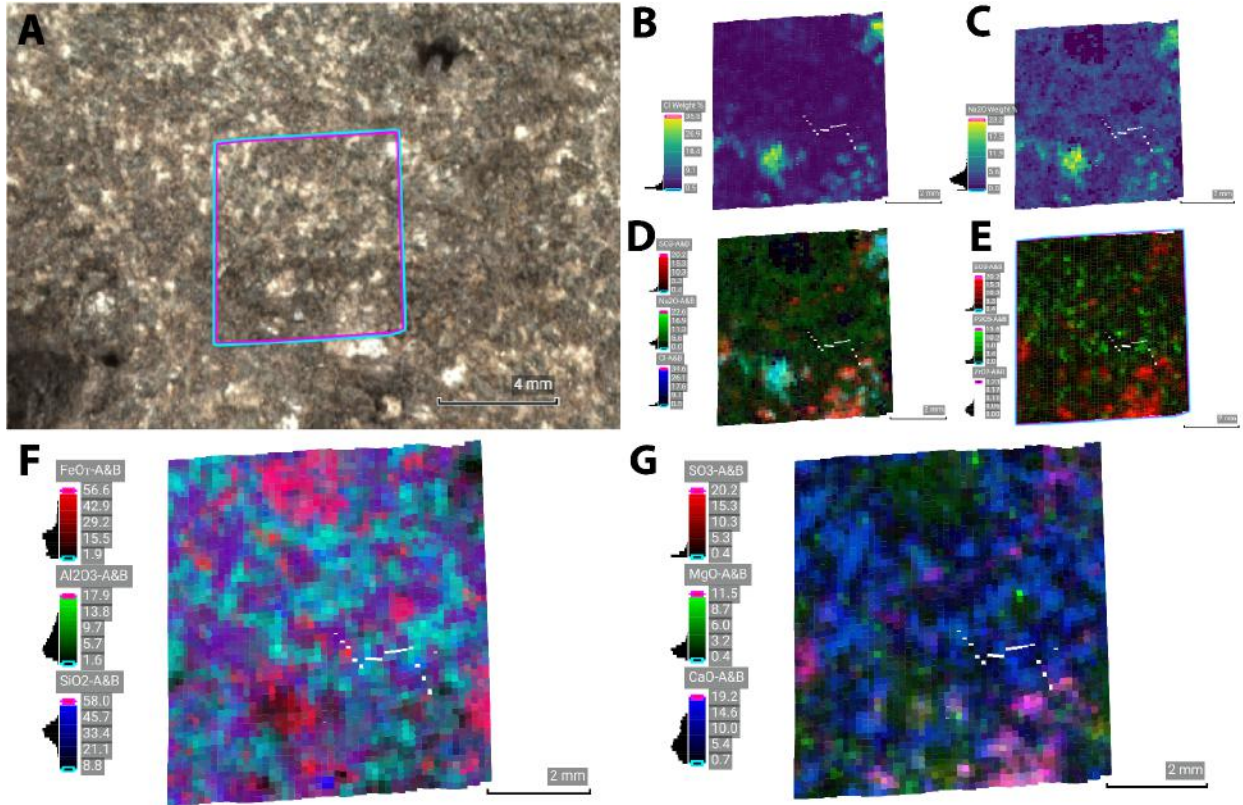
**Fig. S4. Comparison between SHERLOC spectra of perchlorate in Guillaumes target and laboratory measurements of a variety of materials.** (A,B) Spectrum 5 and spectrum 37 of HDR 2 of Guillaumes from Sol 162, compared to normalised spectra of representative perchlorate, phosphate, sulfate, and carbonate standards, showing that overall spectrum shape is most like that of perchlorate. (C) Secondary peak position plotted against primary peak position for the 4 strongest perchlorate spectra from Guillaumes, compared to all perchlorate and phosphate standards, showing that correlated peak positions are best matched to sodium perchlorate. Vertical dotted line indicates the primary peak position of SHERLOC's possible phosphate detections, whereas grey dots indicate peak positions of perchlorate detections.



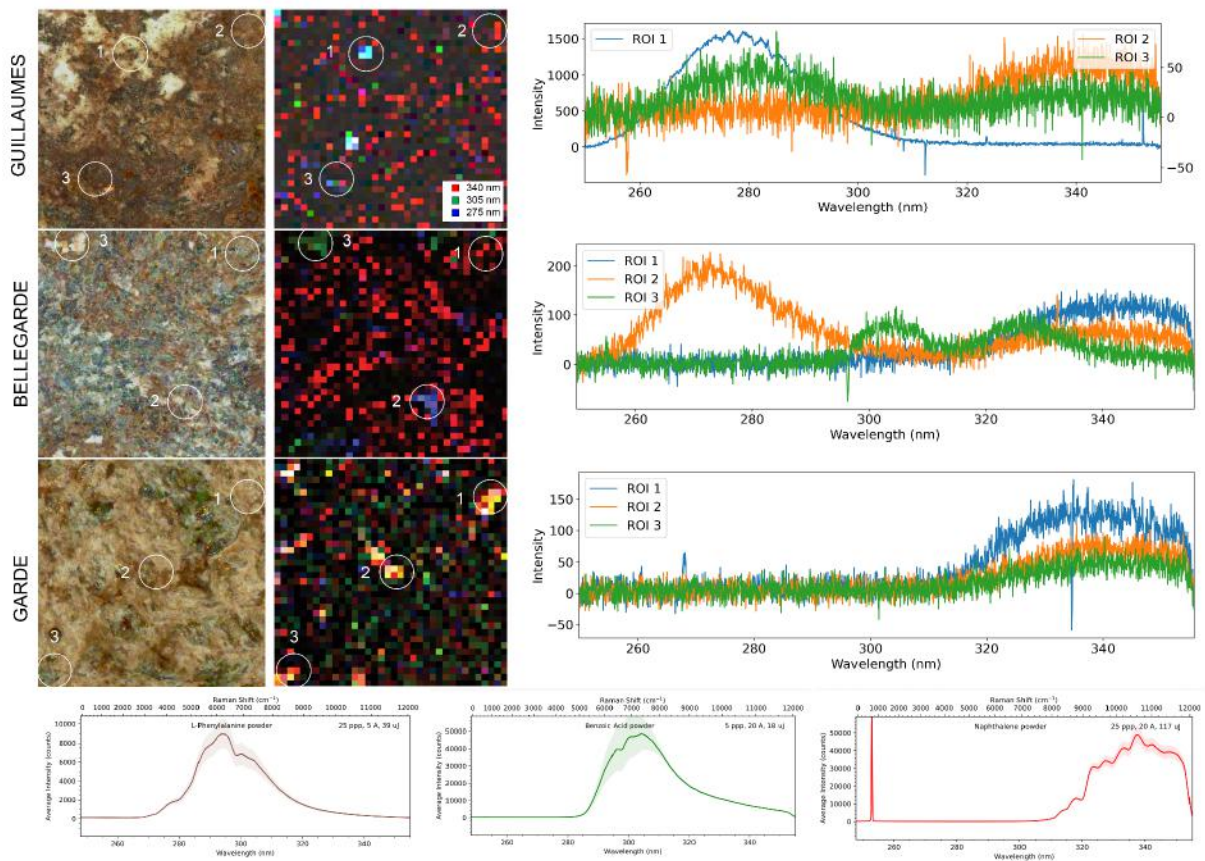
**Fig. S5. Elemental chemistry maps of the Bellegarde target produced by the PIXL instrument on the Perseverance rover in comparison to SHERLOC mineral detections.** (A) SHERLOC context image of survey scan (white rectangle) and HDR scan (cyan rectangle) superposed on WATSON image of the Bellegarde abraded target from Fig. 4. (B-C) Heatmaps of Cl and Na<sub>2</sub>O suggest the presence of a Na- and Cl-rich phase. One SHERLOC 975 cm<sup>-1</sup> peak correlates with a Na-Cl hotspot. (D) Correlations between SO<sub>3</sub> and CaO suggest the presence of Ca-sulfates (pink), which correlate with Ca-sulfate detections in HDR scans (white circles). (E) Distribution of phosphorus (green) does not obviously correlate with 975 cm<sup>-1</sup> peaks. (F) Correlations between SiO<sub>2</sub>, FeO<sub>T</sub>, and Al<sub>2</sub>O<sub>3</sub> in the PIXL map show that the primary lithology consists of silicates (cyan and purple) and Fe-oxides (red) and does not correlate with SHERLOC detections. (G) Correlations between SO<sub>3</sub> and CaO suggest the presence of Ca-sulfates (pink), which correlate with Ca-sulfate detections in survey scans (white circles).



**Fig. S6. Elemental chemistry maps of the Guillaumes target produced by the PIXL instrument on the Perseverance rover.** (A) PIXL footprint (cyan and purple outline) on PIXL context image showing the location of elemental maps in panel B-G. (B-C) Heatmaps of Cl and Na<sub>2</sub>O suggest the presence of a Na- and Cl-rich phase. (D) Spatial relationships between Ca-sulfate (red) and Na- and Cl-rich phases (cyan). (E) Distribution of phosphorus (green) in relation to SO<sub>3</sub> (red). (F) Correlations between SiO<sub>2</sub>, FeO<sub>T</sub>, and Al<sub>2</sub>O<sub>3</sub> showing that the primary lithology consists of silicates (cyan and purple) and Fe-oxides (red). (G) Correlations between SO<sub>3</sub> and CaO suggest the presence of Ca-sulfates (pink).



**Fig. S7. SHERLOC fluorescence spectra compared to laboratory measurements of simple aromatic organics.** Three regions of interest (ROIs) were selected within the fluorescence maps of the three targets, Guillaumes, Bellegarde, and Garde in Fig. 2-4. These demonstrate the variability in fluorescence signatures throughout the rocks that peak at  $\sim 275$  nm,  $\sim 305$  nm, and  $\sim 340$  nm as described in the main text. Below we show laboratory fluorescence measurements of L-phenylalanine, benzoic acid, and naphthalene made with the Brassboard analogue instrument to demonstrate that aromatic organics fluoresce at these same wavelengths. The laboratory measurements show multiple convoluted bands but at the SHERLOC resolution, there would appear as a single broad fluorescence signature similar to those observed in the targets. Note that for Guillaumes spectra, ROI 1 is shown according to the left-hand y-axis, while ROIs 2 and 3 are shown according to the right-hand y-axis.



**Table S1. Terrestrial apatite from igneous, metamorphic, and/or hydrothermal rocks.**  
 Samples used for measurements displayed in Fig. S8. Details about the apatite mineral identifications and/or compositions are provided in the references (52-55).

Standard Name	Mineral Identification	Location	Ce (ppm) <sup>1</sup>	FWHM (nm)	Peak Center (nm)	REF
Ap 001	Hydroxylapatite	Holly Springs, GA USA	400 ± 20	65.1	350.2	(52)
Ap 002	Chlorapatite	Ødegården Verk, Norway	2180 ± 40	51.9	348.5	(53)
Ap 003	Fluorapatite	Durango, Mexico	4900 ± 200	47.3	350.2	(54)
Ap 004	Fluorapatite	Atlas Mountains, Morocco	2200 ± 200	60.1	358.0	(54)
Ap 005	Fluorapatite	Eagle County, CO USA	3880 ± 80	56.7	350.0	(54)
Ap 018	Fluorapatite	Lake Baikal, Russia	111 ± 7	63	357.9	(54)
Ap 020	Mn-rich Fluorapatite	Unknown Pegmatite, India	1060 ± 90	46.3	333.2	(54)
Ap 023	F-OH apatite	Mud Tank Carbonatite, Australia	1760 ± 30	54.6	349.5	(55)

<sup>1</sup>Ce abundances determined by laser ablation inductively coupled mass spectrometry (LA-ICP-MS).

**Fig. S8. SHERLOC fluorescence spectra from the three targets compared to laboratory measurements of phosphates with different trace contents of Ce and aromatic organics.** Representative 340 nm fluorescence spectra from the three targets are compared with laboratory measurements of Ce-containing apatites (Ce contents shown in Table S1) and naphthalene. Ce is known to result in fluorescence signatures that overlap in wavelength with those of 2-ring aromatic organics (e.g. naphthalene) (Fig. S7). Note that co-occurring 275 and 285 nm fluorescence in SHERLOC spectra do not have a known inorganic source and are considered organic in origin. Panel D shows a comparison of a spectrum from the Garde target to laboratory measurements of benzene and naphthalene.

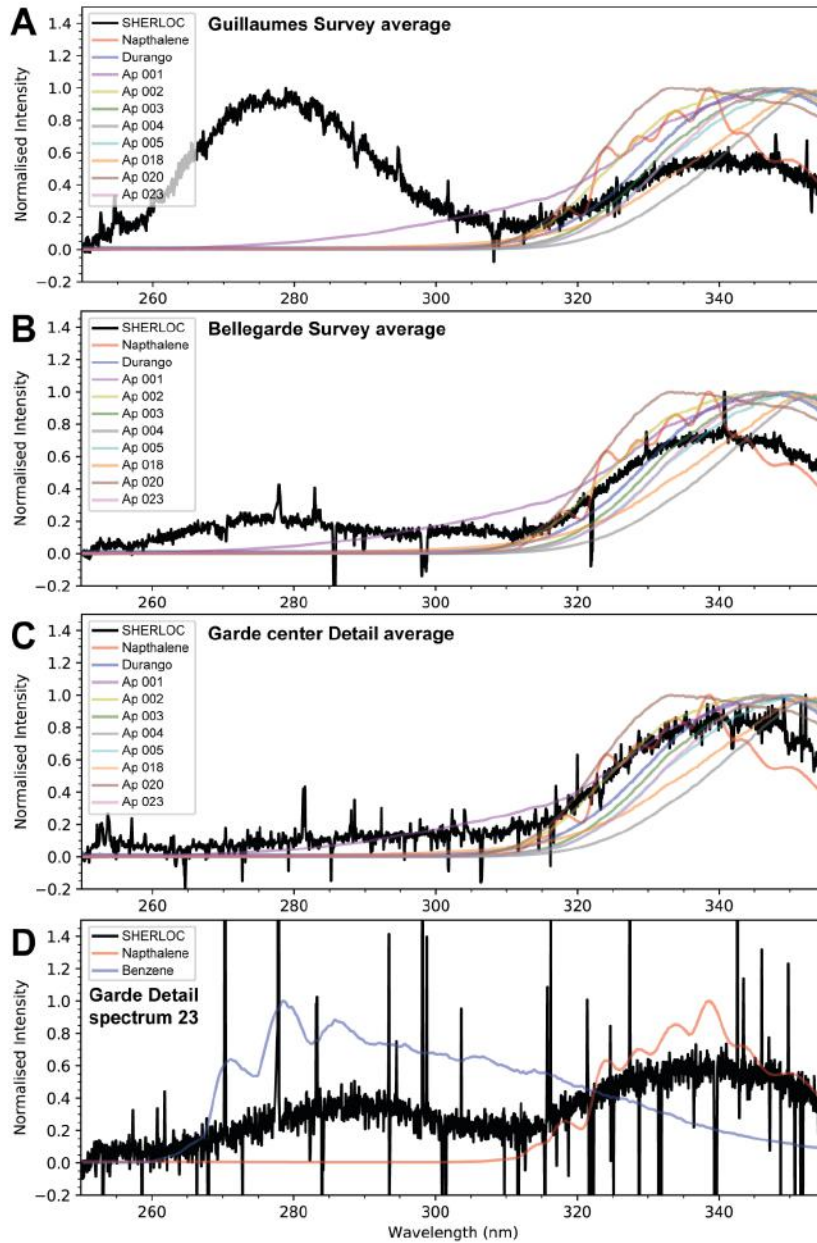


Fig. S9: Grey-scale version of Fig. 1 showing red color-band.

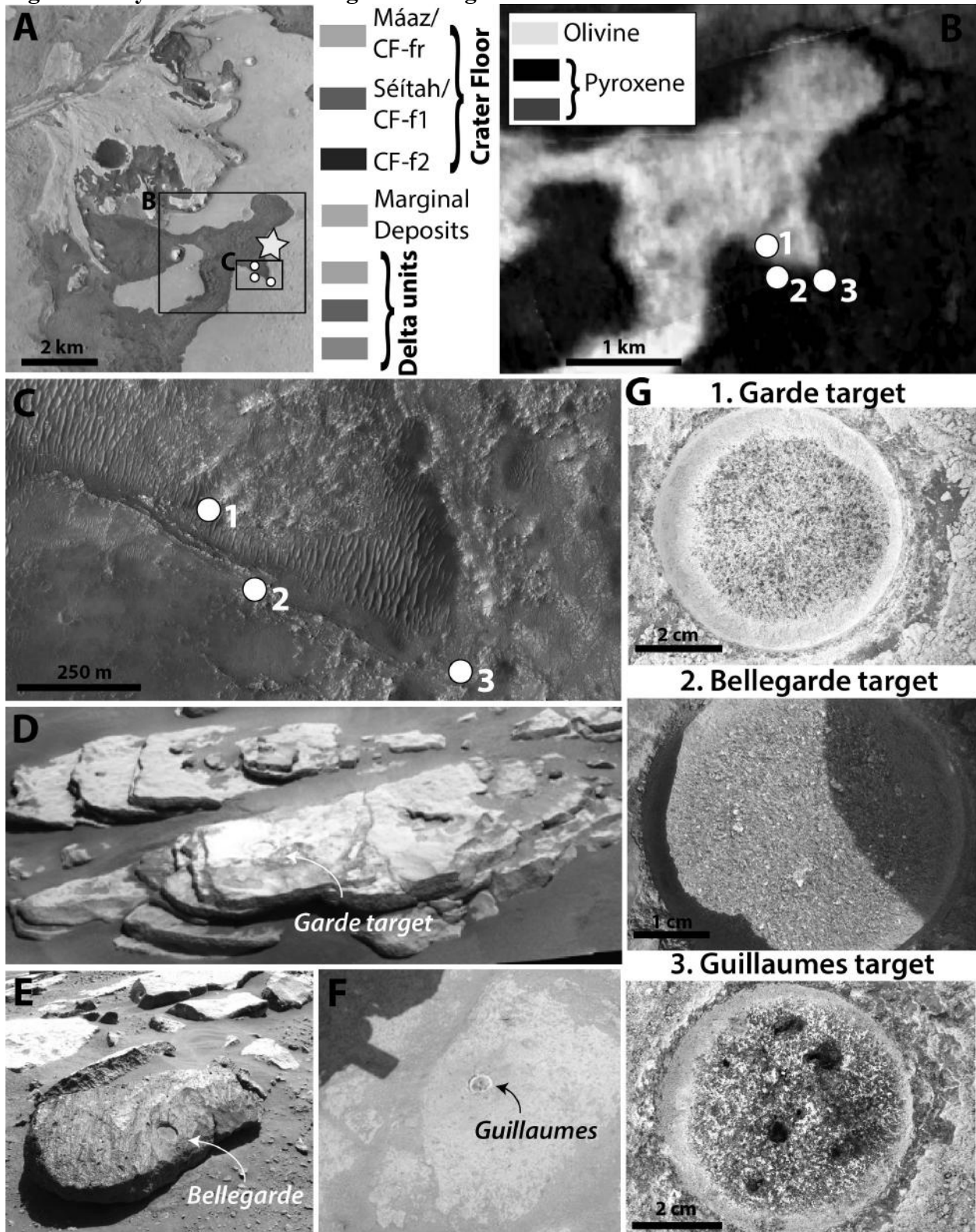


Fig. S10: Grey-scale version of Fig. 1 showing green color-band.

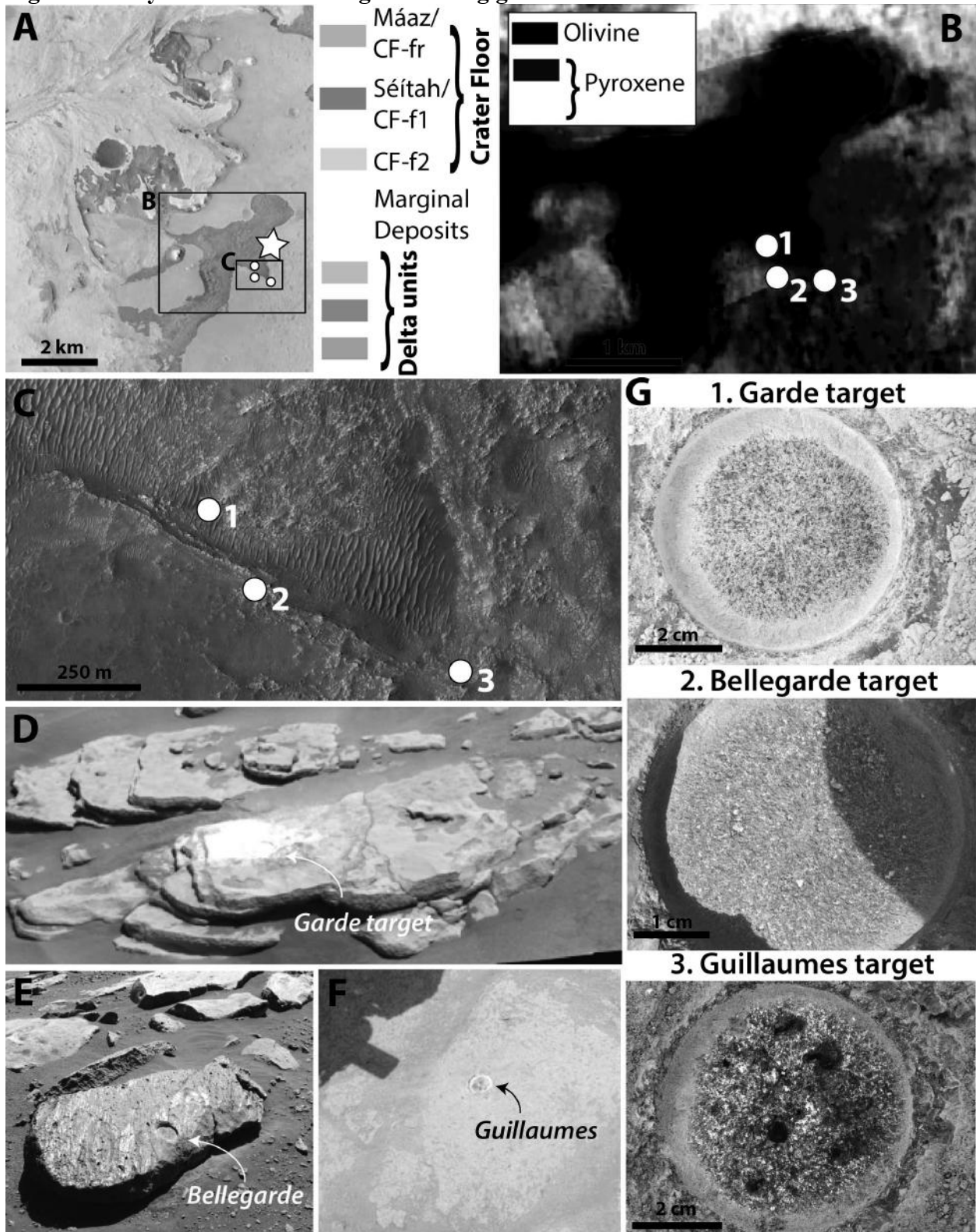


Fig. S11: Grey-scale version of Fig. 1 showing blue color-band.

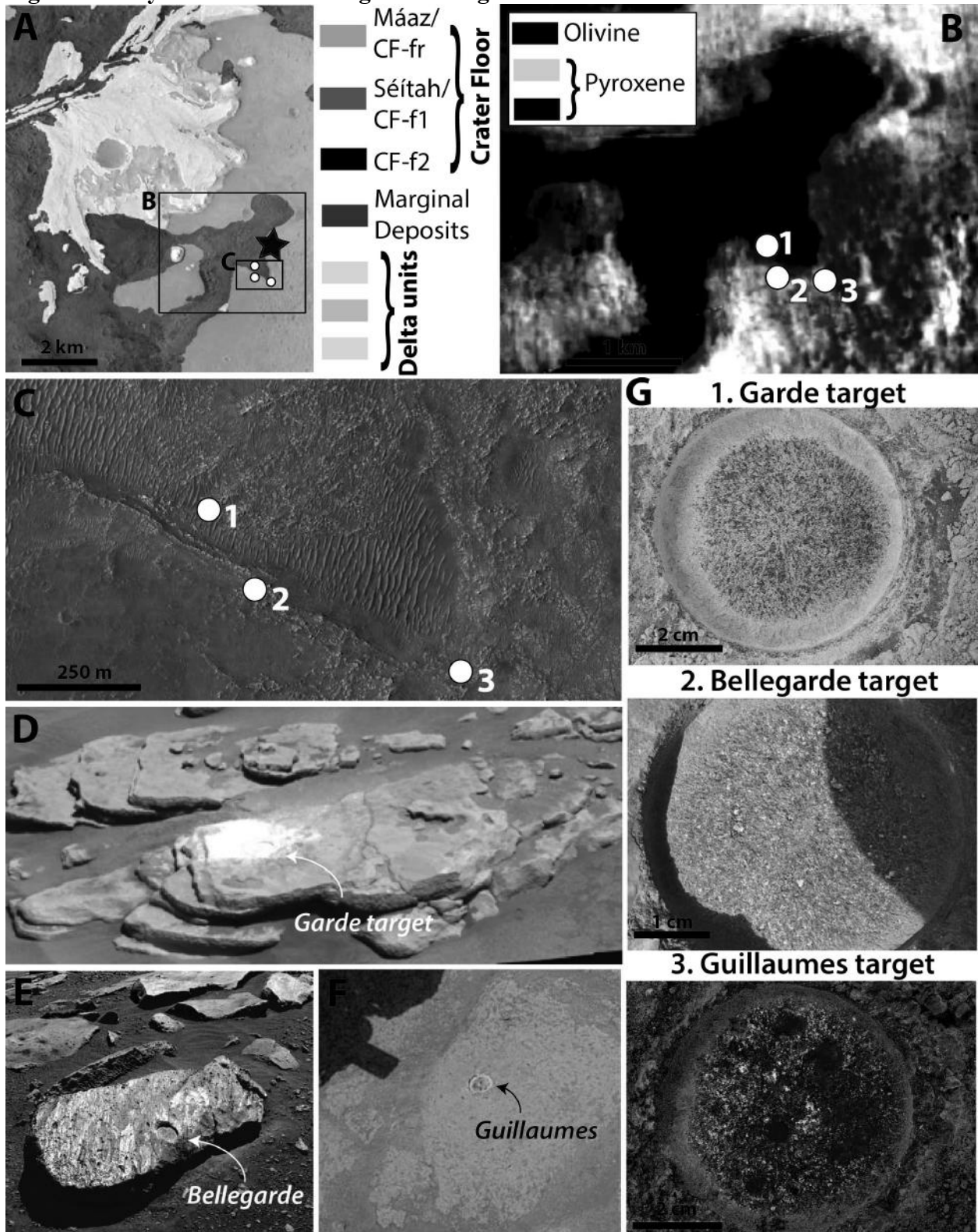


Fig. S12: Grey-scale version of Fig. 2 showing red color-band.

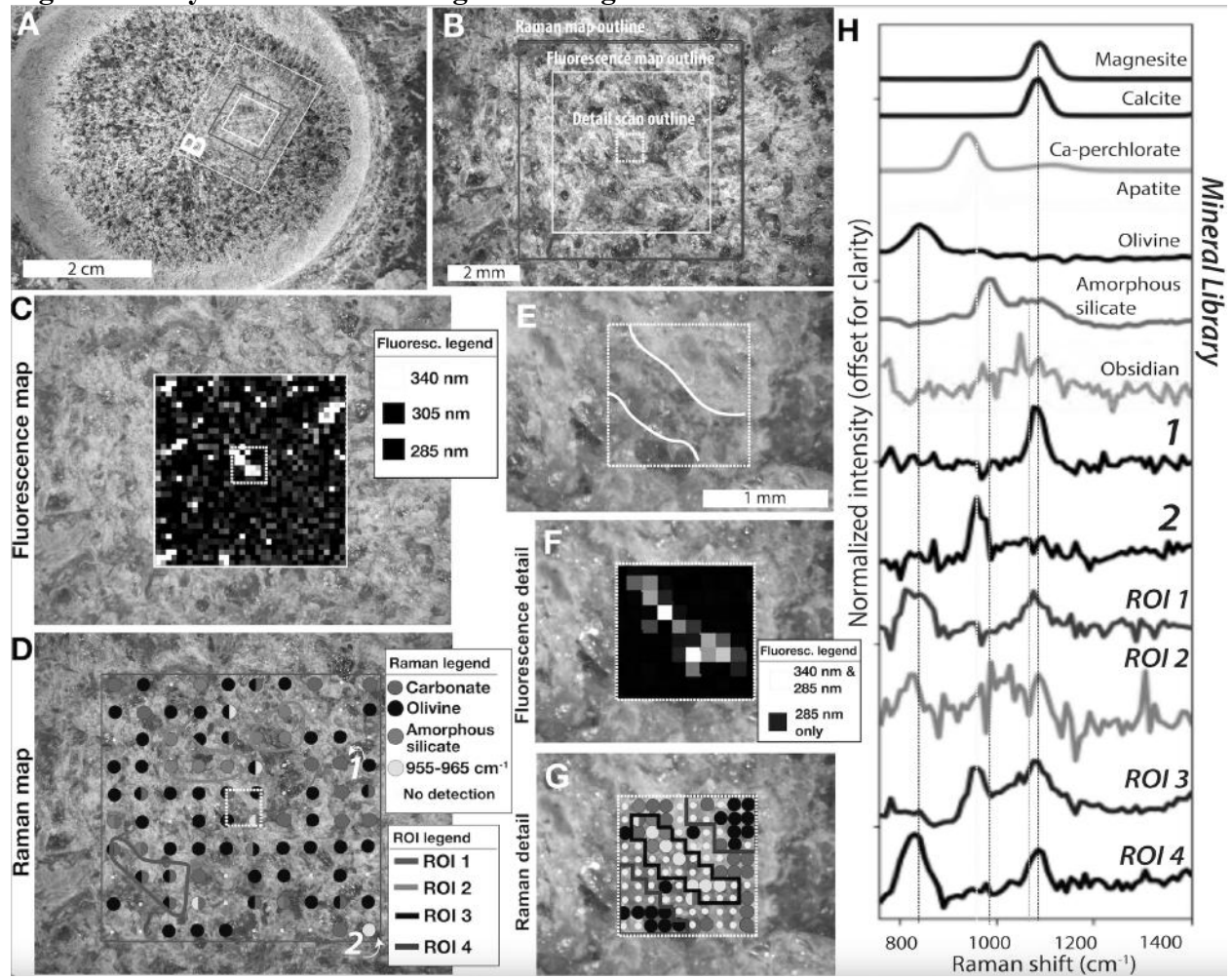


Fig. S13: Grey-scale version of Fig. 2 showing green color-band.

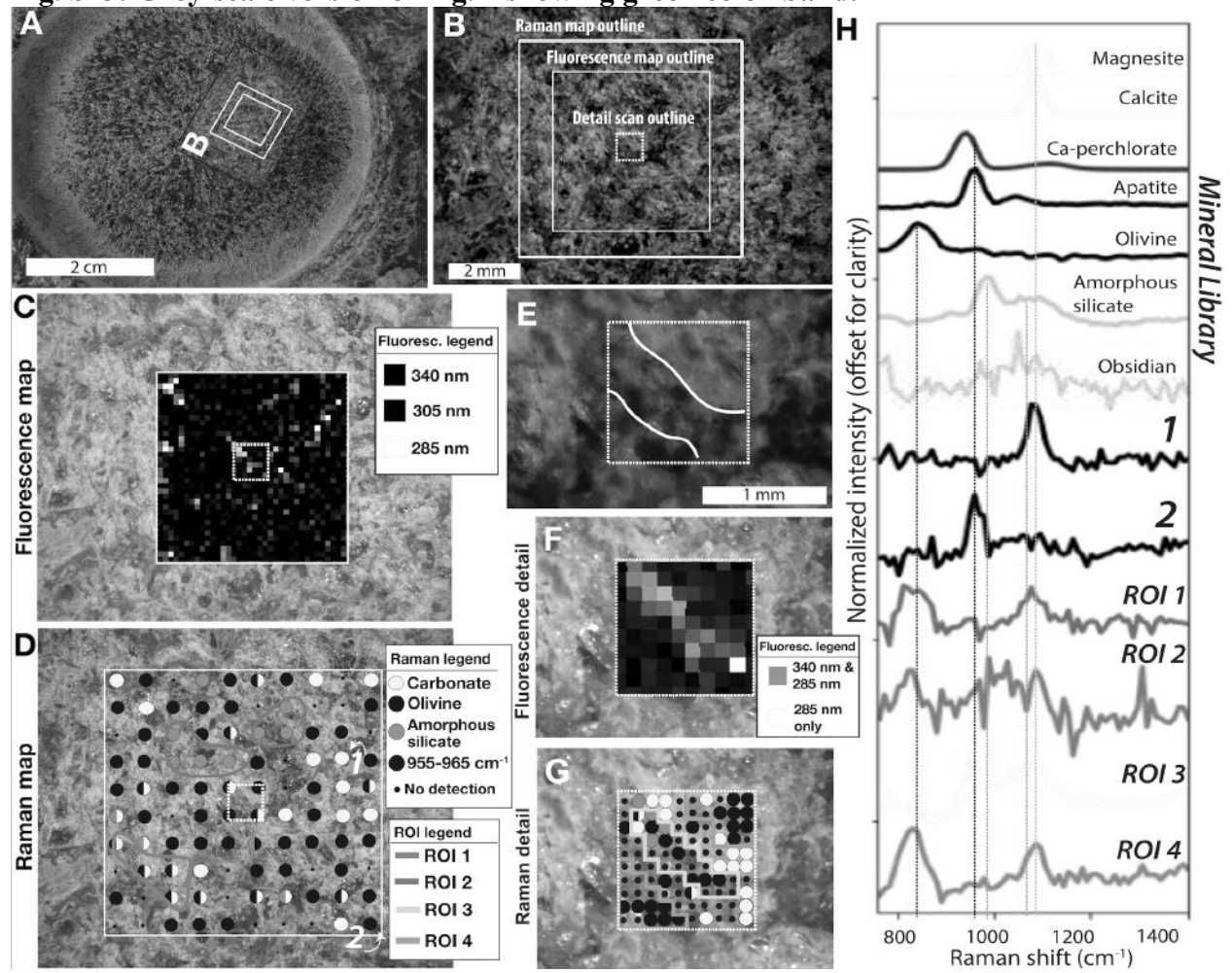


Fig. S14: Grey-scale version of Fig. 2 showing blue color-band.

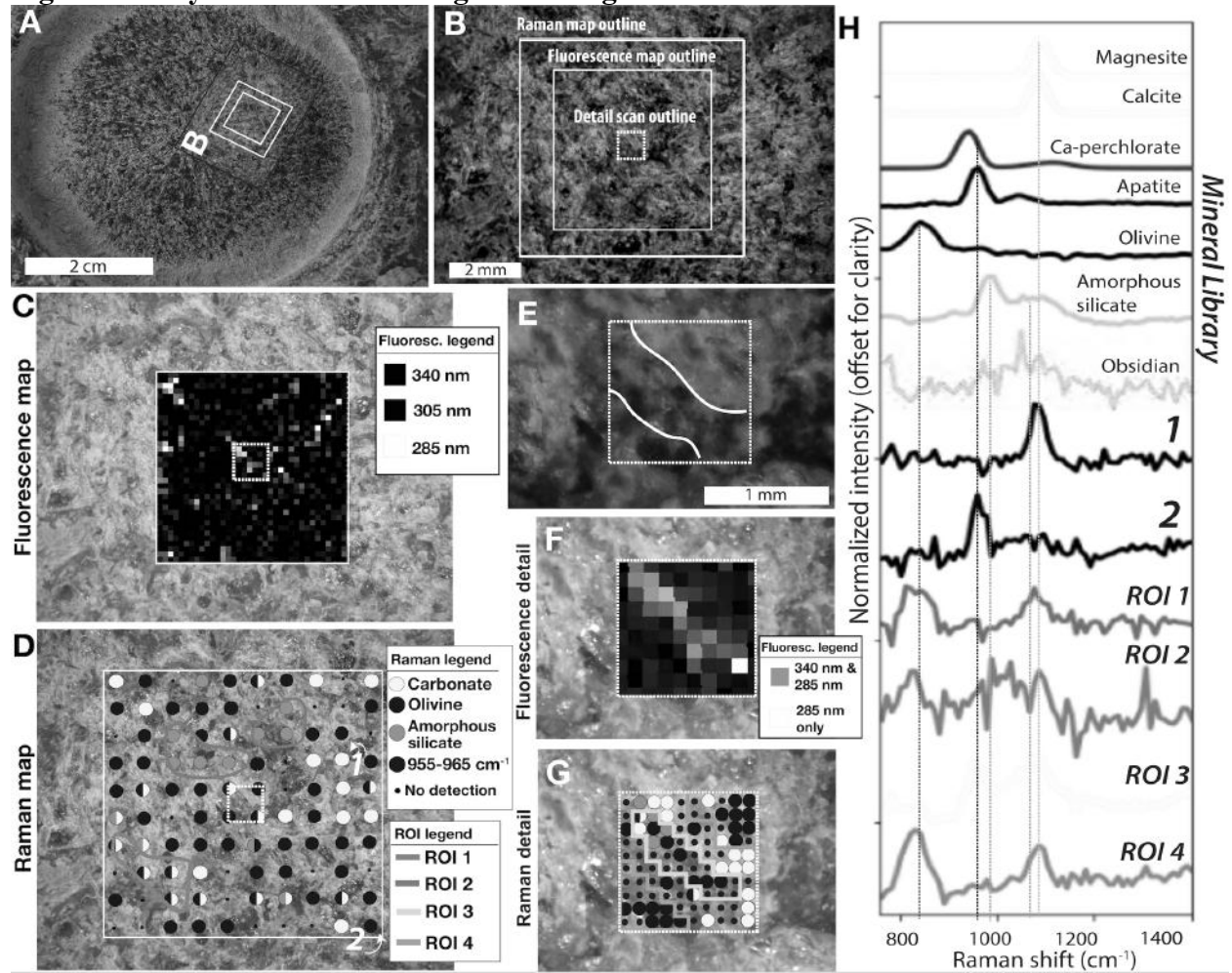


Fig. S15: Grey-scale versions of Garde fluorescence maps from Fig. 2C.

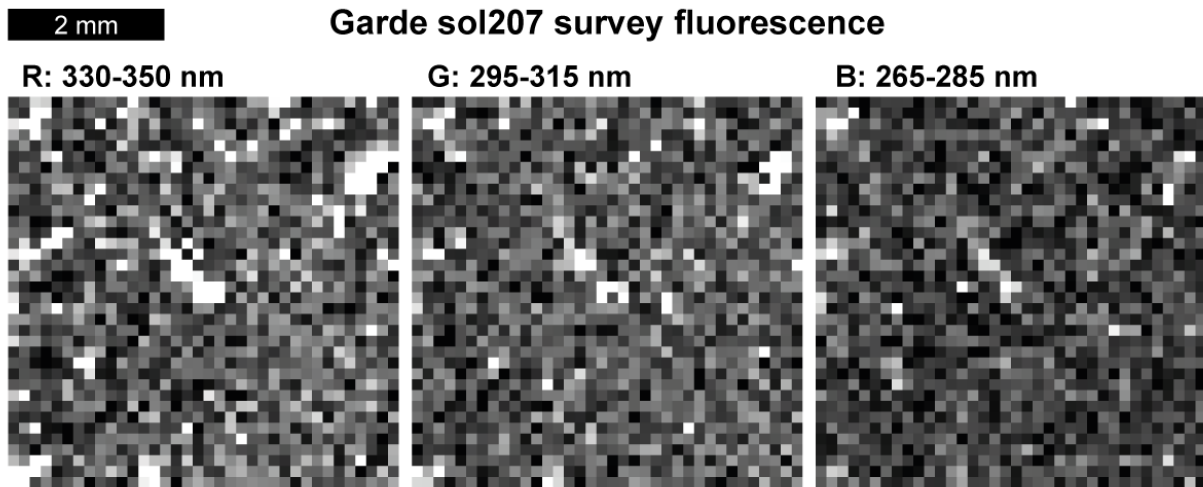


Fig. S16: Grey-scale version of Fig. 3 showing red color-band.

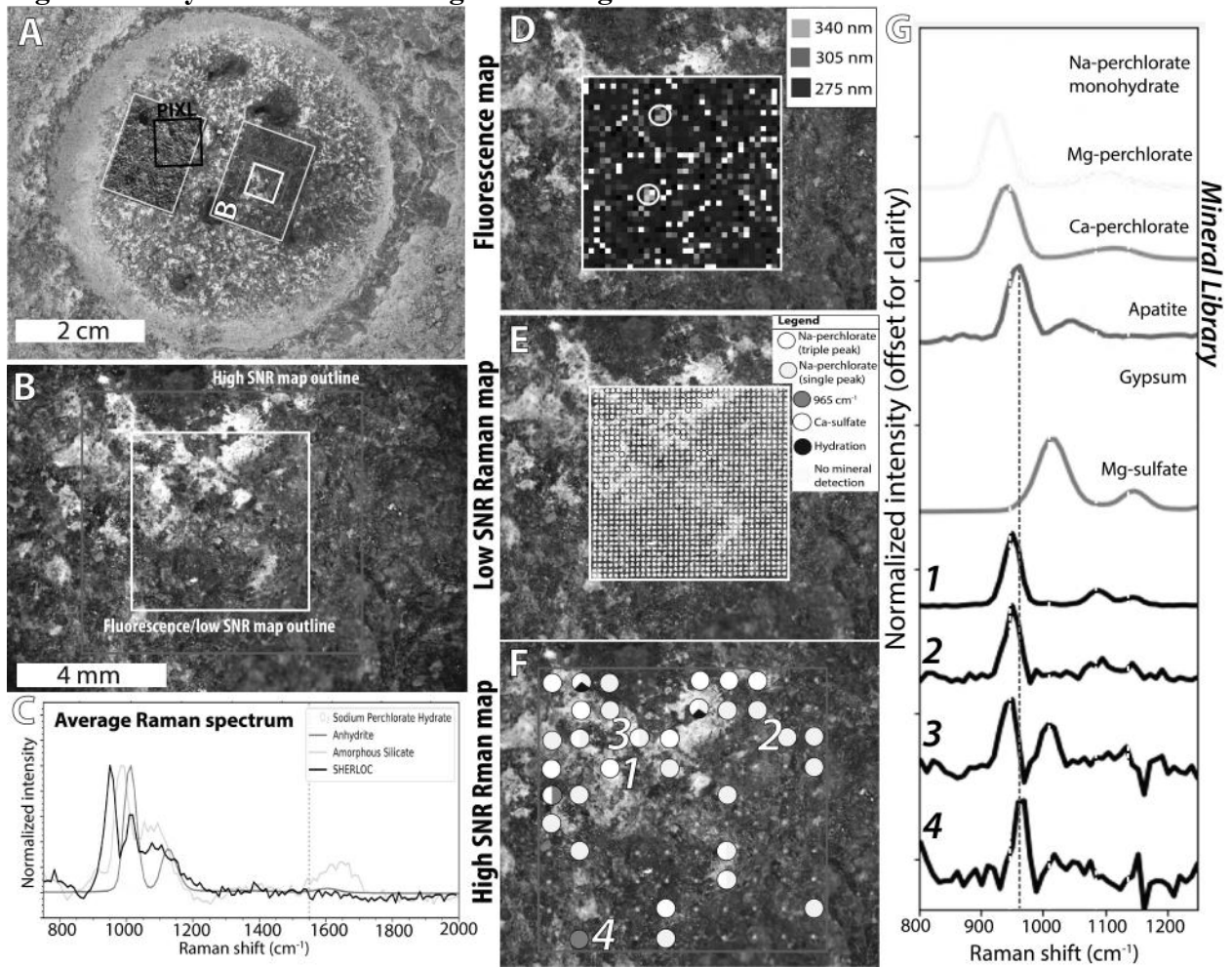


Fig. S17: Grey-scale version of Fig. 3 showing green color-band.

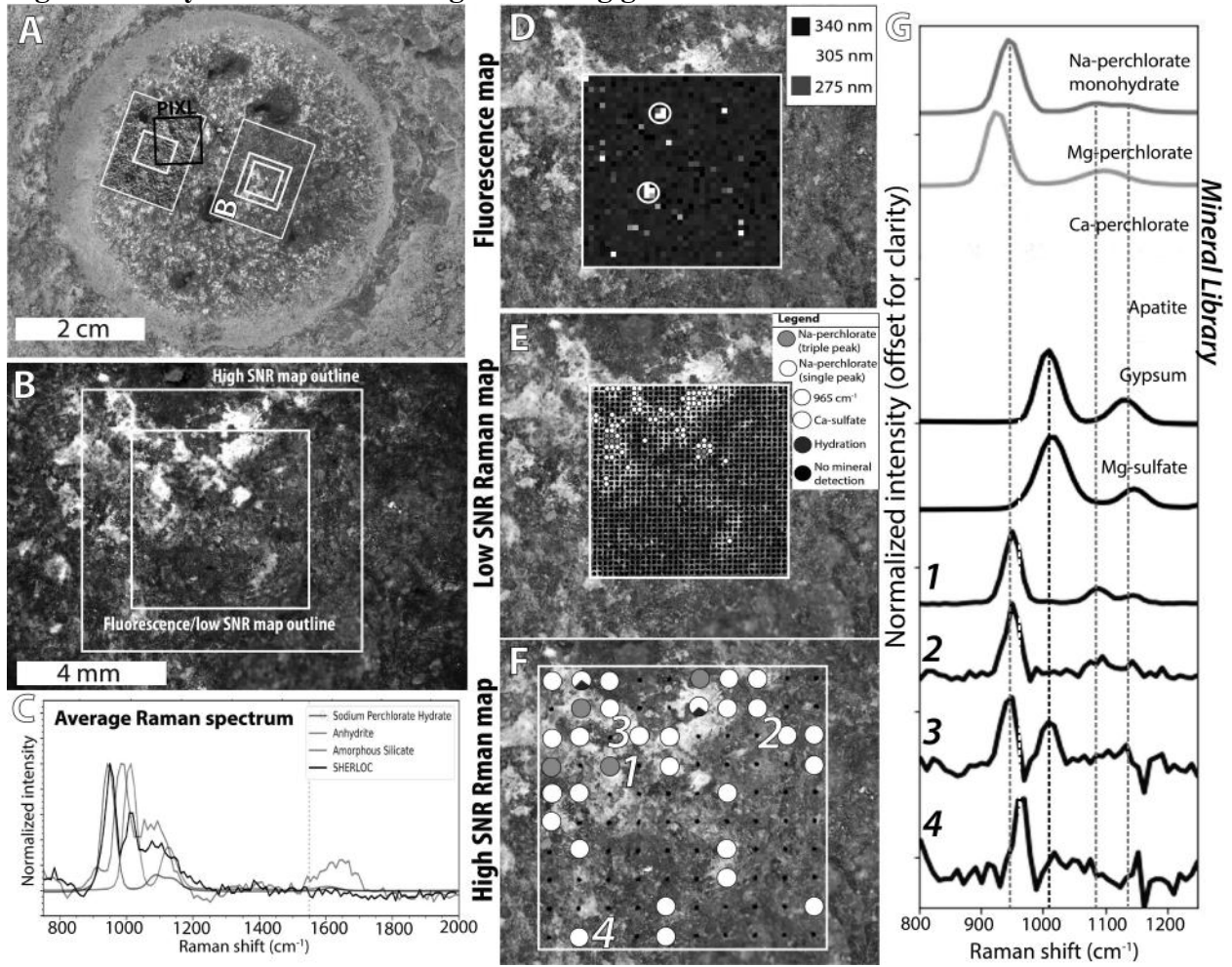


Fig. S18: Grey-scale version of Fig. 3 showing blue color-band.

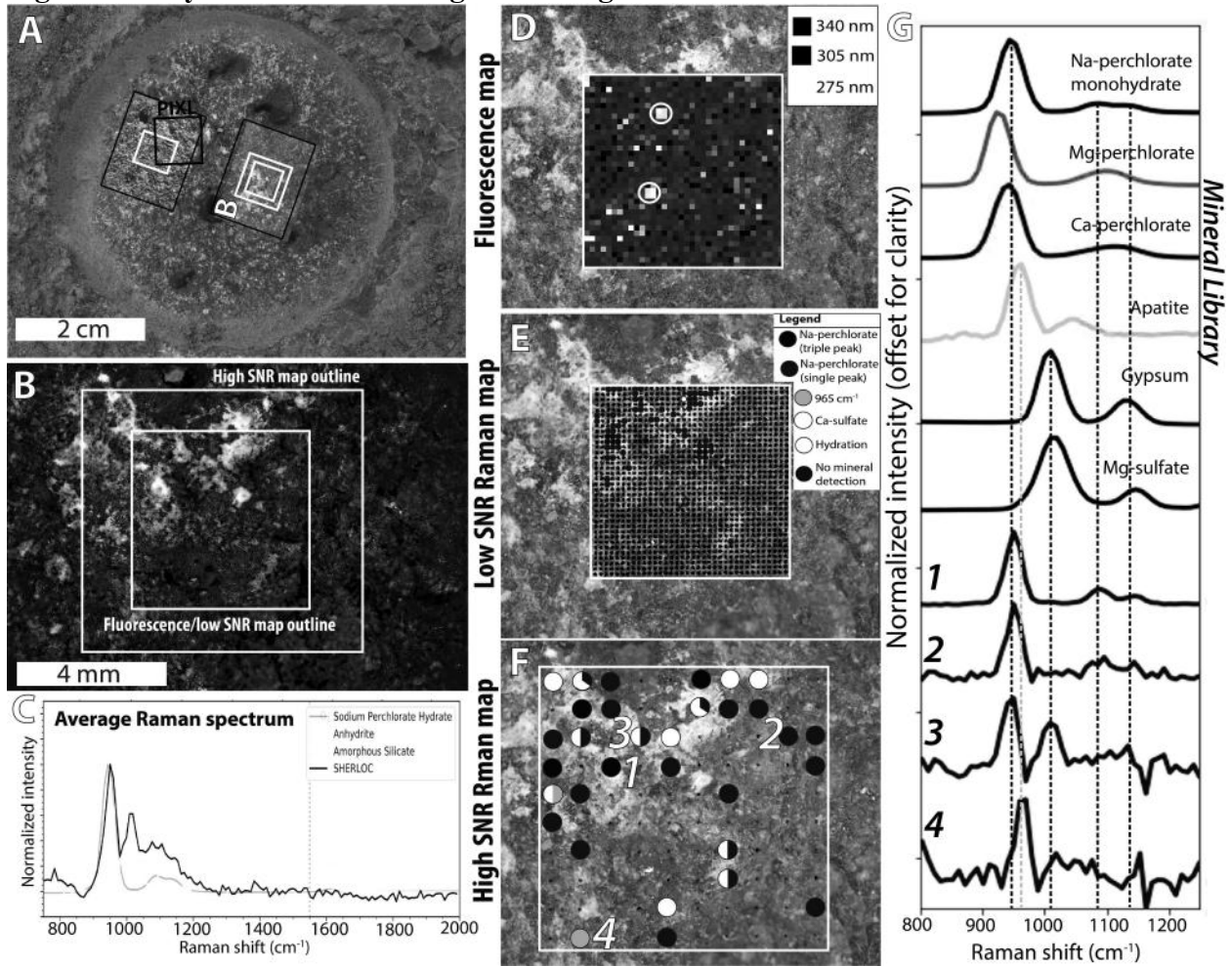


Fig. S19: Grey-scale versions of Guillaumes fluorescence maps from Fig. 3D.

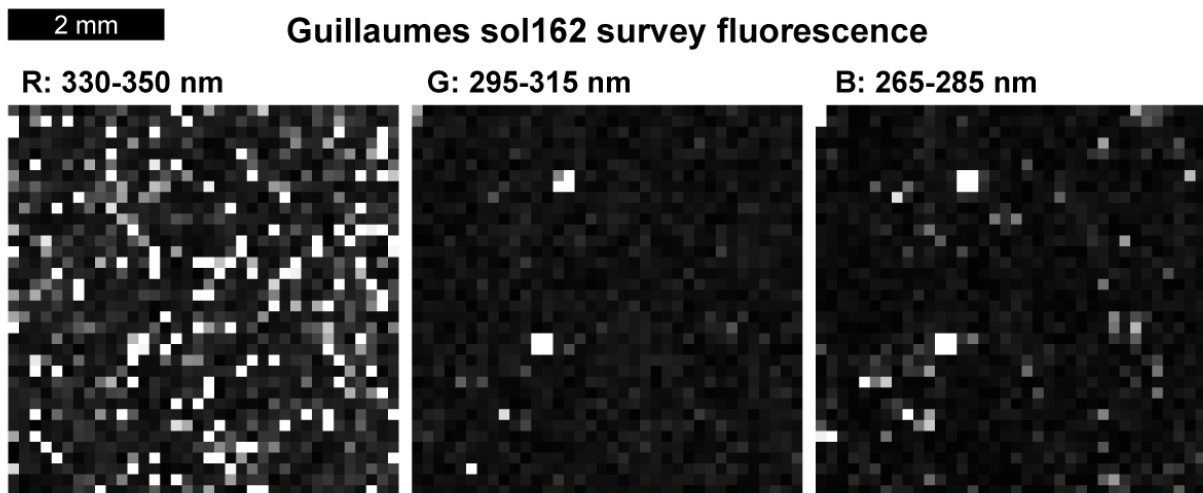


Fig. S20: Grey-scale version of Fig. 4 showing red color-band.

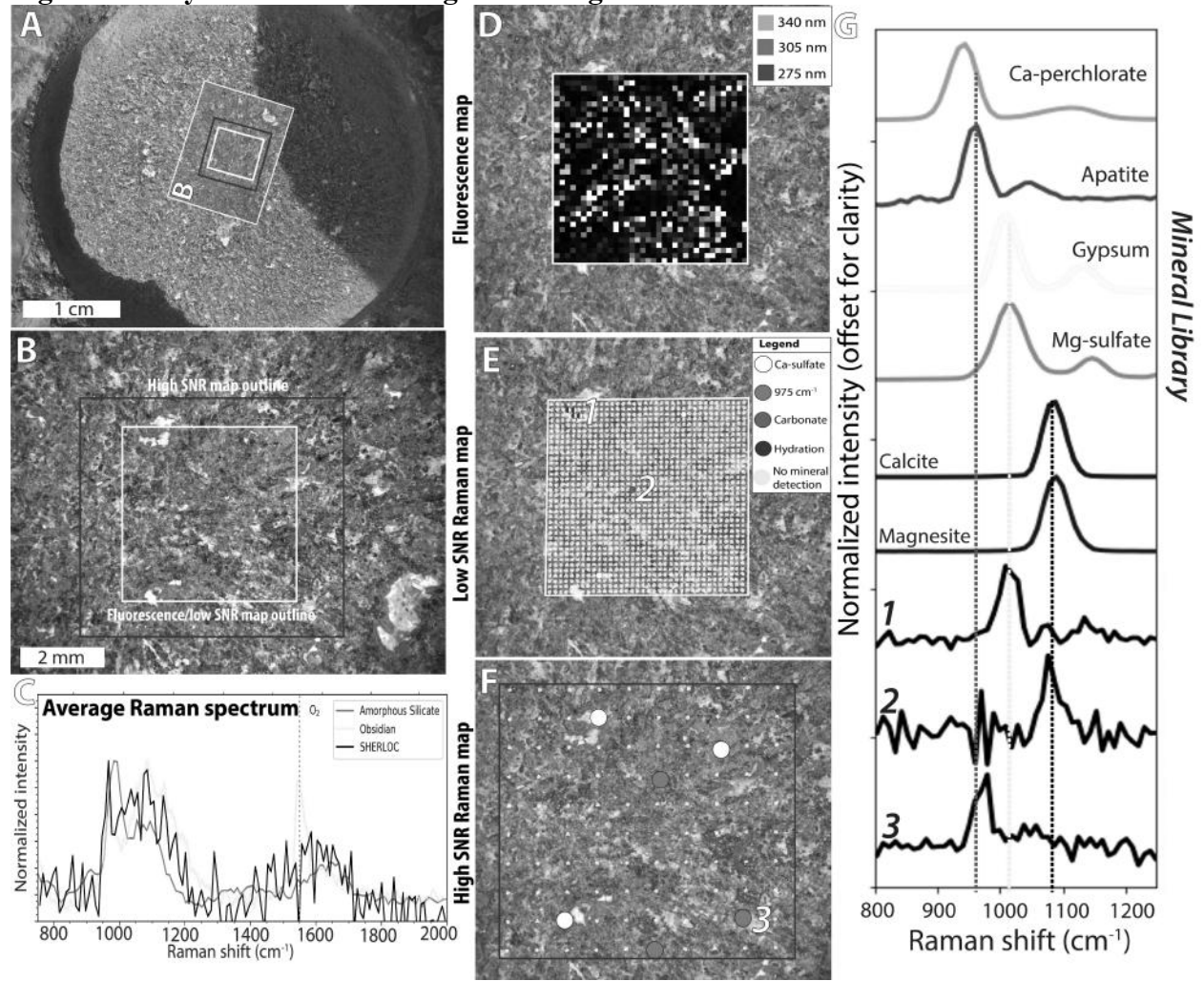


Fig. S21: Grey-scale version of Fig. 4 showing green color-band.

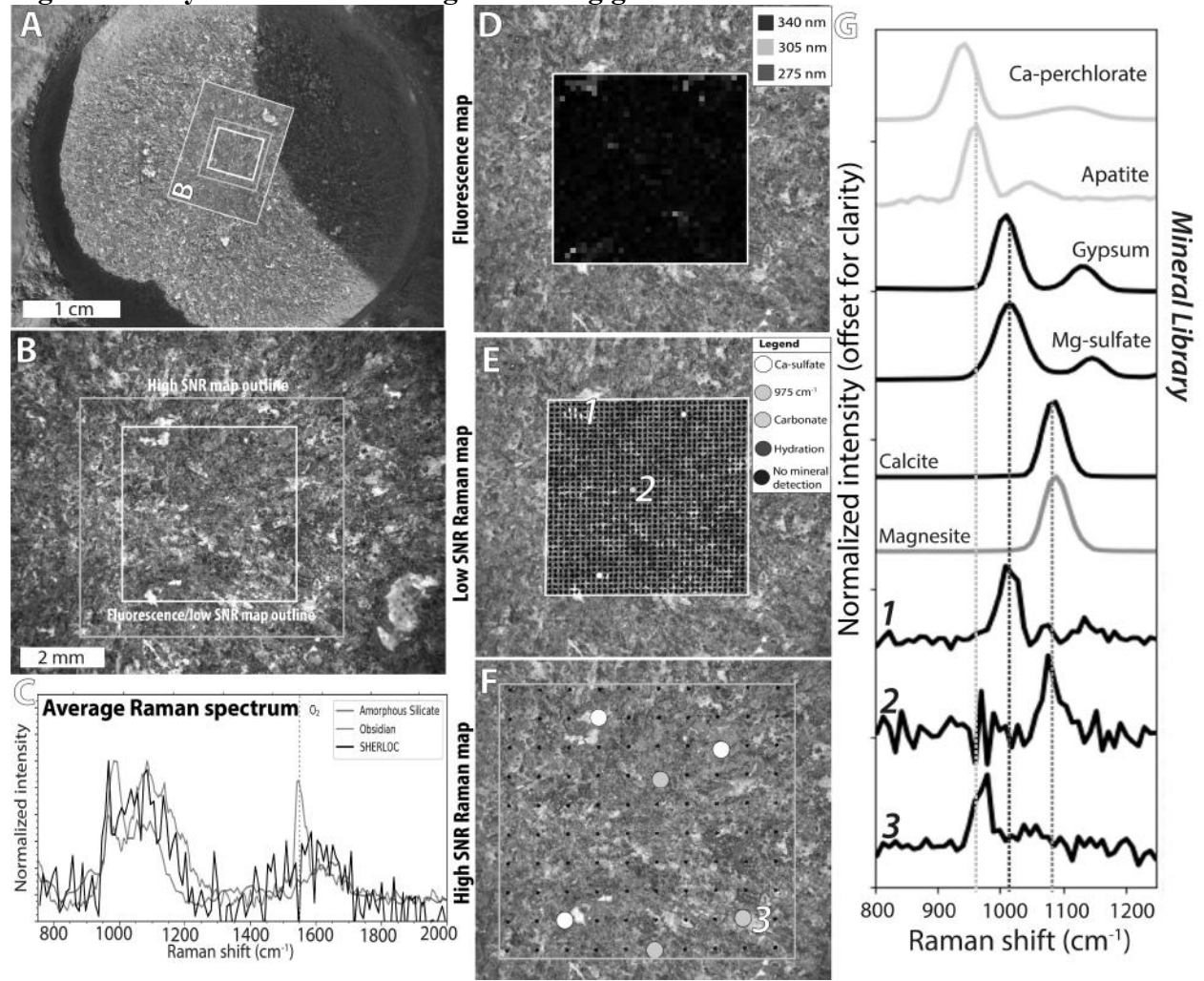


Fig. S22: Grey-scale version of Fig. 4 showing blue color-band

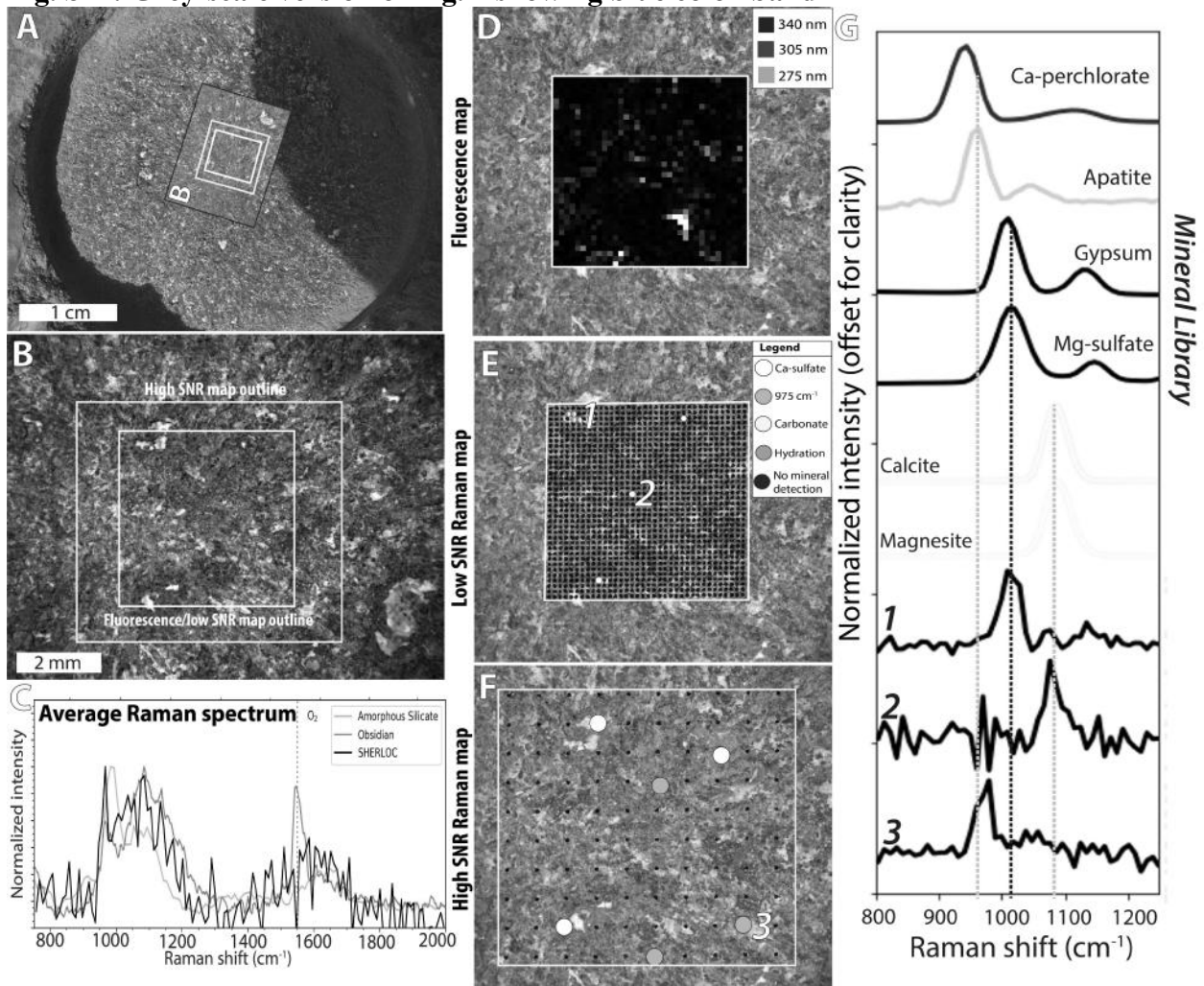


Fig. S23: Grey-scale versions of Bellegarde fluorescence maps from Fig. 4D.

