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5 **Discovery of Alunite in Cross Crater, Terra Sirenum, Mars: Evidence for Acidic, Sulfurous
6 Waters**

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27 infrared spectroscopy

28

Abstract

Cross crater is a 65-km impact crater, located in the Noachian highlands of the Terra Sirenum region of Mars (30°S, 158°W), which hosts aluminum phyllosilicate deposits first detected by the Observatoire pour la Minéralogie, L'Eau, les Glaces et l'Activité (OMEGA) imaging spectrometer on Mars Express. Using high resolution data from the Mars Reconnaissance Orbiter, we examine Cross crater's basin-filling sedimentary deposits. Visible/shortwave infrared (VSWIR) spectra from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) show absorptions diagnostic of alunite. Combining spectral data with high resolution images, we map a large (10 km x 5 km) alunite-bearing deposit in southwest Cross crater, widespread kaolin-bearing sediments with variable amounts of alunite that are layered in <10-m scale beds, and silica- and/or montmorillonite-bearing deposits that occupy topographically lower, heavily fractured units. The secondary minerals are found at elevations ranging from 700 to 1550 m, forming a discontinuous ring along the crater wall beneath darker capping materials. The mineralogy inside Cross crater is different from that of the surrounding terrains and other Martian basins, where Fe/Mg-phyllosilicates and Ca/Mg-sulfates are commonly found. Alunite in Cross crater indicates acidic, sulfurous waters at the time of its formation. Waters in Cross crater were likely supplied by regionally upwelling groundwaters as well as through an inlet valley from a small adjacent depression to the east, perhaps occasionally forming a lake or series of shallow playa lakes in the closed basin. Like nearby Columbus crater, Cross crater exhibits evidence for acid sulfate alteration, but the alteration in Cross is more extensive/complete. The large but localized occurrence of alunite suggests a localized, high volume source of acidic waters or vapors, possibly supplied by sulfurous (H_2S - and/or SO_2 -bearing) waters in contact with a magmatic source, upwelling steam or fluids through fracture zones. The unique, highly aluminous nature of the Cross crater deposits relative to other Martian acid sulfate deposits

53 indicates acid waters, high water throughput during alteration, atypically glassy and/or felsic
54 materials, or a combination of these conditions.

55

Introduction

57 Although geomorphic evidence for the presence of liquid water on Mars has been
58 longstanding (e.g. Carr, 1996 and refs. therein), mineralogic evidence for aqueous alteration of
59 rocks on the Martian surface has been revealed relatively recently by in-situ exploration by the
60 Mars Exploration Rovers (MER; e.g., Squyres et al., 2004a,b; 2008; Arvidson et al., 2006) and
61 by high resolution, orbital infrared spectroscopy. Thermal Emission Spectrometer (TES) data
62 (Christensen et al., 2001), Thermal Imaging System (THEMIS) data (Christensen et al., 2004;
63 Osterloo et al., 2008), and visible shortwave-infrared (VSWIR) imaging spectrometer data from
64 the Observatoire pour la Minéralogie, L'Eau, les Glaces et l'Activité (OMEGA) on Mars
65 Express (Bibring et al., 2005) and the Compact Reconnaissance Imaging Spectrometer for Mars
66 (CRISM) onboard the Mars Reconnaissance Orbiter (MRO; Murchie et al., 2007) have revealed
67 sulfates, carbonates, chlorides, phyllosilicates, and other hydrated silicates on the surface of Mars
68 (e.g., Gendrin et al., 2005; Poulet et al., 2005; Bibring et al., 2006; Mustard et al., 2008; Osterloo
69 et al., 2008; Ehlmann et al., 2008; Murchie et al., 2009a). Salts and secondary minerals indicative
70 of water are heterogeneously distributed. Whereas phyllosilicates are widespread and distributed
71 globally in Noachian and some Hesperian terrains, salts such as chlorides, carbonates, and
72 sulfates show more restricted and spatially distinct geographic distributions (e.g., Ehlmann &
73 Edwards, 2014). Few hydrated minerals are mapped in Amazonian terrains (e.g. Bibring et al.,
74 2006; Carter et al., 2013). Distinctive Martian geochemical environments characterized by
75 different pH, water:rock ratio, and fluid chemistry can thus be inferred. The geologic settings of
76 these salt- and secondary mineral-bearing units vary and include deltaic deposits, basin-filling
77 layered deposits, impact ejecta, and massive units that lack clear bedding.

78 Here, we report the geologic context and environmental implications of the first detection
79 on Mars of alunite, $KAl_3(SO_4)_2(OH)_6$, using diagnostic shortwave-infrared absorptions in

80 CRISM data (after Swayze et al., 2008). In contrast to calcium and magnesium sulfates, which
81 are the predominant sulfates detected on Mars by orbital and surface data (e.g. Gendrin et al.,
82 2005; Murchie et al., 2009a; Vaniman et al., 2014), alunite is rare and found to date only in the
83 Terra Sirenum region (Swayze et al., 2008; Wray et al., 2011). Alunite is an indicator of
84 distinctly acidic geochemical conditions during precipitation, pointing to low pH, sulfurous
85 fluids at or near the Martian surface. We examine the mineral assemblages, their
86 geomorphology, and regional context to understand the controls on spatially extensive alunite
87 formation in Cross crater and the environmental setting(s) of aqueous alteration.

88 **Datasets & Methods**

89 Cross crater, a 65-km-diameter late-Noachian impact crater in the southern highlands of
90 Terra Sirenum (30° S, 158° W; Figure 1), was targeted by MRO based on an absorption at $2.2\text{ }\mu\text{m}$
91 seen in a few pixels of OMEGA data, which suggested the presence of an Al-phyllosilicate such
92 as kaolinite (Gondet et al., 2006). Cross crater is west of the Tharsis rise volcanic edifice in a
93 faulted area with several candidate closed basin lakes (Anderson et al., 2001; Goudge et al.,
94 2015). Seventeen CRISM images were acquired over Cross crater in 544 spectral channels from
95 $0.4\text{-}3.9\text{ }\mu\text{m}$ in full-resolution targeted mode, covering approximately $10 \times 10\text{ km}$ with a spatial
96 sampling of 18-20 m/pixel, and in half-resolution mode targeted mode, covering $10 \times 20\text{ km}$ with
97 a spatial sampling of 35-40 m/pixel (Murchie et al., 2007) (Table 1). In targeted mode, CRISM's
98 effective spectral resolution near $2.2\text{ }\mu\text{m}$ is approximately 10 nm, allowing narrow SWIR
99 absorptions such as the $2.2\text{-}\mu\text{m}$ doublet present in kaolinite group minerals to be resolved.
100 Analyses of data from $0.4\text{-}2.6\text{ }\mu\text{m}$ enable identification of minerals using diagnostic electronic
101 absorptions in the visible and shortwave infrared (VSWIR) from transition metals such as iron as
102 well as vibrational absorptions from OH, H₂O, and CO₃. Additionally, CRISM data were
103 acquired in multispectral mapping mode over the same wavelength range but with decreased

104 spatial and spectral resolution (Murchie et al., 2007; 2009b). VSWIR remote sensing data
105 measure the composition of the upper hundreds of micrometers of the surface; consequently,
106 determination of the mineralogy of lithologic/stratigraphic units requires the bedrock be at least
107 patchily exposed beneath other surface covers, e.g. dust, sand, or overlying units.

108 Raw CRISM spectra were processed to I/F (a ratio of measured radiance to incoming
109 solar flux) following the methodology of Murchie et al. (2009b) and were then photometrically
110 and atmospherically corrected using standard procedures. Assuming a surface that scatters
111 isotropically, i.e., a Lambertian surface, scene I/F was divided by the cosine of the incidence
112 angle, and then corrected for atmospheric gas band absorptions by dividing by a scaled
113 atmospheric transmission spectrum (e.g., Mustard et al., 2008; Ehlmann et al., 2009). To
114 highlight spectral features that differ between terrains and to reduce the effect of systematic,
115 detector-dependent instrument artifacts, individual or average spectra from areas of interest were
116 ratioed to an average spectrum of areas located within the same image column and lacking
117 narrow vibrational absorptions. Spectral summary parameters (Pelkey et al., 2007), which
118 spatially map the strength of absorptions related to Fe, OH, and H₂O at locations diagnostic of
119 minerals and mineral classes were used initially to discover and detect minerals of interest.

120 The locations of minerals with diagnostic infrared absorptions were also mapped using
121 the Tetracorder spectral shape-matching algorithms and expert system (Clark et al., 2003),
122 coupled with the Clark et al. (2007) spectral library, to create color-coded maps of the
123 distribution of minerals and/or spectral endmembers with absorptions in the 1.0-2.6 μm range.
124 Tetracorder compares absorption features in library reference spectra to absorption features in an
125 observed spectrum (e.g., in a CRISM pixel) and then calculates the modified least-squares
126 correlation between them. The algorithm derives a fit (a correlation coefficient) for each of the

127 spectra in its library, applies user-specified constraints on absorption features, and selects the
128 mineral with the highest fit as the best spectral match to the observed spectrum. Maps of the
129 distribution of various minerals are assembled by assigning a unique color to pixels spectrally
130 dominated by a particular mineral or mineral mixture.

CRISM parameter and Tetracorder mineral maps were then map projected and co-registered with MRO high spatial resolution image data collected at 6 m/pixel by the Context Imager (CTX; Malin et al., 2007) and at 0.3 m/pixel by the High Resolution Imaging Science Experiment (HiRISE; McEwen et al., 2007). HiRISE red-blue anaglyphs and digital elevation models provided high resolution topographic information at 1 m/pixel for one location where stereo image pairs were available. Topography at larger scales was determined using 128 pixel/degree Mars Orbiter Laser Altimeter (MOLA) global gridded data as well as point shot data acquired with a ~168 m diameter spot-size at ~300 m spacing with an absolute vertical precision of ~38 cm and accuracy of ~1 m (Smith et al., 2001). Additional daytime and nighttime infrared images from the Thermal Emission Imaging System (THEMIS) mosaics provided context for the high-resolution datasets as well as insight into the thermophysical properties of the geologic materials (e.g., Fergason et al., 2006; Edwards et al., 2011).

Results

144 Cross crater hosts a diverse suite of secondary and primary minerals found in discrete
145 geomorphic units. Sedimentary units, mostly restricted to elevations between 700 m and 1550 m,
146 contain kaolinite group phyllosilicates and certain locales have alunite, silica and/or
147 montmorillonite, Fe/Mg-phyllosilicates, Fe-oxides, and Fe-sulfates. These units are overlain by
148 unconsolidated sediment (sands) as well as a lithified capping unit with weak SWIR absorptions

149 indicative of pyroxene group minerals. The details of the composition inferred from
150 spectroscopy, the geomorphology, and the distribution of key units are described below.

151 **Alunite, Al-phyllosilicates, silica**

152 Three endmember materials have absorptions near 2.2 μm , exhibit consistent and
153 distinctive spectral characteristics (red, blue, green spectra in Figure 2), display spatial coherence
154 when mapped in CRISM images, and occur in multiple localities in different CRISM images
155 (Figure 3). Along the southwestern wall, a ~10 km light-toned deposit occurs within a 860-1020
156 m elevation topographic contour and has a distinctive absorption at 2.17 μm , accompanied by a
157 doublet near 1.4 μm and absorptions at 1.76 μm , 2.32 μm , and 2.52 μm . These absorptions are
158 uniquely characteristic of alunite group minerals ($(\text{K}, \text{Na}, \text{H}_3\text{O})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$) (Figures 2; Hunt
159 et al. 1971; Clark et al., 1990; Swayze, 1997; Bishop and Murad, 2005). The difference between
160 K-bearing alunite and Na-bearing natroalunite is resolvable at CRISM spectral resolution
161 (Swayze, 1997; Bishop & Murad, 2005; Swayze et al., 2006, 2014; McCollom et al., 2014).
162 CRISM spectra of the Cross crater deposit have absorptions at 1.43 and 1.48 μm , which are
163 consistent with alunite, whereas natroalunite has longer wavelength absorptions near 1.44 and
164 1.49 μm , which are not observed. The presence of a 1.9- μm H_2O combination absorption and the
165 relative weakness and shapes of the ~1.4- μm absorptions may be evidence for a poorly
166 crystalline alunite and incorporation of non-stoichiometric water (e.g., Swayze et al., 2006).
167 Mixtures of well-crystalline alunite with another hydrated phase can also generate these spectral
168 characteristics. Alunite-kaolinite mixtures are observed in other locations at 18 m/pixel
169 observation scale (yellow; Figures 2, 3).

170 The second and most widely occurring endmember with a ~2.2- μm absorption, found in
171 every CRISM image of Cross crater floor sediments are kaolinite group minerals (referred to
172 collectively as kaolins). These have a pronounced asymmetry in their ~2.2 μm absorption, which

173 is due to differences in the relative strengths of the Al-OH doublet absorptions at 2.17 and 2.21
174 μm (Hunt 1977 and references therein; Clark et al., 1990; Bishop et al., 2008; Swayze et al.,
175 2014). A similar asymmetry in the weaker 1.41 μm absorption due to the Al-OH overtone can
176 also sometimes be resolved. The doublet is not pronounced in the Cross crater materials. As is
177 the case with other kaolin-bearing materials on Mars (e.g., Ehlmann et al., 2009), there is a 1.9-
178 μm absorption due to water that is not typical of well-crystalline, pure kaolinite, but is present in
179 halloysite, mixed-layer kaolinite-smectite clay, impure/disordered kaolinite, or kaolinite
180 physically mixed with hydrated phases. The breadth of the 2.21- μm absorption is also notably
181 wider than endmember spectral library kaolinite group minerals (Figure 2), indicating the kaolin-
182 bearing phase is likely areally or intimately mixed with other hydroxylated phases, such as
183 montmorillonite, hydrated silica, or alunite at the spatial resolution of CRISM.

184 The third endmember has a 2.2- μm absorption, also centered near 2.21 μm , which lacks
185 the asymmetry of kaolinite group minerals and is substantially broader. The center position and
186 lack of a doublet are characteristic of an Al-smectite phase like montmorillonite or an opaline
187 silica phase, with the absorption caused by Al-OH or Si-OH respectively. The width of the
188 absorption makes opaline silica the most plausible single phase to explain the spectral
189 characteristics; however, mixture of a montmorillonite with opaline silica or another phase, could
190 also cause apparent broadening of the 2.2- μm absorption.

191 **Iron mineralogy**

192 Fe/Mg-phyllosilicates, the most common phyllosilicate on Mars (e.g., Carter et al., 2013;
193 Ehlmann & Edwards, 2014), are uncommon within Cross crater and found so far only in the
194 west, in the vicinity of a small impact crater that impacts Cross crater floor units (Figure 4). In
195 contrast, multiple localities with Fe/Mg-phyllosilicates are located in the Noachian plateau unit
196 into which Cross crater was emplaced (e.g., Figure 1d; Figure 4b). The absorptions due to

197 Fe/Mg-phyllosilicates within Cross crater are centered near 1.43 μm , 1.9 μm , and 2.29 μm ,
198 consistent with an Fe-rich smectite such as nontronite (Figure 4c; Bishop et al., 2002a,b).
199 Outside of Cross crater on the plateau, the terrains have only been observed by CRISM using its
200 multispectral mapping mode so the spectral resolution for discriminating absorption band
201 minima is lower. However, the composition may be different. Observed absorptions in the
202 Fe/Mg phyllosilicate-bearing terrains near Cross crater are centered near 1.39 μm and >2.30 μm ,
203 which may indicate a different, more Mg-rich, Fe/Mg-phyllosilicate chemical composition.

204 Within Cross crater and the alunite- and kaolin-bearing materials, CRISM spectra
205 acquired from 0.4-1.0 μm ('S data') exhibit variations in short wavelength spectral slope at 0.4-
206 0.9 μm . These may be due to the presence of iron oxides and/or iron sulfates within the deposits.
207 In CRISM spectral parameters, variation in dust cover is the primary cause of variability in the
208 0.53- μm band depth parameter rather than crystalline iron oxides; however, certain locations in
209 the sediments and the central ring knobs have absorptions that may indicate an Fe oxide phase.
210 In image FRT0001187B, there are also several small locations (<250 x 250 m) within the
211 alunite- and kaolin-bearing units with a 0.94- μm absorption. One of these has an atypically sharp
212 absorption at 2.22-2.23 μm , likely an indicator of Fe(III)SO₄OH, which has been previously
213 detected on Mars in Aram chaos (Lichtenberg et al., 2010) and in opal-bearing, light-toned
214 layered deposits adjacent to Valles Marineris (Milliken et al., 2008). Additionally, knobs that
215 have a yellow-brown tone in CRISM false-color IR images (R: 2.5 μm , G: 1.8 μm , B: 1.2 μm)
216 have a strong, positive spectral slope downward at wavelengths <1.5 μm , likely caused by one or
217 more Fe-bearing minerals. One small knob in FRT0000987B has spectra consistent with jarosite.
218 A follow-on paper will provide further small-scale geologic mapping of all alteration phases,
219 including iron sulfate phases within Cross crater sediments (Swayze et al., in prep.).

220 Spectral signatures of mafic minerals are uncommon within the crater, found only in
221 overlying sands and certain well-preserved outcrops of caprock. In some locales, the caprock has
222 discernible weak, broad absorptions centered near ~0.9 μm and ~2.1 μm that are consistent with
223 high-calcium pyroxene group minerals. Olivines and low-calcium pyroxenes are not obviously
224 present, although identification of mafic minerals is complicated by the fact the caprock is the
225 most “bland” material in the scene and thus the typical denominator used to remove residual
226 artifacts. There is variability from place to place in apparent pyroxene content, but the signatures
227 are subtle.

228 **Distribution and Geomorphology of Key Intracrater Units**

229 The alunite and Al-phyllosilicates are found in sediments ringing the crater floor,
230 typically exposed between a maximum elevation of approximately 1550 m above the MOLA
231 global datum and a minimum elevation of 700 m. Spatial mapping from Tetracorder analyses of
232 CRISM targeted data shows a concentration of pixels most closely matching spectrally dominant
233 alunite along the southwestern crater wall (Figure 5). Elsewhere, spectral signatures of kaolin-
234 bearing materials are spatially dominant, occurring solely or with variable intermixture of alunite
235 or opaline silica/montmorillonite.

236 A MOLA point shot profile across the largest spatially contiguous concentration of
237 dominantly alunite-bearing materials shows that the alunite- and kaolin-bearing materials are
238 part of a bench (Figure 5b). A break in slope at the transition from the crater wall to the bright-
239 toned sedimentary units suggests that these materials unconformably overlie the crater wall with
240 an upper surface that is nearly horizontal. The alunite is best expressed along the slope,
241 presumably exposed by modern wind erosion (Figure 5b, c). The dominantly alunite portion of
242 the sequence has a lighter-toned, more massive appearance than kaolin-bearing units, and lacks

243 clear bedding, fracturing or other obvious sedimentary structures (Figure 5d, e). The transition
244 from the alunite- and kaolin-bearing materials to the silica/montmorillonite coincides with
245 another break in slope and a change in deposit morphology (position #4 in Figure 5b,c). The
246 alunite- and kaolin-bearing units are massive to layered and form local topographic highs; the
247 silica/montmorillonite-bearing units are polygonally fractured at multiple scales and are
248 topographically lower. The silica/montmorillonite-bearing materials have prominent 500-2000 m
249 long cracks that are 10s of meters wide; buttes of dark caprock rest unconformably atop, in some
250 cases straddling these cracks (Figure 5f). Fracturing in this unit is also common at smaller scales
251 down to a few meters (Figure 5g).

252 Al-phyllosilicate-bearing sedimentary units exposed in cross section are typically layered
253 at a scale of <5 m in thickness (Figure 6). Buttes of the alunite- and kaolin-bearing remnant
254 layers exist in all sectors of the crater, although coverage of stereo data acquired to date does not
255 yet permit tracing whether bed elevations are continuous across the crater. There are two
256 characteristic types of layering: (1) <5 m thick layers of bright and dark materials exposed on
257 relatively smooth-sloped, continuous scarps (Figure 6a, c) and (2) <10-m thick layers of
258 materials with homogeneous albedo properties but variable erodibility such that they form highly
259 irregular scarps with distinct breaks in slope between layers (Figure 6b). Type (2) are areally
260 dominant, especially in the northern part of the crater. Type (1) are rarer but are exposed in both
261 the north (Figure 6a) and in the south (Figure 6c). Notably, the alunite-bearing materials are not
262 associated with these most clearly layered terrains but rather with units with a distinctly massive
263 appearance (Figure 6d).

264 Overlying the sedimentary materials on the margins of the crater from an elevation of
265 700-800 m and extending to lower elevations, including the center of the crater, is a darker,

266 rougher looking cap rock unit that lacks a strong spectral signature in CRISM data but has some
267 characteristics indicative of the presence of high-Ca pyroxene group minerals. This dark unit,
268 which is <50-m thick and possibly considerably thinner, may be a coarse-grained sedimentary
269 unit, ash fall, or lava flow. Where removed by erosion, the underlying alunite-, kaolin-, and
270 silica/montmorillonite-bearing units are exposed (Figure 5e,f). Where the dark caprock is
271 preserved, its presence precludes determination of whether underlying aluminous units extend
272 across the entire basin. In addition to being atop the alunite-, kaolin-, and silica/montmorillonite-
273 bearing units, the dark caprock also embays central topographic highs that have a lower thermal
274 inertia, interpreted to be the peak ring structure of the crater. The dark capping material is
275 brightest in nighttime temperature data (Figure 1c), suggesting that it is the highest thermal
276 inertia material in the crater, which implies coarser grain size, greater cementation, and/or more
277 coherent bedrock relative to the other units.

278 The sole intracrater exposure of Fe/Mg-smectites is found in images FRT0000ACE6 and
279 FRT0000987B, covering an area southeast of a small impact crater, which excavates into
280 caprock and sediments in Cross crater. There is a small area with Fe-smectite in the impact
281 crater's rim in CRISM image FRT0000ACE6 (Figure 4a,c). Additional Fe-smectite deposits are
282 located approximately two crater-radii away from the small impact structure and are slightly
283 higher albedo in the infrared wavelengths than surroundings. Indistinctly layered materials in the
284 upper part of the stratigraphy are the likely host materials. There are some linear features radial
285 to the crater, indicating the presence of ejecta streamers; however, the majority of the small
286 crater's rim rock and ejecta do not have Fe/Mg-phyllosilicate signatures. Consequently, it is not
287 clear if the Fe-smectites are in the ejecta or in underlying materials scoured and exposed by the
288 ejecta. FRT00012E09 also may have spectra of Fe/Mg-smectites in a window beneath the

289 caprock, although the signature is weak, restricted to <10 pixels; and CTX resolution is
290 insufficient to resolve the morphology. Resolving the morphology and stratigraphy of the Fe/Mg
291 phyllosilicates in Cross crater will have to await acquisition of further CRISM and HiRISE data
292 in and around the small crater.

293 **Mineralogy and Geomorphology of the Cross Crater Region**

294 The mineralogy immediately outside of Cross crater is substantially different from that of
295 within (Figure 1d). No Al-phyllosilicates or sulfates are found; but in a survey of the
296 multispectral data within several Cross crater radii, there are at least a half dozen small (~10
297 km²) exposures of Fe/Mg-phyllosilicate-bearing materials. Fe/Mg-phyllosilicates are found in
298 several apparently sedimentary deposits as well as in small crater ejecta north of Cross crater.
299 These occurrences are associated with high thermal inertia materials (e.g. Figure 1c, 1d) yet have
300 a friable, eroded appearance (Figure 4b). To the south Fe/Mg-phyllosilicates are found together
301 with chlorides in a high thermal inertia deposit near 32°S, 157°W (see Osterloo et al., 2010;
302 Figure 13d in Ruesch et al., 2012].

303 Gridded MOLA DEM data of Cross crater paired with visible images show a ~4 km wide
304 valley that breaches the eastern crater rim, entering the Cross crater basin (Figure 7). No outflow
305 is apparent, and thus Cross crater is a closed basin. The valley enters the crater at an elevation of
306 1650 m—slightly above the 1550 m maximum height of the alunite and Al-phyllosilicate units—
307 from the topographic depression immediately east of the crater. The depression's present extent
308 is ~100 km², although its topography has been modified by a nearby impact crater to the east, so
309 the extent may have previously been greater. Interestingly, small knobs in the walls of the inlet
310 exhibit similar composition to the Cross crater sediments with Al-phyllosilicates and possibly

311 alunite. Four knobs in the valley wall have an absorption at 2.18-2.20 μm in materials that also
312 have a 1.9- μm absorption (Figure 7d). Analysis of HiRISE and CTX imagery shows that these
313 knobs are part of the walls of the valley, rather than ejecta or debris from the plateau above and
314 are not layered. They occur at an elevation of \sim 2000 m, i.e., \sim 400-500 m above the highest
315 outcrops of alunite and Al-phyllosilicates minerals within layered Cross crater sediments.

316 **Discussion**

317 **The Cross crater mineral assemblage in a Martian context**

318 A number of intercrater depressions across Mars host chlorides or sulfates (Osterloo et
319 al., 2010; Gaillard et al., 2013; Ehlmann & Edwards, 2014). Carbonates have only been
320 identified in two potential lake basins (Ehlmann et al., 2009; Michalski et al., 2013). Only a few
321 dozen of the $>$ 200 potential closed-basin crater lakes on Mars exhibit evidence of hydrated
322 minerals in existing CRISM and OMEGA data (Goudge et al., 2015). In deep basins filled with
323 sediments (comparable in size and original depth to Cross crater), sulfates are typically the salt
324 present, associated with Fe/Mg-phyllosilicates, hematite, and silica (e.g., in Gale (Milliken et al.,
325 2010) and Terby craters (Ansan et al., 2011)). Meridiani Planum, explored by the Opportunity
326 rover, has jarosite within its spatially extensive sulfate-rich sediments (Klingelhofer et al., 2004;
327 Arvidson et al., 2006; Poulet et al., 2008). The Valles Marineris troughs and associated chaos
328 terrain also host sulfates, with some exposures including interbedded or overlying detrital
329 phyllosilicates or authigenic hydrated silicates (e.g., Gendrin et al., 2005; Murchie et al., 2009a;
330 Bishop et al., 2009; Lichtenberg et al., 2010; Roach et al., 2010; Thollot et al., 2012). Typical
331 Valles Marineris interior layered deposit mineralogy is of monohydrated Mg-sulfates
332 interbedded with or grading up-section into polyhydrated sulfates, both accompanied by
333 crystalline ferric oxides (Bibring et al., 2007; Murchie et al. 2009c). Some locales host evidence

334 for distinctly acidic conditions and sulfur-rich fluids. These include Gusev crater (Hurowitz &
335 McLennan, 2007; Morris et al., 2008; Wang et al., 2008); jarosite in some units at Northeastern
336 Syrtis Major (Ehlmann & Mustard, 2012) and Mawrth Vallis (Farrand et al., 2009; 2014); Valles
337 Marineris plateau deposits with jarosite and Fe(III)SO₄OH (Milliken et al., 2008; Weitz et al.,
338 2010); jarosite in Noctis Labyrinthus troughs (Thollot et al., 2012); szmolnokite and
339 Fe(III)SO₄OH low in the section in Aram chaos (Massé et al., 2008; Lichtenberg et al., 2010);
340 and chasma deposits whose spectra exhibit a “doublet” absorption that may be indicative of clays
341 that have been leached or mixed with jarosite (Roach et al., 2010; Weitz et al., 2011). Alunite has
342 not yet been detected in or around any of these regions.

343 Cross crater contains the first and, as of this writing, largest discovery of alunite deposits
344 on Mars. The outcrop with spectrally dominant alunite in the southwestern portion of the crater is
345 ~10 km x ~5 km in extent, and scattered smaller outcrops occur in several locations in Cross
346 crater, intermixed with kaolinite group minerals. On Mars, known occurrences of alunite are so
347 far restricted to three locations in the Terra Sirenum region: (i) Cross crater, (ii) nearby
348 Columbus crater, where it is found mixed with phyllosilicates in CRISM image, FRT00013EEF,
349 in a few hectometer-scale outcrops on the crater lower wall and floor, and (iii) a small light-
350 toned deposit within the intercrater plateau near Cross and Columbus (25.42°S, 161.17°W). As
351 described by Wray et al. (2011), Columbus crater has light-toned layered deposits similar in
352 morphology to some within Cross crater (Figure 6a, c) but with secondary minerals and
353 precipitates dominated by kaolinite and polyhydrated and monohydrated Ca/Mg/Fe-sulfates,
354 including gypsum and kieserite. Localized outcrops within Columbus contain Al-smectite clays,
355 Fe/Mg-phyllosilicates, jarosite, alunite, and crystalline ferric oxides. The interbedded kaolinite
356 and sulfates at Columbus are inferred to represent fluctuating lake levels within a deep, closed-

357 basin deep lake, fed by upwelling groundwaters (Wray et al., 2011). This mineral assemblage is,
358 however, distinct from that in Cross crater.

359 **Inferred Cross crater water chemistry**

360 At Cross crater, Al-rich and Si-rich phases—specifically, alunite, kaolinite group
361 phyllosilicates, and silica or montmorillonite—are the spectrally and spatially dominant
362 secondary minerals. Iron oxides and iron sulfates are also present but are less spatially
363 widespread at the surface. On Earth, this mineral assemblage is classically characteristic of acid
364 sulfate, advanced argillic alteration. As pH decreases, the solubility of Al^{3+} increases, making it a
365 mobile element and readily available for incorporation into precipitated secondary minerals. The
366 pH of waters implied by the presence of alunite is acidic and possibly as low as 2-3. Figure 8
367 presents mineral stability fields for select slices of the multi-dimensional geochemical parameter
368 space that illustrate key tradeoffs in predominance of alunite with other minerals. Under
369 conditions where Al^{3+} is enriched in fluids, kaolinite and alunite precipitate under similar
370 conditions but with alunite forming at lower pH and/or higher $a\text{SO}_4^{2-}$ than kaolinite (Figure 8a).
371 The formation of alunite also requires acid sulfate solutions that can mobilize K in addition to the
372 aluminum (Rye et al., 1992). Aluminum must be many times more concentrated than iron in
373 solution for alunite formation to be favored relative to jarosite formation (Figure 8b). Jarosite
374 precipitation also requires more oxidizing conditions than alunite precipitation (Figure 8c).
375 Alunite forms near the $\text{H}_2\text{S}-\text{SO}_2$ buffer at low $f\text{O}_2$, commonly in the near-subsurface (Rye et al.
376 1992; Stoffregen et al., 2000).

377 The co-existence of alunite, kaolinite group phyllosilicates, and silica or montmorillonite
378 may indicate temporally fluctuating pH conditions in waters whereby at low $a\text{SO}_4^{2-}$, kaolinite is
379 favored, whereas at lower pHs and/or higher sulfate contents, alunite preferentially precipitates

380 (Figure 8). Alternatively, a two-step formation process is possible. From preexisting Al-
381 phyllosilicates, alunite forms by their leaching with waters with sulfuric acid (e.g., Altheide et
382 al., 2010). In either case, Cross crater hosted distinctly sulfurous, acidic waters during at least
383 one part of its history. Determining the timing and environmental setting(s) of alunite and Al
384 phyllosilicate formation requires additional information, discussed below.

385 **Possible formation environments for large alunite deposits**

386 How could such a large-scale alunite-bearing deposit form on Mars in Cross crater? On
387 Earth, there are three main environmental settings of alunite precipitation: magmatic
388 hydrothermal systems, weathering of massive sulfide deposits (supergene alteration), and in
389 cratonic lakes fed by paleobrines. On Mars, there are at least four possibilities. For the first
390 possibility, in magmatic hydrothermal systems, H₂S or SO₂ gases interact with groundwaters,
391 which are then piped to the surface as brines or steam, often along structurally controlled faults
392 (e.g. John et al., 2008; Varekamp et al., 2009). For example, at Copahue volcano in the Andes,
393 argillaceous deposits along the crater lake and flanks of the volcano host alunite and kaolinite in
394 varying proportions, fed by groundwaters whose flow patterns are controlled by faults.
395 Accessory silica phases are interspersed as crusts and veins, and almost pure siliceous sinters
396 occur in zones with low pH. In this and other fumarolic systems, magmatic fluids contribute SO₂
397 that undergoes disproportionation as it cools to form highly acidic fluids, which boil at the
398 surface of a water table releasing H₂S- and H₂SO₄-rich steam that leaches overlying rocks
399 replacing them with alunite and silica (Rye et al., 1992). Lake margins deposits can also contain
400 jarosite, hematite, montmorillonite, gypsum, kaolinite, goethite and quartz; vent mouths have
401 sulfur and pyrite (Mas et al., 1996). The primary controls on mineralogy are pH, fO₂, and
402 presence of sulfurous species. Variability is driven by volcanic activity (the vigor of outgassing)

403 and seasonal fluxes, which dictate the relative proportion of meteoric waters to magmatic
404 groundwaters. The fluids containing H_2SO_4 , SO_2 , HF, and HCl acquire many rock-forming
405 elements from interaction with basaltic to basaltic-andesite protoliths but are not neutralized by
406 the interaction (Mas et al., 1996; Varekamp et al., 2009). Upon loss of S, either via decreased
407 production of volcanic steam or reaction with host rocks, sulfurous brines transition to alkaline
408 chloride fluids (Rye et al., 1992). On Mars, acid hydrothermal systems have been proposed for
409 sulfate and silica deposits observed by the Spirit Rover in Gusev crater (e.g., Squyres et al.,
410 2008; Wang et al., 2008) and sulfate deposits in Valles Marineris (e.g., Thollot et al., 2012).

411 A second possibility is the formation of acidic waters, and then alunite deposition, driven
412 by acidity produced during oxidative weathering of ferrous minerals, like sulfides and primary
413 mafic phases. Such processes typically result in the precipitation of Fe-rich minerals, including
414 ferrous and ferric sulfates as well as iron oxides and phyllosilicates (e.g., Fernandez-Remolar et
415 al., 2003; 2005; 2011; Swayze et al., 2000; 2008; Swayze et al., 2000). The oxidation and
416 hydrolysis of iron from sulfides releases H^+ and is the source of acidity, which dictates the water
417 chemistry and drives subsequent reactions. In these settings, kaolinite and alunite can sometimes
418 be present when altered rocks are felsic or when leaching is intense. Evidence for large quantities
419 of buried sulfides have not been found on Mars, though sulfide weathering has been proposed to
420 explain sulfate deposits (Poulet et al., 2008; Dehouck et al., 2012), and a similar mechanism of
421 near-surface oxidation of Fe(II)-bearing sulfurous groundwaters has been proposed to generate
422 the acid conditions recorded at Meridiani Planum (Hurowitz et al., 2010).

423 A third possibility is that Cross crater was a paleolake, analogous to the acid saline lakes
424 of Western Australia (WA; e.g., Long et al., 1992; McArthur, 1991; Bowen & Benison, 2009;
425 Story et al., 2010). The WA lakes do not evolve from evapoconcentration of dilute inflow waters

426 but rather are fed by highly evolved, regionally acid-saline groundwaters. Lakes precipitate
427 halite, gypsum, hematite, kaolinite, and small amounts of basaluminite, bassanite, and alunite.
428 Shallow groundwaters in adjacent mudflats precipitate the same minerals, plus jarosite, which
429 forms syndepositionally as cements and displacive crystals (Benison et al., 2007; Story et al.,
430 2010; Bowen et al., 2012; Benison & Bowen, 2015). Alunite is an early diagenetic precipitate
431 within the pores of these deposits. Mixing in of meteoric waters, marine aerosols,
432 evapoconcentration, and mineral precipitation and dilution reactions control the chemistries of
433 individual lakes as well as their time variation. While several theories have been put forward for
434 understanding the origin of the acid saline waters, neither lithologic control (e.g., mafic vs. felsic
435 or presence/absence of massive sulfide), trapped ancient seawaters, or anthropogenic activities
436 can fully explain the observed chemical variability. The lack of natural buffers in a stable, highly
437 weathered craton, coupled with aridity to prevent dilution, may allow ancient acidic brines that
438 have evolved past the carbonate geochemical divide, consuming alkalinity, to acquire acidity
439 from small amounts of Fe, S, and rock weathering (Long et al., 1992; Bowen et al., 2012;
440 Benison & Bowen, 2015). Whether such multigeneration brines—or the equivalent of a
441 weathered craton—exist buried in the Mars subsurface is unknown, though production of
442 subsurface brines from dissolution of ancient salt deposits has been hypothesized (Zolotov and
443 Mironenko, 2014).

444 A fourth possibility may be distinctly Martian: highly acidified snows/rains. A
445 straightforward way to produce the requisite H₂SO₄-bearing solutions for alunite formation is via
446 disproportionation of SO₂ released by volcanism into the atmosphere, and subsequent aerosol
447 deposition (Bullock and Moore, 2007). Any waters – precipitation and/or snow/ice melt – would
448 become acidic by the incorporation of these hydrous sulfate species, present in the atmosphere

449 but also in the Martian soils where there is an imbalance with more anion species than cations
450 (Settle, 1979). These acidified waters could episodically form ponds in Cross crater and in
451 surrounding depressions.

452 **Environment of Alunite Formation in Cross Crater**

453 Geologic associations of minerals present can be used to discriminate between the four
454 possibilities above to establish environmental conditions for the formation of Cross crater's
455 deposits. Most open- and closed-basin lakes on Mars with evidence for secondary minerals
456 exhibit phyllosilicates within the basins that are spectrally identical to materials in the nearby
457 watershed, suggesting transport and deposition may be responsible for the current distribution of
458 these minerals, rather than in situ precipitation (Goudge et al., 2012a; 2015). In Cross crater,
459 however, phyllosilicate mineralization likely occurred in situ because kaolin-bearing sediments
460 within the basin differ markedly from Fe/Mg-phyllosilicates present in plains outside the crater.
461 The existence of extensive kaolinite group minerals and alunite within the basin points to a
462 special geologic process or a peculiar sediment or water chemistry uniquely confined to the
463 Cross crater basin and, perhaps, nearby Columbus crater and the plateaus between.

464 The acid aerosol mechanism may contribute to explaining regional Al-phyllosilicate
465 formation by regional intensification of weathering (e.g., Wray et al., 2011; Ehlmann &
466 Edwards, 2014; Carter et al., 2015), but it does not explain the particular localized concentration
467 of alunite in Cross crater. Iron sulfide dissolution or iron oxidation mechanisms likely provide a
468 source of acidity elsewhere on Mars, but do not alone explain alunite formation here because of
469 the paucity of Fe-bearing alteration phases, which are typical products of this process and are
470 detected with remote sensing at many other Martian localities. Mars is mostly comprised of

471 basaltic rocks, and the paucity of Fe/Mg/Ca secondary minerals and dominance of aluminum
472 minerals in Cross crater is atypical.

473 Mineralized, layered sediments along a contour roughly coincident with the mouth of an
474 inlet valley suggest the past presence of a closed basin lake in Cross crater. Lake levels at 1500
475 m (maximum elevation of layered sediments with Al-phyllosilicates) or 1650 m (inflow channel
476 elevation) would have resulted in lake volumes of approximately 1500 km³ or 1900 km³,
477 respectively, comparable to the volume of terrestrial Lake Ontario (1700 km³). Alternatively,
478 successive episodic periods of sedimentation and fill may have produced the observed sediments
479 via a series of shallow playa lakes or via weathering of airfall deposits. Acquisition of additional
480 HiRISE stereo pairs – only two on the southern wall exist to date – would facilitate the search for
481 shoreline terraces and correlation of bed levels as indicators of lake level.

482 A key question is the source and nature of any waters feeding the basin. Although the
483 depression in which the Cross crater inflow channel is sourced does not constitute a well-
484 bounded basin, the entire region lies just east of the Eridania drainage network (Irwin et al.,
485 2004), thought to be fed at least partially by groundwater (Fassett and Head, 2008). Moreover,
486 Cross crater is located south of the Mangala Vallis outflow, a unique valley system on Mars,
487 where a large outflow is sourced by a small fracture. An extensive groundwater system has been
488 suggested for the eastern flank of Tharsis (Ghatan et al., 2005 and references therein) and may
489 provide a source of waters for a paleo-Cross crater lake. Waters may have acquired acidity by
490 exchange with sulfurous compounds in meteoric waters or via subsurface exchange with
491 hydrothermal fluids, paleobrines, or iron sulfides. As modeled by Andrews-Hanna et al. (2010)
492 and discussed in Wray et al. (2011), Cross and Columbus craters are expected to be sites of
493 groundwater upwelling forming closed basin lakes and evaporate deposits.

494 However, that the most spectrally dominant alunite is geographically restricted to the
495 southwestern portion of the crater in spite of exposure of sedimentary materials with Al
496 phyllosilicates across the whole crater argues for a process that concentrates the alunite
497 formation in that area. In a ~800-m crater-wide deep lake, one would not expect highly localized
498 chemistry except in special circumstances. One possibility is the presence of localized, perhaps
499 fault-controlled, conduits for sulfurous groundwaters to reach the surface that are geographically
500 restricted to the southwest and result in fumarolic or hydrothermal spring deposits. A second
501 possibility is the existence of multiple shallow lakes within the basin, one of which was in the
502 southwest corner. Because the alunite is topographically higher than the silica-rich and kaolin-
503 rich deposits, the former possibility may be more likely than the latter. Additionally, the alunite
504 units are massive, rather than discretely layered. This may reflect their formation in the
505 subsurface as upwelling H₂S- or SO₂-bearing steam or fluids cooled, generating H₂SO₄ through
506 disproportionation. Oxidation upon contacting the Mars atmosphere or fluids in communication
507 with the Mars atmosphere would still further enhance sulfur speciation to SO₄²⁺. Finally, a third
508 inter crater plateau alunite-bearing site was found for which a non-lake-mediated formation
509 process is favored. There, alunite also occurs mixed with kaolinite group minerals within light-
510 toned deposits underlying an eroded cap-rock, but these are not in a topographic low.

511 Thus, localized conduits for escape of steam or waters in contact with magmatic sources
512 at depth is our favored hypothesis for the Cross crater alunite deposits. Numerous basins on Mars
513 show evidence of volcanic resurfacing (Goudge et al., 2012b), and Cross crater is located on the
514 western margin of the Tharsis system (Figure 1), a possible location of dike formation and a
515 location with numerous tectonic fractures, facilitating communication with the subsurface
516 (Anderson et al., 2001). The mineralogy of the Cross crater deposits with alunite, Al-

517 phyllosilicates, silica and scattered Fe oxides and Fe sulfates is similar to that observed in some
518 terrestrial magmatic systems. A flux of steam or waters from a magmatic hydrothermal system
519 into a basin that episodically may have hosted shallow lakes appears to fit the overall deposit
520 morphology and observed mineral assemblages.

521 In terrestrial settings, large alunite deposits are more typically associated with acid
522 alteration of either felsic rocks (e.g., Bigham and Nordstrom, 2000) or preexisting Al
523 phyllosilicates (e.g., Altheide et al., 2010). In basaltic hydrothermal alteration systems, alunite is
524 often a minor phase (Swayze et al., 2002; Guinness et al., 2007; Hynek et al., 2013; Marucci et
525 al., 2013). However, large-scale alteration to alunite and kaolinite assemblages mappable by
526 VSWIR imaging spectroscopy is also occasionally observed, driven in part by the duration of
527 magmatic activity at a particular locale (e.g. Berger et al., 2003; Swayze et al., 2014)
528 Furthermore, the crystallinity of protolith materials can strongly influence weathering products.
529 Weathering experiments by Tosca et al (2004) showed formation of Al-sulfates from basaltic
530 glass but not crystalline basalt of identical chemical composition. This is because Al in a glassy
531 material is released into solution during congruent dissolution whereas Al is typically retained in
532 rock in a dissolution process involving crystalline feldspar. Thus, (a) high throughput of acidic
533 waters, (b) poorly crystalline materials, and/or (c) more felsic precursors may – separately or in
534 combination – be responsible for the unique Cross crater alunite.

535 Future work might include more detailed geochemical modeling of a variety of potential
536 fluid and sediment compositions to further constrain the geochemical setting. Multistep
537 formation scenarios could be modeled with reaction-transport models and compared to the
538 composition and distribution of observed deposit mineralogy. A key question is the fate of
539 leached Fe, Ca and Mg, thus explaining the differences between Cross crater and nearby

540 Columbus crater with its polyhydrated sulfate, gypsum, and kieserite deposits. These salts are
541 either absent in Cross crater (precipitation in the subsurface, brine transport out of Cross crater
542 through highly permeable rocks?) or concealed in the basin center by the caprock. Furthermore,
543 questions of the potential extent, depth, and longevity of a Cross crater lake may be resolvable
544 with additional high spatial resolution mineralogic and topographic data over unimaged regions
545 in Cross crater. A key question whether any paleolakes and magmatic hydrothermal systems
546 facilitating alunite formation were contemporaneous.

547 **Implications**

548 Cross crater hosts the largest-scale alunite deposit discovered to date on Mars. It is
549 associated with basin-ringing, layered kaolin-bearing sediments as well as hydrated silica or
550 montmorillonite in polygonally-fractured sediments within local topographic lows. Evidence for
551 low pH aqueous activity on Mars has been previously provided by ferric sulfates, including
552 jarosite, formed at pH<4. The discovery of alunite adds to the continuum of low pH Martian
553 environments with a distinctly different local geochemistry resulting in relatively iron- (and
554 magnesium- and calcium-) poor assemblages of phyllosilicates and sulfates. Along with the
555 smaller deposits in nearby Columbus crater and on the plateau in between, Cross crater's alunite
556 deposits are indicative of regional conditions. Prevalent alunite and accompanying Al
557 phyllosilicates require acidity and (1) locally high volumes of sulfurous groundwaters with H₂S
558 or SO₂ and high water throughput during alteration; (2) atypically glassy and/or felsic basin-
559 filling materials, more susceptible to dissolution and mobilization of aluminum; or a combination
560 of these. Cross crater, with its advanced argillic alteration, including alunite precipitates, thus
561 represents a new type of ancient Martian aqueous environment.

562 Of four mechanisms considered to produce the observed mineralogy and geomorphology
563 – magmatic hydrothermal waters, massive sulfide weathering, brine-fed acid lakes, and
564 deposition of atmospherically-derived sulfurous aerosols – sulfurous magmatic hydrothermal
565 waters and steam, rising through fractures, leaching local rocks, and then precipitating alunite
566 upon fluid cooling and oxidation best explain the localized nature of the alunite deposits and
567 their geomorphology. Evidence for regional groundwater upwelling, volcanism, and faulting as
568 well as mineral assemblages similar to terrestrial magmatic hydrothermal environments are
569 consistent with this scenario. Cross crater may have also episodically hosted a shallow lake in
570 which the more widespread kaolin- and silica/montmorillonite-bearing sediments were
571 deposited.

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Figure captions

901 **Figure 1.** (a) Location of Cross crater on a MOLA topographic map of Mars where red colors
902 are high elevations and blue are low elevations. Elevation range is approximately -2500 m to
903 10,000 m. (b) MOLA topographic map of Cross crater overlain on CTX. (c) Nighttime thermal
904 infrared map from THEMIS (Christiansen et al., 2004). Bright-toned areas are warmer and
905 higher thermal inertia. Peak ring materials and bright sedimentary layers are relatively lower
906 thermal inertia relative to a later emplaced dark cap rock. (d) CRISM multispectral maps
907 showing the locations of secondary minerals within and around Cross crater using band depth
908 parameterizations (Pelkey et al., 2007). Red: BD1900 for H₂O in mineral structures, Green:
909 Blue: BD2200 for Al-OH and Si-OH, Blue: BD2300 for Fe-OH and Mg-OH.
910
911 **Figure 2.** Spectra of alunite-bearing materials (red), alunite- and kaolin-bearing materials
912 (yellow), kaolin-bearing materials (blue), and silica or Al-smectite-bearing materials (green)
913 from Cross crater CRISM image FRT0000987B compared to library spectra. The low-
914 temperature lacustrine alunite spectrum was acquired of samples from Lake Tyrrell, Australia,
915 and the hydrothermal alunite spectrum was of samples from Marysvale, Utah. The opaline silica
916 acquired under Mars pressure and temperature conditions is from Swayze et al. (2007). All other
917 library spectra are from the Clark et al. (2007) reference database.
918
919 **Figure 3.** Tetracorder maps of CRISM images in Cross crater, showing the spatial distribution of
920 the aluminous endmembers and their mixtures. Colors correspond to the colors of spectra in
921 Figure 2 and images used in the mapping are listed in Table 1 and indicated here by their image
922 IDs with leading zeros removed.

923 **Figure 4.** (a) Fe/Mg-phyllosilicates within Cross crater are found in the rim of a small interior
924 crater as well as at the outer margins of its ejecta blanket. Band depth maps at 2.3 μ m from
925 CRISM images FRT0009878 and FRT0000ACE6 were overlain on CTX image
926 P15_006945_1494_XN_30S158W_080119 and displayed where values >0.0. There is some
927 residual striping from detector artifacts in the mineral map. White, circled regions have Fe/Mg-
928 phyllosilicates; spectra are shown in panel c. A context map for the location is in Figure 3. (b)
929 Example of a friable, Fe/Mg phyllosilicate deposit identified in CRISM mapping data shown in
930 CTX image P20_009028_1495_XI_30S157W_080629. Spectra from the white, circled area are
931 shown in panel c. A context map for the location is in Figure 1d. (c) spectra from the locations in
932 (a) and (b) compared to laboratory measurements of nontronite, an Fe-smectite, and saponite, an
933 Mg-smectite (Clark et al., 2007).

934 **Figure 5.** (a) Context for a MOLA profile of Tetracorder maps on CTX from the southeastern
935 part of Cross crater. The white box shows a portion of (c). (b) MOLA point shot data show the
936 alunite/kaolinite-bearing units form a distinctive bench with topographically lower silica or
937 montmorillonite deposits. (c) Tetracorder maps on CTX from the southwestern part of Cross
938 crater showing the morphology of mineral-bearing units. (d, e) alunite units are massive beneath
939 dark materials in HiRISE PSP_008883_1490_RED. Silica-bearing units are fractured at (f) km-
940 scale and (g) meters-scale in HiRISE ESP_016320_1490_RED. The silica bearing materials
941 occur beneath a dark cap rock.

942 **Figure 6.** Finely layered Al-phyllosilicate-bearing Cross crater sedimentary materials in (a)
943 northwestern Cross crater in ESP_013274_1495_RED, (b) northern Cross crater in
944 PSP_010584_1500_RED,, and (c) southern Cross crater in PSP_010228_1490_RED. Eroded
945 Cross crater sediments have two characteristic types of layering, typified, respectively, by (a, c)

946 and the more spatially widespread (b). (d) a 3D perspective view of the southern wall of Cross
947 crater shows the eroded topography and how the most alunite-enriched area has a distinct lack of
948 bedding. HiRISE digital elevation model from PSP_010228_1490 and ESP_016320_1490.

949 **Figure 7.** (a) MOLA topographic image of Cross crater with color gradient across the
950 topographic range subset to emphasize topography in the vicinity of Cross crater. The range
951 shown is from approximately 600m to 2600 m above the MOLA datum. (b) Zoom of (a)
952 showing the eastern inlet valley and a putative inlet valley into Cross crater. (c) Topographic
953 profile across the valley. (d) A CRISM mineral map tracking the depth of an absorption near
954 2.17-2.20 μm . The strongest signatures are within Cross crater in sediments. Four locations along
955 the inlet valley, 200 m higher in elevation, also exhibit absorptions characteristic of aluminous
956 materials. HiRISE images from (e) ESP_012641_1495_RED and (f) ESP_033383_1495_RED
957 show the outcrops of materials in the valley at finer spatial resolution. (g) CRISM spectra from
958 FRT00014744 at the four locations.

959 **Figure 8.** Predominance area diagrams to illustrate geochemical conditions favorable for alunite
960 kaolinite, and jarosite. Concentration of dissolved species and co-existing solid phases were
961 based on simulated reaction of terrestrial volcanic gas compositions (Symonds et al., 2004) with
962 Martian basaltic composition (Poulet et al. 2009). (a) Plot of Al phases as a function of pH and
963 sulfate activity. Alunite is favored at pH lower than kaolinite and with increasing sulfate activity.
964 (Diagram calculated at: T=5°C, P=0.5 bars, $a\text{Mg}^{2+}=10^{-3}$, $a\text{K}^+=10^{-5}$, $a\text{Ca}^{2+}=10^{-3}$, kaolinite,
965 $\text{SiO}_2(\text{am})$ and $\text{Fe(OH)}_3(\text{am})$ have $a = 1$; pyrophyllite, jurbanite, laumontite is suppressed). (b)
966 Plot of sulfate phases as a function of pH and the ratio of $\text{Al}^{3+}/\text{Fe}^{3+}$, which must be high to favor
967 alunite. (T=5°C, P=0.5 bars, $a\text{Mg}^{2+}=10^{-3}$, $a\text{K}^+=10^{-5}$, $a\text{SO}_4^{2-}=10^{-2}$, $a\text{Ca}^{2+}=10^{-3}$; $\text{SiO}_2(\text{am})$ and
968 Fe(OH)_3 have $a = 1$; jurbanite, and basaluminite are suppressed) C. Superimposed predominance

969 diagrams for Fe and Al phases as a function of pH and fO₂. (T=5°C, P=0.5 bars, aMg²⁺=10⁻³,
970 aK⁺=10⁻⁵, aSO₄²⁻ = 10⁻², aCa²⁺=10⁻³; SiO₂(am), Fe(OH)₃(am), and kaolinite have a = 1; jurbanite,
971 laumontite, pyrophyllite, goethite, and hematite are suppressed). Diagrams calculated using
972 Geochemist's Workbench v.8.0 using the Wateq4 database.

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Tables
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Table 1. CRISM full- and half-resolution images used in this study. Images are listed clockwise around the crater, starting at the inflow valley on the east. Coverage is duplicative in some cases. The best images used for Tetracorder mapping (see Datasets & Methods) are indicated. An asterisk on the image ID indicates data that are short wavelength only, i.e., acquired from 0.4-1.0 μm rather than 0.4-4.0 μm . All CRISM images as well as a map of the image footprints are available at the NASA PDS Geosciences Node website.

CRISM Image ID	Day-of-year	Used in Tetracorder mapping (Fig. 3)
FRT00014744	2009_230	
FRT00011E7D	2009_097	
FRT0000B49F	2008_181	yes
HRL00012386	2009_113	
FRT00019DFE	2010_201	
FRT00021B59	2011_338	
FRT00010AE2	2009_025	
FRT0000D24B	2008_303	yes
FRT00012E09	2009_146	
FRT0000ACE6	2008_136	yes
FRT0000B252	2008_170	yes
FRT0000987B	2008_019	yes
FRT0001EF51*	2011_189	
FRT0001DABB	2011_101	
FRT0001187B	2009_069	
FRT0000CC44	2008_275	yes
FRT000137C2	2009_185	yes

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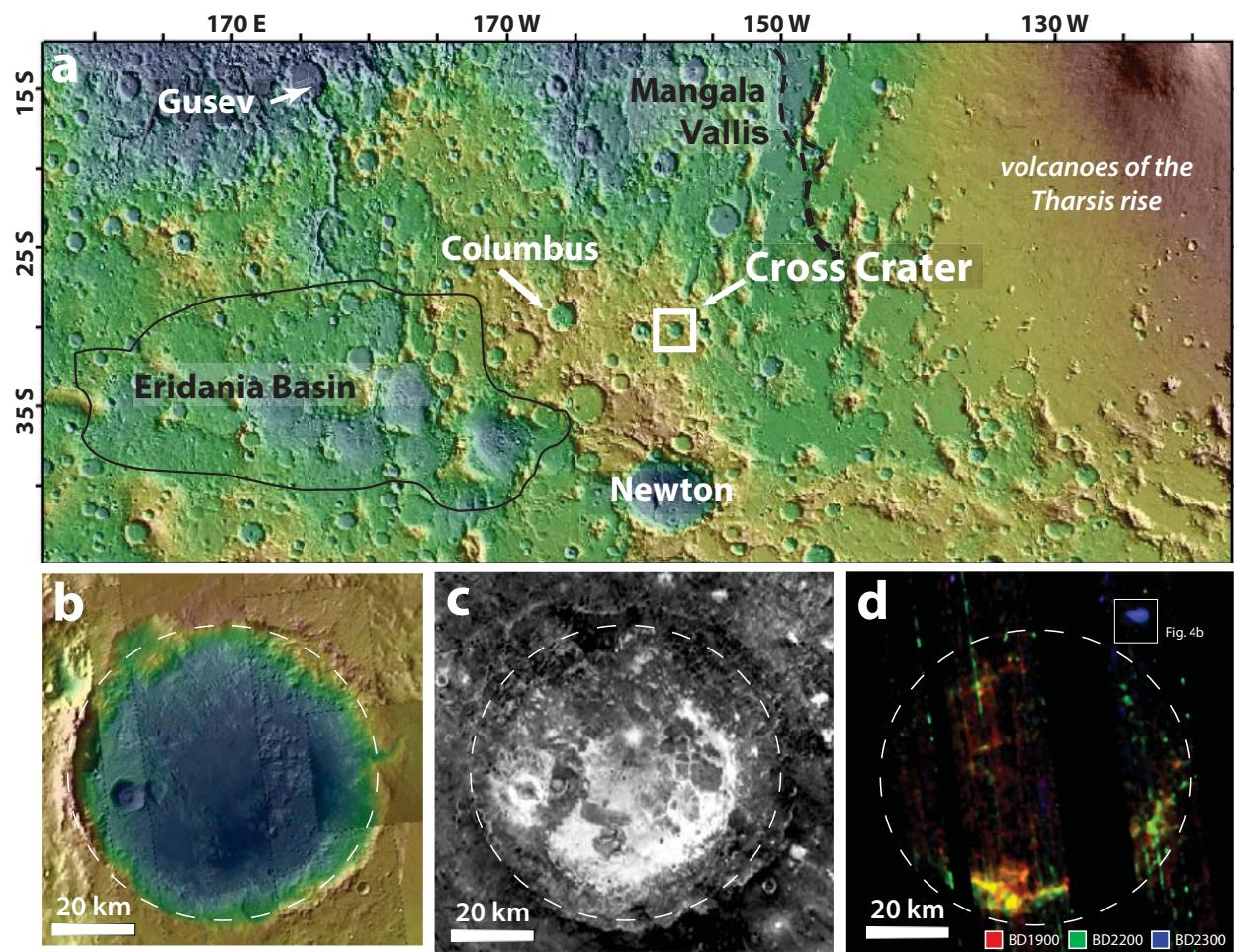
Figures

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Figure 1



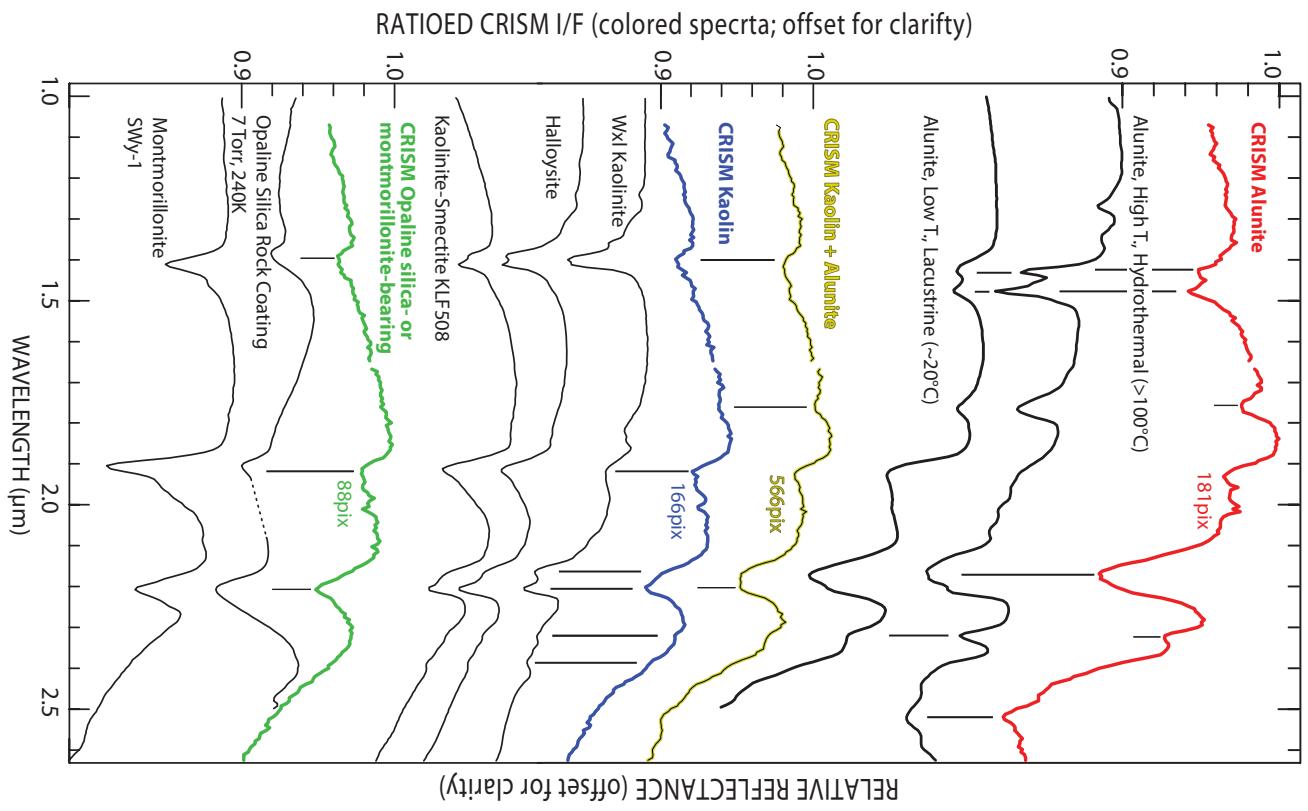
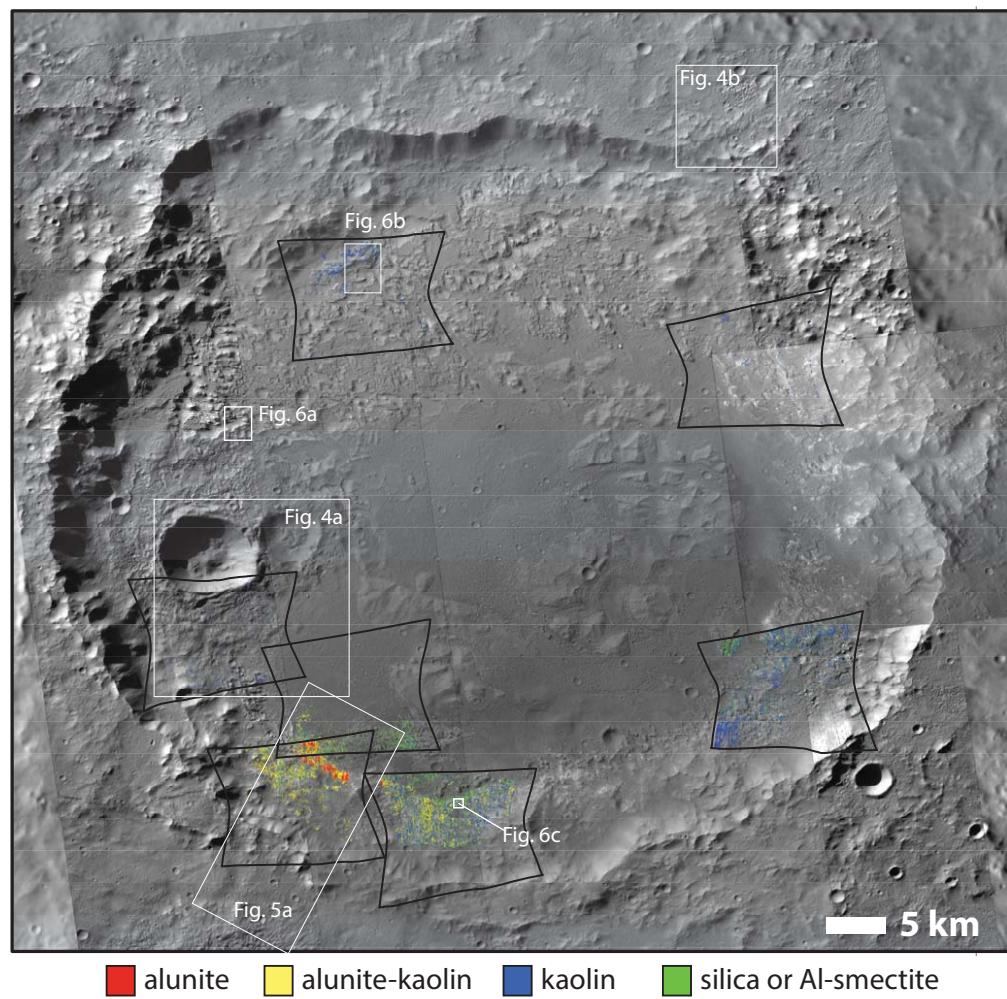


Figure 3



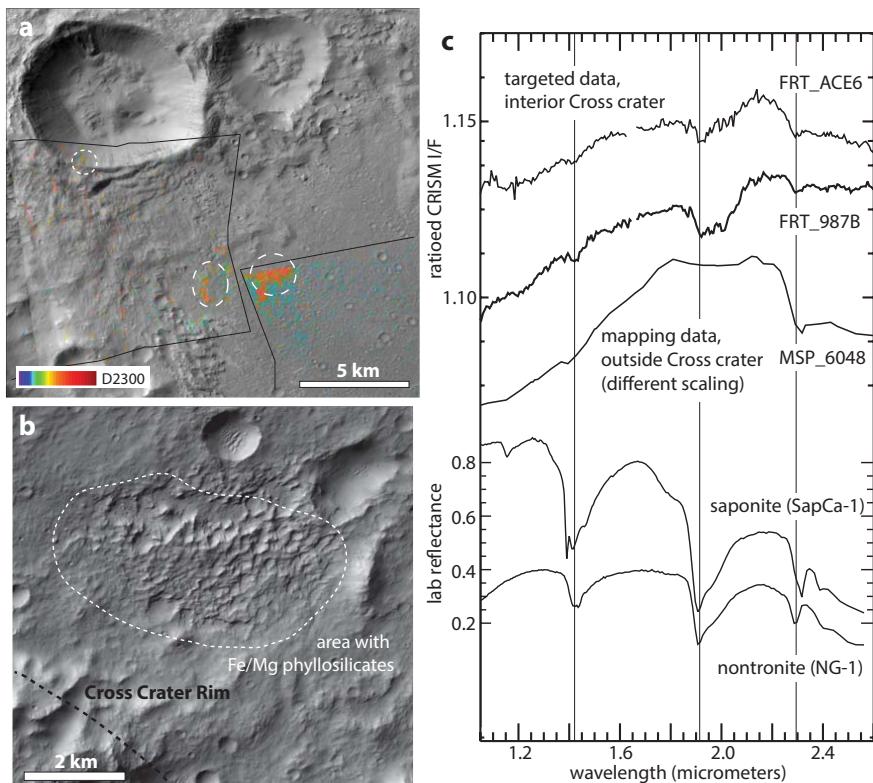


Figure 5

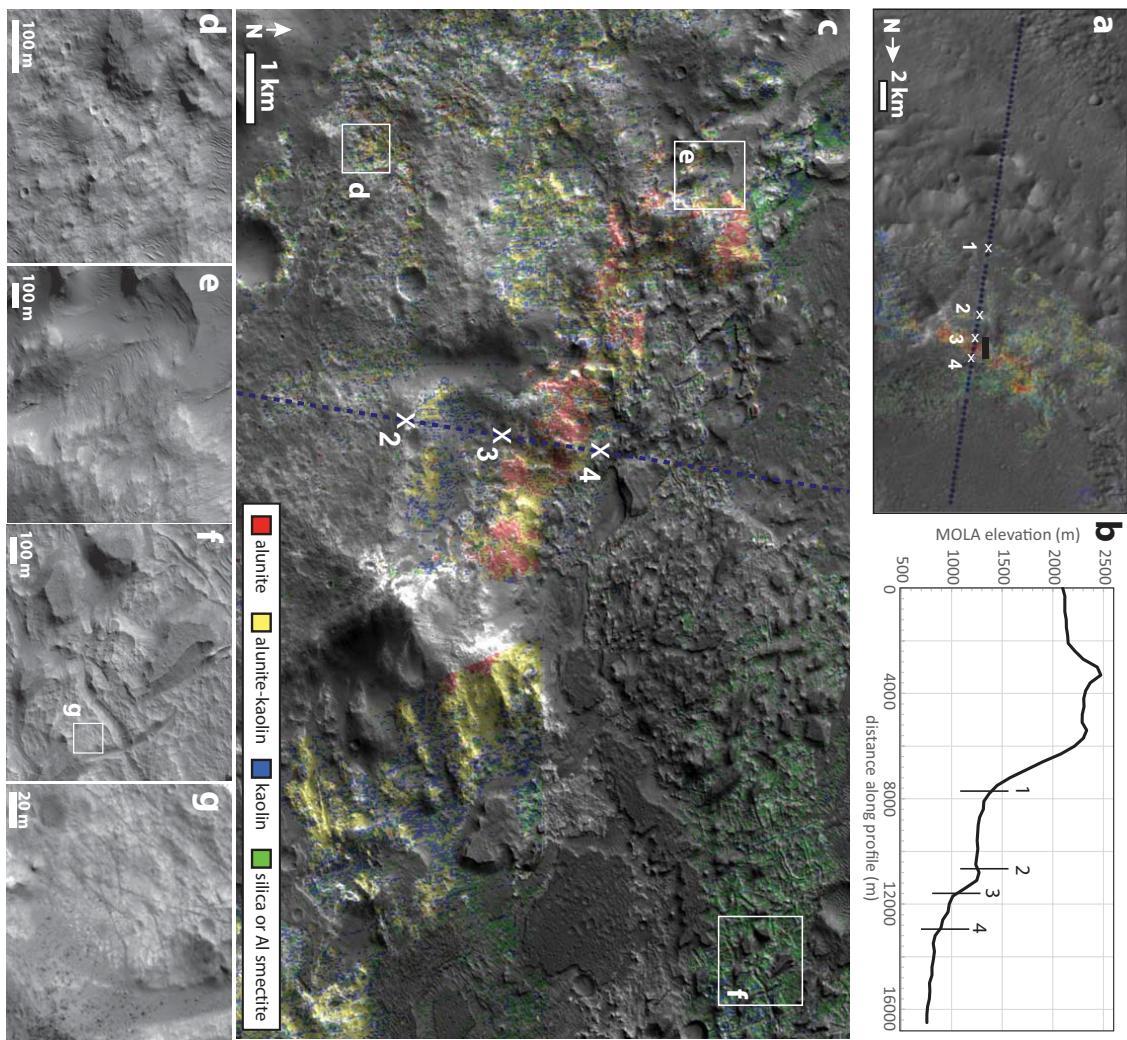


Figure 6

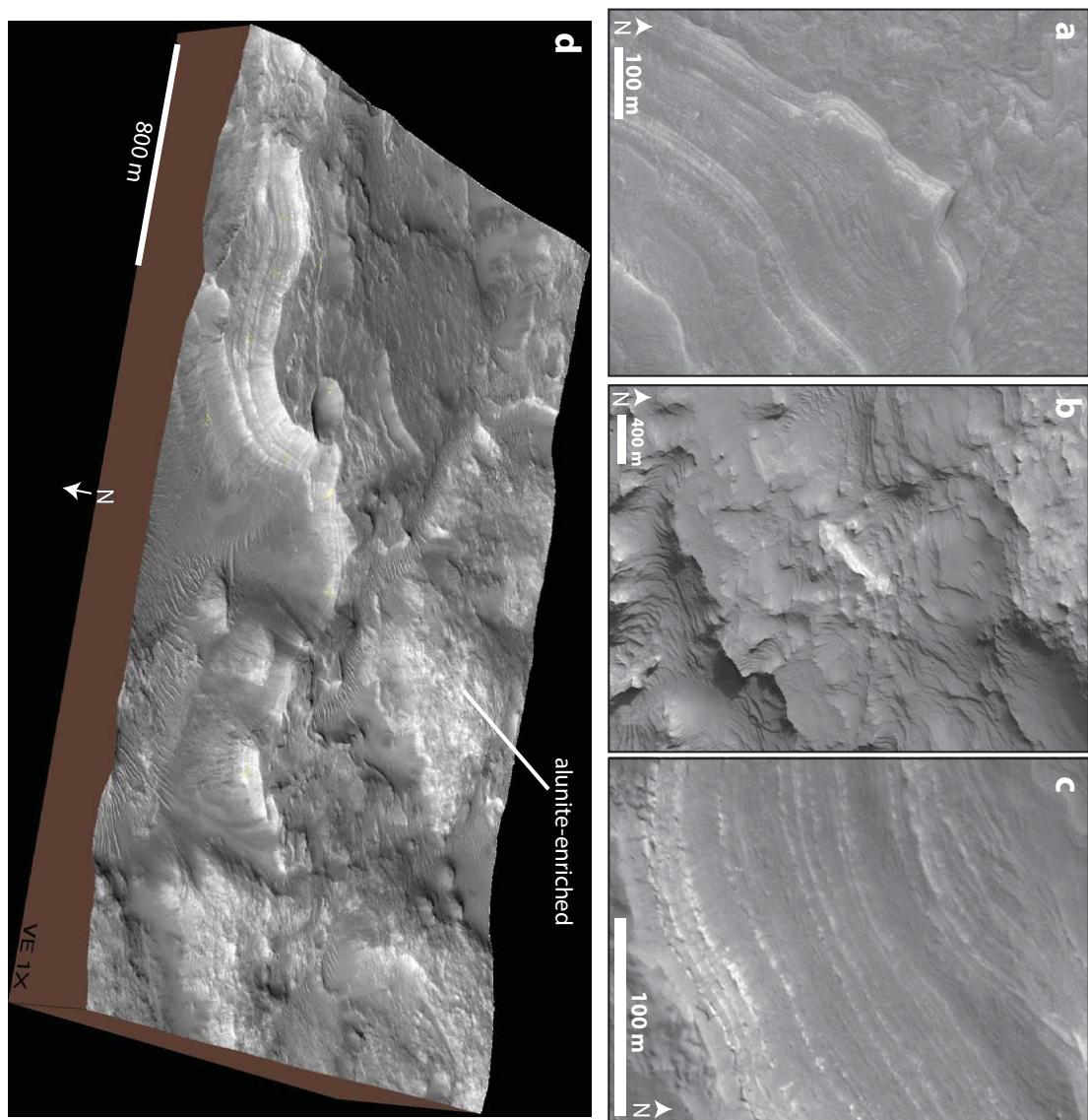


Figure 7

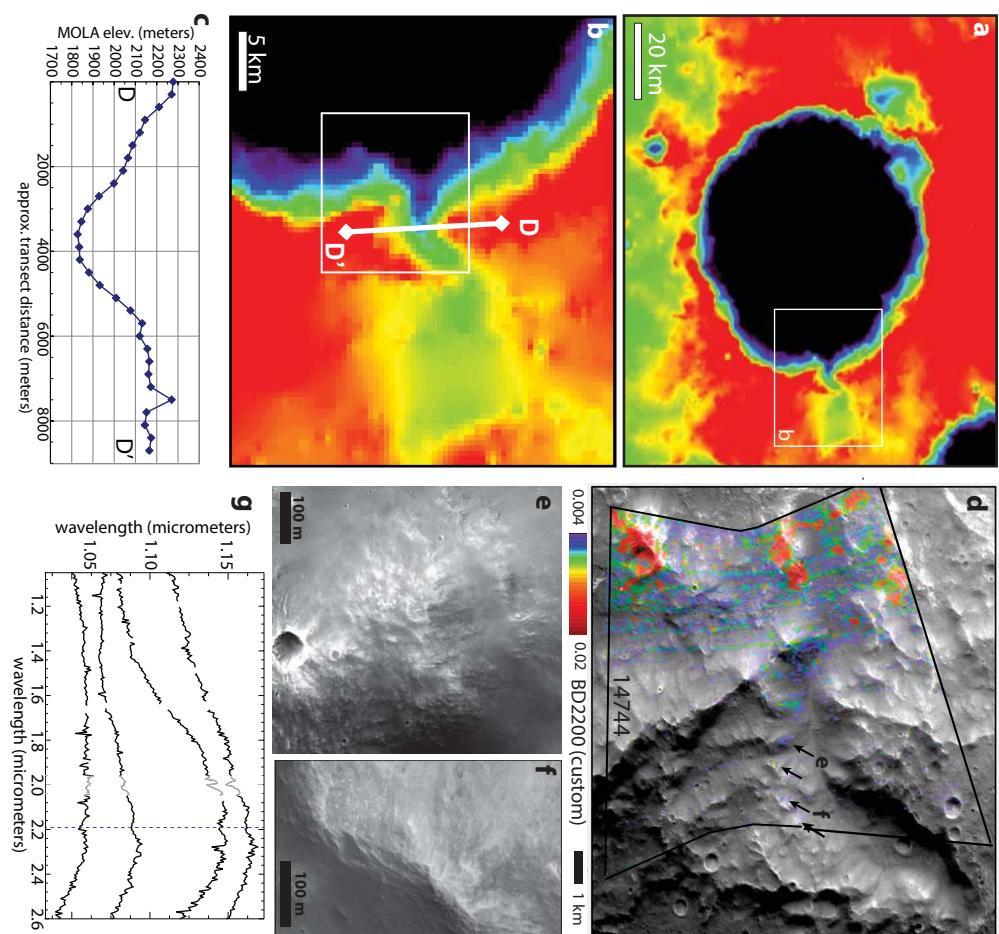


Figure 8

