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#### 37 Abstract

We report the results of geological studies by the Opportunity Mars rover on the 38 Endeavour Crater rim. Four major units occur in the region (oldest to youngest): the Matijevic, 39 Shoemaker, Grasberg and Burns formations. The Matijevic formation, consisting of fine-grained 40 clastic sediments, is the only pre-Endeavour-impact unit and might be part of the Noachian 41 42 etched units of Meridiani Planum. The Shoemaker formation is a heterogeneous polymict impact 43 breccia; its lowermost member incorporates material eroded from the underlying Matijevic 44 formation. The Shoemaker formation is a close analog to the Bunte Breccia of the Ries Crater, 45 although the average clast sizes are substantially larger in the latter. The Grasberg formation is a 46 thin, fine-grained, homogeneous sediment unconformably overlying the Shoemaker formation, 47 and likely formed as an airfall deposit of unknown areal extent. The Burns formation sandstone overlies the Grasberg, but compositions of the two units are distinct; there is no evidence that the 48 Grasberg formation is a fine-grained subfacies of the Burns formation. The rocks along the 49 50 Endeavour Crater rim were affected by at least four episodes of alteration in the Noachian and Early Hesperian: (i) vein formation and alteration of pre-impact Matijevic formation rocks; (ii) 51 low-water/rock alteration along the disconformity between the Matijevic and Shoemaker 52 53 formations; (iii) alteration of the Shoemaker formation along fracture zones; and (iv) differential mobilization of Fe and Mn, and CaSO<sub>4</sub>-vein formation in the Grasberg and Shoemaker 54 formations. Episodes (ii) and (iii) possibly occurred together, but (i) and (iv) are distinct from 55

56 either of these.

#### 57 **1. Introduction**

58 Mars Exploration Rover (MER) *Opportunity* has been exploring the geology of Meridiani 59 Planum within Arabia Terra since landing on 25 January 2004. For over 7 Earth years, 60 Opportunity traversed the hematite-rich plains making observations of sulfate-rich sedimentary 61 rocks and associated hematitic concretions [Arvidson et al., 2011; Squyres et al., 2006] mapped 62 as part of the Hesperian and Noachian highland undivided unit on the global geologic map of Mars [Tanaka et al., 2014]. On Sol (Mars day) 2681 (09 Aug. 2011), Opportunity reached the 63 northwestern rim of Endeavour Crater, a 22 km diameter impact structure (Fig. 1a) formed in 64 65 Noachian aged materials that predate the embaying sulfate-rich sedimentary rocks [Arvidson et al., 2014; Hynek et al., 2002]. The Endeavour Crater rim was chosen as a geological target 66 because the rocks record an ancient epoch in martian history, and because orbital infrared data 67 show that phyllosilicate minerals are present on portions of the rim, thereby implying that a 68 period of aqueous alteration is recorded in the rocks [Wray et al., 2009]. Thus, exploration of the 69 Endeavour Crater rim directly addresses one of the main goals of the MER mission: explore 70 regions and associated rocks and soils where water might have been present and make 71 assessments regarding past habitability [Squyres et al., 2003]. 72

*Opportunity* arrived at the Endeavour Crater rim at Cape York, an ~700 m long segment rising just above the surrounding hematite plains (Fig. 1b). Shoemaker Ridge forms the spine of Cape York and is the type locality for the Noachian impact material of the rim, which has been informally named the Shoemaker formation [*Crumpler et al.*, 2015a; *Squyres et al.*, 2012]. 77 *Opportunity* began investigations of the Endeavour rim at Spirit Point, the southwestern tip of

- 78 Cape York, and then traversed northeast along the western (outboard) side of Cape York,
- climbed to the ridge crest and returned, rounded the northern tip, and traversed southwest along
- 80 the eastern side. Roughly midway down the eastern side, an extensive investigation of the central
- 81 portion of the rim segment was done because information from the Compact Reconnaissance
- 82 Imaging Spectrometer for Mars (CRISM) instrument onboard the Mars Reconnaissance Orbiter
- (MRO) indicated the presence of ferric smectite in this region [*Arvidson et al.*, 2014]. The
   investigation included a looping reconnaissance traverse from the eastern margin of Cape York,
- up to and along the ridge crest, back down to the eastern margin, followed by intensive study of
- selected regions identified as being of especial geological interest.
- Subsequent to the exploration of Cape York, *Opportunity* was commanded to drive south 87 to the next rim segment, Cape Tribulation. Along the way, cursory exploration of two small rim 88 portions named Sutherland Point and Nobbys Head was done (Fig. 1b). Cape Tribulation was 89 reached just east of its northern tip, a region named Solander Point (Fig. 1c). Opportunity 90 rounded the northern tip, climbed along Murray Ridge, which forms the spine of the northern 91 portion of Cape Tribulation, investigated rocks and soils within Cook Haven [Arvidson et al., 92 2016], and then traversed southward along the western side of Murray Ridge. The latter included 93 investigations of the rocks on the outboard bench and up on Murray Ridge. Opportunity also did 94 95 a reconnaissance investigation of a short, ~160 m long SW-NE trending ridge west of the Murray 96 Ridge bench named Wdowiak Ridge (Fig. 1c). On Sol 3847 (18 Nov. 2014) Opportunity reached the northern end of a large, unnamed ridge and investigated bedrock in the Hueytown fracture 97 zone on the outboard side of the ridge (Fig. 1c). 98
- 99 The rocks discussed here are all outcrop, ejecta-block and float-rock targets analyzed 100 between sols 2669 and 3866 (28 July 2011 through 10 Dec. 2014), from the last plains outcrop 101 prior to reaching Spirit Point, through to the Hueytown fracture zone. Subsequent to our 102 investigations at the Hueytown fracture zone, *Opportunity* began investigations in Marathon 103 Valley. Rocks from this region are briefly mentioned for textural comparisons, but they are not a 104 focus of this paper. Soil analyses are not discussed.
- The instruments of the Athena payload [Squyres et al., 2003] were used to investigate 105 materials along the Endeavour rim: the Alpha Particle X-ray Spectrometer (APXS; Rieder et al. 106 107 [2003]), the Microscopic Imager (MI; Herkenhoff et al. [2003]), the Panoramic Camera (Pancam; Bell et al. [2003]) and the Rock Abrasion Tool (RAT; Gorevan et al. [2003]), all 108 109 supported by imaging from the engineering cameras – Navigation Cameras (Navcam) and front and rear Hazard Avoidance Cameras (Hazcam) [Maki et al., 2003]. Prior to arrival at Cape York, 110 the Miniature Thermal Emission Spectrometer [Christensen et al., 2003] had ceased operating. 111 By the time *Opportunity* had reached Cape York, the <sup>57</sup>Co source of the MIMOS II Mössbauer 112 Spectrometer [Klingelhöfer et al., 2003] had decayed to the point where useful measurements 113 114 were no longer possible.
- The major focus of this paper is on the compositional information returned by the APXS and their use in defining alteration processes, but these data are not considered in isolation. We first put our study into geological context using information derived from orbital and *in-situ*

- 118 mapping. Pancam and Navcam images are used to interpret outcrop textures and structures, and
- 119 Pancam spectra are used to constrain mineralogy. The micro-textures of the rocks are interpreted
- 120 from MI images. The Mars observations are then compared to a terrestrial analog site, the Ries
- 121 Crater and tied into information derived from cratering mechanics studies. Finally, the
- 122 observations discussed here are developed into a geological and alteration history for the region
- around Endeavour Crater.

#### 124 2. The APXS Dataset

The APXS determines chemical compositions of rocks and soils using X-ray 125 spectroscopy after irradiation with energetic alpha particles and X-rays. It therefore resembles a 126 combination of the standard laboratory methods of X-ray fluorescence spectrometry (XRF) and 127 particle induced X-ray emission spectrometry [Rieder et al., 2003]. The typical analysis field of 128 view has a diameter of about 38 millimeters, with the instrument response being strongest in the 129 central region. Concentrations are extracted from the X-ray spectra using the empirical method 130 131 described in Gellert et al. [2006]. The areas of the characteristic peaks of each element are determined with a non-linear least-squares-fit algorithm and the peak areas are then quantified 132 133 into elemental concentrations using the calibration sample set for MER, comprised of about 50 geological reference materials and additional simple chemical compounds (cf., Gellert et al. 134 135 [2006]; Rieder et al. [2003]). For each major and minor element, the typical oxide – Na<sub>2</sub>O for quantified Na, MgO for Mg, etc. - is assumed. The major element Cl and trace elements Ni, Zn, 136 and Br are treated as elemental in the data reduction. Iron is reported as FeO because the 137  $Fe^{3+}/Fe^{2+}$  speciation could no longer be determined using the Mössbauer spectrometer. The sum 138 of all components is normalized to 100% to compensate for a variable standoff distance. In the 139 analysis model, self-absorption is taken into account using the assumption of a homogeneous, 140 glass-like sample. This assumption is probably never correct, and is the underlying reason for a 141 lower accuracy compared to analyses of glass disks in standard XRF. The absorption of the 142 emitted X-rays, especially for lower Z elements that come from depths of only a few 143 micrometers, depends on the composition of the host phase. Of necessity, absorption corrections 144 145 for the APXS data use the average sample composition.

The results are reported with uncertainties for each element that represent  $2\sigma$  precision 146 errors of the peak areas (e.g., Gellert et al. [2006]; Ming et al. [2008]). Precision uncertainties 147 are well suited to judge the similarity of samples rather than using the larger accuracy errors, and 148 can be used to group rocks by their similar compositions. The rocks likely share a similar 149 mineralogy and therefore any inaccurate corrections in the APXS analysis stemming from 150 microscopic heterogeneity would be minimized for these rocks. The validity of using precision 151 152 error bars for comparing and grouping rocks in classes is justified by the nearly identical and consistent composition of fine-grained, homogeneous igneous rocks like the Adirondack basalts 153 154 from Gusev Crater analyzed by sister rover Spirit [Gellert et al., 2006; McSween et al., 2006].

The relatively large accuracy error bars can be explained in part by the very different compositions of possible minerals. For example, two possible Cl-rich minerals include NaCl and NaClO<sub>4</sub>, where the difference in oxygen causes differences in the absorption cross sections that are needed for accurate correction. Independent knowledge of the mineralogy and phase distributions within the targets would be required to improve the accuracy of analyses. Table S1

160 of the on-line supplement gives the typical relative accuracy of the measurement, which is

repeated from Table 1 by *Gellert et al.* [2006]. These accuracy measures are compared to the

relative precision for the Shoemaker formation target Transvaal. This target has a composition

163 close to the mean Shoemaker formation breccia, and an integration time close to the median of

all Shoemaker formation target integrations. Thus, the precision of this analysis is typical for the

165 APXS measurements reported here.

## 166 **3. Geological Context**

The oldest geologic structure in the region of Meridiani Planum is an ancient multiring 167 basin that is at least 800, and possibly 1600 km, in diameter (Fig. 2a); the lithologic units of 168 Meridiani Planum were deposited on this structure [Newsom et al., 2003]. Endeavour Crater was 169 formed in materials of Noachian age. The basal unit in the immediate vicinity of the Meridiani 170 plains is the Early to Middle Noachian highlands subdued crater unit (Fig. 2b) which is 171 interpreted to be composed of a mixture of primary (volcanic, pyroclastic) and secondary (impact 172 breccia, fluvial and aeolian sedimentary) rocks with a crater-density model age of ~3.9 Ga 173 174 [Hynek and Di Achille, 2017]. This highlands unit is overlain by several hundreds of meters of Meridiani etched plains units; the lower two are Middle to late Noachian in age; the topmost unit 175 176 is Late Noachian/Early Hesperian in age (Fig. 2b). The etched units are interpreted to be aeolian and/or volcanic deposits, with a combined crater-density model age also of roughly 3.9 Ga 177 [Hynek and Di Achille, 2017; Hynek and Phillips, 2008]. The Burns formation investigated by 178 179 *Opportunity* is the uppermost part of the etched unit stratigraphy. Based on mineralogy, composition, texture, and primary sedimentary features, the Burns formation is interpreted to be 180 a sulfate-rich aeolian sandstone (e.g., Squyres et al. [2006]). The region is capped by the thin, 181 surficial Hematite unit, mapped as Early Hesperian [Hynek and Di Achille, 2017]. This is an 182 unconsolidated lag deposit rich in hematitic concretions derived from erosion of the underlying 183 the Burns formation, plus basaltic sands in aeolian bedforms [Squyres et al., 2006]. 184

Endeavour Crater lies to the northeast of Miyamoto Crater (Fig. 2a) [Grant et al., 2016; 185 Newsom et al., 2003], an ~160 km diameter impact structure containing Fe-Mg-rich smectite 186 phases on its floor [Wiseman et al., 2008]. Formation of the smectites is thought to have been 187 engendered by the hydrological environment of western Arabia Terra in which groundwaters 188 from the highlands to the south emerged from local topographic lows and promoted in-situ 189 alteration of primary or impact-generated rocks [Andrews-Hanna and Lewis, 2011; Andrews-190 Hanna et al., 2007]. The Endeavour impact occurred well within the region where the 191 continuous ejecta blanket of Miyamoto Crater would have been, and the pre-impact target 192 stratigraphy would have included polymict breccias from that earlier impact. These could have 193 been altered as were the Miyamoto Crater floor rocks. 194

Most of Endeavour Crater and portions of its rim are unconformably buried by the sulfate-rich sandstones of the Burns formation (Fig. 2c) [*Arvidson et al.*, 2011; *Grant et al.*, 2016; *Squyres et al.*, 2006]. Portions of the crater rim rise above the Burns formation strata, forming a discontinuous ring of rim segments. There is no evidence, such as fragments of Burns rocks or hematitic concretion clusters high on the rim, that the Burns formation covered these rim segments. *Golombek et al.* [2006] estimated that  $\leq 80$  m of rock has been eroded in Meridiani

- 201 Planum since the Hesperian, and *Grant et al.* [2016] estimated that Burns formation rocks might
- have been 80-100 m higher than at present in the region of Cape Tribulation. These estimates are
- 203 less than the current Cape Tribulation height above the plains. Erosion has variably degraded the
- crater rims with on the order of 100-200 m having been removed, mostly before deposition of the
  Burns formation sands [*Crumpler et al.*, 2015a; *Grant et al.*, 2016]. Some of the rim segments
- show the infrared spectral signature of Fe-Mg-smectite clays in data returned by the CRISM
- instrument onboard MRO [*Fox et al.*, 2016; *Noe Dobrea et al.*, 2012; *Wray et al.*, 2009],
- suggesting that they have undergone aqueous alteration under conditions of circumneutral pH. A
  localized area in the region explored by *Opportunity* during the sols covered here has yielded
  detections of phyllosilicates by CRISM (Fig. 1c). On the inboard side of Cape York is a small
  area on a feature dubbed by the team as Matijevic Hill that is thought to contain a few weight
  percent ferric smectites [*Arvidson et al.*, 2014].

Burns formation sandstones are dominated by Mg-, Ca-, and Fe-sulfates, a silicic 213 component and ferric oxides (e.g., Clark et al. [2005]; Klingelhöfer et al. [2004]; McLennan et 214 al. [2005]; Morris et al. [2006a]). The sandstones are mostly aeolian in origin, with some 215 aqueous facies that indicate local fluvial reworking, and a minor component of mudstones 216 indicating localized deposition in quiet water, possibly a lacustrine setting [Edgar et al., 2012, 217 218 2014; Grotzinger et al., 2005, 2006; Hayes et al., 2011]. The sediments have undergone 219 groundwater-influenced cementation and diagenesis, and are noteworthy for containing abundant hematitic concretions. They document a period of aqueous activity postdating the formation of 220 221 Endeavour Crater in which groundwaters interacted with and altered mafic composition rocks 222 (e.g., Hurowitz et al. [2010]). The solutions evaporated to form sulfate-rich evaporitic muds, 223 which were subsequently redistributed by wind and water under increasingly arid conditions to 224 form sandstones. Rocks of the Burns formation are not a focus of this paper, but we do discuss 225 those Burns formation targets from near the margins of the Endeavour rim for comparison with 226 rocks on the rim proper (Table S2). These targets are referred to here as "Burns margin." We include in Table S2 the last Burns formation target analyzed before reaching Cape York, 227 Gibraltar, and two Burns formation targets from the saddle between Cape York and Cape 228 Tribulation, Tawny and Black Shoulder. These targets are approximately 320, 340 and 190 m 229 from the nearest rim margins and are not included under the sobriquet "Burns margin" in the 230 discussion. 231

232 The rocks of the Endeavour Crater rim have been divided into three units which are, 233 oldest to youngest; the Matijevic, Shoemaker and Grasberg formations (Fig. 2c) [Crumpler et al., 2015a]. A continuous bench of bright rock surrounding Cape York, Sutherland Point and Nobbys 234 Head, and partially along the margin of Cape Tribulation, is discernable in High Resolution 235 Imaging Science Experiment (HiRISE) images of the western rim of Endeavour Crater (Fig. 1b, 236 c). This bench is part of the Grasberg formation [Crumpler et al., 2015a]. Benches of bright rock 237 are visible in HiRISE images around other rim segments of Endeavour Crater and these are 238 239 interpreted to be Grasberg formation outcrops [Grant et al., 2016]. The spine of Cape York is 240 formed by Shoemaker Ridge and is the type locality for the Shoemaker formation. This name is given to the polymict impact breccias of basaltic composition that comprise the major lithology 241

- of the Endeavour Crater rim [*Squyres et al.*, 2012]. The Matijevic formation, consisting of bright
- clastic rock of basaltic composition [*Arvidson et al.*, 2014], has been encountered only on the
- inboard side of Cape York at the base of Matijevic Hill (Fig. 1b). Murray Ridge is notable for
- having localized concentrations of dark-rock float (Figs. 3a, b), and Wdowiak Ridge is capped
- by fine-grained dark rocks (Fig. 3c). The former are allochthonous, while the latter cannot be
- 247 placed within the local stratigraphic framework. Both are of uncertain provenance.

## 248 4. Rock Outcrop and Microscopic Textures

To set the stage for the discussion of unit compositions to follow, we present

250 observations on outcrop morphology, and macroscopic and microscopic textures of the various

251 lithologies on Endeavour Crater rim in this section. We also discuss constraints on mineralogy

derived from Pancam spectra. The order in which the rock units are discussed mirrors the discussion of the compositions of lithelegies in Section 5 and is not in stratigraphic sequence.

discussion of the compositions of lithologies in Section 5 and is not in stratigraphic sequence.
Section 5 is ordered by the specific science issues we wish to explore. Observations for some of

the rock types have been described previously [*Arvidson et al.*, 2014, 2016; *Clark et al.*, 2016;

256 *Crumpler et al.*, 2015a; *Farrand et al.*, 2013, 2014; *Squyres et al.*, 2012]. The outcrop

morphology and textures for the units discussed here are summarized in Table 1. Details for the
Pancam images used in this paper are given in Table S3 of the on-line supplementary material.

## 259 4.1. Grasberg Formation

The Grasberg formation is the oldest of the post-impact formations in the area and occurs as a shallowly tilted bench on the margins of both rim segments investigated by *Opportunity*. The description of the formation given here is largely derived from *Crumpler et al.* [2015a] plus new observations; *Crumpler et al.* [2015a] will be cited for specific interpretations, but not for basic descriptive information.

The Grasberg formation consists of an upper bright unit and a lower dark unit with a total 265 formation thickness estimated as 1-2 m. The rocks are homogeneous and fine-grained, and are 266 planar in outcrop (Fig. 4). The Grasberg formation presents hackly outcrop surfaces that are 267 fractured into polygonal blocks or slabs (Fig. 4a, e). Sedimentary structures are lacking in most 268 outcrops, but an exception is the lower unit target Poverty Bush from Solander Point which 269 shows fine-scale, wavy laminations (Fig. 4e, arrows). Outcrops can exhibit fine-scale jointing 270 (Fig. 4c). Outcrops of the lower Grasberg unit are commonly transected by bright veins tens of 271 cm in length and of roughly cm-scale width (Fig. 4d). Short, bright streaks in the upper Grasberg 272 unit could represent smaller versions of the coarse veins that are common in the lower unit (Fig. 273 274 4a, arrows). The contact between the lower and upper units is defined only by a color transition and no obvious textural or morphological difference is evident; the upper unit might simply 275 reflect an indurated cap rock formed by weathering [Crumpler et al., 2015a]. Rocks of both units 276 are composed of grains with diameters smaller than the  $\sim 100 \ \mu m$  (3 pixels) resolution of the MI 277 (Fig. 5); clastic textures are generally not observed. If the texture is primary, then the 278 homogeneous, fine-grained nature suggests deposition occurred in a relatively low-energy 279 environment. Wind-polished surfaces show small pits that could belie initial porosity (Figs. 5c, 280

d), but these are not evident in the interior of the only Grasberg formation target that was abraded
(Fig. 5a). If that upper unit target is representative of the formation, then the Grasberg formation
consists of homogeneous fine-grained rock later cut by veins (cf., *Crumpler et al.* [2015a]).

The Grasberg formation is distinct from the Burns formation sandstones in mineralogy 284 and texture. The visible to near infrared (VNIR) reflectance spectra of the upper Grasberg 285 resembles purple-colored Burns formation outcrops that have higher 482 to 535 nm slopes as 286 described by Farrand et al. [2007]. However, the upper Grasberg has deeper 535 and 904 nm 287 band depths indicative of higher fractions of crystalline red hematite in that unit and thus is 288 mineralogically distinct from the Burns formation [Farrand et al., 2014]. The very fine-grained 289 nature of the Grasberg formation is also distinct from coarser, sand-sized Burns formation 290 sandstones (e.g., Grotzinger et al. [2005], and see Crumpler et al. [2015a]). 291

On Cape York, the Grasberg formation dips ~10° away from the rim segment in all directions, and is interpreted to lie on an erosional pediment forming the lower slopes of Cape York [*Crumpler et al.*, 2015a]. The geometry of the Grasberg formation indicates that it underlies the Burns formation, and is interpreted to have unconformities as its lower and upper contacts [*Crumpler et al.*, 2015a]. These authors inferred that the Grasberg formation draped paleotopography and could be an airfall deposit that covers an extensive region, for example, a distal deposit of volcanic ash or fine-grained impact ejecta.

## 299 4.2. Matijevic Formation

300 The Matijevic formation occurs on the in-board side of the Cape York rim segment, where the rocks have been described by Arvidson et al. [2014], Crumpler et al. [2015a] and 301 302 Farrand et al. [2014]. Matijevic formation outcrops are most commonly bright, planar and exhibit polygonal jointing (Fig. 6a). The matrix consists of fine-grained clastic material of 303 304 basaltic composition with grains up to ~1 mm in size and contains variable amounts of 2-4 mm-305 sized spherules (Fig. 7a). Local concentrations of the 2-4 mm-sized spherules form small, discontinuous ridge-forming units (Fig. 6b). Broken spherules show a variety of textures -306 307 hollow, partially filled and solid – suggesting a possible diversity of mineralogies (Fig. 7d). Clast-supported textures are evident in places, perhaps indicative of reworking. Note that we 308 309 previously suggested that more resistant outcrops rich in spherules (Fig. 6b) are possibly part of 310 the Shoemaker formation [Crumpler et al., 2015a], but our evaluation of rock compositions (Section 5.2) shows that they are part of the Matijevic formation. Matijevic formation outcrops 311 have relatively flat Pancam VNIR spectra with slight negative sloping near-infrared reflectance 312 [Farrand et al., 2014]. 313

Three types of late modifications to the Matijevic formation are present: (i) thin, bright crosscutting veins; (ii) dark, patchy veneers; and (iii) thicker boxwork veins. Locally, irregular, anastomosing, feathery veins a few-mm wide composed of bright material cut the Matijevic formation matrix (Figs. 6a, 7a, b). Bright outcrops commonly host numerous small, irregular patches of a dark veneer that partially cover exposed surfaces (Figs. 6a, 7c). The dark veneer displays a shallow 904 nm band not observed in the light-toned matrix [*Farrand et al.*, 2014]. These patches are erosional remnants of what was likely a continuous cover [*Crumpler et al.*, 2015a]. Raised irregular ridges in the veneer that can be traced to anastomosing veins in the
underlying matrix (inset, Fig. 6a, arrows) indicate the veneer was formed after the veins were
emplaced. The Matijevic formation locally hosts boxwork veins enriched in Si and Al; these are
discussed in detail in *Clark et al.* [2016]. Veneers, termed coatings in *Clark et al.* [2016], are also
present in the region of the boxwork veins. Imaging of the boxwork veins and coatings shows
that the coatings occur on top of the boxwork veins that crosscut the Matijevic formation

327 outcrops [*Clark et al.*, 2016], suggesting again that the coatings/veneers formed relatively late.

Matijevic formation is interpreted to be a pre-impact lithology [*Arvidson et al.*, 2014; *Crumpler et al.*, 2015a; *Farrand et al.*, 2014]. However, establishing the origin of the formation is hampered by the limited areal extent of unit exposures and the absence of diagnostic structures. It could be a regional deposit, for example airfall fines from a distant impact or volcanic eruption, or a more localized deposit formed by reworking fine-grained clastic material [*Crumpler et al.*, 2015a].

334 The Endeavour Crater rim segments investigated by *Opportunity* are in the equivalent position as the tectonic rim (sometimes referred to as the crater boundary or structural rim) of the 335 26 km diameter Ries Crater (e.g., Pohl et al. [1977]; Stöffler et al. [2013]; cf., Grant et al. 336 [2016]). The pre-impact rocks at the Ries tectonic rim are Jurassic sediments from the uppermost 337 part of the pre-impact stratigraphy. By analogy, the Matijevic formation likely represents part of 338 the Noachian middle or lower etched units, which together might be 350-400 m thick in this area 339 (Fig. 2b, c; Hynek and Di Achille [2017]). However, the etched units are not exposed along the 340 southern edge of the Hesperian Hematite unit (hematitic concretion lag deposit) (Fig. 2a) 341 indicating the etched units must pinch-out in a generally south/southeast direction across 342 Meridiani Planum and could be much thinner than the estimated section given above. The 19 km 343 diameter Bopolu Crater, located 65 km southwest of Endeavour Crater near the margin of the 344 Hematite unit, has a 75-260 m thick section of layered sulfates (Burns equivalent) overlying a 345 Noachian section interpreted to be part of the subdued crater unit of *Hynek and Di Achille* [2017] 346 (Grant et al. [2016], and personal communication). If this is the stratigraphy in the region around 347 Endeavour Crater, then the Matijevic formation would be part of the subdued crater unit. 348

#### 349 **4.3. Shoemaker Formation**

350 The Shoemaker formation makes up the continuous ejecta blanket surrounding Endeavour Crater. The formation has been divided into three informal members on Cape York 351 [Crumpler et al., 2015a]. From the bottom up, they are the Copper Cliff, Chester Lake and 352 Greeley Haven members. These informal member designations will be used here when needed to 353 facilitate discussion of specific compositional distinctions. One of the Chester Lake rocks, 354 Tisdale, is an ejecta block from Odyssey crater at Spirit Point on the southwestern tip of Cape 355 York (Fig. 1b). The targets on this block have some textural, Pancam reflectance properties and 356 compositional differences from the other Shoemaker formation breccias [Squyres et al., 2012]. 357 The Tisdale targets will be highlighted in the discussion as needed. On Murray Ridge the 358 Shoemaker formation is undivided. We investigated a set of outcrops on the northern part of 359 Murray Ridge and a set about 500 m to the south in the general region of Pillinger Point (Fig. 360 1c). These will be referred to as "north" and "central" targets in the discussion. Roughly 1.5 km 361

separate the central Murray Ridge targets from those at the Hueytown fracture zone on the
northern edge of the unnamed ridge south of Wdowiak Ridge (Fig. 1c). Targets from Hueytown
fracture zone are indicated separately on graphs.

Shoemaker formation rocks are coarse, typically unbedded breccias of basaltic 365 composition consisting of dark, relatively smooth, subrounded to angular clasts up to about 10 366 cm in size embedded in a brighter, fractured, fine-grained matrix (Figs. 8, 9) [Crumpler et al., 367 2015a; Squyres et al., 2012]. The matrix and clasts are both relatively dark compared to the 368 Matijevic formation matrix and have negative near-infrared slopes. For the matrix, the negative 369 slope is generally flatter while for the clasts there can be an increase in reflectance from 934 to 370 1009 nm. This could indicate the presence of low-Ca pyroxene in the clasts. Clast sizes and 371 abundances vary within the formation (Figs. 8a-c, e), but sorting is not evident on the outcrop 372 scale. Some clasts have internal textures including brighter patches within a darker matrix (Fig. 373 9c, arrows) suggesting that they are composed of brecciated material. The clasts are commonly 374 more resistant to physical weathering in the current martian environment and often stand in 375 positive relief on outcrops; this texture is especially evident in Fig. 8a (arrows). 376

Lineations are present especially in the Chester Lake member, and consist of trains of clasts and parallel alignments of elongated clasts [*Crumpler et al.*, 2015a; *Squyres et al.*, 2012]. The morphology of these outcrops is similar to that of suevite breccias common in moderate to large impact structures on Earth [*Squyres et al.*, 2012]. Terrestrial suevite contains clasts and matrix rich in impact melt (e.g., *Osinski et al.* [2004]). However, the instrument suite on *Opportunity* does not allow for positive identification of impact-melt glass in the rocks.

The lowest member, Copper Cliff, lies disconformably on the Matijevic formation 383 [Arvidson et al., 2014; Crumpler et al., 2015a]. The Copper Cliff member includes some 384 spherules and fine, bright, anastomosing veins (Figs. 8a, 9a) similar in morphology to those in 385 the underlying Matijevic formation. Spherules in the Copper Cliff member decrease in 386 abundance up section [Arvidson et al., 2014]. These spherules are not hematitic spherules as are 387 present in the Burns formation. This is discussed in Section 5.2.1. Bright veins that are coarser 388 than the fine, anastomosing veins within the Copper Cliff member are present in some outcrops 389 on Murray Ridge and at the Hueytown fracture zone (Figs. 8d, f, 9d). 390

Roughly 750 m further south of the Hueytown fracture zone in the Marathon Valley area 391 392 (Fig. 1c), the Shoemaker formation is divided into lower and upper units, but we have not yet attempted to correlate these with the stratigraphy elsewhere on the rim [Crumpler et al., 2017]. 393 The upper unit is clast-rich with relatively coarse clasts and is similar to many of the rocks 394 forming prominent protuberances on Murray Ridge. The lower unit is clast-poor with relatively 395 396 small clasts. The rocks in the Hueytown fracture zone are texturally more similar to the latter (Fig. 8f). Outcrops at the Cook Haven location on the northern part of Murray Ridge similarly 397 have lower clast abundances and the clasts are relatively small (Fig. 9b). 398

#### 399 4.4. Dark-rock Float and Ejecta

Concentrations of dark-rock float are present at several locations on Solander Point and
 Murray Ridge. On the northeast side of Solander Point a low ridge covered with scattered float

402 lies at the transition from the relatively flat Burns formation/Grasberg formation terrain to the

- 403 lower slopes of Murray Ridge (Fig. 3a). Dark cap rocks and associated float were encountered on
- 404 a series of ridges in the McClure-Beverlin Escarpment region south of the Cook Haven winter-
- 405 over site (Fig. 3b). Coherent outcrop units that could be the sources of the rocks are not
- 406 observed. The distributions are consistent with lenses rich in coarse blocks being present within
- 407 the Shoemaker formation breccias. Alternatively, they could represent inversions of topography.
- For example, the dark rocks could have been emplaced as massive deposits, such as impact melt collected in a local low or as fragments of a massive unit that were mobilized and collected in a
- 410 trough, that then made the trough more resistant to erosion [*Crumpler et al.*, 2015b].

The float rocks are dark, angular, often with conchoidal fracturing and some are vesicular
(Figs. 10a, b). In one instance a rock appears to have the morphology of a hexagonal prism (Fig.
10b), suggesting that it might be a fragment of a massive, columnar-jointed cooling unit – basalt
or impact melt. The rocks are very fine-grained; grains or clasts larger than 100 µm are not
visible (Figs. 11a, b).

Wdowiak Ridge is partially capped by a massive dark-rock unit (Fig. 3c), but 416 Opportunity was not commanded to climb the slope to investigate the unit in situ. Our contact 417 science on Wdowiak Ridge dark rocks was limited to float, and ejecta blocks from the ~30 m 418 diameter Ulysses crater on the southwestern end of the ridge (Fig. 1c). The morphology of most 419 of these rocks is similar to that of the dark-rock float from Solander Point and Murray Ridge: 420 angular and showing conchoidal fracturing (Fig. 10c). Some Wdowiak Ridge rocks have a more 421 irregular, hackly morphology (Fig. 10d). Unlike the float from Solander Point/Murray Ridge, 422 vesicularity is uncommon amongst the Wdowiak Ridge rocks. Planar fractures or partings are 423 common in these rocks [Arvidson et al., 2015]. Remnants of these fractures/partings are 424 expressed as dark flakes on flat surfaces (Fig. 10c). The angular rocks have a very fine-grained 425 texture with no crystals, grains or clasts >100 µm visible (Fig. 11c). A few rocks have hackly-426 427 morphology, and the one investigated in detail shows fracturing in almost orthogonal directions and a few grains  $\geq 100 \ \mu m$  in size are visible (Fig. 11d, arrows). 428

## 429 **5. Rock Compositions**

430 Compositional data for all rock targets discussed here are presented in Table 2, and the uncertainties ( $2\sigma$  precision) are given in Table S4. A listing of the rock targets investigated, from 431 the last Burns formation outcrop analyzed prior to arrival at Cape York through investigation of 432 the Hueytown fracture zone, are presented in the on-line supplementary material (Table S2). The 433 generalized locations of the targets are shown in Fig. 1b, c. The compositions of some of the rock 434 types have been previously described [Arvidson et al., 2014; Crumpler et al., 2015a; Squyres et 435 al., 2012], and some unique lithologic types formed by late-stage alteration have been discussed 436 in detail [Arvidson et al., 2016; Clark et al., 2016]. 437

The elements S, Cl, Zn and Br are the most labile in the recent (possibly current) martian environment (e.g., see *Gellert et al.* [2004]; *Haskin et al.* [2005]; *McSween et al.* [2004]; *Yen et al.* [2005]). Amongst the elements determined by the APXS, these show the greatest variations associated with alteration. We refer to these elements as volatile/mobile elements because their variations in the rocks and soils, coupled with the documented or inferred alteration mineralogy,indicate that these elements were vapor and/or fluid-mobile during alteration.

Most of the analyses are for untreated targets, that is, the rock surfaces as exposed by the 444 martian environment. In most cases, targets were chosen that appeared in Opportunity-based 445 images to have been swept clean by wind. The diamond-impregnated resin pads on the grinding 446 wheel of the RAT are significantly worn down. The remaining abrasion capability has been 447 judiciously used to balance the need to obtain critical knowledge of current lithologies with the 448 need to have an abrasion capability for future use; only 8% of the Endeavour rim targets were 449 abraded. Use of the brush was based on perceived need to clean rock surfaces and concerns for 450 instrument safety; brushing was used on 19% of the targets. 451

452 Wind-swept, untreated rock surfaces can host litter, including lithic debris from the outcrops, aeolian sand and airfall dust. The lithic debris is coarser than the other two components 453 and is likely derived from the outcrops being interrogated; accordingly, inclusion of lithic debris 454 455 should not have a significant impact on determining outcrop compositions. Aeolian sand is mobile in the current environment as saltating sands that form ripples composed of 50-125 µm 456 sized grains [Sullivan et al., 2005]. These sands are dark and basaltic in composition (e.g., Yen et 457 al. [2005]). To evaluate the possible compositional effects of this aeolian sand, referred to here 458 as dark sand, we use the compositions of five Meridiani Planum soil targets that are of uniformly 459 fine grain size and free of lithic clasts as observed in MI images, and have low albedo as seen in 460 Pancam images. 461

462 Dust grains are suspended in the atmosphere as a result of seasonal storms on Mars, and are in the size range 1-3 µm [Pollack et al., 1979, 1995]. This is consistent with dust-size 463 calculations of ~3 µm diameter made for Gusev Crater and Meridiani Planum by the MER rovers 464 [Lemmon et al., 2004]. The estimated sedimentation rate of this airfall dust is 0.002 g/cm<sup>2</sup> per 465 year [Pollack et al., 1979], which could form a 20 µm thick "layer" of dust annually, assuming a 466 density of 1 g/cm<sup>3</sup> for the deposit. To evaluate the possible compositional effects of this airfall 467 dust we use the compositions of five Meridiani Planum soil targets that are bright, of uniformly 468 very-fine grain size, free of lithic clasts as observed in MI images, and have dust spectral-469 characteristics as seen in Pancam images. We refer to these as bright soil. The dark-sand and 470 471 bright-soil targets used for comparisons are given in the on-line supplementary material (Table 472 S5).

473 Compositional characteristics of the rock units discussed here are summarized in Table 1.
474 The characteristics are given in relation to the average of the Shoemaker formation outcrops,
475 excluding compositionally anomalous targets. The adjectival "low" and "high" mean the
476 elements are between 1.5 to 2 times the standard deviation from the mean of the Shoemaker
477 formation, while "very low" and "very high" mean they are more than twice the standard
478 deviation from the Shoemaker mean.

#### 479 **5.1. Grasberg Formation**

480 Analyses were done on lower and upper Grasberg targets, and on two veins cutting across481 the lower member of the Grasberg formation (Table S2). For the eponymous Grasberg outcrop

block, two untreated targets, a brushed target, and an abraded target plus offset were measured. 482 483 The lower-unit rock Monjon included a portion showing the normal purple color in Pancam 484 false-color images and a small patch of grey material (Fig. 4c); both targets were analyzed. Table 3 gives the average compositions for the units, the ratio of lower/upper and an average of the 485 486 vein targets. Table 1 summarizes the compositional characteristics of the two units relative to an 487 average of the Shoemaker formation. Although there are significant compositional differences between the Grasberg and Shoemaker formations, the former is nevertheless of broadly basaltic 488 composition. The veins investigated are narrower than the APXS field of view and thus the 489 compositions of vein targets represent mixtures of vein material, host rock, aeolian sands and 490 possibly other lithic debris (Fig. 4d). The vein targets are higher in CaO and SO<sub>3</sub> compared to the 491 lower Grasberg lithology that hosts them (Table 3). Vein targets from all stratigraphic units are 492 discussed collectively later (Section 5.4). 493

494 As discussed in Section 3 and shown in Fig. 2c, the Burns formation overlies the Grasberg formation [Crumpler et al., 2015a]. Although an unconformity separates them, one 495 issue is whether the Grasberg formation is an earlier facies of the Burns formation. We examine 496 this issue here. The composition of the Grasberg formation is well-resolved from that of the 497 Burns formation (Fig. 12). Compared to the Burns, the Grasberg has lower MgO (Fig. 12a) and 498 SO<sub>3</sub>, and higher SiO<sub>2</sub>, K<sub>2</sub>O, TiO<sub>2</sub>, FeO (Fig. 12c) and Zn (Fig. 12e). The Grasberg formation has 499 500 higher Cl contents than the Burns formation, although a subset of Burns rocks have Cl contents 501 that substantially overlap the range for the Grasberg (Fig. 12e).

The distinction in composition between the two formations is evident even comparing 502 Grasberg targets only with those Burns formation targets located near the contact with the 503 Grasberg (Burns margin in Fig. 12). Two Burns-margin targets – Callitris and Dibbler – plot 504 within the field of Grasberg rocks for some elements (e.g., Figs. 12b-d), but nevertheless can be 505 clearly distinguished from the Grasberg based on overall composition. Burns formation target 506 Tawny, from the saddle between Nobbys Head and Solander Point, has an FeO content within 507 the range of Grasberg formation rocks (Fig. 12c) but otherwise is compositionally distinct from 508 the latter. Similarly, the lower Grasberg target Poverty Bush falls within the field for the Burns 509 formation in Fig. 12c, but is distinct from Burns for most elements. Note that Poverty Bush also 510 has a distinctive outcrop texture, showing fine-scale, wavy laminations (Fig. 4e) that are not 511 present on other Grasberg formation outcrops. Finally, the abraded Grasberg target is distinctly 512 different in composition from abraded Burns formation rocks. Compared to abraded Burns 513 formation targets, abraded Grasberg targets have lower MgO and Ni, and higher Cl, FeO and Zn 514 515 (Fig. 12). The SO<sub>3</sub> content is only ~10 wt% in Grasberg abraded vs. 17.0-28.6 wt% for abraded Burns formation targets. 516

517 The relationship between the upper and lower Grasberg units is difficult to ascertain 518 because Grasberg targets scatter considerably on many element-element plots and the fields for 519 the two units overlap (Fig. 12). The scatter could be caused by surface debris, but the analyses do 520 not appear to be significantly influenced by contamination from sand or dust on untreated 521 surfaces. Some elements, such as Mg, are significantly lower for brushed vs. untreated surfaces, 522 which *could* be consistent with contamination (Fig. 12). However, the compositions of untreated 523 Grasberg targets cannot be explained as simple mixtures of brushed or abraded targets and 524 surface contamination of dust or soil. This aspect is discussed in more detail in Section 5.2.

- 525 Excluding the two abraded targets, the averages of the lower and upper targets cannot be
- 526 distinguished; only the ratio of Na<sub>2</sub>O is outside its uncertainty limit (Table 3). Although upper
- 527 Grasberg is lighter in tone than lower Grasberg, this difference is not reflective of composition as
- 528 determined for untreated surfaces. Note however, that the Grasberg formation is compositionally
- 529 heterogeneous and only five analyses are averaged for each unit (Table 3). For these reasons, the
- averages are not tightly constrained.

The MER team commanded a sequence of target offsets, RAT treatments and APXS 531 analyses for the upper unit target Grasberg in order to gain better knowledge of the true 532 composition of the formation. Of particular importance are the differences between the abraded 533 target and the untreated and brushed targets. Grasberg was a dusty rock surface and brushing 534 resulted in a significant decrease in MgO and increase in Cl in the Grasberg1 target (Figs. 12b, d, 535 e). Because of microtopography on the target surface, the abraded target still contains a 536 substantial fraction of unabraded surface that is below the plane of abrasion (Fig. 5a), but 537 brushing appears to have cleaned the loose debris out of the remaining depressions. Figure 13 538 539 shows the untreated and brushed Grasberg1 targets normalized to the abraded target for all elements. On this diagram, elements with ratios >1 had their concentrations lowered by abrasion. 540 Of the major elements – here defined as those with concentrations  $\geq 2$  wt% – Na<sub>2</sub>O, SiO<sub>2</sub>, CaO 541 542 and FeO were little-affected by the abrasion, suggesting that untreated, wind-cleaned surfaces faithfully record the true compositions for these elements. Magnesia and Al<sub>2</sub>O<sub>3</sub> are much lower 543 in the abraded target, while SO<sub>3</sub> and Cl are much higher. For these elements, the true 544 composition of the Grasberg formation might not be well constrained. 545

A final observation concerns two targets, Monjon Purple and Monjon Grey. Most of the 546 rock has the typical purple color of the Grasberg formation in Pancam false-color images but a 547 small fraction is greyish in this rendition (Fig. 4c). Based on shadowing in the scene, the grey 548 material appears to be a surficial coating or veneer on the rock. The Monjon Grey MI finder 549 frame shows that the APXS target missed the bulk of the grey material (lower box; Fig. 4c), 550 although it does contain more grey material than does Monjon Purple. For many elements, the 551 targets are essentially identical in composition, however, Monjon Grey has roughly twice the 552 MnO content of Monjon Purple; 0.58 vs. 0.27 wt%. There are also lesser enrichments in Ni and 553 Zn, and modest depletions in SO<sub>3</sub> and Br in Monjon Grey. Farrand et al. [2016] noted that the 554 grey material on Monjon, also observed in several other Grasberg exposures, had a positive 555 sloping near-infrared spectrum similar to some Mn oxide minerals, which is borne out by the 556 557 elevated Mn in Monjon Grey.

## 558 **5.2. Matijevic Formation**

There are five main lithic components of the Matijevic formation: matrix; spherules; veneers; thin, bright, anastomosing veins; and boxwork veins. Analyses were done on the matrix, spherule-bearing, veneer-rich and anastomosing-vein-rich materials in flat-lying Matijevic formation outcrops, on spherule-rich, ledge-forming outcrops, and on boxwork veins (Table S2). The compositions of the boxwork veins are discussed by *Clark et al.*, [2016], and are not discussed here in detail. In no case did either veneer material or anastomosing-vein material 565 completely fill the APXS field of view, although the Chelmsford3 veneer nearly did (Figs. 7b, c).

- 566 We can nevertheless infer the compositional characteristics of veneers and anastomosing veins
- from a series of analyses of different targets. We commanded a series of analyses and surface
- treatments, but only in the case of the Sandcherry veneer target did we do the full
- treatment/analysis sequence. Table 1 summarizes the compositional characteristics of the
- 570 Matijevic matrix, spherule-rich and veneer-rich targets relative to an average of the Shoemaker
- 571 formation. Table 4 gives the most representative compositions for the different lithologies.

## 572 5.2.1. Matrix and Spherule-rich Targets

Our best estimate for the matrix composition is an average of the brushed and abraded
Azilda targets weighted by the measurement uncertainty (Table 4). Compared to average
Shoemaker formation breccia, the Matijevic formation matrix is very high in SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> and Ni,
and low in K<sub>2</sub>O, TiO<sub>2</sub> and SO<sub>3</sub> (Table 1).

The spherule-rich targets consist of dense clusters of several-mm-diameter spherules supported by matrix (Fig. 7d) and thus the compositions of these targets represent mixtures. For the best representation of the spherule-rich composition we use the deeply abraded Sturgeon River3 target on a ledge-forming outcrop (Table 4). This target contains an estimated 40-45% spherules by area [*Arvidson et al.*, 2014]. Compared to average Shoemaker formation breccia, spherule-rich Matijevic targets are very high in SiO<sub>2</sub>, high in Ni, low SO<sub>3</sub> and very low in P<sub>2</sub>O<sub>5</sub>, CaO and TiO<sub>2</sub> (Table 1).

584 In general, the spherules are not substantially different in composition from the matrix. 585 The ratio of the deeply abraded Sturgeon River3 spherule-rich target to average matrix 586 composition is shown in Fig. 14b. Several elements have higher concentrations in the spherule-587 rich targets than the matrix – Mg, Cr, Fe and Ni – and several are lower – Na, Al, P, Cl, Ca, Ti, 588 Mn and Br. However, the average matrix is based only on a series of offset measurements of a 589 limited area of one outcrop and the spherule-rich material shown is based on a single target. A 590 considerable fraction of the observed differences between the spherule-rich material and matrix could reflect general compositional variations of the Matijevic formation rather than differences 591 between matrix and spherules. The Fullerton3 target is dominated by matrix, although some 592 593 spherules are within the field of view of the APXS (Fig. 7a); its composition ought to be dominated by matrix. The element-ratio pattern of Fullerton3 mimics that of Sturgeon River3 in 594 its low abundance ratios for Na, P and Mn (Fig. 14b). The low ratios for these elements in 595 596 Sturgeon River3 are thus just as likely to be due to higher contents of these elements in the Azilda targets used for normalization relative to typical matrix, as they are to the spherules being 597 poor in these elements. Amongst the major elements ( $\geq 2 \text{ wt\%}$ ), only Mg is more than 15% 598 divergent from the matrix composition (gray band in Fig. 14b). Thus, although morphologically 599 distinct, the spherules have compositions that are not greatly different from that of the matrix. 600 This compositional similarity is quite different from the case of hematitic concretions (a.k.a. 601 602 blueberries) found in the Burns formation, which are very different in composition from the host 603 rock (e.g., Clark et al. [2005]; Rieder et al. [2004]; Yen et al. [2005]).

604 **5.2.2. Veneers** 

The veneers are thin patches on outcrop surfaces (Figs. 6a, 7c), but not too thin for 605 606 reliable APXS measurement. For the Sandcherry veneer target, we analyzed the target untreated, 607 brushed and abraded (Table S2). The abrasion removed a portion of the veneer, exposing additional underlying matrix in the APXS field of view, but did not abrade the underlying 608 609 bedrock. The outcrop surface was slightly angled with respect to the grind plane, and had a small 610 amount of relief. This resulted in a beveled abrasion surface with an abrasion depth of 0.8 mm. 611 Even given the uncertainties regarding the angle of the abrasion plane, the thickness of the veneer is on the order of the abrasion depth. This is effectively an infinitely thick target for the 612 APXS instrument for all elements (cf., Rieder et al. [2003], Section 6.3]. 613

Amongst the veneer-rich targets, the Sandcherry untreated and brushed targets show the 614 greatest compositional differences from the average matrix; we use the brushed target as the best 615 indicator of this veneer material (Table 4). We brushed the Chelmsford veneer-rich target and 616 did two measurements of it, one slightly offset from the other; we include an average of these 617 two analyses in Table 4. Veneers – a.k.a. coatings – are present in the locality of the boxwork 618 alteration veins and APXS targets there included varying amounts of veneer [Clark et al., 2016]. 619 Those authors derived an estimate of the veneer composition by deconvolving the compositions 620 of the set of analyses; their estimate of the veneer is given in Table 4. 621

The veneer-rich targets have clear compositional distinctions from the matrix (Table 4). 622 The veneer is richer in volatile/mobile elements S, Cl, Zn and Br than the matrix by factors >2.8 623 times for Sandcherry (Fig. 14a) indicating that these elements were substantially mobilized by 624 the process that formed the veneer. The Chelmsford veneer shows lesser enrichments in these 625 volatile/mobile elements - ~1.7-2.3 times - but has an enhancement in MnO not seen in the 626 Sandcherry targets (Fig. 14a). Veneer-rich targets have small enrichments (~25%) in K and Ca, 627 and small depletions (10-20%) in Na, Al, Si and P compared to matrix. The calculated veneer 628 (coating) composition from *Clark et al.* [2016] shows essentially the same compositional trends 629 - large enrichments in S, Cl, Zn and Br, with smaller enrichments in K and Ca (Fig. 14a). 630

The two veneer-rich targets discussed here show variations in composition, most likely 631 due to variations of the amount of veneer material within the APXS field of view. (Because of 632 the attitude of the analyzed surface with respect to the rover, the APXS placement might not 633 634 have been co-registered with the center of the MI mosaics. This misalignment precludes accurate 635 determination of the fraction of the veneer material within the APXS field of view.) The veneerrich targets show a general trend of increasing Zn with Cl (Fig. 15e) consistent with analytical 636 mixing of signal from the matrix with that from the veneer. Veneer-rich targets with the highest 637 Cl and Zn contents have the lowest Al<sub>2</sub>O<sub>3</sub> (Fig. 15c) and SiO<sub>2</sub> (Fig. 15b) contents, indicating the 638 639 veneers are not enriched in aluminosilicates such as clay minerals. The calculated coating composition of *Clark et al.* [2016] is also low in Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and high in S, Cl, Zn and Br 640 (Table 4). The coating composition was calculated by computing the relative instrument 641 responses from the areal fractions of boxwork vein and coating in the fields of view of two of the 642 measurements, and extrapolating to 0% areal coverages to calculate the two components; there is 643 greater uncertainty in the computed coating composition, but this is not quantified [Clark et al., 644 2016]. 645

#### 646 5.2.3. Anastomosing Veins

Amongst the anastomosing-vein-rich targets, Ortiz2B has the highest SO<sub>3</sub> and CaO contents. We use that targets as the best indicator of the composition of the veins. The Ortiz2B vein-rich target is richer in S, Cl, Ca, Mn and Br than the matrix. For most other major elements, Ortiz2B has abundance ratios of ~0.83. This pattern is generally consistent with the Ortiz2B analysis having two components, ~17% vein dominated by Ca-sulfate and ~83% matrix. The thin, feathery bright Ortiz veins have general compositional similarities to the wide veins in the

653 Grasberg formation. Vein-rich targets are discussed in detail in Section 5.4.

#### 654 5.2.4. Comparisons to Burns and Grasberg Formations

In general, the Matijevic formation is compositionally distinct from the Burns and 655 Grasberg formations. Amongst the elements shown in Figure 15, Matijevic rocks have generally 656 higher contents of MgO, Al<sub>2</sub>O<sub>3</sub>, and Ni, but have lower contents of FeO and Zn compared to 657 Grasberg rocks. Excluding the veneer-rich targets, Matijevic rocks also have lower Cl contents 658 than do Grasberg rocks. Similarly, Matijevic formation rocks have higher Al<sub>2</sub>O<sub>3</sub> and Ni but 659 660 lower Zn contents than Burns formation rocks (Fig. 15). Compared to the Grasberg formation, and especially the Burns formation, Matijevic formation rocks have lower SO<sub>3</sub> contents. 661 However, for many other elements, the composition of the Matijevic formation overlaps the 662 ranges for the Burns and/or Grasberg formations. 663

To examine possible compositional similarities between these three formations more 664 rigorously, we did Agglomerative Hierarchical Cluster Analysis (AHCA) on the rocks. This is a 665 multivariate technique that groups observations (APXS targets) by similarities in variables 666 (element concentrations). For our analysis, we used element/Si mole ratios as the variables to 667 minimize problems associated with closure restraint caused by normalizing the APXS data to 668 sum to 100% [Chayes, 1971]. We excluded vein-rich targets from the analysis. We wish to 669 compare the rock target compositions and including the vein-rich samples would return clusters 670 biased by the distinctive vein compositions (e.g., Figs. 12a, 14a). We did include the Matijevic 671 formation veneer-rich targets in order to evaluate their similarity/dissimilarity to the other 672 lithologies. We also included dark-sand and bright-soil targets presented in the on-line 673 supplementary material (Table S5) to help evaluate the possible effects these materials might 674 have on the compositions of untreated surfaces. We ran two calculations; one using all elements 675 and one excluding the volatile/mobile elements S, Cl, Zn and Br. We forced the calculation to 676 677 return five clusters in order to obtain finer granularity on the results. Clusters can easily be merged at higher levels by inspection of dendrograms to yield geologically interpretable results. 678 The resulting dendrograms are given in Figure 16. 679

Using all elements in the AHCA calculation, the highest (most dissimilar) clustering level
separates clusters 1-3 from 4 and 5 (Fig. 16a). Clusters 1 through 3 are composed of Burns
formation targets, the compositionally anomalous Grasberg formation target Poverty Bush (Fig.
12) and two veneer-rich Matijevic formation targets. Poverty Bush also has an unusual texture
compared to other Grasberg formation outcrops (Fig. 4e). The two veneer-rich targets are the
untreated and brushed Sandcherry analyses that have the clearest compositional signature of the

veneer. Cluster 4 includes all the other Matijevic formation targets, the Burns-margin target 686 687 Dibbler, and all the dark-sand and bright-soil targets. With the exception of the two Sandcherry 688 targets, the other Matijevic formation targets cluster at a low level of dissimilarity (cluster 4), shown in more detail in Fig. 16b. Cluster 4 has two main subclusters. One (left side of Fig. 16b) 689 690 contains mostly dark sand, bright soil and the remaining veneer-rich Matijevic targets. The 691 Burns-margin target Dibbler is most similar in composition to the soils (Fig. 16b), as is also 692 evident in Fig. 12. The Dibbler target consisted of soil and dark, rounded-pebble debris on top of a Burns formation outcrop pavement and its inclusion in cluster 4 reflects this rather than 693 compositional similarity with the Matijevic formation. The other subcluster (right side of Fig. 694 16b) contains all but one of the matrix targets and all of the spherule-rich targets, confirming that 695 the spherules are not greatly different in composition from the matrix. The Matijevic formation is 696 well-resolved from the Burns formation, joining clusters 1-3 at the highest level of dissimilarity. 697 698 Cluster 5 is composed solely of Grasberg formation rocks, which are compositionally more similar to the Matijevic formation (cluster 4) than to the Burns formation. 699

700 The Burns formation is composed of sulfate-rich sandstones that resulted from basaltic materials weathered by S-rich fluids [McLennan et al., 2005; Squyres and Knoll, 2005] and has a 701 generally higher SO<sub>3</sub> content than the Grasberg or Matijevic formations. Further, untreated Burns 702 targets have lower SO<sub>3</sub> contents than do abraded targets [*Rieder et al.*, 2005] indicating 703 704 preferential loss or obscuring of SO<sub>3</sub> once bedrock is exposed. Variations in halogens and Zn on 705 rock and soil surfaces, as demonstrated by comparison of untreated, brushed and abraded rock targets and indurated soils in Gusev Crater, shows that they are mobile even in under low 706 water/rock conditions [Gellert et al., 2004; Haskin et al., 2005; McSween et al., 2004]. This 707 708 could have happened in the recent times in the current martian environment, or much earlier, 709 perhaps ~3 Gyr ago. We thus ran the AHCA excluding these volatile/mobile elements to 710 minimize the effects that environmental process would have on the results (Fig. 16c). In this 711 calculation, the distance metric is roughly half that of when the mobile/volatile elements are 712 included, which is consistent with the latter representing a significant component of the compositional variation. 713

As in the previous case, in the calculation sans volatile/mobile elements, the Burns 714 formation dominates clusters 1-3, the Matijevic formation dominates cluster 4, and the Grasberg 715 716 formation dominates cluster 5. However, the structure of linkages is significantly different; the Grasberg is most dissimilar from all other rock units, while the Matijevic formation is more 717 similar to the Burns formation than to the Grasberg. This structure indicates a general 718 719 compositional similarity between what might be called the "basaltic" component of the Burns and Matijevic formations. All Matijevic veneer-rich targets cluster with Burns formation targets, 720 including those that cluster with the matrix and spherule-rich targets when all elements are used. 721 722 Cluster 4 now consists of matrix and spherule-rich Matijevic targets (Fig. 16d) plus one dark sand (the same one in the right subcluster of Fig. 16b). All of the Grasberg formation targets are 723 now collected in cluster 5, including Poverty Bush, which clusters with the Burns formation 724 725 when all elements are used. Cluster 5 includes six Burns-formation targets; one is the Burns-726 margin target Callitris but the other five are from widely dispersed locations on Meridiani 727 Planum. Thus the compositions of the Grasberg and Burns formations are distinct.

Earlier we remarked that we found no evidence suggesting that the untreated Grasberg
targets had their compositions compromised by sand or dust surface contaminants. This is aptly
demonstrated by the AHCA results. The untreated, brushed and abraded Grasberg targets
strongly cluster in both dendrograms (Figs. 16a, c), and are moderately dissimilar from the soils
included in the calculation.

#### 733 **5.3. Shoemaker Formation**

Polymict-impact breccias are chaotic mixtures of the various lithologies excavated by the 734 impact. We undertook compositional investigations of the Shoemaker formation to understand 735 the broad compositional characteristics of the pre-impact terrane, and to identify the 736 737 compositional effects of alteration processes that were documented in CRISM spectra [Fox et al., 2016; Noe Dobrea et al., 2012; Wray et al., 2009]. We did 72 analyses of Shoemaker formation 738 targets, half from Cape York and half from Murray Ridge/Cape Tribulation (Table S2). Targets 739 740 analyzed include a limited number of vein-rich targets from two locations and a series of 9 741 analyses of mineralization deposits on surfaces of two rocks at the Cook Haven location. These two rocks had been overturned by the rover wheels. The results on these latter are given in 742 743 Arvidson et al. [2016] and are only briefly discussed here. The vein-rich targets are discussed 744 separately in the next section. The compositions of some Shoemaker formation rocks were discussed in Arvidson et al. [2014, 2015], Crumpler et al. [2015a] and Squyres et al. [2012]. 745

#### 746 5.3.1. Shoemaker Formation Compositional Diversity

The Shoemaker formation rocks are generally distinct in composition from the Burns,
Grasberg and Matijevic formations although there is some overlap in compositional space. In
CaO vs. MgO, SO<sub>3</sub> vs. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> vs. FeO and Zn vs. Ni the Shoemaker formation rocks are
largely, but not completely, distinguishable from the other formations (Fig. 17a, b, c, f).

751 The Shoemaker formation has been divided into three informal members on Cape York 752 (Section 4.3). From stratigraphically lowest to highest they are the Copper Cliff, Chester Lake 753 and Greeley Haven members [Crumpler et al., 2015a]. The rock Tisdale is distinct in texture and composition from other Chester Lake member targets. The targets on Cape Tribulation are 754 divided here into three groups by location, two from Murray Ridge and a third from the 755 Hueytown fracture zone. The discussion that follows utilizes these groupings. Table 5 gives the 756 average compositions of Shoemaker formation units and the Shoemaker formation in toto. Two 757 compositionally anomalous targets - Spinifex and Sledge Island - were excluded from the 758 759 Murray Ridge north averages. These and the Tisdale targets were excluded from the Shoemaker 760 formation average. Table 1 gives the compositional characteristics of individual Shoemaker units relative to the formation as a whole. 761

The Shoemaker is much more varied in composition than the three formations previously discussed. This variability is especially evident in the SO<sub>3</sub>, FeO, Ni and Zn contents (Figs. 17b, c, f). These variations have both geographic and stratigraphic components. Geographic variation is illustrated by comparing rocks from Murray Ridge with those from Cape York. The former generally have lower Ni and Zn contents than the latter, for example (Fig. 17f). Stratigraphic variations are illustrated by the three Cape York members, which generally increase in FeO inthe sequence Copper Cliff, Greeley Haven, Chester Lake (Fig. 17c).

The ejecta block Tisdale, from the small crater Odyssey at Spirit Point (Fig. 1b), is part of the Chester Lake member [*Crumpler et al.*, 2015a], but it has clear differences in composition

from other Shoemaker formation rocks. It has lower MgO and higher Ni and Zn compared to

other rocks of the Chester Lake member (Figs. 17a, d-f). Most analyses of the Tisdale block are

- higher in  $P_2O_5$ , Ni, Zn and Br, but not  $SO_3$  or Cl, compared to other Chester Lake member
- targets, or the Shoemaker formation more generally. The P<sub>2</sub>O<sub>5</sub>, Ni, Zn and Br contents of Tisdale
- include the highest measurements on the Endeavour Crater rim. As noted in Section 4.3, the
- 776 Copper Cliff member contains spherules as does the underlying Matijevic formation. Copper
- 777 Cliff targets commonly overlap the field for Matijevic formation targets in Fig. 17; we will
- explore this in more detail in Section 6.1.

# 5.3.2. Shoemaker Formation Heterogeneity; Clast-Matrix Comparisons and Outcrop-scale Variations

Clasts in polymict-impact breccias are mostly fragments of the pre-impact lithologies, 781 whereas the matrix is a mixture of materials. To gain a clearer picture of the lithologic diversity 782 of the Shoemaker formation, we have done paired analyses of host and clast-rich targets at four 783 locations, two on each rim segment, and we did an extensive set of offset measurements of the 784 Greeley Haven outcrop in the area of one of the host-clast pairs on Cape York. The host targets 785 included a higher fraction of matrix, but are not pure matrix samples. Similarly, the clast-rich 786 targets were centered on clasts, but have varying amounts of matrix in the field of view 787 depending on the size of the targeted clast. The results of these measurements are shown in Figs. 788 18 and 19. Note that clasts in Shoemaker formation breccias are compositionally distinct from 789 Matijevic formation matrix and spherule-rich rocks (Fig. 19). Although the Matijevic formation 790 represent some portion of the pre-impact target terrane, none of the clasts analyzed are derived 791 from this formation. 792

793 There are some commonalities in compositional differences between clasts and host, but no systematic differences that are always observed. For example, the Geluk/Salisbury, Mount 794 Tempest/Tangalooma and Sarcobatus Clast/Sarcobatus Flat pairs all show higher Al<sub>2</sub>O<sub>3</sub> and CaO 795 in clasts than hosts, but the Komati/Boesmanskop pair does not (Figs. 18b, 19a). All clasts show 796 resolvable enhancements in Mn, have lower Fe/Mn and higher Al/Mg compared to hosts. For the 797 798 Geluk and Sarcobatus Clast targets, lowering of Fe/Mn is significantly contributed to by lower 799 FeO compared to the host (Fig. 19c). The Komati/Boesmanskop clast/host pair is from the Greeley Haven outcrop block that was investigated as a series of 12 Amboy targets over the 800 fourth winter. The variation in composition observed for the Amboy targets encompasses the 801 range of variation observed for the Komati/Boesmanskop pair (Fig. 18b). These clast/host and 802 Amboy series observations are consistent with the inference based on textures that Shoemaker 803 804 formation rocks are heterogeneous polymict breccias composed of materials from different 805 protoliths.

The compositional variations do not solely result from differences between clasts and 806 807 matrix. We did Agglomerative Hierarchical Cluster Analysis on Greeley Haven member rocks -808 the Greeley Haven outcrop plus Transvaal located about 10 m away – and the dark-sand and bright-soil targets (Table S5). We did the analysis using all elements and again excluding the 809 810 volatile/mobile elements. The results of the two calculations are essentially identical; we show 811 the results of the first calculation in Fig. 20a. Three compositional clusters result. Cluster 1 is 812 composed of Amboy 4 through 12, the Transvaal target and all but one of the soil targets. Cluster 2 is composed of Amboy 1 through 3, Boesmanskop (untreated and brushed) and the Komati 813 clast. Cluster 3 consists of one dark-sand target (Fig. 20a), Auk, whose composition is consistent 814 with having the highest plagioclase and lowest ferromagnesian-phases components amongst the 815 dark sand targets (Table S5). Cluster-1 targets occupy a distinct sub-region of the Greeley Haven 816 outcrop (Fig. 20b) suggesting a possible zone of compositionally distinctive material within the 817 818 larger outcrop. The Pancam false-color image shows that the outcrop is generally less dusty in the region of the cluster-2 targets (Fig. 20b). The MI images also show more uniform surfaces 819 for the cluster-2 targets (Fig. 20c) compared to the cluster-1 targets (Figs. 20d, e). 820

One possible explanation for the distinct compositional clusters returned by the AHCA is 821 that surface litter on the cluster-1 targets masks the outcrop composition. We think this is 822 unlikely to be the entire story for the following reasons. Much of the debris on the cluster-1 823 824 target surfaces is lithic fragments that are most likely locally derived (Figs. 20d, e). These lithic 825 fragments would have the same composition as the outcrop. Some fine-grained sand is visible in the MI images and the Pancam image (Fig. 20b) indicates that dust is also present. However, the 826 compositional distinctions between clusters 1 and 2 are not consistent with contamination by 827 828 aeolian sand and/or airfall dust. Cluster-1 targets overlap the fields for dark sand and bright soil 829 in MgO vs. Al<sub>2</sub>O<sub>3</sub> and CaO vs. Al<sub>2</sub>O<sub>3</sub> (Figs. 19a, b), which could suggest the soils dominate the 830 compositions of some cluster-1 rocks. However, cluster 1 overlaps cluster 2 in Zn vs. Cl but not 831 the soils, and cluster 1 extends from cluster 2 in FeO vs. MnO towards high MnO content and 832 away from the soils (Figs. 19c, d). Dark sand and bright soil are members of cluster 1 (Fig. 20a), but we think this likely reflects a general similarity between these materials and the Shoemaker 833 formation breccias rather than sand/dust completely masking of outcrop compositions. We 834 conclude that while aeolian sand and airfall dust obscure to some extent the true rock 835 compositions, the differences in composition between clusters 1 and 2 are in part due to the rocks 836 themselves. This indicates that the polymict breccias include multi-decimeter-scale 837 heterogeneities caused by differences in compositions of "packets" of impact debris deposited on 838 839 the rim.

#### 840 5.4. Vein-rich Targets

Crosscutting veins contained within outcrops document late additions of volatile/mobile elements resulting from alteration of preexisting rocks. The compositions and mineralogies of veins provide evidence constraining the nature of the alteration processes. We analyzed vein-rich targets in the Grasberg, Matijevic and Shoemaker formation rocks in order to understand the types of alteration that occurred around the Endeavour Crater rim (Table S2; Fig. 21). The 846 Shoemaker formation targets are from Murray Ridge/Cape Tribulation whereas the others are

847 from Cape York.

#### 848 5.4.1. CaSO<sub>4</sub>-dominated Veins

We previously noted that the compositions of the coarse veins in the Grasberg formation 849 are consistent with CaSO<sub>4</sub> [Squyres et al., 2012]. This is illustrated in Fig. 21a which shows that 850 a mixing line between the composition of Deadwood, host of the Homestake vein, and CaSO<sub>4</sub> 851 passes through the compositions of the coarse vein targets. These targets did not completely fill 852 the APXS field of view and some of the host rock plus surficial litter contribute to the 853 compositions determined by the instrument. Roughly 45-48% of the instrument response for 854 855 Homestake2, the target with the highest CaO and SO<sub>3</sub> contents, is derived from the vein, assuming it is pure CaSO<sub>4</sub>. The veins have distinctive Pancam spectra that show drops in 856 reflectance from 934 to 1009 nm that is consistent with the H<sub>2</sub>O overtone absorption in gypsum 857 reflectance spectra [Farrand et al., 2013]. The Pancam spectra for the hydrated CaSO<sub>4</sub> bassanite 858 859 would be distinct from that of gypsum in having a much weaker H<sub>2</sub>O absorption feature; we concluded that the Homestake vein is not composed of bassanite [Squyres et al., 2012]. 860

861 The veins cutting Shoemaker formation breccias are similarly consistent with being pure CaSO<sub>4</sub>, and they show the drop in Pancam spectral reflectance from 934 to 1009 nm indicative 862 of gypsum. We commanded three offset measurements of the Bristol Well target to sample an 863 irregular patch of bright vein material, lithic debris and aeolian drift sand (Fig. 22a). As in the 864 previous case, the vein did not fill the field of view of the instrument and the integration centered 865 on the vein includes response from surrounding non-vein materials. The Bristol Well3 target was 866 commanded to be centered on lithic debris and drift sand (Fig. 22b). A mixing line between 867 Bristol Well3 and CaSO<sub>4</sub> passes through the other Bristol Well target consistent with a pure Ca-868 sulfate vein (Fig. 21b). However, the vein material would only make up ~9% of the APXS 869 response signal. Because of this we cannot definitively assign a composition to the vein other 870 than to note that it is dominantly CaSO<sub>4</sub>. Two offset integrations on the bright vein Cottondale 871 (Fig. 8f) from the Hueytown fracture zone do not form a mixing line between the average 872 Hueytown outcrop composition and CaSO<sub>4</sub> (solid line, Fig. 21c). Again, because the vein 873 material did not fill the field of view of the instrument, lithic debris and aeolian drift sand were 874 included in the instrument response. The Cottondale vein target compositions are consistent with 875 a response that includes CaSO<sub>4</sub>, the average Hueytown outcrop and average dark sand (dotted 876 line, Fig. 21c). The simplest interpretation of the data from vein-rich targets in the Shoemaker 877 878 formation breccias is that the veins are composed mostly of Ca-sulfate.

879 In the case of the Matijevic formation, mixing the average matrix composition with Casulfate does not pass through the compositions of the Ortiz targets that contain the anastomosing 880 veins (solid line, Fig. 21d). Regressing the CaO and SO<sub>3</sub> data for the vein-rich targets results in a 881 correlation with one endmember consistent with the average Matijevic formation matrix, but the 882 high CaO-SO<sub>3</sub> endmember would have molar Ca/S < 1, inconsistent with pure CaSO<sub>4</sub> (dotted 883 line, Fig. 21d); the vein endmember has excess S compared to pure Ca-sulfate. The Matijevic 884 formation vein-rich targets have decreasing MgO and FeO with increasing CaO (e.g., Fig. 15a) 885 and SO<sub>3</sub>, suggesting that the excess S is not due to Mg- or Fe-sulfates. Indeed, with the exception 886

- of Ca, none of the cations measured by the APXS are positively correlated with S. One possible
- conclusion is that the vein-rich material includes one or more unknown S-bearing phases.
- 889 However, the data could be explained if the anastomosing veins are some mixture of Mg- and/or
- 890 Fe-sulfates with Ca-sulfate such that as the Ca-sulfate content increases, other sulfates
- systematically decrease. Nevertheless, the anastomosing veins are dominated by CaSO<sub>4</sub>. The
- 892 Ortiz veins show the same drop in reflectance from 934 to 1009 nm in Pancam spectra as
- 893 observed for the Grasberg veins and we interpret this as evidence for gypsum [*Arvidson et al.*,
- 894 2014].

Calcium sulfate is only slightly soluble in aqueous solutions and the common presence of 895 CaSO<sub>4</sub>-rich veins in rocks along the Endeavour Crater rim indicates movement of relatively large 896 volumes of water through the fractures. Calcium sulfate is soluble in solutions from acidic to 897 mildly alkaline (e.g., Shukla et al. [2008]), and solubility is modestly enhanced in solutions 898 containing chlorides and other sulfates (e.g., Azimi and Papangelakis [2010]; Azimi et al. [2007]; 899 Zhang et al. [2013]). Solubility of CaSO<sub>4</sub> has a maximum in pure water around 30-50°C; the 900 veins likely were formed at moderate temperatures. The identification of gypsum in Ca-sulfate 901 veins in all three formations [Arvidson et al., 2014; Farrand et al., 2013; this work] indicates 902

temperatures of <50°C [*Nachon et al.*, 2014].

## 904 5.4.2. Aluminosilicate-dominated Boxwork Veins

905 In addition to the Ca-S-rich veins, the Matijevic formation hosts bright boxwork veins in some locations [Arvidson et al., 2014; Crumpler et al., 2015a]. Two targets at one location were 906 analyzed, with one including abrasion to expose the interior [Clark et al., 2016]. Unlike the 907 common CaSO<sub>4</sub>-rich veins on Endeavour Crater rim, the boxwork veins have high Al<sub>2</sub>O<sub>3</sub> and the 908 highest SiO<sub>2</sub> measured at Meridiani Planum. The calculated "pure" vein composition is 909 consistent with a mixture dominated by montmorillonite and a silica phase [Arvidson et al., 910 2014; Clark et al., 2016]. Pancam spectra of the boxwork veins also display a drop in reflectance 911 from 934 to 1009 nm as seen in the CaSO<sub>4</sub>-rich veins, but display subtle spectral differences 912 from those veins [Farrand et al., 2014]. For the boxwork veins, the silica phase might be 913 hydrated silica as observed by the Spirit rover near Home Plate [Rice et al., 2010]. Clark et al. 914 [2016] suggest that the boxwork veins formed from solutions with pH values that were 915 circumneutral to mildly alkaline. Deposition of aluminosilicates in cm-wide, crosscutting 916 boxwork veins suggests that the solutions were hydrothermal (few hundred C) to allow 917 918 dissolution of primary feldspar from their source (cf., Catalano [2013]) with relatively high water/rock ratios. The differences in alteration conditions inferred for the aluminosilicate 919 boxwork veins and the Ca-sulfate-dominated anastomosing veins in the Matijevic formation 920 indicates that they were distinct events. 921

## 922 5.5. Dark-rock Float and Ejecta

923 The dark rocks encountered as float on Murray Ridge and as a capping rock on Wdowiak
924 Ridge have an uncertain origin. They potentially could be fragments of a pre-impact lithology,
925 materials formed during the impact (e.g. impact melt), or even a post-impact addition to the

region. Compositional data can help constrain their origin and how they fit into the impact and 926 927 alteration history of the region. Two analyses were done on the dark vesicular float-rock Tick 928 Bush (Figs. 10a, 11a) from the Solander Point region, and two separate dark float-rocks -929 Augustine (Fig. 10b) and Point Bede (Fig. 11b) - from the McClure-Beverlin Escarpment region (Table S2). These were untreated targets. From Wdowiak Ridge we analyzed a total of four dark 930 931 rocks. Two of these were untreated, and one brushed. For the remaining rock we did analyses 932 before and after brushing on the main rock, and two slightly offset analyses of a dark flake on the opposite side of that rock. Mount Edgecumbe was found as float off the northeast tip of 933 Wdowiak Ridge, while the others were ejecta blocks from Ulysses crater on the southwestern 934 end (Fig. 1c). 935

The analysis results are shown in Fig. 23. Table 1 gives the compositional characteristics 936 of the dark rocks relative to the average Shoemaker formation composition. Amongst the dark-937 rock float targets, Tick Bush is compositionally distinct from any of the major lithologies found 938 on the Endeavour Crater rim. The low MgO and FeO contents, coupled with high Al<sub>2</sub>O<sub>3</sub> (Figs. 939 23a, b) and SiO<sub>2</sub> (not shown) would be consistent with Tick Bush being an evolved mafic 940 volcanic rock, but this origin is not compatible with the high Ni and Zn contents (Figs. 23c, d). 941 Tick Bush also has higher MnO contents than any other rock from the Endeavour rim, excluding 942 the salt-encrusted surfaces of two rocks dislodged by Opportunity's wheels - Pinnacle Island and 943 944 Stuart Island [Arvidson et al., 2016]. We will return to the origin of Tick Bush in Section 6.2.

The two float rocks from the McClure-Beverlin Escarpment have major element 945 compositions that are generally within family of the Shoemaker formation impact breccias 946 although their Al<sub>2</sub>O<sub>3</sub> contents are higher than those of the breccias (Fig. 23b). These two rocks 947 plot at the low MgO and low FeO ends of arrays of compositions of Gusev Crater mafic volcanic 948 rocks (Figs. 23a-c). The fine-grained homogeneous textures of the rocks are compatible with a 949 volcanic origin. These two rocks are low in Zn and Cl compared to the Shoemaker formation 950 breccias or the Matijevic formation (Fig. 23d), and again they are similar to the Gusev Crater 951 mafic volcanic rocks in volatile/mobile element contents [Gellert et al., 2006; McSween et al., 952 2006a, b, 2008; Ming et al., 2006, 2008]. The compositional and textural characteristics of 953 Augustine and Point Bede are consistent with an origin as mafic volcanic rocks. 954

955 Rocks from Wdowiak Ridge are compositionally distinct from all other Endeavour rim 956 lithologies (Fig. 23). They typically have a heterogeneously distributed coating of dust on some 957 surfaces (Fig. 10c) that is effectively removed by brushing (Fig. 11c). Comparing the untreated 958 and brushed compositions of the target Lipscomb-Margaret (hereafter, Margaret), the brushing resulted in lowering of the SO<sub>3</sub> and Cl by about 10%, but all other elements are within 959 960 measurement uncertainty for the two analyses. The only other brushed target is Hoover (Figs. 10c, 11c), and this target is compositionally anomalous compared to all other Wdowiak Ridge 961 targets. It has by far the lowest Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> contents, and highest SO<sub>3</sub>, Cl, FeO 962 and Zn contents (e.g., Figs. 23b, d). The high SO<sub>3</sub>, Cl and Zn contents suggest that this rock has 963 an altered composition. The planar fractures [Arvidson et al., 2015] that result in dark flakes on 964 flat surfaces after physical weathering (Fig. 11c) are evidence for late alteration of the dark cap 965 rocks prior to impact excavation and deposition in the ejecta field of Ulysses crater. The flake 966 target Lipscomb-Victory (hereafter, Victory) is smaller than the APXS field of view and thus the 967

968 underlying Margaret substrate contributed to the instrument response. We did two integrations

- on Victory that were slightly offset, but the two compositions are almost identical. Compared to
- 970 the Margaret brushed target, the Victory flake targets have ~50% higher Cl contents, and ~18%
- lower MnO and ~55% lower Ni contents. A small decrease in  $Al_2O_3$  and a small increase in FeO
- are also evident in the analyses, but these could simply reflect small variations in the Margaret
- 973 rock composition rather than differences between the flakes and the rock. The change from
- 974 Margaret to Victory are shown by dashed arrows in Figs. 23b-d.

975 Compositional variations between Margaret and Victory are unlike the differences
976 between Hoover and the other Wdowiak Ridge rocks indicating that the alteration that we infer
977 occurred along the planar fractures in these rocks was not the same alteration that engendered the
978 Hoover composition. There are general increases in SO<sub>3</sub> and Zn with Cl amongst the Wdowiak
979 Ridge rocks indicating that the suite likely represents a series of variably altered rocks of broadly
980 mafic composition.

## 981 6. Discussion

The geological, textural, mineralogical and compositional evidence presented is used below to explore several aspects of the nature and origin of the lithologies seen in the Endeavour Crater rim: (i) the nature of the pre-impact surface; (ii) which rocks, if any, are pristine; (iii) which are altered; (iv) the origin of the dark rocks; (v) formation of veneers; and (vi) the origin of the Grasberg formation. The discussion ends with a scenario developed to explain the geological and alteration history of rocks on the rim of Endeavour Crater.

## 988 6.1. Nature of the Pre-impact Terrane

As discussed in Sections 4 and 5, we have several types of materials whose textures and compositions can inform us of the lithologic diversity of the pre-impact terrane: the Matijevic formation, clasts within the Shoemaker formation breccias, and dark rocks from Murray and Wdowiak Ridges. The latter are discussed in Section 6.4. Interpretations of the former two are explored in this section.

The Matijevic formation is interpreted as representing a pre-impact lithology upon which 994 the polymict impact breccias of the Shoemaker formation on Cape York were deposited 995 [Arvidson et al., 2014; Crumpler et al., 2015a]. The limited areal and stratigraphic extent of the 996 Matijevic formation outcrops hampers interpretation of the origin and scope of the formation. It 997 could be regional or localized in extent [Crumpler et al., 2015a], but it is plausible that it is part 998 999 of the Noachian etched unit of Meridiani Planum (Figs. 2b, c). However, because of uncertainty 1000 in the thickness of the etched unit in the location of Endeavour Crater, the Matijevic formation could instead be part of the Noachian subdued crater unit that is exposed to the south of the 1001 1002 hematite-spherule lag deposits [Hynek and Di Achille, 2017]. Rocks similar to the Matijevic 1003 formation have yet to be identified on the Cape Tribulation segment of the rim, but as of the time 1004 this paper was accepted, we have not investigated a similar location – the inboard side of the rim 1005 - for this segment. The impact process also plausibly resulted in differing degrees of motion of 1006 blocks around the rim which would have affected exposures of the pre-impact surface (e.g.,

*Crumpler et al.* [2015a]; *Grant et al.* [2016]). The Matijevic rocks give us our only definitive
direct look at the nature of the pre-impact surface, albeit very limited in geographic extent.

1009 A broader-scale, but fragmented view of the pre-impact terrane can be attained by examining clasts in the Shoemaker formation breccias, informed by knowledge gained from the 1010 study of terrestrial craters. Close to the rims of small craters, low-velocity ejecta can form 1011 "inverted stratigraphy" in which the local stratigraphic column can be recognized in the ejecta 1012 blanket, albeit upside down. However, for larger, complex craters such as Endeavour, the 1013 transient crater rim, where low-velocity ejecta would occur, slumps inward forming the inner 1014 1015 ring of the final crater. This inner ring and possible preserved inverted stratigraphy is not accessible by *Opportunity*. At the location of the tectonic rim where *Opportunity* has worked, 1016 ejecta strikes the surface at high velocity, effectively mixing the ejecta blanket. Material is 1017 ejected from a crater only to a depth of about 1/3 the transient crater depth, or approximately 0.1 1018 times the transient crater diameter (see Melosh [1989], page 78). The clast suite in the 1019 1020 Shoemaker formation thus represents a mixture of the lithologic diversity of the upper portion of the pre-impact geology. Comparison with a terrestrial crater can aid in the interpretation of the 1021 1022 Matijevic formation and clast suite.

#### 1023 6.1.1. Ries Crater; a Terrestrial Analog

1024 The Ries Crater is a well-studied Miocene impact crater in southern Germany that is 1025 similar in size – 26 km diameter – to Endeavour Crater and thus serves as a useful analog; the 1026 discussion here is summarized from *Hörz* [1982], *Hörz et al.* [1983], *Pohl et al.* [1977] and 1027 *Stöffler et al.* [2013], except as noted. The pre-impact target of the Ries consisted of 550-750 m 1028 of terrestrial and marine sediments overlying a metamorphic/granitic crystalline basement. The 1029 surface topography and the unconformity surface each had on the order of  $10^2$  m of relief.

1030 Two types of polymict breccia occur on the tectonic rim of the Ries, the Bunte Breccia 1031 and the outer suevite. The Bunte Breccia is almost exclusively derived from the sedimentary 1032 target rocks that are modestly shocked, if at all, whereas the suevite derives predominantly from the crystalline basement and contains shocked rocks and impact melts. Within the Bunte Breccia 1033 deposits, blocks >25 m across are classified as megablocks and mapped individually as to 1034 1035 stratigraphic source region, while blocks <25 m across are subsumed as part of the Bunte Breccia. The Bunte Breccia is much coarser grained than the suevite and forms the bulk of the 1036 continuous ejecta blanket. It is roughly 100 m thick at the tectonic rim (see Fig. 35 of Hörz et al. 1037 1038 [1983]) and directly overlies the pre-impact surface. The Bunte Breccia is thus stratigraphically equivalent to the Shoemaker formation, which formed the continuous ejecta blanket around the 1039 Endeavour Crater tectonic rim. Note that the Bunte Breccia is substantially coarser-grained than 1040 is the Shoemaker formation at Endeavour. At the position of the tectonic rim of the Ries, the 1041 mean fragment size of the Bunte Breccia is ~50 cm (using eq. 4 of Hörz et al. [1983]), whereas 1042 the *largest* clasts we have observed in the Shoemaker formation are ~10 cm across. The 1043 1044 instrumentation on-board Opportunity does not allow for characterization of shock state of rocks and we cannot thus determine whether Shoemaker formation clasts are of low shock stage as is 1045 1046 the case for the Bunte Breccia.

Outer suevite overlies the Bunte Breccia with very sharp contacts and is a finer-grained 1047 1048 polymict breccia. The unit is presently discontinuous and is thought to have been emplaced as 1049 discontinuous patches, likely of varying thicknesses. The maximum thickness of suevite 1050 observed outside the tectonic rim is ~30 m. In some locations, a top quenched zone is present 1051 indicating little erosion. The outer suevite was not part of the primary ejecta curtain that 1052 deposited the Bunte Breccia but its mode of transportation and emplacement is uncertain. Based on a synthesis of observations and modeling, Artemieva et al. [2013] and Stöffler et al. [2013] 1053 concluded that the outer and crater suevite of the Ries represent polymict fallback deposits from 1054 a secondary plume engendered by interaction of volatiles ( $H_2O \pm CO_2$ ) with impact melt and hot 1055 breccia on the crater floor. This follows earlier work that concluded that the suevite of the 1056 1057 Onaping Formation of the Sudbury impact structure was formed by a melt-fuel-coolantinteraction process rather than as primary ejecta [Grieve et al., 2010]. A 20-40 cm thick basal 1058 1059 sublayer of the Ries outer suevite – a miniscule fraction of the total suevite – might be fallback 1060 breccia from the primary ejecta plume, but this is uncertain [*Stöffler et al.*, 2013].

1061 Osinski et al. [2016] have compared the morphologic and petrologic characteristics of Ries suevite with those of volcanic rocks formed by a melt-fuel-coolant-interaction process, and 1062 with the Onaping Formation suevite, and concluded that an origin of the Ries suevite as proposed 1063 by Artemieva et al. [2013] and Stöffler et al. [2013] is not supported. Osinksi et al. [2016] 1064 1065 affirmed an origin for the Onaping suevite as deposits from secondary, phreatomagmatic 1066 eruption plumes. However, these authors concluded that the Ries suevite was emplaced as meltrich flows on the Bunte Breccia. Osinksi et al. [2016] documented that emplacement of melt-rich 1067 1068 flows on top of continuous ejecta blankets is commonly observed on the inner planets, the Moon and asteroid 4 Vesta. 1069

1070 We earlier noted that Shoemaker formation rocks bear a textural resemblance to suevite [Crumpler et al., 2015a; Squyres et al., 2012]. Note that because Opportunity cannot determine 1071 1072 whether glass is present, the textural resemblance cannot extend to the presence of impact-melt, a hallmark of Ries Crater suevite (e.g., Osinski et al. [2004]; Siegert et al. [2017]). Given that (i) 1073 suevite overlies the continuous ejecta blanket at the Ries, (ii) Reis suevite was deposited as 1074 discontinuous patches only a few tens of meters thick, (iii) 100-200 m of erosion has occurred on 1075 the Endeavour Crater rim [Grant et al., 2016], which would have removed any suevite that might 1076 initially have been present, and (iv) the Shoemaker formation directly overlies pre-impact rocks, 1077 comparison of Shoemaker formation rocks with the Bunte Breccia is more apt. 1078

1079 The lithic clast population in the Bunte Breccia is dominated by sedimentary rocks from the upper 550-750 m of the target stratigraphy and <1% of the clast population is derived from 1080 the approximately 800-1000 m of crystalline basement excavated by the impact. As a crude 1081 approximation, clasts in the Bunte Breccia are dominantly from the upper ~40% of the target 1082 1083 zone. Melosh [1989] states (page 144) that a typical result of crater studies is that a transient crater expands by about 60% of its diameter to form the final diameter of a complex crater, and 1084 the transient crater diameter is roughly equivalent to the floor diameter of the final crater. This 1085 would put the transient crater and final floor diameter for Endeavour at ~14 km. This is 1086 consistent with the inner diameter of 17-19 km defined by terrace blocks [Grant et al., 2016] 1087 which would be somewhat greater than the floor diameter. Material is excavated from a depth of 1088

roughly 0.1 times the transient crater diameter, or ~1400 m for Endeavour. However, the depth
of Endeavour Crater is estimated to have been 1500-2200 m before infilling with Burns
formation sands [*Grant et al.*, 2016], which suggests a greater excavation depth than that
estimated here. Using a range of excavation depths of 1400-2200 m, and based on the results
from the Ries crater, we expect the clasts in the Shoemaker formation to have been derived
mostly from the upper 560-880 m of the pre-impact surface.

### 1095 **6.1.2. Matijevic Formation; Origin and Mixing During Impact**

None of the clasts in Shoemaker formation breccias resemble pre-impact Matijevic 1096 formation rocks. Although there is some overlap in composition for some elements in some 1097 clasts with Matijevic rocks, no clasts fall within the fields for the latter for all elements (see Fig. 1098 19). The textures for clasts are also distinct from the Matijevic rocks (compare Figs. 7a, 9c). 1099 More generally, clasts are typically dark in Pancam images in contrast to the bright Matijevic 1100 formation matrix and are distinct from the Matijevic matrix in terms of their VNIR Pancam 1101 1102 spectra. Thus, none of the few clasts we have analyzed are from a Matijevic protolith, and it 1103 likely was not a major component of the pre-impact terrane.

1104 Although clasts of Matijevic formation have not been identified within the Shoemaker 1105 formation, there is nevertheless evidence for localized contamination of the lowermost 1106 Shoemaker formation with material derived from the Matijevic formation. In Section 4.3 we noted that spherules like those found in the Matijevic formation are present in the Copper Cliff 1107 member of the Shoemaker formation that lies in direct contact with it. In Section 5.3 we noted 1108 that there is some compositional overlap for some elements between the Matijevic and 1109 Shoemaker, and that Copper Cliff member rocks commonly overlapped. We ran an AHCA 1110 calculation for all Matijevic, Shoemaker and Grasberg formation targets for all elements except 1111 the volatile/mobile elements. All of the Matijevic formation matrix and spherule-rich targets but 1112 one cluster with six of the nine Copper Cliff member targets. No Grasberg or other Shoemaker 1113 formation targets are in this cluster. This indicates a general compositional similarity between the 1114 Matijevic formation and the overlying Copper Cliff member. At the Ries crater, emplacement of 1115 the Bunte Breccia on the rim caused erosion of the paleosurface and incorporation of the eroded 1116 debris into the Bunte Breccia [Hörz et al. 1983]. The textural and compositional data from the 1117 Cape York rim segment are consistent with this same process occurring locally at Endeavour 1118 1119 Crater.

1120 As mentioned in Section 4.2, one possible origin for the Matijevic formation is as volcanic ash [Crumpler et al., 2015a]. We can compare this lithology with pristine, ancient 1121 Adirondack-class olivine basalts that form the cratered plains of Gusev Crater [McSween et al., 1122 2004, 2006; Morris et al., 2004, 2006b]. These were analyzed by sister rover Spirit using an 1123 identical instrument. The cratered plains unit is of Early Hesperian age [Tanaka et al., 2014] with 1124 an estimated age based on crater counting of 3.65 Ga [Greeley et al., 2005; Parker et al., 2010]. 1125 These are near-primary melts of the martian mantle and are likely representative of basalts that 1126 were formed during early martian history [Filiberto et al., 2008; Monders et al., 2007; Schmidt 1127 1128 and McCoy, 2010]. Basaltic cobbles (Group 1) with fairly primitive compositions (high MgO)

have also been analyzed by the Chemical Camera (ChemCam) instrument on the Mars Science
Laboratory rover *Curiosity* in Gale Crater [*Cousin et al.*, 2017].

1131 Compared to the abraded interiors of Adirondack-class basalt targets, Matijevic 1132 formation matrix and spherule-rich targets are higher in SiO<sub>2</sub> and lower in MgO, CaO and FeO 1133 (Fig. 15); all consistent with a more evolved magmatic composition. However, the Ni contents of 1134 Matijevic formation rocks are much higher than for Adirondack-class basalts (Fig. 15d); higher 1135 Ni coupled with lower MgO is inconsistent with igneous fractionation. The Matijevic formation 1136 rocks are similarly lower in MgO and FeO than the primitive Group 1 basalts from Gale Crater, 1137 but overlap the latter in SiO<sub>2</sub> and CaO (cf., Table 6, *Cousin et al.* [2017]).

1138 The abraded interiors of Matijevic formation are slightly higher in Cl (~0.5 wt%) and 1139 SO<sub>3</sub> (2-3 wt%) compared to the Adirondack-class (0.2-0.3 wt% and ~1.5 wt%), but Zn and Br contents are similar. The veneer-rich targets of the Matijevic formation are substantially enriched 1140 in these volatile/mobile elements (Fig. 14a) plausibly as a result of leaching from the matrix and 1141 deposition on the surface. Thus, the concentrations of the volatile/mobile elements measured in 1142 matrix/spherule-rich targets are likely lower than when the rocks were deposited. Together, the 1143 compositional data indicate that the Matijevic formation is composed of altered rocks, but 1144 whether alteration occurred prior to or after the Endeavour impact is unclear. If Ni 1145 concentrations were enhanced by the alteration, the fine-grained clastic Matijevic formation 1146 might have originated as moderately evolved volcanic ash or impact debris from an evolved 1147 igneous terrane. 1148

## 1149 6.1.3. Origin of Clasts

1150 Some clasts appear to be breccias (Fig. 9c), which could suggest that their protolith was 1151 an earlier-formed impact breccia, possibly from Miyamoto Crater for example (see Section 3; 1152 Fig. 2a). However, polymict-breccia clasts can be formed in a single impact event, and multiple 1153 generations of breccia are observed at the Ries (see Hörz et al. [1983], page 1681). For this 1154 reason, the protoliths for breccia clasts in the Shoemaker formation could have been primary crustal units. More generally, clasts in Shoemaker breccias have textures that indicate that they 1155 are very fine-grained or glassy rocks (Figs. 9a, b). Potentially, they are fine-grained primary 1156 volcanic rocks. 1157

We have done only a small number of analyses of clasts from the Shoemaker formation, 1158 and they do not allow firm conclusions to be drawn regarding the origin of their protoliths. The 1159 clast data scatter on major-element diagrams (Fig. 19). This is not surprising as they likely 1160 represent material from widely separated locations and depths within the pre-impact terrane. 1161 They do not match Adirondack-class basalts in composition, nor are they obvious magmatic 1162 progenitors or derivatives from similar basalts. The clasts are also distinct in major element 1163 1164 composition from the primitive Group 1 basalts from Gale Crater [Cousin et al., 2017]. There is some evidence that the clasts were derived from altered materials. Many of the clasts have 1165 FeO/MnO ratios much lower than observed for pristine martian magmatic rocks (Fig. 19c). 1166 1167 Igneous processes do not greatly fractionate FeO and MnO, and pristine igneous rocks from Mars, such as the Adirondack-class basalts, have a limited range in FeO/MnO; the Mars line in 1168

- 1169 Fig. 19c is an average derived from compositions of abraded Adirondack-class-basalt targets.
- 1170 Most of the Shoemaker formation host targets and the dark sands plot along this line, indicating
- their FeO/MnO ratios are primary. Many of the clasts and some of the Amboy outcrop targets
- 1172 have low ratios as a result of high MnO contents. This indicates likely Mn mobility in the
- 1173 precursor lithologies as a result of alteration of the pre-impact terrane. Manganese mobility is
- 1174 explored in more detail in the next section.
- 1175 Although definitive conclusions cannot be reached, the textures and compositions of 1176 clasts within the Shoemaker formation suggest that they are fragments of mildly altered volcanic 1177 units.

## 1178 6.2. Iron and Mn Variations with Alteration

- 1179 The geochemical behaviors of Fe and Mn vary greatly depending on oxidation state. Iron and Mn behave very similarly in geochemical systems when in their divalent states. Because of 1180 their similar ionic radii,  $Fe^{2+}$  and  $Mn^{2+}$  are not greatly fractionated by the major ferromagnesian 1181 minerals crystallizing from magmas, and igneous rocks from a given planetary body have 1182 relatively limited ranges in FeO/MnO [Papike et al., 2003]. However, aqueous alteration 1183 processes can lead to substantial fractionation of these elements because of differences in 1184 solubility with oxidation state and solution chemistry (e.g., Drever [1997]; Lindsay [1979]; 1185 1186 Stumm and Morgan [1996]). Fractionation of Mn from Fe in an aqueous environment is demonstrated by Mn-rich dark coatings on surfaces of rocks flipped by *Opportunity*'s wheels in 1187 the Cook Haven fracture zone of Murray Ridge [Arvidson et al., 2016], and in Mn- rich veins 1188 crosscutting Kimberley formation sandstones in Gale Crater [Lanza et al., 2016]. The targets in 1189 the Cook Haven fracture zone (rock alteration in Fig. 24a; Table 2) have low and widely varying 1190 molar Fe/Mn (13.7 – 4.3) caused by increasing MnO content with only modest variation in FeO 1191 content. The coatings on these rocks are interpreted as having two main components: an earlier 1192 bright coating dominated by Mg-rich sulfates; a later dark, Mn-rich precipitate composed of 1193 Mn<sup>3+</sup> and Mn<sup>4+</sup> oxide phases [Arvidson et al., 2016]. Chemical modeling in which a solution 1194 calculated to be in equilibrium with Shoemaker formation composition rock is allowed to 1195 precipitate at low T produces a sequence of secondary phases that is consistent with the 1196 observations [Arvidson et al., 2016]. The physicochemical conditions of this alteration process 1197 are poorly constrained at present, but late-stage oxidation to form  $Mn^{3+}$  and  $Mn^{4+}$  oxide phases is 1198 1199 required. Similarly, the Mn-rich veins in Gale Crater are composed of Mn oxides and indicate deposition from highly oxidizing aqueous solutions, which is considered to be evidence for more 1200 1201 abundant O in the ancient martian atmosphere than observed today [Lanza et al., 2016].
- 1202 The dark-rock float target Tick Bush has high MnO and low Fe/Mn (10.9 for the higher Mn target) compared to Mars (Fig. 24). (The Mars line shown corresponds to a molar Fe/Mn of 1203 44.9, an average for abraded targets of Early Hesperian Adirondack-class basalts. For 1204 comparison, an average Fe/Mn for Late Amazonian martian basaltic meteorites is 36.3 based on 1205 1206 compiled literature data.) Tick Bush has lower FeO (13.2-14.0 wt%) compared to the other darkrock float and Wdowiak Ridge targets (15.2-17.1 wt%, excluding Hoover), but the low Fe/Mn is 1207 1208 largely a result of its higher MnO. We did not abrade or brush the surface of Tick Bush, but the composition of this rock is not consistent with dark-sand or bright-soil contamination (Fig. 23), 1209

nor does Pancam imaging indicate the presence of a coating (Fig. 10). The high MnO is 1210 1211 consistent with enrichment via an alteration process, which could also be the cause of its high Ni 1212 and Zn contents (Fig. 23). In particular, the high Ni content associated with low MgO, high 1213 Al<sub>2</sub>O<sub>3</sub> (Fig. 23) and high SiO<sub>2</sub> in Tick Bush is inconsistent with magmatic fractionation 1214 processes and indicates later addition by an alteration process. High Ni contents could result 1215 from chondritic contamination (e.g., in an impact-generated rock), but this can be ruled out for Tick Bush because of its association with high MnO and Zn, neither of which would be enriched 1216 by chondritic contamination. Note that the SO<sub>3</sub> and Cl contents of Tick Bush are not 1217 exceptionally high; they overlap the ranges for dark rock from Wdowiak Ridge that have Mars-1218 like Fe/Mn. Tick Bush is vesicular and very fine grained, possibly glassy (Fig. 11a) indicating a 1219 melt origin. Together, the textural and compositional data support an origin as an impact melt of 1220 a moderately altered protolith, possibly of evolved volcanic materials. Impact melting plausibly 1221 1222 allowed volatilization of SO<sub>3</sub> and Cl, lowering their content and contributing to the vesiculation of the melt. 1223

1224 Figure 24b shows an expanded view of the FeO-MnO relationships for Endeavour rim rocks compared to the Fe/Mn ratio for Mars as represented by abraded Adirondack-class basalts 1225 from Gusev Crater analyzed by sister rover Spirit [McSween et al., 2004, 2006]. With the 1226 exception of the Monjon Grey target, the Grasberg formation is high in Fe/Mn, low in MnO and 1227 1228 high in FeO compared to the average Shoemaker formation breccia (Table 1). As discussed in 1229 Section 5.1, the grey material on Monjon appears to be a coating, with only a portion of the APXS field of view of the Monjon Grey target including this coating. The high MnO content of 1230 1231 Monjon Grey is accompanied by the highest Zn content of any Grasberg formation target, and the two Monjon targets have the lowest CaO contents (Fig. 12). The halogen, SO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> 1232 1233 contents of Monjon are not dramatically different between the Grey and Purple targets, which are 1234 similar to those of most Grasberg formation targets. However, Pancam spectra of these grey 1235 coatings are distinct from purple Grasberg targets and are consistent with some fraction of the 1236 coating consisting of Mn-oxides [Farrand et al., 2016]. Thus, the grey material on Monjon could 1237 be an oxide coating rich in MnO similar to those seen at Cook Haven, but we have insufficient data to test this hypothesis further. 1238

There is a dichotomy in Fe/Mn ratios of the Shoemaker formation on the two Endeavour 1239 rim segments investigated; rocks on Murray Ridge tend to have Mars-like or higher Fe/Mn while 1240 those on Cape York tend to have Mars-like or lower Fe/Mn (Fig. 24b). Separate fields for the 1241 anomalous Tisdale block and Shoemaker formation members on Cape York are shown, and 1242 1243 compositionally anomalous and clast targets are plotted separately. Two bulk-rock targets, Amboy12 (Greeley Haven, Cape York) and Spinifex (Murray Ridge) have high MnO, but have 1244 FeO typical of other rocks from those regions. Clast samples Geluk and Komati similarly have 1245 modestly higher MnO, but only marginally higher than some of the Greeley Haven cluster 2 1246 rocks; in the case of Geluk, it has substantially lower FeO compared to its host breccia (cf., Fig. 1247 1248 19c).

We did a series of three measurements of the Murray Ridge Sarcobatus target, a bulk sample and two integrations on a large clast (Fig. 8e), the second of which was better-centered on the clast. For most elements, there is a progression from either low to high contents (Al<sub>2</sub>O<sub>3</sub>,

SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, CaO, TiO<sub>2</sub>), high to low (MgO, SO<sub>3</sub>, Cl, Cr<sub>2</sub>O<sub>3</sub>, FeO, Br) or roughly constant within 1252 1253 measurement precision (Na<sub>2</sub>O, K<sub>2</sub>O, Ni) (cf., Fig. 18d, 19). This is consistent with the Clast2 1254 target representing the purer sampling of clast material than the first clast target. However, MnO 1255 and Zn are exceptions; they are much higher in the first clast target than either the host or Clast2, 1256 which are almost identical (Fig. 18d). Sarcobatus Clast has internal variations in MnO and Zn 1257 that suggest alteration mobilized these elements. The clast appears fine-grained and homogeneous in Pancam (Fig. 8e) and MI imaging, with no coatings evident. The data and 1258 observations are consistent with the alteration having occurred in the protolith of the clast prior 1259 to impact excavation. 1260

#### 1261 **6.3. Sulfur and Fe/Mn Relationships**

We have previously noted a correlation between the S contents and Fe/Mn ratios for 1262 rocks from the Endeavour Crater rim that we concluded provided evidence for differential 1263 mobilization of Fe and Mn in S-bearing solutions [Ming et al., 2015]. In general, data for coarse 1264 1265 CaSO<sub>4</sub> veins (Grasberg formation) or targets containing finer-scale CaSO<sub>4</sub> veins (Hueytown vein, Murray Ridge vein-rich) have Fe/Mn that are Mars-like (Fig. 24b). An exception is the 1266 1267 Matijevic formation vein-rich targets, which have Fe/Mn ratios that are lower than the Mars 1268 igneous and Matijevic-formation-matrix-target ratios. The relationship between S mobilization 1269 and Fe/Mn variation is explored in Fig. 25. As discussed in Section 5.4, the sulfate veins in the Grasberg formation, Bristol Well on Murray Ridge and Cottondale at the Hueytown fracture 1270 zone are consistent with being composed of CaSO<sub>4</sub>, but the Ortiz veins in Matijevic formation 1271 1272 are inconsistent with simply being CaSO<sub>4</sub> crosscutting typical Matijevic formation matrix rock. A curious characteristic of the vein-rich targets, excluding the Ortiz veins, is that their 1273 compositions closely approach the Mars Fe/Mn ratio even though the host rocks might have a 1274 distinctly different ratios (Fig. 25a). The difference for the Bristol Well vein on Murray Ridge is 1275 small, but the host is already close to the Mars Fe/Mn ratio. For the vein sampled at the 1276 Hueytown fracture zone, the Fe/Mn ratio is higher than that of the modeled bedrock-dark sand 1277 mixed composition that is plausible for the substrate hosting the vein (Fig. 21c). The largest 1278 1279 difference is for the Deadwood-Homestake host-vein pair from the Grasberg formation (Fig. 25a). The CaO and SO<sub>3</sub> data are consistent with CaSO<sub>4</sub> contributing ~45-48% of the instrument 1280 response for Homestake2 compared to an assumed substrate equivalent to Deadwood. 1281

1282 For the Deadwood-Homestake host-vein pair, the Mn/Si ratio of the host and vein are very similar (Fig. 26a) indicating that the Grasberg formation substrate included in the 1283 1284 Homestake analysis field of view has the same Mn/Si ratio as the nearby Deadwood target, and 1285 the lower member of the Grasberg formation more generally. (This assumes that the Homestake 1286 vein is free of Si and Mn.) In contrast, the Homestake targets have substantially lower Fe/Si than does Deadwood, or any of the targets of the lower member of the Grasberg formation. The 1287 1288 substrate included in the APXS field of view is depleted in FeO compared to the Grasberg 1289 formation and indicates that FeO was mobilized by the solutions responsible for the veins, but 1290 MnO was not. Although the signal is less clear for the other vein-rich targets because of the 1291 lower fraction of vein material in the APXS field of view, the Bristol Well vein similarly shows little difference in Mn/Si and lower Fe/Si whereas the Hueytown fracture zone vein shows lower 1292

ratios for both, with a proportionally greater decrease in Mn/Si (Fig. 26). The Ortiz veins in the
Matijevic formation are the oddballs, showing essentially no difference in Fe/Si but a large
increase in Mn/Si. We noted in Section 5.4 that the Ortiz veins are compositionally distinct from
the other Ca-sulfate veins we have analyzed.

As noted in Section 6.2, Fe and Mn behave nearly identically in basaltic magma systems, 1297 but they can be quantitatively fractionated in some aqueous systems. Mildly acidic to 1298 circumneutral solutions at low  $a_{O_2}$  can precipitate Fe as oxides/hydroxides while  $Mn^{2+}$  remains in 1299 solution (see Stumm and Morgan [1996], Fig. 7.7). Varying the redox condition is a candidate 1300 mechanism for Mn mobilization, but we cannot rule out mobilization by changes in pH. Our 1301 hypothesis is that oxidized solutions from the overlying Burns formation interacted with 1302 Grasberg formation sediments leading to redox exchange of Fe and Mn. Initially immobile, 1303 oxidized Mn was mobilized via reduction by late stage fluxes of Fe<sup>2+</sup>-rich fluids through the 1304 Grasberg sediments via the reaction: 1305

1306

$$MnO_2 + 2Fe^{2+} + 4H_2O \rightarrow Mn^{2+} + 2Fe(OH)_3 + 2H^+$$

This reaction produces acidity similar to that calculated by *Hurowitz et al.* [2010] for interaction
of groundwaters with basaltic rock as a mechanism for formation of jarosite and other sulfates in
the Burns formation. Regional groundwater upwelling, possibly with recharge from the southern
highlands [*Andrews-Hanna et al.*, 2007, 2011] might have been a source for the water. This
process could have depleted the Grasberg formation in Mn and slightly elevated it in Fe. Fluids
that precipitated CaSO<sub>4</sub> differentially mobilized FeO from MnO in the vicinity of the veins.

Enrichments of Mn are associated with S. This is suggested by the Fe/Mn and S 1313 1314 relationships shown in Figs. 24 and 25 for the Matijevic formation veneers and Ortiz veins, and by the rock alteration targets discussed by Arvidson et al. [2016]. This relationship suggests that 1315 Mn<sup>2+</sup> and possibly other ions (e.g., Ni<sup>2+</sup>, [*Ming et al.*, 2015]) were transported with S-rich fluids 1316 through fractures and porous substrates in Endeavour Crater rim materials. Manganese, S, and 1317 other ions such as Ni precipitated in veins (e.g., Matijevic formation veins) and on other surfaces 1318 1319 that came into contact with the fluids. Redox reactions appeared to have played a role in the 1320 mobilization and transportation of redox sensitive elements in Endeavour Crater rim deposits. 1321 These reactions are likely late-stage diagenetic processes.

#### 1322 6.4. Origin of Dark Rocks

We have already touched upon the compositional characteristics of some of the dark 1323 rocks that relate to evidence for alteration. Here we will summarize the compositional and 1324 textural evidence and discuss possible origins for these rocks. Dark rocks were encountered on 1325 Solander Point, near Cook Haven on Murray Ridge and on Wdowiak Ridge. The reasons for 1326 1327 these concentrated occurrences of dark rocks are unresolved. Those on Solander Point and Murray Ridge could be examples of inverted topography [*Crumpler et al.*, 2015b], or perhaps 1328 remnants of breccia lenses rich in exceptionally large clasts. Several possible origins for the dark 1329 rocks capping Wdowiak Ridge have been put forth: (i) impact melt emplaced with ejecta during 1330 formation of Endeavour Crater [Grant et al., 2015], (ii) an exhumed mega-block of target rock 1331 [Mittlefehldt et al., 2015], (iii) relief on the pre-impact surface [Mittlefehldt et al., 2015], (iv) an 1332

1333 upraised fault block created during impact [*Crumpler et al.*, 2015b], or (v) inverted topography

- 1334 of resistant rock of former valley-fill materials remaining after erosion of less competent rock
- 1335 [*Crumpler et al.*, 2015b]. Wdowiak Ridge is one of several structural elements in the Murray
- 1336 Ridge-Cape Tribulation area with a general NE-SW strike that includes topographic breaks
- 1337 within the bounding rim segments; these might have been engendered by the Endeavour impact
- 1338 [*Crumpler et al.*, 2015a; *Grant et al.*, 2016]. If so, this would suggest that mechanisms (ii), (iii)
- and (v) are less likely because that would suggest coincidental alignment of Wdowiak Ridge
- 1340 with impact-generated structures.

The dark rocks from these three locations share a common aphanitic texture, and some are vesicular. As discussed in Sections 5.5 and 6.2, Tick Bush is compositionally distinct from the other dark-rock targets and we interpret it to be an impact-melt rock. It is the only dark rock target from Solander point analyzed using the APXS. If Tick Bush is representative of those rocks, then the scattering of dark rocks on Solander Point (Fig. 3a) plausibly represents a brokenup remnant of an impact-melt lens in the rim ejecta.

1347 The dark rocks from the McClure-Beverlin Escarpment region (Fig. 3b) of Murray Ridge - Augustine and Point Bede - have compositions consistent with their being mafic volcanic 1348 rocks. They are distinct in composition from the erratic block Bounce Rock that is a close match 1349 to some of the martian basaltic meteorites [Zipfel et al., 2011]. Thus, Augustine and Point Bede 1350 are not sourced from the same location as Bounce Rock. These two dark rocks are closest in 1351 composition to some of the brushed targets on Adirondack-class olivine basalts from Gusev 1352 Crater [McSween et al., 2006], but are not identical to them. Augustine and Point Bede have 1353 generally low SO<sub>3</sub>, Cl, Zn and Br contents (see Fig. 23d); Zn and Br are within range of abraded 1354 1355 targets on Adirondack-class basalts; SO<sub>3</sub> and Cl are higher. Their Fe/Mn is higher than the typical Mars value (Fig. 24b). These data indicate that they are modestly altered, plausibly as a 1356 result of mild weathering. The compositional data for Augustine and Point Bede do not allow for 1357 a firm conclusion regarding a volcanic versus impact-melt origin for them, but the simplest 1358 interpretation is that they are weathered mafic volcanic rocks. 1359

Wdowiak Ridge rocks have compositions that are very distinct from the Shoemaker 1360 formation (Fig. 23; Table 1). Hoover from Wdowiak Ridge is compositionally distinct from the 1361 1362 other dark rocks on the ridge, and we conclude that it is substantially altered (see Section 5.5). 1363 The Victory flake differs slightly in composition from the Margaret target. Victory has higher Cl 1364 and Fe/Mn, which is consistent with slightly greater degree of alteration for material composing the flake. However, the rocks from Wdowiak Ridge in general are not highly altered. Several of 1365 them have Fe/Mn close to the primary martian ratio (Fig. 24b) and have SO<sub>3</sub>, Cl and Zn contents 1366 similar to those of brushed basalt targets from Gusev Crater (Fig. 23d) and generally lower than 1367 those of Shoemaker formation breccias (Table 1). Further, CRISM spectra of Wdowiak Ridge 1368 have relatively deep olivine and pyroxene absorption features compared to surrounding regions 1369 1370 [Arvidson et al., 2015], which suggests that rocks on the ridge are less altered.

As was the case for Tick Bush, Wdowiak Ridge rocks have lower MgO and FeO, but
higher Al<sub>2</sub>O<sub>3</sub> than do Gusev Crater basalts, consistent with a more evolved volcanic composition
(Fig. 23). However, these rocks show little variation in MgO coupled with substantial variation

in Ni content; the high end of the range being similar to the Ni contents of Tick Bush (Fig. 23c). 1374 1375 Excluding the Victory alteration flake, the Margaret target has the lowest Ni content amongst 1376 Wdowiak Ridge dark rocks. Its Ni content is similar to those of Gusev Crater basalts with much higher MgO contents (Fig. 23c). The Ni-MgO distribution for Wdowiak Ridge is inconsistent 1377 with magmatic trends in which MgO and Ni are typically well correlated. This suggests that 1378 1379 either the Wdowiak Ridge rocks are fragments of impact melt variably contaminated with 1380 chondritic impactor material, or that Ni was mobilized during the modest alteration experienced by these rocks. Robust correlations between Ni and other volatile/mobile elements do not exist 1381 for these rocks, but there are general trends of increasing Ni with increasing SO<sub>3</sub>, Cl and Zn, 1382 suggesting that Ni was indeed mobilized by alteration. 1383

As discussed above, the two hypotheses for the origin of dark capping rocks on Wdowiak 1384 Ridge that are consistent with its common orientation with Endeavour Crater structural-elements 1385 are that they are impact melt emplaced with ejecta during formation of Endeavour Crater [Grant 1386 et al., 2015], or that Wdowiak Ridge is an upraised fault block created during impact [Crumpler 1387 et al., 2015b]. The first hypothesis implies that Wdowiak Ridge should contain a lithologic suite 1388 generally similar to the rocks elsewhere on the rim. Thus, the dark capping rock would be 1389 erosion-resistant material allowing formation of the topographic feature, while below the cap one 1390 would expect to find impact breccias, which are the dominant lithologic type of the rim. The 1391 1392 abundance of unbrecciated rocks and an absence of impact breccias on Wdowiak Ridge suggest 1393 that this hypothesis is unlikely to be correct. The second hypothesis indicates that the dark capping rocks could represent a pre-impact surface. The many fracture planes within the rocks 1394 seem consistent with damage done during movement of a fault block during the impact. The 1395 1396 compositions of the dark capping rock indicate that it is variably altered volcanic rock. Wdowiak 1397 Ridge is much smaller than the km-scale terrace blocks observed on the eastern side of 1398 Endeavour Crater [Grant et al., 2016], but these were formed by a different mechanism -1399 collapse of the transient crater wall – and occur in the crater interior rather than outside the rim. 1400 Other linear ridges of the same scale as Wdowiak Ridge and subparallel to it occur nearby (see Grant et al., 2016, figure 5), but Opportunity was not commanded to investigate them. 1401 Considering the geological and compositional evidence, an origin for the Wdowiak Ridge dark 1402

rocks as an uplifted block of the pre-impact surface is more plausible.

## 1404 6.5. Formation of Veneers on Matijevic formation Outcrops; Timing and Mechanism

1405 The relative timing of veneer formation can be deduced using standard geological superposition criteria. As discussed in Section 4.2, veneers on Matijevic formation outcrops are 1406 1407 small erosional remnants of a formerly more extensive coating on the outcrop (Fig. 6a). In one 1408 area (Fig. 6a inset), bright veins underlie a patch of veneer. Vein morphology is imposed on the veneer surface, but the veins do not cut the veneer. None of the images of Matijevic formation 1409 1410 show instances where the bright Ca-sulfate-rich veins crosscut veneer. Similarly, dark veneer 1411 patches are present on the Lihir/Espérance boxwork vein that crosscuts the Matijevic formation 1412 [Clark et al., 2016]. These relationships indicate that veneer formation post-dated formation of 1413 veins in the Matijevic formation, regardless of vein type.

Veins are also present in the overlying Shoemaker and Grasberg formations, but these 1414 1415 represent a distinct episode of fluid movement from those that formed the veins in the Matijevic 1416 formation. As noted in Sections 5.4 and 6.3, the fine, bright anastomosing veins in the Matijevic 1417 formation are compositionally distinct from the CaSO<sub>4</sub> veins that crosscut the Shoemaker and 1418 Grasberg formations, and the Lihir/Espérance boxwork vein is composed dominantly of 1419 aluminosilicate-rich phases, not Ca-sulfate [Clark et al., 2016]. Farrand et al. [2014] noted 1420 VNIR spectral differences between the Ca-sulfate veins in the Matijevic and Grasberg formations on the one hand, and between them and the boxwork veins on the other. These 1421 differences were most pronounced in the form of differences in 535 nm band depth, a good 1422 indicator for hematite or other ferric oxides. Together, the evidence indicates that the veins in the 1423 Matijevic formation are products of an earlier episode of fluid flowing through the Endeavour 1424 Crater rim rock suite than that which produced Ca-sulfate veins in the Grasberg and Shoemaker 1425 1426 formations, a conclusion reached by Farrand et al. [2014].

One possible piece of contrary evidence is that fine, bright anastomosing veins, possibly
of Ca-sulfate, occur in the Copper Cliff outcrop of the Shoemaker formation that directly
overlies the Matijevic formation (Fig. 9 of *Arvidson et al.* [2014]). However the contact is often
obscured by soil and lithic fragments (see Fig. 14 of *Crumpler et al.* [2015a]). Veins cannot be
traced from Matijevic into Shoemaker rock.

The surface of the Matijevic formation was modified by the Endeavour impact. As 1432 discussed in Section 6.1, the composition of the Copper Cliff member and occurrences of 1433 spherules in it are consistent with erosion of the Matijevic formation during emplacement of the 1434 Endeavour ejecta and incorporation of eroded debris in the lowest unit of the Shoemaker 1435 formation. For comparison, emplacement of the Bunte Breccia at the Ries Crater caused tens of 1436 1437 meters of erosion of the paleosurface [Hörz et al., 1983]. Erosion of the Matijevic formation surface thus would have removed the ~mm-thick veneer had it been present on the pre-impact 1438 1439 surface.

Finally, geological evidence suggests that veneer formation predates development of the current surface. Veneer patches are present on the Matijevic surface below the Copper Cliff outcrop, but not on the smooth, gently sloped top surface of the Copper Cliff outcrop only a few tens of cm above veneer patches on the Matijevic formation. We conclude that it is unlikely that the veneers were formed on the current erosional surface.

Previously we concluded that the veneers were formed either on an ancient surface or 1445 1446 along bedding plane fractures [Arvidson et al., 2014; Crumpler et al., 2015a]. Because dark veneers are present on the eroded surface of the crosscutting Lihir/Espérance boxwork vein, we 1447 1448 conclude that the veneers were formed on an ancient erosional surface. Previously, we concluded that this occurred prior to deposition of the Shoemaker breccias [Crumpler et al., 2015a]. 1449 However, in view of the evidence presented here that the Matijevic was eroded and incorporated 1450 1451 into the lower Shoemaker breccias during emplacement of the latter, we suggest that the veneers were formed by fluids moving through the Matijevic formation, altering the rock and 1452 precipitating salts along the Matijevic-Shoemaker unconformity. 1453
We have concluded that the veneers are the host of the ferric smectite signature observed 1454 1455 from orbit for this location [Arvidson et al., 2014]. The most likely smectite is nontronite, but the 1456 veneers do not show a strong enrichment in Fe as would be expected for a nontronite-rich rock. 1457 However, nontronite only needs to be a small fraction of the scene to engender the spectral signature detected by the CRISM instrument [Arvidson et al., 2014]. The veneer is enriched in 1458 1459 the volatile/mobile elements (S, Cl, Zn and Br), K and Ca, with or without Mn compared to Matijevic formation matrix (Figs. 14, 15). A scenario consistent with the in-situ and orbital data 1460 is that small amounts of aqueous fluid mobilized the more labile elements, deposited them along 1461 the unconformity and altered a fraction of the silicates to ferric smectite with little change in bulk 1462 major element composition. 1463

Thermodynamic modeling shows that ferric smectites can form on Mars through low-1464 temperature oxidative weathering of basalt, or through later oxidative alteration of ferrous 1465 smectites produced during anoxic weathering [Catalano, 2013]. The calculations presented in 1466 that study were done for  $T = 25^{\circ}C$  with different fluid contents of  $H_2SO_4$  and  $HCO_3^{-1}$ ; the 1467 solutions were mildly acidic. The water/rock ratio for veneer formation cannot be constrained 1468 based on these calculations because we have no information on the total mineral assemblage. 1469 1470 However, the veneers are thin, roughly mm-thickness, and are enriched, not depleted, in the more soluble elements (Fig. 14a). Together, this suggest relatively low water/rock ratios for the 1471 alteration process. 1472

We infer that the sequence of events experienced by the Matijevic formation was: (i)
deposition of clastic sediments; (ii) formation of fine, anastomosing Ca-sulfate veins and
aluminosilicate boxwork veins; (iii) erosion exposing a pre-impact surface close to the present
surface of the Matijevic formation; (iv) further erosion and deposition of Shoemaker formation
breccias by the Endeavour impact; (v) veneer and ferric smectite formation along the
unconformity; and (vi) erosion to form the present surface with remaining veneer scattered in
patches.

### 1480 6.6. Origin of the Grasberg Formation

1481 The origin of the Grasberg formation is enigmatic. The consensus view of the MER 1482 science team, presented in Crumpler et al. [2015a], is that the Grasberg formation is a thin unit 1483 unconformably lying on an erosion surface (pediment) forming the lower slopes of the Endeavour Crater rim segments explored by *Opportunity*. Similar benches are present elsewhere 1484 at the contact between Endeavour Crater rim segments/terrace blocks and the Burns formation, 1485 and these are interpreted to be Grasberg formation [Grant et al., 2016]. An erosional 1486 unconformity in turn forms the upper contact with the overlying Burns formation [Crumpler et 1487 1488 al., 2015a]. A contrary view, that the Grasberg formation overlies and is younger than the Burns formation [Ruff, 2013], is not well-supported by the geological observations as discussed in 1489 Crumpler et al. [2015a]. Our hypothesis is that the Grasberg formation was emplaced as a fine-1490 grained airfall deposit that mantled paleotopography, and is a local expression of a widespread, 1491 homogeneous unit, possibly fine volcanic ash or distal debris from an impact [Crumpler et al., 1492 1493 2015a].

Assuming textures are primary, the fine-grained nature and general lack of sedimentary 1494 1495 structures suggest formation in a low-energy environment such as by air fall of ash or dust. The 1496 only interior view we have of textures for the Grasberg formation are from the abrasion hole in 1497 the upper unit target Grasberg (Fig. 5a). As noted [Crumpler et al., 2015a], the lack of 1498 identifiable contact structures between the lower and upper Grasberg suggest that the upper unit 1499 might be a weathering cap rather than a distinct depositional unit. This is generally consistent with the compositions of the two units; we find no significant compositional differences between 1500 the two (Table 3). However, because the Grasberg formation is compositionally heterogeneous 1501 (Fig. 12) and few targets were analyzed, the compositional averages of the two units are not 1502 tightly constrained. If the upper unit is a weathering cap, then the featureless texture of the 1503 1504 Grasberg target could simply reflect recrystallization that destroyed primary textures. In this case, we could make no conclusion regarding the environment of deposition from rock textures. 1505

1506 Two Burns formation targets, Guadalupe and Lion Stone, are composed of crystalline material with primary textures poorly preserved, possibly because of more extensive cementation 1507 and/or recrystallization [McLennan et al., 2005]. The specific grind energies for Guadalupe and 1508 Lion Stone were 46.2 and 18.1 J/mm<sup>3</sup>, much higher than the values of <2 J/mm<sup>3</sup> typical for 1509 Burns formation targets (Table 20.4 of Herkenhoff et al. [2008]), and within or higher than the 1510 range of terrestrial limestone [Arvidson et al., 2004]. The compositions of Guadalupe and Lion 1511 1512 Stone are within the ranges for other abraded Burns formation targets (Fig. 12). Erosion-resistant 1513 fracture fills present within the Burns formation are possibly cemented by Fe-oxides and/or silica [Knoll et al., 2008]. Guadalupe and Lion Stone are amongst the more FeO-poor abraded Burns 1514 1515 formation targets (Fig. 12c), and their SiO<sub>2</sub> contents (36.2 and 37.2 wt%) are within the range of other abraded Burns formation targets; most are between 34.4 and 41.1 wt%. Thus, there is no 1516 1517 compositional evidence for mineralization of Guadalupe or Lion Stone that could explain their 1518 high specific grind energy. The strengths of these two targets reflect a higher degree of 1519 recrystallization and/or cementation under isochemical conditions than experienced by most Burns formation rocks. 1520

The specific grind energy for Grasberg is 7.6 J/mm<sup>3</sup> [*Crumpler et al.*, 2015a], 1521 substantially less than that for Guadalupe or Lion Stone. Because Grasberg is considerably 1522 weaker than either of those Burns formation rocks, and the latter still retain some evidence of 1523 their primary sedimentary structures, we conclude that Grasberg originated as a very fine-grained 1524 sediment. However, the lower Grasberg unit target Poverty Bush shows fine-scale wavy 1525 laminations in outcrop (Fig. 4e), yet appears homogeneous and very fine-grained in MI images 1526 1527 (Fig. 5d). This could be contrary evidence to our conclusion: Poverty Bush could be completely 1528 recrystallized with primary macroscopic sedimentary structures remaining as pseudomorphs. Pancam and MI observations on untreated and abraded targets of a Grasberg formation rock like 1529 Poverty Bush would be required to address this issue. Note that the fine-scale wavy lamination 1530 texture of Poverty Bush does not obviously fit with an interpretation as an airfall deposit, but is 1531 not entirely inconsistent with that hypothesis. For example, localized reworking of the sediment 1532 1533 prior to lithification, possibly by water, could explain the textures. Additional observations of the 1534 Grasberg formation would be needed to address this issue.

Absent definitive evidence to the contrary, we continue to carry the working hypothesis 1535 1536 that the Grasberg formation is a widespread airfall deposit draped on an erosional pediment. 1537 Originally, the Grasberg sediments would have also formed a layer on the ridges of Endeavour 1538 rim segments, but must have been eroded from them. The rim segments have been degraded by 1539 100-200 m since formation, but much of that occurred prior to deposition of the Burns formation 1540 [Grant et al., 2016]. The interpretation that the Grasberg formation sits on an erosional pediment 1541 [Crumpler et al., 2015a] indicates that much of the rim degradation also occurred prior deposition of the Grasberg sediments. Continuing erosion during the Hesperian [Golombek et al., 1542 2006] would have been sufficient to remove a thin draping unit such as the Grasberg from the 1543 1544 ridges.

The composition of the Grasberg formation is distinct from the other lithologies in the 1545 region, especially so if volatile/mobile elements are excluded from consideration (Fig. 16c). We 1546 posited that the Grasberg could be either volcanic or impact-derived in origin [Crumpler et al., 1547 2015a]. Grasberg rocks are broadly basaltic in composition, but are not well-matched by 1548 expectations for volcanics. The MgO contents are lower than likely martian basalts (e.g., Fig. 1549 23a) which could indicate an evolved magma. However, the Al<sub>2</sub>O<sub>3</sub> contents are low and FeO 1550 contents are high (Fig. 23b) which preclude such an origin. The high Fe/Mn, most likely caused 1551 by low MnO contents (Fig. 24), indicates mobilization of elements during alteration as discussed 1552 1553 in Sections 6.2 and 6.3. For this reason, we cannot infer a plausible origin for the Grasberg 1554 formation based on composition. The origin of the Grasberg formation remains enigmatic, and study of further outcrops are required to test our working hypothesis. 1555

## 1556 **6.7. Geological and Alteration History of the Endeavour Crater Rim**

Based on the geological and compositional evidenced presented above, we suggest the
following scenario for the geological and alteration history of the region of the western rim of
Endeavour Crater:

- 1. Alteration of pre-impact rocks prior to the impact, including formation of fine, 1560 anastomosing Ortiz CaSO<sub>4</sub>-rich veins and aluminosilicate (boxwork) veins that 1561 crosscut the Matijevic formation [Arvidson et al., 2014; Clark et al., 2016]. Calcium-1562 1563 sulfate-rich veins were likely precipitated from dilute solutions at moderate (<50°C 1564 temperatures. The formation of the boxwork veins was a hydrothermal process. Modest alteration by low-temperature weathering processes of dark rocks that were 1565 ultimately emplaced on the rim and the cap rock on Wdowiak Ridge may also have 1566 occurred at this time. 1567 2. Erosion to form the pre-impact surface. 1568
- 15693. The Endeavour impactor excavated the crater, eroded the surface outside the crater1570and deposited polymict-breccia ejecta.
- 4. Alteration under low water/rock mobilized elements within the Matijevic formation and formed veneers along the unconformity between the Matijevic and Shoemaker.
  This was a low-temperature alteration process in mildly acidic solutions at a low

| 1574<br>1575   |                               | water/rock ratio. These are the presumed carriers of the ferric-smectite signature observed in CRISM spectra [ <i>Arvidson et al.</i> , 2014].   |
|--|-------------------------------|--|
| 1576<br>1577<br>1578<br>1579<br>1580<br>1581<br>1582<br>1583         | 5.                            | Fracture zones served as conduits for alteration fluids, possibly mobilized by heat from the impact. The Cook Haven region lies within one such fracture zone [ <i>Arvidson et al.</i> , 2016]. The Shoemaker formation targets from this region have generally higher SO <sub>3</sub> and Cl contents indicative of alteration. Rocks in this region that were flipped by <i>Opportunity's</i> wheels have compositions and mineralogies that reflect precipitation of sulfate salts and Mn oxides precipitated from solutions formed through alteration of basaltic-composition protoliths, but the processes that produced the solutions are not well-constrained by data [ <i>Arvidson et al.</i> , 2016].                         |
| 1584<br>1585<br>1586   | 6.                            | Following a period of erosion, the deposition of fine-grained Grasberg formation sediments as airfall unconformably on the Shoemaker formation and any exposed pre-impact surfaces occurred [ <i>Crumpler et al.</i> , 2015a].   |
| 1587<br>1588<br>1589<br>1590   | 7.                            | After additional erosion, the sulfate-rich sands of the Burns formation were deposited<br>on the Grasberg and Shoemaker formations. The timing of the diagenesis of the Burns<br>formation [ <i>Grotzinger et al.</i> , 2005; <i>McLennan et al.</i> , 2005; <i>Squyres and Knoll</i> , 2005]<br>in this sequence is unclear.  |
| 1591<br>1592<br>1593<br>1594<br>1595<br>1596<br>1597<br>1598<br>1599 | 8.                            | The final alteration event was formation of CaSO <sub>4</sub> veins in the Grasberg and<br>Shoemaker formations under conditions similar to those described above for the Ortiz<br>veins. The coarsest veins crosscut the Grasberg formation. A hydrologic head is<br>required to have forced fluids up to locations as high as Bristol Well on Pillinger<br>Point, suggesting that this episode likely occurred later, after a thick section of Burns<br>formation was in place. Groundwaters flushed through the region and redox exchange<br>differentially mobilized Fe and Mn in the Grasberg and Shoemaker formations in<br>mildly acidic to circumneutral solutions. This event might have indurated the<br>Grasberg formation. |
| 1600<br>1601<br>1602<br>1603   | 9.                            | Degradation of the rim likely began as soon as, or shortly after, it was formed [ <i>Grant et al.</i> , 2016], but degradation since the final alteration event would have been sufficient to remove Grasberg formation sediments from higher positions on the rim (cf., <i>Golombek et al.</i> [2006]).   |
| 1604<br>1605<br>1606   | En<br>We infer t<br>formation | deavour Crater is Noachian in age and events 1 through 3 occurred during that epoch.<br>hat events 5 and 6 are also Noachian, but we have no hard constraints on this. Because<br>of CaSO <sub>4</sub> veins in the Grasberg and Shoemaker formations likely occurred after  |

1607 deposition of the Burns formation, this alteration was Early Hesperian in age.

## 1608 7. Conclusions

1609 The imaging of and compositional data for pre-Burns-formation rocks from along the 1610 Endeavour Crater rim allow us to further refine our interpretations of the origin of the rocks and 1611 the alteration processes that affected them:

The Matijevic formation is a unit of fine-grained clastic sediments that, because of the 1612 • limited exposure, is of unknown areal and stratigraphic extent. It is the only definitive 1613 intact, pre-impact unit examined, and might be part of the Noachian etched units of 1614 Meridiani Planum (cf., Hynek and Di Achille [2017]). Dark cap rocks on Wdowiak 1615 Ridge might be a pre-impact lithology, but the case is less compelling for them. 1616 1617 The Shoemaker formation is a heterogeneous polymict breccia. The lowermost unit on Cape York incorporates material eroded from the underlying Matijevic formation 1618 1619 during deposition of the ejecta. The Shoemaker is heterogeneous on the cm to km scale as revealed by compositional differences between clasts and matrix, variations 1620 within outcrops (Greelev Haven) and differences between rim segments. The 1621 Shoemaker formation is an analog to the Bunte Breccia of the Ries Crater, but 1622 average clast sizes are substantially smaller in the Shoemaker. 1623 1624 The Grasberg formation is a 1-2 m thick fine-grained, homogeneous sedimentary unit that lies unconformably on the Shoemaker formation. It typically does not show 1625 sedimentary structures, consistent with deposition in a low-energy environment. It 1626 likely represents an airfall deposit of widespread areal extent. Although the Burns 1627 formation overlies the Grasberg, the compositions of two units are quite distinct. 1628 There is no evidence, compositional or textural, that the Grasberg formation might be 1629 a separate, fine-grained facies of the Burns formation as has been argued for the rare 1630 mudstones found on the plains in the ejecta from Santa Maria crater [Edgar et al. 1631 2014]. The composition of Grasberg rocks was changed by aqueous alteration which 1632 1633 cause differential mobility of Mn and Fe, and possibly other elements, and deposition of CaSO<sub>4</sub> in coarse veins. 1634 At least four episodes of alteration occurred in the Noachian and Early Hesperian in 1635 the region, not counting diagenesis of the Burns formation sandstones: (i) pre-impact 1636 1637 alteration of regional rocks, including formation of CaSO<sub>4</sub>-rich and aluminosilicate veins in the Matijevic formation; (ii) low water/rock alteration along the 1638 1639 disconformity between the Matijevic and Shoemaker formations forming veneers; 1640 (iii) alteration along fracture zones in the rim segments; and (iv) differential 1641 mobilization of Fe and Mn, and CaSO<sub>4</sub> vein formation. Episodes (ii) and (iii) possibly 1642 occurred together, but (i) and (iv) are distinct. Acknowledgements-Rover operations described in this paper were conducted at the Jet 1643

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soil targets acquired by *Opportunity* through Sol 4000 are available on the NASA Planetary Data
System website: <a href="http://pds-geosciences.wustl.edu/">http://pds-geosciences.wustl.edu/</a>.

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| formation  | unit             | morphology and texture <sup>1</sup>   | "silicate" characteristic <sup>2</sup>  | volatile/mobile<br>element<br>characteristic <sup>3</sup> |
|------------|------------------|---|---|---|
| Burns      | n/a              | laminated to cross-laminated<br>medium to coarse, well-sorted<br>sand, 1-2 mm,    | low to very low Al; very<br>high K; abraded only: high<br>P, Fe; very high Mg | very high S; high to<br>very high Zn                      |
| Grasberg   | upper            | planar, fractured,<br>homogeneous, <100 μm  | low Al, Mn; very low Mg;<br>very high K, Fe                                   | very high Cl, Zn, Br                                      |
|            | lower            | devoid of structure,<br>homogeneous, <100 μm                                      | low Mn; very low Mg; very<br>high K, Fe                                       | very high Zn, Br  |
| Shoemaker  | Greeley<br>Haven | breccia, cm-sized<br>angular/subrounded clasts in<br>fine-grained matrix          | (average)   | (average)   |
|            | Chester Lake     | as for Greeley Haven; with prominent lineation of clasts                          | low Si  | (average)   |
|            | Copper Cliff     | as for Greeley Haven; with1-2<br>mm spherules, fine,<br>anastomosing bright veins | high Ni   | (average)   |
|            | Tisdale          | as for Chester Lake   | low Ca; very low Mg; high<br>Fe; very high P, Ni                              | very high Zn, Br  |
|            | Murray Ridge     | as for Greeley Haven  | (average)   | (average)   |
|            | Hueytown         | as for Greeley Haven; poorer<br>in clasts, generally smaller<br>size              | (average)   | very high S   |
| Matijevic  | matrix           | tabular, clastic, poorly<br>laminated, <100 μm                                    | low K, Ti; very high Si, P,<br>Ni   | low S   |
|            | spherule-rich    | linear, fin-like, 2-4 mm<br>matrix-supported spherules                            | very low P, Ca, Ti; high<br>Ni; very high Si                                  | low S   |
|            | veneer           | tabular surface lamination, homogeneous   | high Ni; very high P  | very high Cl, Br  |
| dark rocks | float            | allochthonous blocks,<br>homogeneous, <100 µm                                     | low Fe; very low Mg, Cr;<br>very high Al, Mn                                  | low S, Cl   |
|            | Wdowiak<br>Ridge | as for float  | low Cr; very low Mg; high<br>Na; very high Al                                 | low S, Cl   |

| 1950 | Table 1. | Summary | of rock | units at | Endeavour  | Crater | rim. |
|------|----------|---------|---------|----------|------------|--------|------|
|      | 10010 11 |         | 0110011 |          | 2matul our | 010001 |      |

1951

<sup>1</sup>*Arvidson et al.* [2014]; *Crumpler et al.* [2015a]; *Edgar et al.* [2012]; *Grotzinger et al.* [2005,

1953 2006]; *Squyres et al.* [2012]; this work.

<sup>2</sup>Elements normalized to be free of volatile/mobile elements (S, Cl, Zn and Br); compared to an
 average of Shoemaker formation breccias, excluding Tisdale and anomalous targets (see text).

<sup>3</sup>Volatile/mobile elements compared to an average of Shoemaker formation breccias, excluding

1957 Tisdale and anomalous targets.

| Target            | Sol  | treatment | unit/identifier | hours | Na <sub>2</sub> O | MgO          | $Al_2O_3$          | SiO <sub>2</sub> | $P_2O_5$ | SO <sub>3</sub> | Cl   | K <sub>2</sub> O | CaO   | TiO <sub>2</sub> | $Cr_2O_3$ | MnO  | FeO  | Ni   | Zn   | Br        |
|-------------------|------|-----------|-----------------|-------|-------------------|--------------|--------------------|------------------|----------|-----------------|------|------------------|-------|------------------|-----------|------|------|------|------|-----------|
|                   |      |           |                 |       | Wt%               | wt%          | wt%                | wt%              | wt%      | wt%             | wt%  | wt%              | wt%   | wt%              | wt%       | wt%  | wt%  | µg/g | µg/g | µg/g      |
| Cibraltar         | 2660 | untrastad | n/o             | 2.4   | 2.12              | 7 41         | surns jor.<br>רר ר | <i>mation</i>    | 1.02     | 12 70           | 1.01 | 0.57             | 6 10  | 0.84             | 0.22      | 0.20 | 16.0 | 126  | 414  | 408       |
| Dioranai          | 2009 | untreated | n/a<br>margin   | 2.4   | 2.13              | 7.41<br>6.07 | 7.60               | 41.0             | 0.05     | 12.01           | 0.05 | 0.37             | 0.19  | 0.64             | 0.22      | 0.30 | 17.2 | 420  | 200  | 490       |
| Tawny             | 3027 | untreated | niaigin<br>n/a  | 23.9  | 2.03              | 6.80         | 7.09               | 40.8             | 0.95     | 11.03           | 0.95 | 0.49             | 6.54  | 0.80             | 0.23      | 0.28 | 20.0 | 379  | 390  | 210       |
| Black Shoulder    | 3378 | untreated | n/a             | 9.0   | 1.85              | 8 35         | 6.81               | 38.4             | 1.03     | 10.72           | 1 18 | 0.54             | 4.66  | 0.82             | 0.27      | 0.27 | 16.0 | 677  | 275  | J48<br>46 |
| Black Shoulder?   | 3380 | untreated | n/a<br>n/a      | 3.0   | 1.01              | 7 73         | 7.16               | 30.7             | 1.03     | 17.65           | 1.10 | 0.55             | 5 59  | 0.84             | 0.20      | 0.25 | 16.5 | 616  | 310  | +0<br>77  |
| Black Shoulder3   | 3381 | untreated | n/a<br>n/a      | 2.0   | 1.75              | 7.96         | 6.69               | 37.6             | 1.00     | 19.86           | 1.17 | 0.53             | 6.00  | 0.82             | 0.22      | 0.21 | 15.6 | 660  | 252  | 60        |
| Black Shoulder    | 3383 | abraded   | n/a<br>n/a      | 2.2   | 1.78              | 8 15         | 5.95               | 36.5             | 1.00     | 22.36           | 1.10 | 0.55             | 4 28  | 0.02             | 0.18      | 0.21 | 16.5 | 612  | 294  | 40        |
| Red Poker         | 3390 | untreated | margin          | 3.1   | 2.07              | 7.14         | 7.50               | 40.6             | 1.04     | 15.53           | 1.05 | 0.57             | 6.16  | 0.85             | 0.20      | 0.29 | 16.8 | 545  | 538  | 632       |
| Dibbler           | 3415 | untreated | margin          | 10.0  | 2.12              | 6.84         | 8.85               | 44.5             | 0.95     | 8.05            | 0.79 | 0.52             | 7.12  | 0.91             | 0.33      | 0.35 | 18.6 | 378  | 431  | 222       |
| Callitris         | 3445 | brushed   | margin          | 6.2   | 1.54              | 5.52         | 6.71               | 39.4             | 1.06     | 18.77           | 0.84 | 0.49             | 7.46  | 0.82             | 0.21      | 0.15 | 16.9 | 275  | 330  | 65        |
| Cape Fairweather1 | 3741 | untreated | margin          | 3.4   | 1.86              | 7.31         | 7.15               | 39.6             | 1.02     | 17.88           | 0.88 | 0.51             | 6.38  | 0.78             | 0.19      | 0.18 | 16.2 | 311  | 276  | 114       |
| Cape Fairweather2 | 3742 | untreated | margin          | 2.4   | 2.01              | 7.39         | 7.71               | 42.3             | 0.98     | 12.66           | 0.83 | 0.55             | 6.29  | 0.94             | 0.32      | 0.34 | 17.5 | 318  | 477  | 297       |
|                   |      |           |                 |       |                   | Gr           | asberg fo          | ormation         | 1        |                 |      |                  |       |                  |           |      |      |      |      |           |
| Homestake1        | 2764 | untreated | lower, vein     | 1.2   | 1.63              | 4.77         | 4.78               | 25.4             | 0.71     | 32.71           | 1.02 | 0.28             | 22.02 | 0.29             | 0.15      | 0.17 | 6.1  | 21   | 126  | 77        |
| Homestake2        | 2765 | untreated | lower, vein     | 3.5   | 1.72              | 4.52         | 4.70               | 24.6             | 0.77     | 33.25           | 0.99 | 0.25             | 22.28 | 0.22             | 0.12      | 0.12 | 6.5  | 0    | 94   | 71        |
| Homestake3        | 2767 | untreated | lower, vein     | 3.6   | 1.50              | 4.67         | 4.91               | 25.8             | 0.85     | 32.03           | 0.85 | 0.28             | 21.78 | 0.29             | 0.13      | 0.16 | 6.8  | 86   | 143  | 55        |
| Deadwood          | 2771 | untreated | lower           | 3.2   | 2.17              | 5.70         | 8.32               | 44.0             | 1.13     | 9.19            | 1.12 | 0.62             | 6.68  | 0.98             | 0.30      | 0.22 | 19.4 | 410  | 521  | 301       |
| Oostark1          | 2974 | untreated | lower, vein     | 6.4   | 1.21              | 5.03         | 5.35               | 25.8             | 0.85     | 31.32           | 1.11 | 0.34             | 22.10 | 0.30             | 0.08      | 0.14 | 6.3  | 51   | 170  | 106       |
| Oostark2          | 2976 | untreated | lower, vein     | 3.0   | 1.61              | 5.02         | 5.27               | 28.0             | 0.82     | 29.67           | 1.08 | 0.31             | 20.67 | 0.27             | 0.09      | 0.17 | 7.0  | 110  | 165  | 146       |
| Grasberg1         | 2990 | untreated | upper           | 9.4   | 2.28              | 6.03         | 8.21               | 44.4             | 1.09     | 8.49            | 1.88 | 0.63             | 5.71  | 0.97             | 0.23      | 0.22 | 19.6 | 425  | 863  | 448       |
| Grasberg2         | 2992 | untreated | upper           | 4.6   | 2.23              | 5.89         | 8.07               | 43.9             | 1.00     | 9.76            | 1.74 | 0.63             | 6.73  | 0.97             | 0.23      | 0.22 | 18.4 | 372  | 762  | 343       |
| Grasberg1         | 2995 | brushed   | upper           | 3.3   | 2.25              | 5.30         | 7.83               | 45.1             | 1.14     | 8.76            | 2.54 | 0.67             | 5.11  | 0.96             | 0.25      | 0.19 | 19.7 | 365  | 923  | 479       |
| Grasberg1         | 3001 | abraded   | upper           | 3.9   | 2.57              | 3.93         | 7.24               | 44.0             | 1.24     | 10.12           | 2.74 | 0.73             | 5.85  | 0.92             | 0.23      | 0.19 | 20.0 | 452  | 955  | 524       |
| Grasberg3         | 3006 | abraded   | upper           | 4.1   | 2.49              | 3.63         | 7.36               | 44.3             | 1.23     | 9.75            | 2.60 | 0.71             | 6.02  | 0.92             | 0.23      | 0.19 | 20.3 | 444  | 935  | 540       |
| Mons Cupri        | 3022 | untreated | upper           | 3.5   | 2.22              | 5.73         | 8.40               | 45.3             | 1.20     | 8.12            | 1.71 | 0.71             | 5.91  | 0.97             | 0.25      | 0.18 | 19.2 | 470  | 558  | 286       |
| Gnarlaroo         | 3332 | untreated | lower           | 10.5  | 2.11              | 5.49         | 8.56               | 47.2             | 0.89     | 6.30            | 0.98 | 0.69             | 5.03  | 1.07             | 0.30      | 0.18 | 21.1 | 427  | 514  | 268       |
| Platypus          | 3403 | brushed   | lower           | 3.0   | 2.13              | 4.43         | 8.22               | 46.2             | 1.00     | 8.65            | 1.44 | 0.78             | 5.91  | 1.05             | 0.27      | 0.18 | 19.5 | 368  | 764  | 1004      |
| Monjon Purple     | 3422 | untreated | lower           | 3.7   | 2.09              | 4.24         | 8.79               | 47.9             | 1.05     | 6.28            | 1.56 | 0.83             | 4.58  | 1.04             | 0.26      | 0.27 | 20.9 | 268  | 877  | 444       |
| Monjon Grey       | 3423 | untreated | lower           | 4.6   | 2.10              | 4.29         | 9.02               | 48.0             | 0.98     | 5.86            | 1.58 | 0.81             | 4.47  | 1.06             | 0.26      | 0.58 | 20.8 | 412  | 995  | 352       |
| Poverty Bush      | 3427 | untreated | lower           | 6.5   | 2.01              | 4.87         | 7.60               | 42.6             | 1.08     | 13.06           | 1.68 | 0.60             | 7.62  | 0.90             | 0.22      | 0.21 | 17.4 | 134  | 800  | 685       |
| Wally Wombat      | 3434 | brushed   | upper           | 2.9   | 2.22              | 4.37         | 8.53               | 45.5             | 1.06     | 9.55            | 1.70 | 0.79             | 6.30  | 0.96             | 0.25      | 0.24 | 18.5 | 196  | 553  | 293       |
| Rosebud Canyon    | 3734 | untreated | upper           | 9.0   | 2.17              | 5.33         | 8.37               | 46.0             | 0.85     | 7.82            | 1.59 | 0.70             | 5.75  | 1.03             | 0.26      | 0.12 | 19.8 | 419  | 718  | 559       |
|                   |      |           |                 |       |                   | Sho          | emaker f           | formatio         | n        |                 |      |                  |       |                  |           | a    |      |      |      |           |
| Timmins1          | 2694 | untreated | Tisdale block   | 2.9   | 1.84              | 6.20         | 8.86               | 42.6             | 3.14     | 8.57            | 1.23 | 0.43             | 7.13  | 0.99             | 0.16      | 0.38 | 17.6 | 950  | 6267 | 779       |
| Timmins2          | 2695 | untreated | Tisdale block   | 3.2   | 2.16              | 6.04         | 9.97               | 46.2             | 1.22     | 6.01            | 0.93 | 0.50             | 6.78  | 1.05             | 0.27      | 0.38 | 18.0 | 1405 | 1798 | 722       |
| Timmins3          | 2696 | untreated | Tisdale block   | 2.0   | 2.54              | 6.19         | 10.10              | 45.4             | 1.20     | 6.50            | 1.00 | 0.53             | 5.88  | 1.05             | 0.23      | 0.23 | 18.8 | 2030 | 710  | 377       |
| Shaw1             | 2699 | untreated | Tisdale block   | 3.0   | 2.16              | 6.22         | 8.56               | 42.8             | 2.27     | 6.81            | 1.52 | 0.53             | 5.61  | 1.08             | 0.21      | 0.54 | 21.3 | 852  | 1813 | 967       |
| Shaw2             | 2701 | untreated | Tisdale block   | 2.9   | 2.12              | 6.04         | 8.61               | 45.2             | 2.24     | 5.87            | 1.21 | 0.56             | 5.18  | 1.10             | 0.24      | 0.51 | 20.7 | 770  | 1853 | 1324      |

# Table 2. Compositional data for Endeavour Crater rim rocks organized by formation and measurement Sol.

| Target              | Sol  | treatment                 | unit/identifier     | hours       | Na <sub>2</sub> O | MgO          | $Al_2O_3$ | SiO <sub>2</sub> | $P_2O_5$         | SO <sub>3</sub> | Cl   | K <sub>2</sub> O | CaO  | TiO <sub>2</sub> | $Cr_2O_3$ | MnO  | FeO  | Ni         | Zn   | Br   |
|---------------------|------|---------------------------|---------------------|-------------|-------------------|--------------|-----------|------------------|------------------|-----------------|------|------------------|------|------------------|-----------|------|------|------------|------|------|
|                     |      |                           |                     |             | wt%               | wt%          | wt%       | wt%              | wt%              | wt%             | wt%  | wt%              | wt%  | wt%              | wt%       | wt%  | wt%  | µg/g       | µg/g | µg/g |
| Show?               | 2702 | untrooted                 | Tindala bloak       | 2.2         | 2.00              | 5 00         | emaker fo | ormation         | <i>i</i><br>2.01 | 5 90            | 1.27 | 0.62             | 1 02 | 1.01             | 0.27      | 0.46 | 21.4 | 1005       | 2214 | 1470 |
| Snaw5               | 2702 | untreated                 | Charter Lala        | 3.2<br>12.5 | 2.09              | 5.90         | 8.10      | 45.0             | 2.01             | 5.89            | 1.27 | 0.62             | 4.85 | 1.01             | 0.27      | 0.40 | 21.4 | 1005       | 2314 | 1470 |
| Salisbury 1         | 2/15 | untreated<br>hereological | Chester Lake        | 13.5        | 2.45              | 7.57         | 9.00      | 44.5             | 1.02             | 0.10<br>6.42    | 1.31 | 0.49             | 0.70 | 1.00             | 0.24      | 0.45 | 19.2 | 4/4        | 283  | 18   |
| Salisbury 1         | 2717 | obrashed                  | Chester Lake        | 5.2         | 2.34              | 0.01         | 0.92      | 45.9             | 1.04             | 0.42            | 1.54 | 0.48             | 6.07 | 1.00             | 0.25      | 0.43 | 19.4 | 435        | 215  | 10   |
| Salisbury 1         | 2726 | abraded                   | Chester Lake        | 0.0         | 2.74              | 0.01         | 0.02      | 45.5             | 1.00             | 2.09            | 1.02 | 0.41             | 6.77 | 1.09             | 0.25      | 0.48 | 20.1 | 482        | 240  | 124  |
| Galuk               | 2720 | uptracted                 | Chester Lake        | 2.9         | 2.47              | 0.09         | 0.51      | 45.4             | 0.99             | J.40<br>1 91    | 1.03 | 0.36             | 0.78 | 1.04             | 0.23      | 0.49 | 17.0 | 400        | 245  | 68   |
| Transvool           | 2734 | untreated                 | Crealey Heyen       | 2.9         | 2.09              | 7.45         | 0.10      | 40.1             | 1.15             | 4.04<br>6.25    | 0.08 | 0.40             | 6.56 | 1.15             | 0.27      | 0.03 | 17.0 | 401<br>565 | 244  | 120  |
| Poormanskon         | 2709 | untreated                 | Greeley Haven       | 5.0         | 2.32              | 7.47<br>9.96 | 9.19      | 45.5             | 1.04             | 5.74            | 0.96 | 0.49             | 5.70 | 1.11             | 0.20      | 0.41 | 17.0 | 515        | 294  | 159  |
| Bruch               | 2790 | brushed                   | Greeley Haven       | 2.9         | 2.37              | 0.00<br>8.05 | 9.55      | 45.5             | 1.22             | 5.74            | 0.99 | 0.54             | 5.79 | 1.03             | 0.22      | 0.43 | 17.6 | 615        | 340  | 150  |
| Komati              | 2801 | untreated                 | Greeley Haven       | 2.5         | 2.39              | 8.95         | 9.32      | 43.0             | 1.21             | 5.81            | 0.99 | 0.51             | 6.12 | 1.05             | 0.23      | 0.41 | 18.7 | 461        | 266  | 220  |
| Amboy1              | 2805 | untreated                 | Greeley Haven       | 43          | 2.37              | 0.42         | 9.32      | 44.7             | 1.10             | 6.12            | 0.92 | 0.38             | 6.00 | 1.08             | 0.18      | 0.39 | 17.8 | 401        | 200  | 104  |
| Amboy?              | 2834 | untreated                 | Greeley Haven       | 4.J         | 2.15              | 0.08         | 0.17      | 45.7             | 1.00             | 6.10            | 0.85 | 0.42             | 5.80 | 1.05             | 0.17      | 0.44 | 17.0 | 524        | 280  | 06   |
| Amboy2              | 2805 | untreated                 | Greeley Haven       | 5.5<br>4 7  | 2.19              | 9.08<br>8.60 | 9.17      | 45.7             | 1.07             | 6.16            | 0.85 | 0.42             | 5.83 | 1.01             | 0.18      | 0.44 | 17.0 | 576        | 200  | 13/  |
| Amboy4              | 2020 | untreated                 | Greeley Haven       | 3.1         | 2.13              | 7 53         | 9.97      | 46.0             | 1.04             | 5.41            | 0.70 | 0.47             | 7 48 | 1.00             | 0.23      | 0.37 | 17.5 | 306        | 194  | 103  |
| Amboy5              | 2922 | untreated                 | Greeley Haven       | 2.4         | 2.55              | 7.02         | 9.23      | 45.9             | 0.99             | 6 47            | 0.89 | 0.30             | 6 96 | 1.07             | 0.15      | 0.40 | 17.1 | 249        | 328  | 132  |
| Amboy6              | 2924 | untreated                 | Greeley Haven       | 2.1         | 1.77              | 7.02         | 9.12      | 45.9             | 1 11             | 673             | 0.02 | 0.45             | 6.99 | 1.03             | 0.20      | 0.30 | 17.7 | 221        | 317  | 177  |
| Amboy7              | 2927 | untreated                 | Greeley Haven       | 5.2         | 2 37              | 7.27         | 9.36      | 45.2             | 1.07             | 6.57            | 0.90 | 0.15             | 7 10 | 1.05             | 0.25      | 0.45 | 17.9 | 472        | 244  | 121  |
| Amboy8              | 2929 | untreated                 | Greeley Haven       | 3.6         | 2.30              | 7.08         | 9.48      | 46.1             | 0.99             | 6.09            | 0.83 | 0.45             | 6.95 | 1.15             | 0.29      | 0.39 | 17.7 | 447        | 255  | 108  |
| Amboy9              | 2931 | untreated                 | Greeley Haven       | 2.9         | 2.34              | 7.57         | 9.38      | 45.8             | 1.03             | 6.50            | 1.04 | 0.45             | 6.89 | 1.12             | 0.29      | 0.53 | 16.9 | 410        | 309  | 90   |
| Amboy10             | 2935 | untreated                 | Greelev Haven       | 3.4         | 2.24              | 7.37         | 9.25      | 45.5             | 1.03             | 6.68            | 0.98 | 0.47             | 7.05 | 1.16             | 0.26      | 0.51 | 17.4 | 353        | 295  | 84   |
| Amboy11             | 2937 | untreated                 | Greeley Haven       | 3.7         | 2.07              | 7.44         | 9.24      | 45.8             | 1.08             | 6.58            | 0.93 | 0.44             | 6.97 | 1.10             | 0.25      | 0.38 | 17.7 | 376        | 267  | 158  |
| Amboy12             | 2940 | untreated                 | Greeley Haven       | 7.4         | 2.23              | 7.57         | 9.25      | 44.9             | 1.12             | 6.44            | 0.90 | 0.46             | 6.80 | 1.12             | 0.19      | 0.84 | 18.0 | 523        | 340  | 119  |
| Onaping1            | 3158 | untreated                 | Copper Cliff        | 12.7        | 2.24              | 8.21         | 11.26     | 47.0             | 0.99             | 6.74            | 1.04 | 0.27             | 6.99 | 0.90             | 0.28      | 0.39 | 13.6 | 684        | 212  | 62   |
| Onaping2            | 3162 | untreated                 | Copper Cliff        | 10.5        | 2.18              | 8.57         | 10.83     | 46.5             | 1.02             | 7.27            | 1.07 | 0.29             | 7.00 | 0.86             | 0.27      | 0.42 | 13.6 | 808        | 245  | 48   |
| Vermillion Cliffs1  | 3168 | untreated                 | Copper Cliff        | 7.3         | 2.25              | 8.09         | 10.27     | 45.0             | 1.04             | 8.71            | 1.27 | 0.31             | 7.16 | 0.83             | 0.26      | 0.40 | 14.2 | 868        | 216  | 312  |
| Vermillion Cliffs1  | 3171 | untreated                 | Copper Cliff        | 8.8         | 2.26              | 8.18         | 10.25     | 45.0             | 1.05             | 8.72            | 1.26 | 0.30             | 7.17 | 0.83             | 0.23      | 0.38 | 14.2 | 844        | 211  | 326  |
| Vermillion Lake1    | 3174 | untreated                 | Copper Cliff        | 8.9         | 2.14              | 7.23         | 8.63      | 44.4             | 1.12             | 9.26            | 1.47 | 0.51             | 7.33 | 1.00             | 0.26      | 0.40 | 16.1 | 741        | 577  | 93   |
| Vermillion Lake2    | 3177 | untreated                 | Copper Cliff        | 3.3         | 1.93              | 7.28         | 8.60      | 44.4             | 1.14             | 9.27            | 1.52 | 0.50             | 7.27 | 1.01             | 0.29      | 0.38 | 16.2 | 818        | 600  | 80   |
| Vermillion Cliffs2a | 3179 | untreated                 | Copper Cliff        | 5.3         | 2.43              | 8.51         | 10.34     | 46.1             | 1.13             | 6.86            | 1.27 | 0.33             | 6.15 | 0.85             | 0.26      | 0.41 | 15.2 | 916        | 188  | 229  |
| Fecunis Lake        | 3214 | brushed                   | Copper Cliff        | 4.5         | 2.36              | 8.33         | 9.91      | 46.3             | 0.93             | 6.77            | 1.50 | 0.39             | 5.90 | 0.87             | 0.27      | 0.33 | 15.9 | 938        | 228  | 108  |
| Maley               | 3224 | brushed                   | Copper Cliff        | 6.1         | 2.24              | 8.17         | 8.94      | 43.6             | 0.99             | 9.79            | 1.70 | 0.41             | 7.02 | 0.87             | 0.25      | 0.36 | 15.5 | 863        | 414  | 85   |
| Spinifex            | 3463 | brushed                   | Murray Ridge, north | 4.1         | 2.32              | 8.85         | 8.76      | 45.7             | 1.18             | 5.52            | 0.95 | 0.70             | 6.18 | 1.04             | 0.22      | 0.78 | 17.6 | 537        | 460  | 706  |
| Baobab              | 3468 | untreated                 | Murray Ridge, north | 4.4         | 2.38              | 7.38         | 9.51      | 46.1             | 1.03             | 6.94            | 0.91 | 0.44             | 6.68 | 1.09             | 0.28      | 0.35 | 16.8 | 377        | 353  | 137  |
| Tangalooma          | 3498 | untreated                 | Murray Ridge, north | 4.9         | 2.04              | 8.58         | 9.43      | 45.7             | 1.15             | 7.82            | 0.74 | 0.23             | 6.29 | 1.09             | 0.20      | 0.36 | 16.2 | 523        | 118  | 97   |
| MountTempest        | 3502 | untreated                 | Murray Ridge, north | 4.7         | 2.39              | 7.48         | 10.30     | 46.3             | 1.18             | 6.25            | 0.75 | 0.30             | 7.14 | 1.16             | 0.21      | 0.40 | 16.1 | 342        | 87   | 43   |
| Cape Darby          | 3522 | untreated                 | Murray Ridge, north | 3.6         | 2.25              | 6.96         | 9.39      | 46.3             | 0.97             | 7.20            | 1.06 | 0.46             | 6.67 | 1.13             | 0.25      | 0.31 | 17.0 | 394        | 258  | 112  |
| Cape Darby2         | 3535 | untreated                 | Murray Ridge, north | 4.1         | 2.37              | 7.13         | 9.23      | 45.5             | 0.98             | 7.66            | 1.17 | 0.49             | 6.47 | 1.18             | 0.27      | 0.35 | 17.1 | 394        | 203  | 110  |
| Cape Elizabeth      | 3542 | brushed                   | Murray Ridge, north | 2.3         | 2.54              | 8.01         | 9.06      | 44.7             | 0.89             | 9.17            | 1.12 | 0.36             | 5.92 | 0.96             | 0.20      | 0.26 | 16.7 | 447        | 121  | 78   |

Table 2 (continued). Compositional data for Endeavour Crater rim rocks organized by formation and measurement Sol.

Table 2 (continued). Compositional data for Endeavour Crater rim rocks organized by formation and measurement Sol.

| Target            | Sol  | treatment        | unit/identifier       | hours | Na <sub>2</sub> O | MgO    | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | $P_2O_5$ | SO <sub>3</sub> | Cl   | K <sub>2</sub> O | CaO   | TiO <sub>2</sub> | Cr <sub>2</sub> O <sub>3</sub> | MnO  | FeO  | Ni   | Zn   | Br   |
|-------------------|------|------------------|-----------------------|-------|-------------------|--------|--------------------------------|------------------|----------|-----------------|------|------------------|-------|------------------|--------------------------------|------|------|------|------|------|
|                   |      |                  |                       |       | wt%               | wt%    | wt%                            | wt%              | wt%      | wt%             | wt%  | wt%              | wt%   | wt%              | wt%                            | wt%  | wt%  | µg/g | µg/g | µg/g |
| <b>N</b> 1 1 1    |      |                  |                       | •     |                   | Shoem  | iker form                      | ation            |          | ~~              |      |                  |       |                  |                                |      |      |      | 105  |      |
| Pinnacle Island1  | 3546 | untreated        | rock alteration       | 3.8   | 1.01              | 12.06  | 5.75                           | 28.1             | 1.57     | 25.44           | 0.92 | 0.32             | 5.45  | 0.76             | 0.21                           | 1.67 | 16.6 | 661  | 185  | 262  |
| Pinnacle Island2  | 3548 | untreated        | rock alteration       | 4.3   | 1.02              | 13.26  | 4.70                           | 23.8             | 2.18     | 28.81           | 0.95 | 0.17             | 6.08  | 0.62             | 0.12                           | 2.12 | 16.0 | 884  | 130  | 476  |
| Pinnacle Island3  | 3551 | untreated        | rock alteration       | 3.8   | 0.86              | 13.00  | 3.48                           | 18.1             | 2.37     | 34.51           | 0.66 | 0.14             | 7.66  | 0.44             | 0.10                           | 3.48 | 15.1 | 1001 | 155  | 334  |
| Pinnacle Island4  | 3560 | untreated        | rock alteration       | 3.0   | 1.57              | 9.43   | 7.57                           | 36.2             | 1.33     | 16.44           | 0.91 | 0.41             | 5.69  | 0.91             | 0.22                           | 1.30 | 17.9 | 354  | 204  | 144  |
| Pinnacle Island5  | 3564 | untreated        | rock alteration       | 3.1   | 0.84              | 11.50  | 3.68                           | 20.1             | 2.44     | 32.70           | 0.65 | 0.13             | 8.26  | 0.58             | 0.10                           | 3.35 | 15.5 | 736  | 116  | 269  |
| Green Island      | 3569 | brushed          | Murray Ridge, north   | 4.0   | 2.53              | 7.31   | 8.89                           | 43.3             | 0.99     | 10.48           | 1.54 | 0.37             | 6.38  | 1.02             | 0.19                           | 0.27 | 16.7 | 376  | 152  | 65   |
| Stuart Island1    | 3573 | untreated        | rock alteration       | 4.6   | 0.93              | 12.31  | 5.67                           | 27.3             | 1.08     | 28.20           | 0.22 | 0.18             | 5.36  | 0.78             | 0.13                           | 1.57 | 16.2 | 547  | 82   | 40   |
| Stuart Island2    | 3574 | untreated        | rock alteration       | 3.1   | 0.82              | 14.49  | 4.38                           | 22.5             | 0.91     | 33.31           | 0.26 | 0.12             | 3.75  | 0.65             | 0.17                           | 2.01 | 16.5 | 715  | 111  | 88   |
| Stuart Island3    | 3575 | untreated        | rock alteration       | 3.3   | 0.53              | 15.58  | 3.60                           | 16.1             | 0.98     | 38.21           | 0.21 | 0.09             | 4.05  | 0.57             | 0.14                           | 2.85 | 17.0 | 1024 | 175  | 77   |
| Stuart Island4    | 3577 | untreated        | rock alteration       | 3.8   | 0.86              | 11.65  | 4.87                           | 25.6             | 1.40     | 28.95           | 0.33 | 0.28             | 4.85  | 0.65             | 0.16                           | 3.37 | 16.8 | 1022 | 231  | 77   |
| Sledge Island1    | 3587 | untreated        | Murray Ridge, north   | 4.1   | 2.48              | 6.35   | 10.44                          | 47.6             | 0.82     | 7.74            | 0.65 | 0.28             | 9.65  | 0.63             | 0.21                           | 0.30 | 12.8 | 123  | 138  | 94   |
| Turnagain Arm     | 3598 | brushed          | Murray Ridge, north   | 1.7   | 2.32              | 8.05   | 9.10                           | 44.5             | 0.95     | 9.37            | 1.36 | 0.36             | 5.98  | 1.04             | 0.20                           | 0.28 | 16.4 | 453  | 114  | 167  |
| Ash Meadows       | 3657 | untreated        | Murray Ridge, central | 9.0   | 2.34              | 7.25   | 9.43                           | 45.3             | 1.07     | 7.38            | 0.92 | 0.45             | 6.85  | 1.05             | 0.23                           | 0.29 | 17.4 | 364  | 148  | 273  |
| Bristol Well1     | 3664 | untreated        | Murray Ridge, central | 9.0   | 2.15              | 6.98   | 8.50                           | 42.8             | 1.01     | 11.00           | 0.95 | 0.49             | 9.42  | 0.94             | 0.27                           | 0.34 | 15.1 | 312  | 321  | 75   |
| Bristol Well2     | 3666 | untreated        | Murray Ridge, central | 9.0   | 2.03              | 6.86   | 8.25                           | 41.9             | 1.06     | 12.04           | 0.97 | 0.45             | 10.00 | 0.92             | 0.26                           | 0.33 | 14.8 | 269  | 302  | 81   |
| Bristol Well3     | 3667 | untreated        | Murray Ridge, central | 3.7   | 2.03              | 7.14   | 8.89                           | 45.4             | 1.00     | 7.36            | 1.05 | 0.50             | 7.17  | 1.15             | 0.27                           | 0.36 | 17.6 | 365  | 361  | 102  |
| Sarcobatus Flat   | 3671 | brushed          | Murray Ridge, central | 5.0   | 2.30              | 7.78   | 8.84                           | 44.9             | 1.17     | 7.10            | 1.92 | 0.48             | 6.38  | 0.98             | 0.23                           | 0.24 | 17.6 | 293  | 162  | 98   |
| Sarcobatus Clast1 | 3675 | untreated        | Murray Ridge, central | 2.7   | 1.90              | 6.98   | 9.89                           | 46.0             | 1.09     | 6.40            | 1.06 | 0.51             | 7.72  | 1.15             | 0.20                           | 0.51 | 16.5 | 193  | 295  | 69   |
| Sarcobatus Clast2 | 3676 | untreated        | Murray Ridge, central | 9.0   | 2.00              | 6.21   | 11.23                          | 46.2             | 1.61     | 6.12            | 0.83 | 0.44             | 8.17  | 1.41             | 0.14                           | 0.27 | 15.3 | 292  | 151  | 69   |
| Landshut          | 3679 | untreated        | Murray Ridge, central | 9.0   | 2.21              | 7.14   | 9.08                           | 45.0             | 1.00     | 6.88            | 0.88 | 0.52             | 7.24  | 1.09             | 0.34                           | 0.36 | 18.2 | 352  | 331  | 95   |
| Mayfield          | 3700 | untreated        | Murray Ridge, central | 3.2   | 2.24              | 7.42   | 9.07                           | 45.0             | 1.10     | 7.21            | 1.23 | 0.50             | 7.16  | 1.02             | 0.27                           | 0.27 | 17.4 | 415  | 273  | 96   |
| Sodaville         | 3707 | untreated        | Murray Ridge, central | 12.0  | 2.29              | 7.42   | 9.18                           | 45.4             | 1.01     | 6.69            | 1.12 | 0.55             | 6.56  | 1.11             | 0.28                           | 0.25 | 18.0 | 391  | 372  | 71   |
| Tuscaloosa        | 3708 | untreated        | Murray Ridge, central | 3.9   | 2.13              | 8.20   | 9.10                           | 45.9             | 1.11     | 7.18            | 1.19 | 0.41             | 6.20  | 1.05             | 0.19                           | 0.14 | 17.1 | 371  | 132  | 117  |
| Sodaville2        | 3709 | untreated        | Murray Ridge, central | 12.0  | 2.22              | 7.34   | 9.25                           | 45.6             | 1.07     | 6.56            | 1.24 | 0.52             | 6.75  | 1.12             | 0.24                           | 0.23 | 17.7 | 305  | 325  | 87   |
| Cottondale1       | 3848 | untreated        | vein                  | 2.6   | 1.88              | 6.03   | 7.18                           | 36.1             | 1.02     | 19.15           | 0.85 | 0.39             | 13.24 | 0.72             | 0.25                           | 0.27 | 12.9 | 199  | 192  | 102  |
| Cottondale2       | 3849 | untreated        | vein                  | 2.7   | 1.90              | 6.27   | 7.87                           | 39.3             | 1.11     | 15.17           | 0.87 | 0.44             | 10.70 | 0.91             | 0.20                           | 0.34 | 14.9 | 254  | 171  | 98   |
| Caleral           | 3851 | brushed          | Hueytown              | 9.0   | 2.30              | 7.02   | 8.73                           | 43.2             | 1.19     | 10.69           | 0.99 | 0.43             | 6.56  | 1.10             | 0.20                           | 0.46 | 17.1 | 483  | 163  | 78   |
| Calera2           | 3853 | brushed          | Hueytown              | 2.9   | 2.08              | 6.90   | 8.72                           | 43.6             | 1.18     | 10.76           | 0.89 | 0.46             | 6.47  | 1.08             | 0.20                           | 0.50 | 17.1 | 420  | 133  | 86   |
| Locust Fork       | 3856 | brushed          | Hueytown              | 2.3   | 2.32              | 6.88   | 8.93                           | 43.4             | 1.19     | 11.04           | 1.11 | 0.42             | 6.28  | 1.10             | 0.20                           | 0.50 | 16.6 | 332  | 161  | 60   |
|                   |      |                  |                       |       |                   | Matije | vic form                       | ition            |          |                 |      |                  |       |                  |                                |      |      |      |      |      |
| Kirkwood          | 3064 | untreated        | spherule-rich         | 12.0  | 2.28              | 8.30   | 9.88                           | 49.4             | 0.75     | 4.57            | 1.04 | 0.50             | 5.11  | 0.83             | 0.29                           | 0.23 | 16.7 | 817  | 131  | 100  |
| Kirkwood1         | 3067 | brushed          | spherule-rich         | 13.2  | 2.44              | 8.47   | 9.91                           | 49.1             | 0.74     | 4.50            | 1.08 | 0.49             | 5.03  | 0.79             | 0.30                           | 0.22 | 16.7 | 881  | 134  | 112  |
| Azilda            | 3073 | untreated        | matrix                | 11.8  | 2.39              | 7.19   | 9.72                           | 46.6             | 1.13     | 6.51            | 0.90 | 0.43             | 6.60  | 0.97             | 0.27                           | 0.37 | 16.8 | 1004 | 207  | 158  |
| Azilda1           | 3076 | brushed          | matrix                | 12.3  | 2.56              | 7.74   | 10.64                          | 48.7             | 1.41     | 4.05            | 0.78 | 0.34             | 6.30  | 0.90             | 0.26                           | 0.35 | 15.8 | 1033 | 151  | 155  |
| Azilda2           | 3078 | brushed          | matrix                | 13.8  | 2.48              | 7.40   | 10.48                          | 50.3             | 1.39     | 3.78            | 0.73 | 0.30             | 6.07  | 0.90             | 0.24                           | 0.35 | 15.4 | 898  | 153  | 128  |
| Azilda3           | 3080 | brushed          | matrix                | 10.7  | 2.57              | 7.98   | 10.36                          | 47.7             | 1.37     | 4.46            | 0.87 | 0.37             | 6.13  | 0.93             | 0.26                           | 0.45 | 16.4 | 976  | 168  | 112  |
| Azilda2           | 3085 | abraded          | matrix                | 14.8  | 2.75              | 7.67   | 10.84                          | 50.6             | 1.44     | 2.35            | 0.52 | 0.28             | 6.06  | 0.91             | 0.24                           | 0.37 | 15.8 | 951  | 128  | 43   |
| Azilda2           | 3087 | abraded, brushed | matrix                | 20.9  | 2.55              | 7.91   | 10.60                          | 51.2             | 1.50     | 2.47            | 0.53 | 0.28             | 5.98  | 0.87             | 0.24                           | 0.36 | 15.4 | 922  | 134  | 48   |

| Table 2 (continued). Compositional data for Endeavour Crater rim rocks organized by formation and measured | ement Sol |
|--|-----------|
|--|-----------|

| Target            | Sol  | treatment       | unit/identifier        | hours | Na <sub>2</sub> O | MgO  | $Al_2O_3$   | SiO <sub>2</sub> | $P_2O_5$ | SO <sub>3</sub> | Cl   | K <sub>2</sub> O | CaO   | TiO <sub>2</sub> | Cr <sub>2</sub> O <sub>3</sub> | MnO  | FeO  | Ni   | Zn   | Br   |
|-------------------|------|-----------------|------------------------|-------|-------------------|------|-------------|------------------|----------|-----------------|------|------------------|-------|------------------|--------------------------------|------|------|------|------|------|
|                   |      |                 |                        |       | wt%               | wt%  | wt%         | wt%              | wt%      | wt%             | wt%  | wt%              | wt%   | wt%              | wt%                            | wt%  | wt%  | µg/g | µg/g | µg/g |
|                   |      |                 |                        |       |                   | Mat  | tijevic for | mation           |          |                 |      |                  |       |                  |                                |      |      |      |      |      |
| Chelmsford2       | 3094 | brushed         | veneer-rich            | 12.5  | 2.46              | 7.58 | 9.46        | 46.4             | 1.25     | 6.64            | 1.36 | 0.35             | 6.79  | 0.93             | 0.24                           | 0.61 | 15.8 | 813  | 261  | 172  |
| Chelmsford3       | 3096 | brushed         | veneer-rich            | 19.5  | 2.42              | 7.60 | 8.98        | 45.1             | 1.28     | 7.62            | 1.63 | 0.37             | 7.15  | 0.92             | 0.25                           | 0.53 | 16.0 | 815  | 331  | 154  |
| Sandcherry        | 3138 | untreated       | veneer-rich            | 2.8   | 2.24              | 7.59 | 8.33        | 43.5             | 1.24     | 9.06            | 1.76 | 0.42             | 7.58  | 0.88             | 0.23                           | 0.36 | 16.6 | 762  | 445  | 318  |
| Sandcherry        | 3144 | brushed         | veneer-rich            | 10.1  | 2.32              | 7.79 | 8.23        | 43.3             | 1.29     | 8.86            | 1.98 | 0.40             | 7.64  | 0.92             | 0.22                           | 0.38 | 16.4 | 888  | 453  | 348  |
| Sandcherry        | 3146 | abraded         | veneer-rich            | 18.7  | 2.83              | 8.64 | 9.02        | 44.7             | 1.33     | 6.42            | 1.75 | 0.31             | 7.05  | 0.86             | 0.24                           | 0.39 | 16.3 | 914  | 373  | 332  |
| Ortiz1            | 3190 | untreated       | vein-rich              | 9.0   | 2.21              | 6.44 | 8.69        | 42.6             | 1.17     | 12.14           | 0.90 | 0.33             | 9.81  | 0.78             | 0.25                           | 0.54 | 14.0 | 694  | 167  | 227  |
| Ortiz2            | 3192 | untreated       | vein-rich              | 9.0   | 2.21              | 6.58 | 9.62        | 46.5             | 1.23     | 7.87            | 0.92 | 0.32             | 7.91  | 0.92             | 0.23                           | 0.47 | 15.1 | 723  | 193  | 157  |
| Ortiz3            | 3194 | untreated       | vein-rich              | 18.0  | 2.18              | 6.60 | 9.14        | 45.3             | 1.14     | 9.43            | 0.84 | 0.35             | 8.47  | 0.89             | 0.27                           | 0.48 | 14.8 | 668  | 198  | 208  |
| Ortiz2B           | 3200 | untreated       | vein-rich              | 11.4  | 2.09              | 6.28 | 8.57        | 42.0             | 1.17     | 13.51           | 0.95 | 0.27             | 10.35 | 0.78             | 0.22                           | 0.47 | 13.2 | 670  | 144  | 208  |
| Fullerton         | 3207 | untreated       | spherule-rich          | 17.9  | 2.31              | 7.41 | 10.37       | 48.0             | 1.62     | 5.39            | 0.96 | 0.36             | 5.51  | 0.96             | 0.22                           | 0.29 | 16.4 | 935  | 194  | 54   |
| Fullerton2        | 3208 | untreated       | spherule-rich          | 3.1   | 2.21              | 7.99 | 10.51       | 50.3             | 0.87     | 4.54            | 0.84 | 0.35             | 5.96  | 0.98             | 0.26                           | 0.28 | 14.8 | 741  | 199  | 182  |
| Fullerton3        | 3209 | brushed         | spherule-rich          | 7.4   | 2.25              | 8.22 | 10.47       | 50.1             | 0.89     | 4.64            | 0.85 | 0.33             | 5.81  | 0.96             | 0.29                           | 0.28 | 14.7 | 738  | 176  | 159  |
| Lihir             | 3239 | untreated       | boxwork vein           | 2.9   | 1.66              | 5.89 | 12.92       | 58.4             | 1.19     | 6.25            | 1.58 | 0.37             | 4.03  | 1.16             | 0.32                           | 0.16 | 5.8  | 644  | 304  | 114  |
| Sturgeon River1   | 3247 | untreated       | spherule-rich          | 12.0  | 2.17              | 7.76 | 9.65        | 48.9             | 0.80     | 5.22            | 1.04 | 0.46             | 5.50  | 0.87             | 0.29                           | 0.29 | 17.0 | 691  | 199  | 88   |
| Sturgeon River2   | 3248 | untreated       | spherule-rich          | 10.5  | 2.41              | 8.14 | 10.06       | 48.8             | 0.88     | 4.78            | 0.99 | 0.30             | 5.46  | 0.81             | 0.28                           | 0.25 | 16.7 | 724  | 159  | 53   |
| Sturgeon River1a  | 3249 | untreated       | spherule-rich          | 4.9   | 2.15              | 8.24 | 9.87        | 49.4             | 0.74     | 4.67            | 0.88 | 0.41             | 5.17  | 0.81             | 0.32                           | 0.24 | 17.0 | 806  | 155  | 48   |
| Sturgeon River3   | 3252 | abraded         | spherule-rich          | 4.5   | 2.13              | 8.71 | 9.92        | 50.1             | 0.66     | 4.08            | 0.76 | 0.33             | 5.11  | 0.81             | 0.30                           | 0.28 | 16.6 | 798  | 122  | 52   |
| Sturgeon River3   | 3253 | second abrasion | spherule-rich          | 3.1   | 2.21              | 9.29 | 9.61        | 49.5             | 0.59     | 3.32            | 0.47 | 0.36             | 5.11  | 0.81             | 0.36                           | 0.29 | 17.9 | 1165 | 132  | 57   |
| Espérance         | 3262 | untreated       | boxwork vein           | 13.0  | 2.28              | 6.19 | 11.47       | 53.3             | 1.30     | 7.88            | 2.53 | 0.39             | 5.05  | 1.02             | 0.30                           | 0.28 | 7.8  | 606  | 377  | 213  |
| Espérance2        | 3264 | untreated       | boxwork vein           | 14.5  | 2.16              | 6.49 | 10.36       | 50.6             | 1.26     | 8.93            | 2.61 | 0.45             | 5.80  | 0.99             | 0.28                           | 0.27 | 9.6  | 707  | 484  | 233  |
| Espérance3        | 3267 | untreated       | boxwork vein           | 24.3  | 2.25              | 6.13 | 11.36       | 53.9             | 1.23     | 7.88            | 2.95 | 0.42             | 4.56  | 1.01             | 0.30                           | 0.23 | 7.6  | 670  | 413  | 142  |
| Espérance4        | 3298 | untreated       | boxwork vein           | 4.9   | 2.28              | 6.12 | 11.72       | 55.5             | 1.15     | 7.28            | 2.97 | 0.39             | 3.93  | 1.04             | 0.28                           | 0.23 | 6.9  | 728  | 361  | 144  |
| Espérance5        | 3301 | abraded         | boxwork vein           | 11.8  | 2.54              | 4.79 | 14.61       | 61.0             | 1.19     | 3.98            | 2.80 | 0.25             | 2.49  | 0.95             | 0.34                           | 0.19 | 4.6  | 633  | 253  | 58   |
| Espérance6        | 3305 | abraded         | boxwork vein           | 8.9   | 2.25              | 4.73 | 15.37       | 62.5             | 1.14     | 3.28            | 2.32 | 0.24             | 2.14  | 0.93             | 0.34                           | 0.19 | 4.4  | 622  | 238  | 35   |
|                   |      |                 |                        |       |                   | dark | -rock floo  | at/ejecta        |          |                 |      |                  |       |                  |                                |      |      |      |      |      |
| Tick Bush         | 3392 | untreated       | dark-rock float        | 6.7   | 2.89              | 5.65 | 12.47       | 48.2             | 1.21     | 4.49            | 0.98 | 0.57             | 7.16  | 1.08             | 0.11                           | 1.00 | 14.0 | 913  | 696  | 51   |
| Tick Bush2        | 3396 | untreated       | dark-rock float        | 5.0   | 3.10              | 4.90 | 13.97       | 49.8             | 1.27     | 2.67            | 0.67 | 0.49             | 7.29  | 1.17             | 0.10                           | 1.20 | 13.2 | 985  | 670  | 40   |
| Augustine         | 3603 | untreated       | dark-rock float        | 4.2   | 2.15              | 7.95 | 11.00       | 46.7             | 0.98     | 4.66            | 0.53 | 0.32             | 7.09  | 1.20             | 0.21                           | 0.29 | 16.9 | 449  | 101  | 15   |
| Point Bede        | 3616 | untreated       | dark-rock float        | 10.5  | 2.19              | 7.77 | 11.01       | 46.1             | 0.65     | 5.35            | 0.61 | 0.28             | 6.77  | 1.23             | 0.20                           | 0.31 | 17.5 | 438  | 107  | 58   |
| Mount Edgecumbe   | 3753 | untreated       | dark-rock ejecta/float | 10.5  | 2.67              | 6.71 | 11.42       | 46.7             | 1.16     | 4.66            | 0.68 | 0.45             | 7.63  | 1.33             | 0.21                           | 0.34 | 15.9 | 794  | 252  | 56   |
| Hoover            | 3796 | brushed         | dark-rock ejecta/float | 9.0   | 2.04              | 6.54 | 7.56        | 42.2             | 1.19     | 9.71            | 1.61 | 0.54             | 7.72  | 0.97             | 0.22                           | 0.34 | 19.2 | 549  | 666  | 44   |
| Lipscomb-Victory1 | 3800 | untreated       | dark-rock ejecta/float | 7.5   | 2.65              | 6.15 | 11.99       | 47.7             | 1.29     | 4.02            | 0.64 | 0.41             | 7.53  | 1.21             | 0.19                           | 0.30 | 15.9 | 116  | 112  | 20   |
| Lipscomb-Victory2 | 3802 | untreated       | dark-rock ejecta/float | 9.0   | 2.72              | 6.09 | 12.30       | 47.8             | 1.31     | 3.73            | 0.61 | 0.38             | 7.46  | 1.31             | 0.17                           | 0.30 | 15.8 | 152  | 124  | 31   |
| Lipscomb-Margaret | 3809 | untreated       | dark-rock ejecta/float | 7.5   | 2.82              | 6.05 | 12.56       | 48.2             | 1.17     | 4.02            | 0.46 | 0.39             | 7.32  | 1.21             | 0.17                           | 0.35 | 15.2 | 303  | 103  | 17   |
| Lipscomb-Margaret | 3812 | brushed         | dark-rock ejecta/float | 2.5   | 2.75              | 6.23 | 12.56       | 48.4             | 1.20     | 3.72            | 0.42 | 0.36             | 7.35  | 1.23             | 0.18                           | 0.36 | 15.2 | 289  | 111  | 20   |
| Birmingham        | 3819 | untreated       | dark-rock ejecta/float | 7.5   | 2.46              | 6.47 | 11.23       | 46.7             | 1.28     | 4.93            | 0.98 | 0.47             | 7.56  | 1.15             | 0.15                           | 0.34 | 16.1 | 452  | 262  | 153  |

|                   |      | lowe | r unit | uppe | r unit | ve   | ein  | upper | /lower |
|-------------------|------|------|--------|------|--------|------|------|-------|--------|
|                   |      | ave  | std    | ave  | std    | ave  | std  | ratio | ±      |
| number            |      | 5    |        | 5    |        | 5    |      |       |        |
| Na <sub>2</sub> O | wt%  | 2.10 | 0.06   | 2.23 | 0.03   | 1.53 | 0.20 | 1.058 | 0.034  |
| MgO               | wt%  | 4.95 | 0.64   | 5.44 | 0.60   | 4.80 | 0.22 | 1.106 | 0.196  |
| $Al_2O_3$         | wt%  | 8.30 | 0.45   | 8.24 | 0.25   | 5.00 | 0.29 | 1.002 | 0.058  |
| SiO <sub>2</sub>  | wt%  | 45.6 | 2.2    | 45.0 | 0.8    | 25.9 | 1.3  | 0.988 | 0.052  |
| $P_2O_5$          | wt%  | 1.03 | 0.09   | 1.06 | 0.12   | 0.80 | 0.06 | 1.011 | 0.153  |
| SO <sub>3</sub>   | wt%  | 8.69 | 2.78   | 8.75 | 0.77   | 31.8 | 1.4  | 1.006 | 0.337  |
| Cl                | wt%  | 1.35 | 0.29   | 1.86 | 0.35   | 1.01 | 0.10 | 1.273 | 0.287  |
| K <sub>2</sub> O  | wt%  | 0.70 | 0.10   | 0.69 | 0.06   | 0.29 | 0.03 | 0.985 | 0.168  |
| CaO               | wt%  | 5.96 | 1.23   | 5.92 | 0.55   | 21.8 | 0.6  | 1.020 | 0.222  |
| TiO <sub>2</sub>  | wt%  | 1.01 | 0.07   | 0.98 | 0.03   | 0.28 | 0.03 | 0.972 | 0.073  |
| $Cr_2O_3$         | wt%  | 0.27 | 0.03   | 0.25 | 0.01   | 0.11 | 0.03 | 0.910 | 0.113  |
| MnO               | wt%  | 0.21 | 0.03   | 0.20 | 0.04   | 0.15 | 0.02 | 0.922 | 0.265  |
| FeO               | wt%  | 19.7 | 1.5    | 19.2 | 0.6    | 6.53 | 0.37 | 0.970 | 0.080  |
| Ni                | µg∕g | 321  | 122    | 375  | 95     | 53   | 45   | 1.172 | 0.553  |
| Zn                | µg/g | 695  | 167    | 729  | 153    | 140  | 31   | 0.994 | 0.308  |
| Br                | µg/g | 541  | 307    | 401  | 111    | 91   | 36   | 0.714 | 0.459  |

1967 Table 3. Average compositions of Grasberg formation lower and upper units and1968 vein targets, plus the ratio of upper unit to lower unit.

|                   |      | Az   | ilda | Sturgeon | n River3 | Sande  | herry  | Cheln | nsford  | veneer | Ortiz | z2B  |  |
|-------------------|------|------|------|----------|----------|--------|--------|-------|---------|--------|-------|------|--|
|                   |      | ma   | trix | spheru   | le-rich  | veneer | r-rich | venee | er-rich | calc.* | vein- | rich |  |
|                   |      | ave  | std  | meas.    | ±        | meas.  | ±      | ave   | ±       |        | meas. | ±    |  |
| number            |      | 5    |      |          |          |        |        | 2     |         |        |       |      |  |
| Na <sub>2</sub> O | wt%  | 2.58 | 0.08 | 2.21     | 0.25     | 2.32   | 0.21   | 2.44  | 0.12    | 1.98   | 2.09  | 0.19 |  |
| MgO               | wt%  | 7.75 | 0.04 | 9.29     | 0.15     | 7.79   | 0.10   | 7.59  | 0.05    | 10.15  | 6.28  | 0.08 |  |
| $Al_2O_3$         | wt%  | 10.6 | 0.1  | 9.61     | 0.16     | 8.23   | 0.10   | 9.19  | 0.06    | —      | 8.57  | 0.11 |  |
| SiO <sub>2</sub>  | wt%  | 49.5 | 0.2  | 49.5     | 0.5      | 43.3   | 0.4    | 45.7  | 0.2     | 25.8   | 42.0  | 0.4  |  |
| $P_2O_5$          | wt%  | 1.42 | 0.03 | 0.59     | 0.08     | 1.29   | 0.08   | 1.27  | 0.05    | 1.49   | 1.17  | 0.08 |  |
| SO <sub>3</sub>   | wt%  | 3.09 | 0.02 | 3.32     | 0.08     | 8.86   | 0.10   | 7.13  | 0.05    | 20.70  | 13.5  | 0.1  |  |
| Cl                | wt%  | 0.64 | 0.01 | 0.47     | 0.02     | 1.98   | 0.03   | 1.49  | 0.01    | 3.21   | 0.95  | 0.02 |  |
| K <sub>2</sub> O  | wt%  | 0.31 | 0.02 | 0.36     | 0.06     | 0.40   | 0.06   | 0.36  | 0.04    | 0.89   | 0.27  | 0.06 |  |
| CaO               | wt%  | 6.10 | 0.02 | 5.11     | 0.06     | 7.64   | 0.06   | 6.98  | 0.03    | 13.4   | 10.3  | 0.1  |  |
| TiO <sub>2</sub>  | wt%  | 0.90 | 0.03 | 0.81     | 0.09     | 0.92   | 0.07   | 0.93  | 0.04    | 1.12   | 0.78  | 0.06 |  |
| $Cr_2O_3$         | wt%  | 0.25 | 0.01 | 0.36     | 0.04     | 0.22   | 0.03   | 0.25  | 0.02    | 0.17   | 0.22  | 0.03 |  |
| MnO               | wt%  | 0.37 | 0.01 | 0.29     | 0.02     | 0.38   | 0.01   | 0.56  | 0.01    | 0.44   | 0.47  | 0.01 |  |
| FeO               | wt%  | 15.8 | 0.1  | 17.9     | 0.2      | 16.4   | 0.1    | 15.9  | 0.1     | 20.3   | 13.2  | 0.1  |  |
| Ni                | µg∕g | 952  | 20   | 1165     | 76       | 888    | 50     | 814   | 30      | 884    | 670   | 44   |  |
| Zn                | µg/g | 144  | 4    | 132      | 20       | 453    | 16     | 300   | 7       | 995    | 144   | 10   |  |
| Br                | µg/g | 92   | 7    | 57       | 19       | 348    | 19     | 162   | 11      | 644    | 208   | 17   |  |

1972 Table 4. Average or representative compositions of Matijevic formation lithologies.1973

1974

1975 \*From *Clark et al.* [2016].

|                   |      | a     | 01:00    | <b>C</b> 1 | <b>T</b> 1 |      | Tisdale |      | eley | Murra | y Ridge, | Murray | Ridge, | Huevtown |      | 01    | 1 2                |
|-------------------|------|-------|----------|------------|------------|------|---------|------|------|-------|----------|--------|--------|----------|------|-------|--------------------|
|                   |      | Coppe | er Cliff | Cheste     | er Lake    | Tis  | dale    | Ha   | ven  | no    | orth     | cen    | itral  | Huey     | town | Shoer | naker <sup>2</sup> |
|                   |      | ave   | std      | ave        | std        | ave  | std     | ave  | std  | ave   | std      | ave    | std    | ave      | std  | ave   | std                |
| number            | •    | 9     |          | 5          |            | 6    |         | 16   |      | 8     |          | 10     |        | 3        |      | 51    |                    |
| Na <sub>2</sub> O | wt%  | 2.22  | 0.14     | 2.57       | 0.13       | 2.15 | 0.23    | 2.24 | 0.16 | 2.35  | 0.16     | 2.17   | 0.15   | 2.23     | 0.13 | 2.27  | 0.18               |
| MgO               | wt%  | 8.06  | 0.49     | 8.00       | 0.78       | 6.10 | 0.13    | 7.92 | 0.76 | 7.61  | 0.55     | 7.29   | 0.52   | 6.93     | 0.07 | 7.72  | 0.69               |
| $Al_2O_3$         | wt%  | 9.89  | 0.96     | 9.07       | 0.60       | 9.04 | 0.80    | 9.33 | 0.20 | 9.36  | 0.43     | 9.40   | 0.71   | 8.79     | 0.12 | 9.39  | 0.62               |
| $SiO_2$           | wt%  | 45.4  | 1.1      | 45.1       | 0.9        | 44.6 | 1.5     | 45.6 | 0.4  | 45.3  | 1.1      | 45.5   | 0.4    | 43.4     | 0.2  | 45.3  | 0.9                |
| $P_2O_5$          | wt%  | 1.05  | 0.07     | 1.04       | 0.06       | 2.01 | 0.73    | 1.08 | 0.07 | 1.02  | 0.10     | 1.12   | 0.18   | 1.19     | 0.01 | 1.08  | 0.11               |
| $SO_3$            | wt%  | 8.16  | 1.23     | 4.80       | 1.51       | 6.61 | 1.03    | 6.23 | 0.41 | 8.11  | 1.43     | 6.89   | 0.43   | 10.83    | 0.18 | 7.12  | 1.67               |
| Cl                | wt%  | 1.34  | 0.22     | 1.12       | 0.20       | 1.19 | 0.21    | 0.91 | 0.08 | 1.08  | 0.28     | 1.15   | 0.31   | 1.00     | 0.11 | 1.09  | 0.25               |
| K <sub>2</sub> O  | wt%  | 0.37  | 0.09     | 0.44       | 0.05       | 0.53 | 0.06    | 0.47 | 0.04 | 0.38  | 0.09     | 0.49   | 0.04   | 0.43     | 0.02 | 0.44  | 0.08               |
| CaO               | wt%  | 6.89  | 0.50     | 6.82       | 0.18       | 5.90 | 0.90    | 6.57 | 0.57 | 6.44  | 0.40     | 7.02   | 0.61   | 6.44     | 0.14 | 6.71  | 0.53               |
| $TiO_2$           | wt%  | 0.89  | 0.07     | 1.05       | 0.07       | 1.05 | 0.04    | 1.08 | 0.06 | 1.08  | 0.07     | 1.11   | 0.12   | 1.10     | 0.01 | 1.05  | 0.11               |
| $Cr_2O_3$         | wt%  | 0.26  | 0.02     | 0.25       | 0.01       | 0.23 | 0.04    | 0.23 | 0.04 | 0.22  | 0.04     | 0.24   | 0.06   | 0.20     | 0.01 | 0.24  | 0.04               |
| MnO               | wt%  | 0.39  | 0.03     | 0.50       | 0.07       | 0.41 | 0.11    | 0.48 | 0.12 | 0.32  | 0.05     | 0.29   | 0.10   | 0.49     | 0.02 | 0.40  | 0.12               |
| FeO               | wt%  | 15.0  | 1.1      | 19.2       | 1.3        | 19.6 | 1.7     | 17.7 | 0.4  | 16.6  | 0.4      | 17.3   | 0.8    | 16.9     | 0.3  | 17.1  | 1.4                |
| Ni                | µg/g | 831   | 80       | 471        | 15         | 1169 | 476     | 440  | 116  | 413   | 58       | 334    | 65     | 412      | 76   | 485   | 186                |
| Zn                | µg/g | 321   | 166      | 266        | 31         | 2459 | 1939    | 292  | 41   | 176   | 90       | 255    | 96     | 152      | 16   | 261   | 103                |
| Br                | µg/g | 149   | 109      | 91         | 24         | 940  | 405     | 131  | 37   | 101   | 40       | 108    | 60     | 75       | 13   | 118   | 61                 |

1977 Table 5. Average compositions of Shoemaker formation units and the formational average.

1978

<sup>1</sup>Excluding anomalous targets Spinifex and Sledge Island.

<sup>2</sup>Excluding anomalous targets Spinifex and Sledge Island, and the Tisdale block.

#### 1982 Figure captions

- 1983 Figure 1: HiRISE-based mosaic showing Endeavour Crater (upper right). Locator images
- showing rover track (courtesy of T. Parker), APXS target sites and geographic names used in the
  text. Close up images cropped from HiRISE image file ESP\_018846\_1775\_RED.
- 1986 Figure 2: Portion of the geologic map (a) and cross section (b) of the Meridiani Planum region
- surrounding the Mars Exploration Rover *Opportunity* area of investigation [*Hynek and Di*
- 1988 *Achille*, 2017], and the schematic stratigraphy of the region explored by *Opportunity* (c)
- 1989 (modified after [*Crumpler et al.*, [2015a]). Unit key only covers those discussed in the text.
- 1990 Cross section vertical exaggeration is ~78×. White dotted circle approximate location of
- 1991 Miyamoto Crater rim; yellow dotted arcs approximate inner rim crest and first ring of multiring
- 1992 basin that underlies Meridiani Planum [after *Newsom et al.*, 2003].
- 1993 Figure 3: a. Portion of the sols 3387-3389 site 179/position 0 Navcam mosaic showing dark-rock
- 1994 float on Solander Point; Murray Ridge in the background. Tick Bush is ~20 cm across. b. Portion
- 1995 of the Sol 3609 Pancam L257 false-color mosaic showing dark-rock float on the McClure-
- 1996 Beverlin Escarpment of Murray Ridge. Labeled boulders A and are 16 and 18 cm across at their
- 1997 bases. c. Portion of the Sol 3750 L257 Pancam false-color mosaic showing the dark cap-rock on
- 1998 the northeast tip of Wdowiak Ridge. (The left Pancam filters numbers 2, 5 and 7 are centered on
- 1999 753, 535 and 432 nm. Unless otherwise noted, all Pancam false-color images used are based on
- 2000 these filters.)
- Figure 4: Pancam false-color images showing examples of macrotextures of Grasberg formation
- targets: a. Grasberg, upper unit (portion of Sol 3000 image), Pancam left filters 4, 5 and 6
- centered on 601, 535 and 482 nm. Arrows indicate possible fine Ca-sulfate veins; b. Rosebud
- 2004 Canyon, upper unit (Sol 3734); c. Monjon (Sol 3425), lower unit. Boxes indicate the locations of
- 2005 MI frames for the purple (upper box) and grey (lower box) targets discussed in the text; d.
- 2006 Homestake (Sol 2769), vein in lower unit; e. Poverty Bush, lower unit, showing fine-scale
- 2007 laminations (arrows) (Sol 3426).
- 2008 Figure 5: Microscopic Imager mosaics showing examples of microtextures of Grasberg
- 2009 formation targets: a. Grasberg, upper unit (Sol 3006, abraded, illuminated from upper right); b.
- 2010 Wally Wombat, upper unit (Sol 3434, brushed, fully shadowed); c. Monjon Purple, lower unit
- 2011 (Sol 3422, untreated, illuminated from upper right); d. Poverty Bush, lower unit (Sol 3427,
- 2012 untreated, fully shadowed). Scale bars are 1 cm.
- 2013 Figure 6: Pancam false-color images showing examples of macrotextures of Matijevic formation
- 2014 outcrops: a. Fine-grained bright lithology showing matrix (M), patches of dark veneer (Vr),
- 2015 bright veins (Vn) locally traceable below the veneer (white arrows, inset), and rare spherules (S)
- 2016 (Sol 3203); b. Outcrop of ledge-forming spherule-rich lithology (portion of Sol 3062 mosaic).
- 2017 Figure 7: Microscopic Imager mosaics showing examples of microtextures of Matijevic
- 2018 formation targets: a. Fullerton3 showing matrix, scattered spherules and bright veins in the top
- right (Sol 3209, brushed, illuminated from upper left); b. Ortiz2B with the highest vein
- 2020 concentration targeted (center of circles) (Sol 3200, untreated, fully shadowed); c. Chelmsford3
- showing dark veneer on top of bright matrix (Sol 3096, brushed, illuminated from upper left); d.

Spherule-rich target Sturgeon River3 (Sol 3251, very light abrasion – arrows, illuminated from
upper left). Scale bars are 1 cm. On a-c, solid circles are the 3.8 cm inside diameter of the APXS;
dotted circles are the approximate regions from which 75% of the APXS response signal is
derived.

Figure 8: Pancam false-color images showing examples of macrotextures of Shoemaker

2027 formation outcrops: a. Vermilion on Matijevic Hill, Copper Cliff member (Sol 3156), arrows

2028 mark several clasts standing in relief above the surface; b. Mpangeni on Shoemaker Ridge,

- Greeley Haven member (Sol 2786), Pancam left filters 2, 4 and 6 centered on 753, 601, and 482
- 2030 nm; c. Kangaroo Paw on Murray Ridge (Sol 3466); d. Bristol Well at Pillinger Point on Murray
- 2031 Ridge showing bright CaSO<sub>4</sub> vein (Sol 3669); e. Sarcobatus at Pillinger Point on Murray Ridge
- showing targets Flat (brushed), Clast1 and Clast2 (Sol 3676); f. Hueytown on Cape Tribulation
  showing brushed outcrop targets Calera and Locust Fork, and vein target Cottondale (Sol 3868).
- Figure 9: Microscopic Imager mosaics (except c) showing examples of microtextures of
- 2035 Shoemaker formation targets: a. Onaping from the Copper Cliff outcrop, Matijevic Hill (Sol
- 2036 3158, untreated, illuminated from top); b. Green Island from Cook Haven on Murray Ridge (Sol
- 2037 3569, brushed, illuminated from bottom); c. Portion of Mount Tempest image showing large
- clast with texture suggesting bright clasts (arrows) in dark matrix, from the Moreton Island

2039 outcrop, Murray Ridge (Sol 3502, untreated, fully shadowed); d. Cottondale CaSO<sub>4</sub> vein at

- 2040 Hueytown (between arrows) on Cape Tribulation (Sol 3848, untreated, illuminated from left).
- 2041 Bright vertical streaks in lower right of a are artifacts caused by saturation of specular
- 2042 reflections. Scale bars are 1 cm.
- 2043 Figure 10: Pancam false-color images of dark rocks: a. Tick Bush from Solander Point (Sol
- 2044 3391); b. Concentration of dark-rock float between Cook Haven and the McClure-Beverlin
- 2045 Escarpment, A Augustine and, c possible columnar-jointed (hexagonal prism) block (Sol
- 2046 3601); c. Dark-rock ejecta from Ulysses crater, Wdowiak Ridge, H Hoover and, f dark flakes
- 2047 commonly observed on local rocks (Sol 3793); d. Birmingham from Wdowiak Ridge in the2048 Ulysses crater ejecta field (Sol 3814).
- Figure 11: Microscopic Imager mosaics showing examples of microtextures of dark rocks: a.
- 2050 Tick Bush from Solander Point (Sol 3392, untreated, fully shadowed); b. Point Bede from near
- 2051 Cook Haven (Sol 3616, untreated, illuminated from upper right); c. Hoover from Wdowiak
- Ridge (Sol 3795, brushed, illuminated from upper right); d. Crimson Tide target on rock
- 2053 Birmingham from Wdowiak Ridge, arrows indicate grains or clasts (Sol 3819, untreated,
- 2054 illuminated from right). Scale bars are 1 cm.
- 2055 Figure 12: Compositional data for Grasberg formation targets compared to Burns formation, dark 2056 sands and bright soils. "Burns; margin" refers to targets from near the contact with the Grasberg formation; see text. Symbols with "×" were brushed; those with "•" were abraded. Arrow shows 2057 2058 progression of analyses of untreated, brushed and abraded Grasberg1. Panel b expands the 2059 ordinate of a to show details of the non-vein targets. Compositionally anomalous Grasberg (red) 2060 and Burns margin (black) targets are labeled; G and P refer to Monjon Grey and Purple. Circled 2061 abraded Burns formation analyses are for Guadalupe and Lion Stone (see discussion in Section 2062 6.6).

- Figure 13: Element ratio diagram for Grasberg1 untreated and brushed targets normalized to the abraded target; u – untreated, b – brushed, a – abraded. Y-axis is log scale.
- Figure 14: Element ratio diagrams for Matijevic formation veneer-rich (a) and spherule-rich (b)
- targets relative to matrix composition (average Azilda, Table 4). In a, coating is the calculated
- veneer composition from *Clark et al.* [2016]. In b, Fullerton3 is a different matrix target. Y-axisis log scale.
- 2069 Figure 15: Compositional data for Matijevic formation targets compared to Burns and Grasberg
- 2070 (G) formation targets, abraded Adirondack-class (A) basalts from Gusev Crater, dark sands and
- bright soils. Stars are the best representations of the Matijevic matrix composition (Table 4);arrows point towards veneer-rich targets.
- 2073 Figure 16: Results of Agglomerative Hierarchical Cluster Analysis on Matijevic, Burns and
- 2074 Grasberg formation targets, dark sands and bright soils for all elements (a, b) and excluding S,
- 2075 Cl, Zn and Br (c, d). Panels b and d show details of cluster 4.
- Figure 17: Compositional data for Shoemaker formation targets compared to Burns formation targets, fields Grasberg (G) and Matijevic (M) formations, dark sands and bright soils.
- Figure 18: Element ratio diagrams for clast/host pairs; u = untreated, b = brushed, a = abraded.
- 2079 Dashed lines in panel b show the maximum and minimum measurements on the Amboy outcrop
- ratioed to the median values. Ratios >1 are elements with <u>lower</u> concentrations in the host
- 2081 targets. The Y axis are log scales and are the same on all panels.
- 2082 Figure 19: Compositional data for Shoemaker formation clast and bulk rock targets compared to
- 2083 Transvaal, multiple analyses of Greeley Haven target Amboy, fields for Matijevic formation
- 2084 matrix  $(M_m)$  and spherule-rich  $(M_s)$  targets, abraded Adirondack-class basalt targets (A), dark
- sands, and bright soils. Symbols with "×" were brushed; those with "•" were abraded. Dotted
- envelope cluster 1 rocks; solid envelope cluster 2 rocks (see text). Sarcobatus Clast1 and
  Clast2 are labeled.
- 2087 Clast2 are labeled.
- 2088 Figure 20: a. Results of Agglomerative Hierarchical Cluster Analysis on Greeley Haven member
- targets, dark sand and bright soil using all elements. b. Target locations color coded by cluster on
- a portion of the Greeley Haven Pancam mosaic (Sol 2803); locations of images shown in panels
- 2091 c e are indicated. Microscopic Imager images of: c. Boesmanskop (Sol 2800, untreated, fully
- shadowed); d. Amboy 4 (Sol 2921, untreated, illuminated from top); e. Amboy 12 (Sol 2940,
- untreated, illuminated from top). Scale bar in d is 0.5 cm and also applies to c and e.
- Figure 21: CaO vs. SO<sub>3</sub> for vein-rich targets compared to fields for host lithologies for (a) the
- 2095 Grasberg formation, (b) the Murray Ridge, Bristol Well targets, (c) Hueytown fracture zone, and
- 2096 (d) the Matijevic formation. Labeled fields are:  $G_L$  Grasberg formation, lower unit; H –
- 2097 Shoemaker formation, Hueytown;  $M_m$  Matijevic formation matrix; MR Shoemaker
- 2098 formation, Murray Ridge. Dark sands and bright soils are shown for comparison. Solid lines are
- 2099 mixing lines between outcrop host and pure  $CaSO_4$  veins (see text). Star in panel c is a mixture
- of Hueytown outcrop and dark sand, and the dotted line is a mixing line between this
- composition and CaSO<sub>4</sub>; see text. Dotted line in d is a regression through the Matijevic formation
- 2102 vein-rich targets (see text).

- Figure 22: Bristol Well targets on: a. Pancam false-color image (Sol 3669); and b. MI mosaic
- (Sol 3664, untreated, fully shadowed). Approximate centers and APXS fields of view of thethree Bristol Well targets are shown in b.
- Figure 23: Compositional data for dark-rock Wdowiak Ridge and float targets compared to
- 2107 Gusev Crater basalts, dark sands, bright soils and fields for Endeavour rim lithologies.
- 2108 Abbreviations are: G Grasberg formation; M Matijevic formation; S<sub>Y</sub> Shoemaker formation
- 2109 on Cape York;  $S_T$  Shoemaker formation, Tisdale block;  $S_M$  Shoemaker formation on Murray
- 2110 Ridge (individual labeled point is the anomalous Sledge Island target); T Tick Bush, H –
- 2111 Hoover. Dashed arrows: Lipscomb-Margaret (rock) to Lipscomb-Victory (flake) targets; see text.
- Figure 24: FeO vs. MnO for clasts, anomalous or altered targets compared to fields for host
- 2113 lithologies and abraded Adirondack-class basalts. Panel b expands the x axis to highlight details
- of low-MnO targets. Abbreviations in a are: CY Shoemaker formation, Cape York; G –
- 2115 Grasberg formation; M Matijevic formation; MR Shoemaker formation on Murray Ridge.
- 2116 Abbreviations in b are: A Adirondack-class basalts;  $M_m$  Matijevic formation matrix;  $M_s$  –
- 2117 Matijevic formation spherule-rich;  $S_{CC}$  Shoemaker formation, Copper Cliff member;  $S_{CL}$  –
- 2118 Shoemaker formation Chester Lake member; S<sub>GH</sub> Shoemaker formation Greeley Haven
- 2119 member;  $S_T$  Shoemaker formation, Tisdale block. Line labeled Mars is average Fe/Mn of
- abraded Adirondack-class basalts; dotted lines in b are  $\pm 10\%$  on the average, and are merely
- meant to aid in visualizing the scale of departure of the Endeavour Crater rim rocks from the
- average. Some symbols from panel a legend carry over to panel b.
- Figure 25: S vs. Fe/Mn for select lithologies. Blue arrows show trends from host towards CaSO<sub>4</sub>
- veins; see text. Dashed lines show trends of higher Fe/Mn with slight S increase in some outcrop
- 2125 lithologies (Matijevic spherule-rich; Grasberg) and lower Fe/Mn with large S increase in some
- 2126 vein-rich and altered targets. Abbreviations in a are: Dw Deadwood outcrop target; G –
- 2127 Grasberg formation; Hs Homestake vein target. Abbreviations in b are: A abraded
- 2128 Adirondack-class basalts; H Shoemaker formation, Hueytown; m martian meteorites; M<sub>m</sub> –
- 2129 Matijevic formation matrix; M<sub>s</sub> Matijevic formation spherule-rich; MR Shoemaker
- 2130 formation, Murray Ridge;  $S_{CC}$  Shoemaker formation, Copper Cliff member;  $S_{CL}$  Shoemaker
- 2131 formation Chester Lake member;  $S_{GH}$  Shoemaker formation Greeley Haven member;  $S_T$  –
- 2132 Shoemaker formation, Tisdale block. Line labeled Mars is average Fe/Mn of abraded
- 2133 Adirondack-class basalts.
- Figure 26: Element/Si vs. Ca/Si mole-ratio diagrams for CaSO<sub>4</sub> vein-rich targets compared to
- 2135 host outcrop and unit fields. Abbreviations in a are:  $G_L$  Grasberg formation, lower unit; H –
- 2136 Shoemaker formation, Hueytown; M<sub>m</sub> Matijevic formation matrix; MR Shoemaker
- formation, Murray Ridge. Symbols for host outcrop are Deadwood target (Grasberg), average
- 2138 Matijevic matrix (Table 4), Bristol Well on Murray Ridge, and mixed Hueytown outcrop and
- 2139 dark sand.

Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.


Figure 6.



Figure 7.



Figure 8.



Figure 9.



Figure 10.



Figure 11.



Figure 12.



Figure 13.



Figure 14.



Figure 15.



Figure 16.



Figure 17.



Figure 18.



Figure 19.



Figure 20.



Figure 21.



Figure 22.



Figure 23.


Figure 24.



Figure 25.



Figure 26.

