1 2 3 4 5 6 7		R Multispectral Observations of Aqueous Alteration Materials by the Pancams on the Spirit and Opportunity Mars Exploration Rovers
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28	Abstract
29	Multispectral visible and near infrared (VNIR) observations from the Mars Exploration
30	Rover Pancam multispectral stereo camera systems are consistent with materials having been
31	subjected to a variety of aqueous processes. Ferric oxides in the form of hematite in the Burns
32	and Grasberg formations of Meridiani Planum have been well characterized by Opportunity on
33	the basis of strong 535 and 864 nm absorptions and positive 754 to 1009 nm and 934 to 1009 nm
34	slopes. On the Noachian-aged rim of Endeavour crater, Opportunity has observed light-toned
35	veins with high Ca and S, as determined by the rover's Alpha Particle X-ray Spectrometer
36	(APXS), and a negative 934 to 1009 nm slope in VNIR spectra extracted from Pancam,
37	indicative of a 1000 nm H ₂ O overtone absorption- together these observations indicate that the
38	veins are composed of gypsum. Rocks overturned by Opportunity on the Murray Ridge portion
39	of the Endeavour crater rim display dark and light-toned coatings. The dark toned coatings have
40	a red, featureless slope that is consistent with that observed in laboratory spectra of high valence
41	manganese oxide minerals. Potential Mn oxide coatings may also be associated with some
42	exposures of the Grasberg formation. APXS results for high Mg and S in the light-toned coatings
43	of the Murray Ridge overturned rocks, and a negative 934 to 1009 nm slope are consistent with
44	hydrated Mg-sulfates. Opportunity has also observed spectral features in rocks consistent with
45	orbital observations of Fe-smectites, as well as Al-smectites and possible hydrated silica in light-
46	toned fracture-fill materials. The Spirit rover observed sulfate-rich light-toned soils exposed by
47	the rover's wheels. Several of these soil observations contained spectral features, such as a broad
48	absorption centered near 800 nm, consistent with ferric sulfate minerals, a finding confirmed by
49	the rover's Mössbauer spectrometer. Spirit also excavated light-toned Si-rich soils. These soils
50	have a flat near infrared spectrum with a drop in reflectance from 934 to 1009 nm that is
51	consistent with free water contained in voids or adsorbed onto the surface of the silica.

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- 52 Keywords: Mars remote sensing, visible/near-infrared, Mars spectroscopy, iron oxides, ferric
- 53 sulfates, manganese oxides, phyllosilicates

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Introduction

57	Since January 2004, the Panoramic Cameras (Pancams) on-board the Mars Exploration
58	Rovers Spirit and Opportunity have been imaging the martian surface along their traverse paths.
59	A key objective of the Mars Exploration Rover (MER) mission has been to detect signs of
60	ancient aqueous activity and determine the role of water in affecting geology at the two MER
61	landing sites. The role of the Pancams has been to provide stereoscopic imaging to aid in the
62	navigation of the rovers and to assess rock and outcrop morphology. The Pancams also possess
63	multispectral imaging capability through the use of their two 8-position filter wheels with filter
64	band centers and widths listed in Table 1. Aside from neutral density filters and an empty
65	position, there are 13 filters devoted to geology observations between the two "eyes" of the
66	Pancam with 11 distinct (non-overlapping) wavelengths from 432 to 1009 nm. From a Pancam
67	13 filter ("13f") observation, we obtain an image cube that provides a visible-to-near-infrared
68	(VNIR) spectrum for each picture element, or pixel, for a total of 1024x1024 pixels in the
69	imaged scene. This multispectral imaging enables us to characterize the VNIR reflectance
70	character of targets of interest. The remote sensing aspect of Pancam has also proven important
71	in cases where a target cannot be reached by the rover's robotic arm for <i>in situ</i> examination or
72	where other operating constraints might preclude such an <i>in situ</i> examination.
73	This paper describes the Pancam instrument, data calibration, and how reflectance spectra
74	from multispectral Pancam observations have been used to help constrain the identity of a
75	number of minerals produced through aqueous alteration. The observations and results portion
76	of the paper is divided according to several mineral and material groups: oxides, hydrous
77	sulfates, hydrated silica, and presumed phyllosilicate-bearing rocks.
78	Examining how the VNIR multispectral imaging capabilities on the Spirit and

79 Opportunity rovers have been used to characterize minerals associated with aqueous alteration is

80	relevant for ongoing studies by the MSL rover Curiosity (Bell et al., 2013; Wellington et al., this
81	issue), as well as similar capabilities planned for the ExoMars (e.g., Cousins et al., 2012) and
82	Mars 2020 rovers. This paper also examines a number of spectrally distinctive materials
83	observed by Opportunity since its departure from the Cape York rim segment of Endeavour
84	crater. This paper furthers the multispectral examination of surface materials at Endeavour crater
85	that was introduced in Farrand et al. (2013a, 2014) and is discussed in part by Arvidson et al.
86	(this issue).

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The Pancam Instrument and Calibration of Data

89 The Pancam instrument was described in detail by Bell et al. (2003). A description of 90 mission operational calibration was provided by Bell et al. (2006). In brief, the Pancam on each 91 rover has two 1024 by 1024 active-area charge-coupled devices (CCDs) with a 30 cm stereo 92 separation and a 0.27 mrad per pixel resolution. Each Pancam is mounted 1.5 m above the 93 ground on the mast referred to as the Pancam Mast Assembly (PMA). Each rover is also equipped with identical calibration targets (Bell et al., 2003) for the Pancam observations. Each 94 95 Pancam was calibrated before launch (Bell et al., 2003; 2006). Operational surface procedures 96 for the collection of multispectral images involve the close-in-time imaging of the calibration 97 target (in extended mission operations with Opportunity, calibration target imaging is sometimes 98 omitted if the calibration target was imaged on the previous sol at a similar time; acceptable 99 given the relatively uniform atmospheric conditions from sol-to-sol on Mars). Multispectral 100 image data from the calibration target, in conjunction with pre-launch calibration information, 101 are utilized to convert raw image data to calibrated radiance and then to radiance factor (I/F, or 102 more properly I/ π F, where I is the measured radiance and π F is the incident solar irradiance).

103	Accumulation of airfall dust on the calibration target over the course of the mission led to
104	development of a correction for dust on the calibration target based on a two-layer Hapke model
105	along with the known photometric properties of the calibration target (Bell et al., 2006, Sohl-
106	Dickstein et al., 2005). The measurements presented here are I/F divided by the cosine of the
107	incidence angle at the time of image acquisition, a quantity described as relative reflectance, or
108	R*, by Reid et al. (1999) and Bell et al. (2006). Bell et al. (2006) estimated that the absolute
109	reflectance levels of Pancam multispectral data are accurate to within ~10% at the shortest
110	wavelengths, and slightly more accurate at longer wavelengths. Relative filter-to-filter
111	uncertainties in R* were estimated to be smaller, typically 1-5%, providing confidence in the
112	reality of even very small-scale spectral variations detected in the scene. The 13-geology filter
113	data sets examined here were typically compressed using the ICER wavelet-based compression
114	routine (Kiely and Klimesh, 2003) so that blue stereo bands (the L7 and R1 bands) were at 2
115	bits-per-pixel and all other bands were at 1 bit-per-pixel for transmission and uncompressed back
116	to the full dynamic range once received on Earth. Effects on the radiometric precision due to the
117	compression were estimated to be < 1% based on pre-launch tests (Bell et al., 2006).
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119	Multispectral Processing Tools Used on Pancam Spectra

120 Multispectral Approaches

Analysis of Pancam data has been performed using both image processing and spectral analysis paradigms. The image processing approach consists of successive analyses of the separate multispectral sequences of the left and right eye image data. Purely spectral analysis has been conducted using combined eye spectra of materials of interest that have been compiled and examined as 11 band datasets. As described in Farrand et al. (2006, 2007, 2008, 2013a,

126	2014), the use of a number of established image processing approaches has been applied to left-
127	and/or right-eye image sequences including decorrelation stretch composites, spectral
128	parameterization, spectral mixture analysis (Farrand et al., 2006), and supervised classification
129	approaches. These techniques have been used to define regions of interest (ROIs) over spectrally
130	distinctive or representative areas. Spectra from the ROIs in both the left and right eye data are
131	averaged and are combined at the L2 and R2 bands (at 753 to 754 nm). These combined-eye
132	spectra have been used for 11-band processing of assemblages of spectra. The combined-eye
133	spectra have been analyzed as collections of vectors using clustering approaches (Anderson and
134	Bell, 2013; Farrand et al., 2013a; 2014) and various endmember determination approaches
135	(Farrand et al., 2008; 2013a; 2014).
136 137	Spectral Parameters
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139	characteristics such as slope, band depth, and the position of spectral features. Table 2 lists a
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140 141 142 143 144 145 146 147	number of spectral parameters that have been used in various Pancam data analyses (e.g., Farrand et al., 2006, 2007, 2008, 2013, 2014; Rice et al., 2010). Geologic Setting The aqueous alteration minerals observed by Spirit and Opportunity are best understood in the geologic context of the Gusev crater and Meridiani Planum sites examined by these rovers. Overviews of the geology of Gusev crater as it was known prior to the landing of Spirit include

in Arvidson et al. (2008)). The materials in the Columbia Hills have been interpreted as being
Noachian in age (Squyres et al., 2006). The materials making up Home Plate, at least its lower
Barnhill unit, were interpreted by Squyres et al. (2007) as being pyroclastic, potentially
hydrovolcanic, in origin. Sulfate-rich and silica-rich soils and nodules observed around Home
Plate have been interpreted as being the result of hydrothermal processes (Schmidt et al., 2009;
Ruff et al., 2011).

157 The geology of Terra Meridiani, and the Meridiani Planum subregion examined by 158 Opportunity, were discussed prior to Opportunity's landing by Arvidson et al. (2003). From the 159 time of its landing to its arrival at the rim of Endeavour crater, Opportunity explored the Burns 160 formation, named in honor of geochemist Roger Burns, which comprise the bedrock of 161 Meridiani Planum. The Burns formation is a sulfate-bearing "sandstone" composed of 162 siliciclastic materials derived from the mechanical and chemical erosion of basalt (Grotzinger et 163 al., 2005; McLennan et al., 2005; Clark et al., 2005). The Burns formation has been interpreted 164 as being late Noachian to early Hesperian in age (Arvidson et al., 2006). The rim of the 22 km 165 diameter Endeavour crater, which is currently the subject of Opportunity's explorations, has been 166 interpreted as being Noachian in age (Squyres et al., 2012). Orbital observations made with the 167 Mars Reconnaissance Orbiter (MRO) Compact Reconnaissance Imaging Spectrometer for Mars 168 (CRISM) instrument revealed the presence of Fe/Mg smectite minerals on the rim of Endeavour 169 (Wray et al., 2009; Noe Dobrea et al., 2012). Discussion of place names and units as well as 170 traverse maps are provided in Squyres et al. (2012), Arvidson et al. (2014), and Crumpler et al. 171 (2015). Observations by Opportunity around the bench of the raised rim segments revealed the 172 presence of another sulfate-bearing stratigraphic unit that is chemically distinct from the Burns 173 formation, the Grasberg formation (Crumpler et al., 2015). Other materials making up the rim of

- Endeavour included an impact breccia, dubbed the Shoemaker formation and nominally older,clay-bearing, materials of the Matijevic formation (Squyres et al., 2012).
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Pancam Observations of Aqueous Alteration Minerals

179 Oxides

180 **Ferric Oxides.** Hematite (Fe_2O_3) is a mineral that is widespread on Mars (Bell et al., 181 1996). The airborne and dune-forming bright drift deposits that blanket much of the planet's 182 surface contain nanophase hematite (Singer et al., 1982). Crystalline (red) hematite and coarsely 183 crystalline (gray) hematite are not as widespread (or at least not as apparent from telescopic and 184 orbital observations) and, when observed, are indicate aqueous alteration. Opportunity was 185 targeted to land in Meridiani Planum on the basis of orbital observations by the Mars Global 186 Surveyor (MGS) Thermal Emission Spectrometer (TES) of coarsely crystalline gray hematite in 187 the Meridiani Planum region (Christensen et al., 2000). Before Opportunity's landing, the type 188 of surface materials hosting the gray hematite was unknown. After landing, it became apparent 189 through observations by the rover's Miniature Thermal Emission Spectrometer (Mini-TES) and, 190 later, *in situ* observations by the rover's Mössbauer spectrometer that the gray hematite was 191 hosted both in spherules, interpreted as concretions, weathering out of the light-toned sulfate-192 bearing Burns formation outcrop (Klingelhöfer et al., 2004) and disseminated within the Burns 193 formation itself (Glotch et al., 2006). 194 The first grind into Burns formation outcrop by Opportunity's Rock Abrasion Tool 195 (RAT) produced red cuttings from the grind (Fig. 1A). The cuttings and the abraded rock 196 surface displayed spectra with a strong 535 nm band, a near infrared (NIR) absorption band with

a minimum in the Pancam R4 (864 nm) band and strongly positive 754 to 1009 nm and 934 to

198	1009 nm slopes. These spectral parameters match that of red hematite. However, the narrower
199	reflectance maximum and deeper band depth of laboratory hematite compared to the Pancam
200	spectrum of the RAT grind (Fig. 1B) indicates the influence of nanophase hematite and possibly
201	other Fe-bearing phases on the spectral shape.
202	The spherules, colloquially referred to by the rover team as "blueberries", have
203	reflectance spectra with a strongly positive 934 to 1009 nm slope, and a reflectance minimum
204	appearing in some blueberry spectra in the Pancam R4 (864 nm) and in others in the R5 (904
205	nm) band. These spectral characteristics are consistent with coarsely crystalline (dark red)
206	hematite (Fig. 2), but not of specular hematite which has a flat reflectance spectrum in the
207	Pancam spectral range (Fig. 3). The presence of a 864 to 904 nm absorption band in the
208	blueberry spectra suggests that the surfaces of the blueberries either have a patina of red to dark-
209	red hematite, possibly produced by wind-driven dust abrasion, or that the grain size of the
210	hematite in the blueberries is less than approximately 90 μ m (Lane et al., 1999).
211	As noted in Farrand et al. (2007), Burns formation rock surfaces could be divided into
212	those that are lighter-toned to buff-colored in composites such as L357 (673, 535, 432 nm) or
213	L256 (753,535, 432 nm) (Fig. 4), which had a higher 482 to 535 nm slope (and was labeled in
214	that paper as the HFS class for Higher Four hundred eighty-two to 535 nm Slope). The redder or
215	more purple (again in composites such as L357 or L256; Fig. 4), cleaner (nominally wind-
216	abraded) Burns formation outcrop surfaces also have red hematite-like spectra (Fig. 5a) although
217	the near-infrared (NIR) band is not as well-defined and the 754 to 1009 nm slopes are
218	diminished. Nevertheless, these surfaces referred to in Farrand et al. (2007) as the "LFS" (for
219	Lower Four hundred eighty-two to 535 nm Slope) Burns formation surfaces have elevated 535
220	nm band depths and 904 nm band depths relative to other surface materials.

The Grasberg formation was first encountered on the bench of the Cape York rim segment of Endeavour crater, and was interpreted alternatively as immediately underlying or overlying the Burns formation (Crumpler et al., 2015). Natural, wind abraded surfaces of the Grasberg formation have an even closer resemblance to red hematite (**Fig. 5b**) with stronger 535 nm band depths, polynomial-fitted NIR band minimums at shorter wavelengths, and steeper 754 to 1009 nm slopes (**Fig. 6**) than are observed in the "purple" (LFS) Burns formation surfaces (Farrand et al., 2014).

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Manganese Oxides. On the Murray Ridge portion of the Endeavour crater rim south of 229 230 Solander Point, a turn-in-place maneuver by Opportunity resulted in the overturning of at least 231 two rocks and the moving of others (Arvidson et al., this issue). The smaller and larger of the 232 overturned rocks were named respectively Pinnacle Island and Stuart Island (Fig. 7). The newly 233 exposed surfaces of both rocks have two different coatings on them. Both rocks displayed a 234 dark-toned coating with a red, featureless spectral slope (Fig. 8A) and also a lighter-toned 235 coating spectrally similar to the gypsum veins and the Lihir/Esperance fracture-fill discussed 236 below. The nature of the light-toned coating is discussed in section 5.2.3 below in the discussion 237 of sulfate minerals. As shown in **Fig. 8b**, the dark coating spectrum resembles that of terrestrial desert varnish. Desert varnish is generally composed of birnessite ((Na,Ca)_{0.5}(Mn⁴⁺, 238 $Mn^{3+})_2O_4 \cdot 1.5H_2O$ mixed with clay minerals and hematite (Potter and Rossman, 1979). The 239 240 comparison here to desert varnish is purely a comparison of spectral shape and is not intended as 241 a process analogue. Fox et al., (2015) and Arvidson et al. (this issue) have provided a 242 comparison of the dark coatings to pure and mixed Mn oxide mineral reflectance spectra and 243 found that the spectra of the dark coatings are consistent with high-valence-state Mn oxide

244 minerals. Indeed, the Mn-rich nature of the dark coatings was confirmed by APXS investigation
245 (Arvidson et al., this issue).

Possible Mn-oxide minerals have also been observed by Pancam and APXS at several 246 247 locations in association with the Grasberg formation. These include several small two-toned 248 rocks on the north end of Cape York (occurring among rocks of the Grasberg formation) 249 observed on sol 3038, a large patch of material, potentially a coating, on the target Monjon 250 examined by APXS on sol 3419, and also on rocks observed along the eastern border of the rim 251 on the bench imaged on sols 3739. These materials appear blue in left-eye composites such as 252 L256, Fig. 9A, and purple in right-eye composites such as R731 (Fig. 9B) and the 535 nm band 253 depth of these coatings is very weak with comparison to other surface materials (Fig. 9C). The 254 spectra of these coatings (Fig. 10) have a positive, featureless red slope in the NIR and a broad, 255 weak 535 nm band in the visible wavelengths. The Monjon "blue" spectrum, and the other 256 occurrences noted from sols 3038 and 3419, occur amongst representative rocks of the Grasberg 257 formation. Grasberg formation rocks have spectra more typical of the Monjon sol 3419 "purple" 258 spectrum (Fig. 10 and also as shown in Fig. 5B). Mn in the blue-gray portion of the Monjon 259 target was twice that of the purple portion when measured by the APXS on sol 3419 (R. Gellert, 260 pers. comm.). 261 As noted by Arvidson et al. (this issue) and Lanza et al. (2014) the presence of high-

valence Mn oxides is significant since such minerals are formed in highly oxidizing, aqueous

263 environments. Moreover, the presence of Mn-rich minerals is a potential indicator of a habitable

264 environment on account of their association with water and highly oxidizing conditions.

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266 Sulfates

267	Sulfate-rich Soils Observed by Spirit. The first recognition of sulfate-rich soils by the
268	Spirit rover was during the investigation of the Big Hole (sol 113-115) and Boroughs trench (sol
269	135-142) targets on the Gusev crater volcanic plains between Bonneville crater and the
270	Columbia Hills (Haskin et al., 2005). Although sulfates (with a maximum > 20 mass % of the
271	examined soils) were implied by APXS and Mössbauer data analyses of trench regolith (Wang et
272	al., 2006), no spectral features of sulfates were identified in Pancam spectra because, as indicated
273	by the APXS data, the major sulfates were spectrally neutral Mg sulfates, rather than Fe sulfates
274	that exhibit characteristic absorption features in the VNIR spectral range.
275	Five major exposures of sulfate-rich soils, containing Fe-sulfates, were excavated from
276	depths of ~10 cm by Spirit (Arvidson et al. 2008, 2011; Wang et al., 2008; Rice et al. 2011).
277	The namesake location for this class of soils (e.g., Ming et al., 2008) was the Paso Robles site on
278	the crest of the Cumberland Ridge portion of Husband Hill (sol 399-432). Although examples of
279	these soils were encountered after Paso Robles, another example was not examined in situ again
280	until Spirit reached the Inner Basin (to the north of Husband Hill) at the Dead Sea/Arad region
281	(sol 721-728, Fig. 11a). The failure of the rover's right front wheel led to the excavation of the
282	Tyrone target on the eastern side of Home Plate (sol 784-798, sol 864-1062, sol 1098-1306), the
283	Hamilton target on the north side of Home Plate (sol 1804 – 1852), and the Ulysses target on the
284	west side of Home Plate (sol 1864-2186). Fig. 11B shows the typical Pancam spectra of
285	"yellow" and "white" Fe ³⁺ -sulfate-rich soils of the Arad site. These light-toned soils were found
286	to have SO_3 concentrations measured by the APXS of up to 38 wt.% (Ming et al., 2006; 2008).
287	Mössbauer spectrometer data indicated ferric-bearing sulfates in these soils (Morris et al., 2008),
288	and the soils' distinctive Pancam and Mini-TES spectra are consistent with a heterogeneous

289 mixture of hydrated ferric sulfate phases (*e.g.*, Johnson et al., 2007; Lane et al., 2008; Ruff et al.,
2008; Arvidson et al., 2011).

291 Johnson et al. (2007) selected six typical Pancam spectra from the sulfate-bearing 292 exposed soils at the Paso Robles, Dead Sea, and Tyrone sites, and used a database of 84 293 laboratory spectra and a multiple end-member spectral mixing model approach to identify 294 candidate Fe-sulfate assemblages that may contribute to the observed Pancam spectra. Among 295 the sulfate and ferric oxide/oxyhydroxide mineral spectra in the database, they found six ferric 296 sulfates that could make significant contributions to the observed Pancam spectra. They are ferricopiapite $[Fe_{2/3}^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O]$, hydronium jarosite $[(H_3O)Fe_3^{3+}(SO_4)_2(OH)_6]$. 297 fibroferrite [Fe³⁺(SO₄)(OH) \cdot 5H₂O], rhomboclase HFe³⁺(SO₄)₂ \cdot 4H₂O], paracoquimbite 298 $[Fe_2^{3+}(SO_4)_3 \cdot 9H_2O]$, and a mixture of anhydrite $[CaSO_4]$ with coquimbite $[Fe_2^{3+}(SO_4)_3 \cdot 9H_2O]$. 299 300 The analyses of Johnson et al. (2007) suggested that ferricopiapite, hydronium jarosite, 301 fibroferrite, rhomboclase composed a significant fraction of Tyrone yellowish light-toned soil, 302 while fibroferrite, (anhydrite + coquimbite), and paracoquimbite were consistent with spectra of 303 Paso Robles whitish light-toned soil, and hydronium jarosite and fibroferrite were likely present 304 in Arad soils at the Dead Sea site (Johnson et al., 2007). Fig. 12 compares a Pancam spectrum of 305 Arad soil and library spectra of phases suggested by Johnson et al. (2007). Other minerals have been suggested as important components of the soils, including Fe³⁺-bearing phosphates (Lane et 306 307 al., 2008), hydrated silica (Wang et al., 2008), and elemental sulfur (Morris et al., 2008). These ferric sulfates are considered to be precipitates from a Fe^{3+} and SO_4 -rich hydrothermal brine 308 309 (Wang et al., 2008) or to have formed directly from fumarolic processes (Yen et al., 2008). 310 Wang et al. (2008) suggested that some of these minerals may be unstable under present 311 Mars surface temperature and pressure conditions, and that repeated Pancam observations on

312	exposed light-toned soils at Tyrone indicated spectral changes, namely a decrease in the spectral
313	slope from the L7 (432 nm) to L3 (673 nm) bands, consistent with ferric sulfate phase changes.
314	Specifically, laboratory experiments (Wang and Ling, 2011) on the stability and phase
315	transformation of ferricopiapite (a potential component of Tyrone yellowish soils based on
316	Johnson et al., 2007) demonstrated that under Mars-relevant conditions, the potential dehydration
317	products of ferricopiapite are rhomboclase, kornelite Fe2 ³⁺ (SO ₄) ₃ ·7H ₂ O, pentahydrate
318	Fe ₂ ³⁺ (SO ₄) ₃ ·5H ₂ O, paracoquimbite, and two types of amorphous ferric sulfates. Wang and Ling
319	(2011) found reductions of the L3 vs. L7 ratio reflectance in laboratory sulfate dehydration
320	studies similar to those noted by Wang et al. (2008) in the Tyrone yellow sulfate-bearing soils.
321	The dehydration of ferricopiapite in Tyrone yellowish soil after exposure would suggest a very
322	different temperature and relative humidity environment within the subsurface. In another
323	examination of the data, Rice et al. (2011) studied the same Pancam observations and concluded
324	that temporal variations in Pancam spectra were more consistent with deposition of airfall dust
325	than with mineralogical changes, suggesting that the bright soils were stable over the observation
326	timescales (100+ sols). Further analysis of these data appear warranted to resolve differences in
327	interpretation.
328	Finally, the presence of a drop in reflectance from the 934 (R6) to 1009 nm (R7) band in
329	some of the sulfate-bearing soils (such as the Arad white soil spectrum in Fig. 11B and Fig. 12)

is potentially evidence of the presence of a water overtone feature centered near 1000 nm. This

drop in reflectance was recognized as a feature of the Tyrone white soils by Wang et al. (2008)

and was discussed as a possible hydration feature by Wang et al. (2008) and Wang and Ling

333 (2011).

Ca-Sulfate Minerals Encountered by Opportunity. Most of Opportunity's traverse on 334 335 the flat terrain of Meridiani Planum was over sulfate-bearing bedrock, as confirmed by 336 Mössbauer (Klingelhöfer et al., 2004) and Mini-TES observations (Glotch et al., 2006). 337 However, spectral features in the Pancam VNIR spectral range that could clearly be assigned to 338 sulfate minerals in the Burns formation bedrock of Meridiani Planum were lacking. Upon 339 reaching the rim of Endeavour crater, Opportunity has encountered at least two types of sulfate-340 bearing materials which have spectral features observable in the Pancam spectral range: gypsum 341 veins and light-toned subsurface rock coatings. 342 In its traverse over the Cape York rim segment of Endeavour crater, examples of light-343 toned materials in linear to curvilinear veins were observed intermittently in Opportunity's 344 Navcam images over the course of the traverse along Cape York. On the northwest bench of 345 Cape York, Opportunity examined one of these veins *in situ*, the Homestake target (Squyres et 346 al., 2012) (Fig. 13). Since that first examination, a number of veins have been examined *in situ* 347 (most on the Endeavour rim bench unit). However, thinner veins on the Matijevic Hill portion of 348 Cape York (in the Matijevic formation), and veins in the rim segments south of Cape York were 349 also encountered. While displaying higher Ca and S in APXS results, the case for identifying the 350 veins as consisting of the hydrated mineral gypsum $[CaSO_4 \cdot 2(H_2O)]$ was bolstered by the drop 351 in reflectance from the Pancam R6 to R7 bands (934 to 1009 nm), which was attributed to a 1.0 352 μ m H₂O overtone feature (Cloutis et al., 2006; Rice et al., 2010). The equivalent overtone feature 353 in bassanite $[CaSO4 \cdot 0.5H_2O]$ occurs at 0.95 µm and anhydrite $[CaSO_4]$ is anhydrous and thus 354 does not have this absorption feature. Gypsum laboratory reflectance spectra convolved to the 355 Pancam bandpasses show this 934 to 1009 nm drop in reflectance (Fig. 14). This drop in 356 reflectance caused by a 1000 nm water overtone band has also been observed by multispectral

imaging of light-toned veins using the Mastcam on the Mars Science Laboratory Curiosity rover(Vaniman et al., 2014; Wellington et al., this issue).

359 Ca-sulfates in the form of gypsum would precipitate at temperatures lower than basanite 360 and anhydrite. The retaining of the highest hydration degree (as gypsum) is consistent with its 361 extremely slow dehydration rate under current Mars surface conditions that was experimentally 362 evaluated by Robertson and Bish (2013).

363 The gypsum veins observed by Opportunity are also characterized by high 535 nm band 364 depth values. Terrestrial gypsum veins formed in ferric oxide-rich sediments often incorporate 365 some of those ferric oxide-rich grains into the vein and this is likely the case with the veins 366 observed on the Endeavour rim. Farrand et al. (2014) found spectral differences between the 367 veins observed on the bench unit of Cape York and those occurring in the Matijevic Hill area. 368 These two sets of veins also expressed differences when compared against the spectrally similar 369 boxwork veins such as those hosting the Lihir and Esperance targets discussed below. The 370 spectral differences between the bench unit veins, those on Matijevic Hill and the boxwork 371 fracture fills are expressed primarily in terms of parameters related to the presence and/or degree 372 of crystallinity of ferric oxide minerals such as 535 nm band depth and 754 to 1009 nm slope. 373 Fig. 15 shows a spectral parameter plot of the Cape York bench unit and Matijevic formation 374 veins for the 754 to 1009 nm slope and 535 nm band depth parameters indicating spectral 375 differences between the two sets of veins. The Matijevic formation veins have an overall flatter 376 NIR spectral shape while the Cape York bench units have an overall red slope in the NIR leading 377 to positive 754 to 1009 nm slopes. The higher 535 nm band depth of the Cape York bench veins 378 also indicates a higher fraction of crystalline ferric oxides. Differences between the veins in 379 terms of the parameter related to the 1000 nm hydration feature, the drop in reflectance from 934

to 1009 nm, are minimal as can be seen in Fig. 10 of Farrand et al. (2014). Spectral differences
between the different sets of veins potentially indicate different episodes of fluid flow and vein
formation.

383 Mg-Sulfates Encountered on Murray Ridge. Arvidson et al. (this issue) describe the 384 Pinnacle Island and Stuart Island rocks overturned by Opportunity on the Murray Ridge portion 385 of the Endeavour rim. As noted above, these rocks were characterized by both a dark, nominally 386 Mn oxide-bearing coating and by a light-toned coating with a 934 to 1009 nm downturn in 387 reflectance similar to that in the gypsum veins (Fig. 16A). As noted by Rice et al. (2010) a 388 number of hydrated or hydroxylated minerals display a 1 um overtone feature that at Pancam 389 spectral resolution would display the R6 to R7 drop in reflectance. 390 The Pinnacle and Stuart Island APXS observations that were centered principally over 391 the light-toned portions of those rocks showed high Mg and S values- indicating the presence of 392 Mg sulfate minerals (Arvidson et al., this issue). Kieserite $[MgSO_4 \cdot H_2O]$ and epsomite 393 [MgSO₄•7H₂O] both display drops in reflectance in the longest Pancam channel (**Fig. 16B**). For 394 epsomite, the H₂O absorption is broader leading to a decrease in reflectance extending to 395 Pancam's R6 (934 nm) and R5 (904 nm) bands. Hence, the multispectral evidence from Pancam 396 is consistent with the light-toned coatings on Pinnacle and Stuart Island containing a Mg sulfate 397 phase, potentially kieserite.

398

399 Hydrated Silica

400 One of the most striking discoveries of the Spirit mission was the discovery of nearly-

401 pure hydrated silica in a subsurface soil in the "Eastern Valley" on the eastern side of Home

- 402 Plate. The highest Si content (> 90 wt.%) was in the Gertrude Weise (Fig. 17B) soil target
- 403 (Squyres et al., 2008). The "white" soils at the sulfate-bearing exposures Tyrone and Troy also

404	were found to contain a SiO ₂ component (Wang et al., 2008; Arvidson et al., 2011). SiO ₂ made
405	up 32.9% of the Mt. Darwin observation within the Tyrone soils (Ming et al., 2008) and up to
406	46% of the Tyrone soils (Arvidson et al., 2011). Friable, nodular outcrops containing significant
407	amounts of hydrated silica $(61.8 - 72.8 \text{ wt.\%})$ were also observed in the vicinity of Home Plate
408	(Fig. 17A). The Si-rich deposits have been alternatively interpreted as volcanic fumarolic
409	deposits (Squyres et al., 2008) or as the result of precipitation from geothermal waters (Ruff et
410	al., 2011; Wang et al., 2008). Recently morphologic similarities have been observed between the
411	Si-rich nodules in the Eastern Valley and high-altitude silica sinter deposits in the El Tatio hot
412	springs region in Chile (Ruff, 2015; Nicolau et al., 2014).
413	The soil and nearby silica-rich outcrops are spectrally distinct from other Gusev crater
414	materials in VNIR wavelengths: Wang et al. (2008) identified a drop in reflectance from 934 to
415	1009 nm that characterizes Pancam spectra of all known hydrated silica targets observed by
416	Spirit, which Rice et al. (2010) showed is due to the $2v_1 + v_3 H_2O$ combination band and/or the
417	3ν OH overtone centered near ~1000 nm. In a study of these spectral features in terrestrial high-
418	silica materials, Rice et al. (2013) showed that most opaline silica samples exhibit these features
419	near ~950-960 nm, which is between Pancam's R6 and R7 filters and would thus be undetectable
420	to the instrument. However, the spectra of water-saturated silica reproduce the spectral downturn
421	at 1009 nm that characterizes the Pancam silica spectra, leading to the interpretation that the
422	silica-rich materials observed by MER Spirit must contain large amounts of free water contained
423	in voids or adsorbed onto the silica surface.
424	The silica-rich materials are characterized by flat NIR spectra from 864 to 934 nm, which
425	allows the narrow hydration band to be distinguished from broad absorptions near 1000 nm in

426 the spectra of iron-bearing minerals. The broader ferric or ferrous iron absorptions near 1000 nm

result in lower reflectance in additional Pancam bands besides the R7 (1009 nm) band- e.g. these 427 428 absorptions reduce the reflectance in the R6 (934 nm) down to the R4 (864 nm) bands, or to even 429 shorter wavelengths. Using criteria based on these parameters, Rice et al. (2010) defined a 430 Pancam "hydration signature" that characterizes the spectra of the hydrated minerals to which the 431 instrument is sensitive (including hydrated silica, some hydrated Mg- and Ca-sulfates, water ice, 432 and some carbonates). Rice et al. (2010) showed that the Pancam spectra of some dust-covered 433 rock surfaces can mimic the hydration signature when tilted away from the rover's line of sight 434 and/or when viewed at very low Sun elevations. To avoid these false detections, the Pancam 435 hydration signature has typically only been used to identify potentially hydrated materials in 436 observations made at low (~0°-30°) incidence (i) and emission (e) angles. The contributing 437 factors to the negative 934 to 1009 nm spectral slope of these rock surfaces have not yet been 438 fully identified, but Rice et al. (2010) proposed two main hypotheses: (1) the NIR slope is due to 439 hydration in the Martian surface dust; or (2) the NIR slope effect is due to Pancam calibration 440 inaccuracies at specific viewing geometries. Example hydrated silica outcrop and soils are shown 441 in **Fig. 17C**. This Pancam hydration signature has since been used to interpret the mineralogy of 442 other high-silica surface targets at Gusev crater (e.g., Ruff et al., 2011; Arvidson et al., 2011) and 443 hydrated Ca-sulfate at Meridiani Planum (Squyres et al., 2012; Farrand et al., 2013a, b, 2014) 444 (Section 3.2.2.1).

445

446 **Phyllosilicate-bearing Outcrops**

By the time that Opportunity reached the rim of Endeavour crater, its instruments that
were most sensitive to diagnostic mineral identification (Mössbauer spectrometer and MiniTES), had ceased to function. However, through the orbital reflectance spectroscopy of CRISM
and rover observations, the Whitewater Lake type outcrops of the Matijevic formation (Fig. 18A)

and 18B) were identified as being the host of a weak Fe-smectite signature (Arvidson et al.,
2014). Also, in its exploration of the Matijevic Hill area, Opportunity encountered
morphologically distinctive boxwork structures (Fig. 18C). APXS examination of the lighttoned fracture fill material of these structures indicated Al- and Si-rich compositions which
geochemical modeling (Arvidson et al., 2014; Clark et al., this issue) was consistent with Al
smectite compositions plus a potential hydrated silica component.

Pancam spectra of the Whitewater Lake type outcrops could be divided into the lighttoned, fine-grained matrix materials exemplified by the Azilda IDD location (Fig. 18A) and the
darker-toned coatings such as the Chelmsford IDD target (Fig. 18B). Spectra of these materials
are shown in Fig. 19.

461 The light-toned matrix materials are characterized by a broad reflectance peak centered 462 near 770 nm and negative slope from 864 to 1009 nm. The darker-toned coatings exhibit a more 463 convex reflectance peak and weak near-infrared absorption centered near 950 nm and also a 464 higher 535 nm band depth than the matrix materials. The deeper 535 and 904 nm band depths 465 were noted by Farrand et al. (2014) as being consistent with the coatings having more partially to 466 well-crystalline ferric iron minerals than are present in the matrix materials. Also, while not 467 diagnostic of the presence of nontronite, a third degree polynomial fitted to the four bands from 468 864 to 1009 nm of the dark coatings has a median band minimum of 950 nm which is close to 469 the continuum-removed band center of nontronite of 955 to 960 nm.

In an exploratory "walk-about" of Matijevic Hill, Opportunity observed the presence of
boxwork structures in several locations. A prominent boxwork structure, with thick, light-toned
fracture-fill materials was briefly examined with the rover's MI and APXS at the Lihir target.

473 The APXS indicated that Lihir had the highest Al and Si yet detected in any target examined by

474 Opportunity to that time (Al₂O₃ of 12.92% and SiO₂ of 58.44%; Clark et al., this issue).

475 Opportunity returned to this fracture fill in order to investigate it more fully with a RAT brush 476 and grind on a new target, Esperance (yellow circle in **Fig. 18C**). The geochemistry of the 477 Esperance target is described by Clark et al. (this issue). Pancam spectra of the Lihir/Esperance 478 fracture fill resembled the gypsum veins observed on the bench of Cape York and on Matijevic 479 Hill with a high reflectance, relatively high 535 nm band depth, and a convex shape in the NIR 480 with a drop in reflectance from the Pancam R6 to R7 bands (934 to 1009 nm) (Fig. 20). 481 However, in terms of more subtle spectral parameters, the boxwork fracture fills have lower 535 482 nm band depths and have a fifth degree polynomial fitted band position with a median position 483 shorter than that of both sets of gypsum veins (Fig. 21). 484 Also, since geochemical modeling of Esperance has allowed for the possibility of excess 485 silica (Clark et al., this issue), the presence of the 934 to 1009 nm drop of reflectance, suggests 486 the presence of hydrated silica, potentially similar to that observed by Spirit in the Eastern Valley 487 near Home Plate (section 3.3). Representative spectra from the Eastern Valley nodules (broken 488 surfaces from the Innocent Bystander target which was rolled over by Spirit) are compared 489 against a wind-abraded, light-toned portion of Esperance in **Fig. 22**. Although similar, the NIR 490 reflectance of the Si nodules is flat whereas that of Esperance is more convex. Also, as shown in 491 Fig. 23, the Si nodules have a lower 754 to 1009 nm slope and a higher R6/R7 (934/1009 nm) 492 ratio compared to Esperance and Lihir measurements. If the 934 to 1009 nm drop in reflectance 493 in Esperance is attributable to hydrated silica, the higher R6/R7 ratio of the Eastern Valley Si-494 rich nodules is nominally attributable to a higher fraction of hydrated silica (62 to 69% SiO_2 in 495 the Innocent Bystander target) in the nodules compared to Esperance. Esperance has $\sim 66\%$ 496 SiO₂, most of which Clark et al. (this issue) attribute to montmorillonite (which does not have the

497	934 to 1009 nm drop in reflectance when convolved to Pancam bandpasses), but the geochemical
498	modeling of those authors attributes one-sixth to one-fourth of the SiO_2 to silica and thus
499	Esperance would have a lower fraction of hydrated silica compared to the Eastern Valley silica
500	nodules and this would be consistent with the lower R6/R7 ratio compared to the silica nodules.
501 502	
503	Key Observations for Mineralogical Identifications
504	The multispectral reflectance measurements provided by the Pancam on both Spirit and
505	Opportunity have provided complementary information on rocks and soils to that provided by
506	the other MER instruments. Since the loss of Opportunity's Mini-TES and Mössbauer
507	spectrometers, Pancam has become the only instrument on the rover providing mineralogical
508	constraints. In this paper, we highlight instances in which Pancam multispectral observations
509	have contributed to mineralogical identifications. These include:
510	
511	1. The observation of red hematite in multiple locations visited by Opportunity including
512	Burns and Grasberg formation outcrops and the gray hematite spherules, interpreted as
513	concretions, that weather out of the Burns formation outcrop and that blanket the
514	Meridiani Planum plains.
515	
516	2. Dark coatings with a "red" (reflectance increasing with increasing wavelength) generally
517	featureless slope that are consistent with Mn oxides. These coatings include more Mn-
518	rich coatings on the overturned rocks Pinnacle and Stuart Island and the previously
519	unreported on "blue" coatings on some Grasberg formation outcrops.
520	

521	3.	The observation of spectral features consistent with Fe-bearing sulfate minerals at several
522		exposures of sulfur-rich soils excavated from the subsurface by the wheels of the Spirit
523		rover and examined in situ by Spirit.
524		
525	4.	The 934 to 1009 nm drop in reflectance in Si-rich light toned soils and nodules in the
526		Eastern Valley of the Home Plate region examined by Spirit have been attributed to free
527		water contained in voids or adsorbed onto the surface of the silica associated with these
528		materials.
529		
530	5.	The drop in reflectance associated with a 1 μ m water overtone feature in gypsum veins
531		on the bench of the Cape York rim segment of Endeavour crater, another set of gypsum
532		veins exposed in the outcrop of Matijevic Hill, also on Cape York, and gypsum veins
533		observed on the southern rim segment of Murray Ridge/Cape Tribulation.
534		
535	6.	The light-toned coatings on the overturned rocks Pinnacle and Stuart Island, which
536		display enrichments in Mg and S as determined by the APXS, have a drop in reflectance
537		from 934 to 1009 nm that is consistent with the spectra of some Mg sulfate minerals,
538		specifically kieserite.
539		
540	7.	The 934 to 1009 nm drop in reflectance that is observed in gypsum veins was also
541		observed in the Al and Si rich fracture fills in boxwork structures on Matijevic Hill.
542		Based on APXS modeled geochemistry (Clark et al., this issue) this feature, also

attributed to a H₂O overtone absorption, is more likely caused by hydrated silica in the 543 544 fracture fill material. 545 Implications 546 547 The ability to detect minerals altered by aqueous activity using visible and near-infrared (VNIR) multispectral imaging data on the surface of Mars has been demonstrated in this paper. 548 549 This ability has relevance for the Opportunity's on-going exploration of the western rim of 550 Endeavour Crater. The use of Pancam for the definition of spectrally unique materials is 551 especially important in the near term for Opportunity's exploration of the Marathon Valley area 552 where orbital data has indicated the presence of phyllosilicate minerals. Also, the potential to use VNIR multispectral imaging for the detection of aqueous alteration minerals also has 553 554 importance for the use of the Curiosity rover's Mastcam and will be used in the future with the 555 ExoMars PanCam and the Mars 2020 Mastcam-Z. 556 557 558 Acknowledgements 559 The first author is supported as a Participating Scientist on MER through the Jet 560 Propulsion Laboratory. We would like to thank Ralf Gellert of the University of Guelph for 561 helpful discussions on APXS results. We also thank Ed Cloutis and an anonymous reviewer for 562 helpful reviews. 563 564

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References

566	Anderson, R.B. and Bell, J.F. III (2013) Correlating multispectral imaging and compositional
567	data from the Mars Exploration Rovers and implications for Mars Science Laboratory. Icarus,
568	223, 157-180.
569	
570	Arvidson, R.E., Seelos, F.P. IV, Deal, K.S., Koeppen, W.C., Snider, N.O., Kieniewicz, J.M.,
571	Hynek, B.M., Mellon, M.T., and Garvin, J.B. (2003) Mantled and exhumed terrains in Terra
572	Meridiani, Mars. Journal of Geophysical Research-Planets, 108, No. E12, doi:
573	10.1029/2002JE001982.
574	
575	Arvidson, R.E., Ruff, S.W., Morris, R.V., Ming, D.W., Crumpler, L.S., Yen, A.S., Squyres,
576	S.W., Sullivan, R.J., Bell, J.F. III, Cabrol, N.A., and others (2008) Spirit Mars Rover Mission
577	to the Columbia Hills, Gusev Crater: Mission overview and selected results from the
578	Cumberland Ridge to Home Plate. Journal of Geophysical Research-Planets, 113, E12S33,
579	doi:10.1029/2008JE003183.
580	
581	Arvidson, R.E., Ashley, J.W., Bell, J.F. III, Chojnacki, M., Cohen, J., Economou, T.E., Farrand,
582	W.H., Fergason, R., Fleischer, I., Geissler, P., and others (2011) Opportunity Mars Rover
583	mission: Overview and selected results from Purgatory ripple to traverses to Endeavour
584	crater. Journal of Geophysical Research-Planets, 116, E00F15, doi:10.1029/2010JE003746.
585	
586	Arvidson, R.E., Squyres, S.W., Bell, J.F. III, Catalano, J.G., Clark, B.C., Crumpler, L.S., De
587	Souza, P.A., Fairen, A.G., Farrand, W.H., Fox, V.K., and Gellert, R. (2014) Ancient aqueous
588	environments at Endeavour Crater, Mars. Science, 343, doi:10.1126/science.1248097.

209	J	8	9
-----	---	---	---

590	Arvidson, R.E., Squyres, S.W., Morris, R.V., Knoll, A.H., Gellert, R., Clark, B.C., Catalano,
591	J.G., Jolliff, B.L., McLennan, S.M., Herkenhoff, K.E., and others (2016) High concentration
592	manganese and sulfur-bearing deposits on Murray Ridge, Endeavour crater, Mars. American
593	Mineralogist, in press.
594	
595	Bell, J.F III (1996) Iron, sulfate, carbonate, and hydrated minerals on Mars. In M.D. Dyer, C.
596	McCammon, and M.W. Schaefer, Eds., Mineral Spectroscopy: A Tribute to Roger G. Burns,
597	Geochem. Soc. Spec. Pub. No. 5, p. 359-380, Houston.
598	
599	Bell, J.F. III, Squyres, S.W., Herkenhoff, K.E., Maki, J.N., Arneson, H.M., Brown, D., Collins,
600	S.A., Dingizian, A., Elliot, S.T., Hagerott, E.C., and others (2003) The Mars Exploration
601	Rover Athena Panoramic Camera (Pancam) Investigation. Journal of Geophysical Research-
602	Planets, 108, doi:10.1029/2003JE002070.
603	
604	Bell, J.F. III, Joseph, J., Sohl-Dickstein, J.N., Arneson, H.M., Johnson, M.J., Lemmon, M.T., and
605	Savransky, D. (2006) In-flight calibration and performance of the Mars Exploration Rover
606	Panoramic Camera (Pancam) instruments. Journal of Geophysical Research-Planets,
607	111, E02S03, doi:10.1029/2005JE002444.
608	
609	Bell, J.F. III, Godber, A., Rice, M.S., Fraeman, A.A., Ehlmann, B.L., Goetz, W., Hardgrove,
610	C.J., Harker, D.E., Johnson, J.R., Kinch, K.M., and others (2013) Initial multispectral imaging

- 611 results from the Mars Science Laboratory Mastcam investigation at the Gale crater field site.
- 612 44th Lunar and Planetary Science Conference, abstract #1417.
- 613
- Burns, R.G. (1987) Ferric sulfates on Mars. Proceedings of the 17th Lunar and Planetary Science
- 615 Conference, Journal of Geophysical Research, 92, E570-E574.
- 616
- 617 Cabrol, N.A., Grin, E.O., Carr, M.H., Sutter, B., Moore, J.M., Farmer, J.D., Greeley, R.,
- 618 Kuzmin, R.O., DesMarais, D.J., Kramer, M.G., and others (2003) Exploring Gusev Crater
- 619 with Spirit: Review of science objectives and testable hypotheses. Journal of Geophysical
- 620 Research-Planets, 108 (E12), 8076, doi:10.1029/2002JE002026.
- 621
- 622 Christensen, P.R., Bandfield, J.L., Clark, R.N., Edgett, K.S., Hamilton, V.E., Hoefen, T., Kieffer,
- H.H., Kuzmin, R.O., Lane, M.D., Malin, M.C., and others (2000) Detection of crystalline
- hematite mineralization on Mars by the Thermal Emission Spectrometer: Evidence for near-
- surface water, Journal of Geophysical Research-Planets. 105, 9623-9642.
- 626
- 627 Clark, B.C., Morris, R.V., McLennan, S.M., Gellert. R., Jolliff, B.L., Knoll, A.H., Squyres, S.W.,
- 628 Lowenstein, T.K., Ming, D.W., Tosca, N.J. and Yen, A. (2005) Chemistry and mineralogy of
- outcrops at Meridiani Planum. Earth and Planetary Science Letters, 240, 73–94.
- 630
- 631 Clark, B.C., Morris, R.V., Herkenhoff, K.E., Farrand, W.H., Gellert. R., Jolliff, B.L., Arvidson,
- 632 R.E., Squyres, S.W., Mittlelfehldt, D.W., Ming, D.W., and Yen A. (2016) Esperance:

- 633 Multiple episodes of aqueous alteration involving fracture fills and coatings at Matijevic Hill,
- 634 Mars. American Mineralogist, in press.

635

- 636 Clark, R.N., Swayze, G.A., Wise, R., Livo, E., Hoefen, T., Kokaly, R., and Sutley, S.J. (2007)
- 637 USGS digital spectral library splib06a, U.S. Geological Survey, Digital Data Series 231.
- 638
- 639 Cloutis, E.A., Hawthorne, F.C., Mertzman, S.A., Krenn, K., Craig, M.A., Marcino, D., Methot,

640 M., Strong, J., Mustard, J.F., Blaney, D.L., and Bell, J.F. (2006) Detection and discrimination

- of sulfate minerals using reflectance spectroscopy. Icarus, 184, 121-157.
- 642
- 643 Cousins, C.R., Gunn, M., Prosser, B.J., Barnes, D.P., Crawford, I.A., Griffiths, A.D., Davis, L.E.
- and Coates, A.J. (2012) Selecting the geology filter wavelengths for the ExoMars Panoramic
- Camera instrument. Planetary and Space Science, 71, 80-100, doi:10.1016/j.pss.2012.07.009.
- 647 Crumpler, L.S., Arvidson, R.E., Bell, J., Clark, B.C., Cohen, B.A., Farrand, W.H., Gellert, R.,
- 648 Golombek, M., Grant, J.A., Guinness, E., and Herkenhoff, K.E. (2015) Context of ancient
- 649 aqueous environments on Mars from in situ geologic mapping at Endeavour Crater. Journal of

650 Geophysical Research-Planets, 120, 538–569, doi:10.1002/2014JE004699.

- 651
- Farrand, W.H., Bell, J.F. III, Johnson, J.R., Squyres, S.W., Soderblom, J., and Ming, D.W.
- 653 (2006) Spectral variability among rocks in visible and near infrared multispectral Pancam data
- 654 collected at Gusev Crater: Examinations using spectral mixture analysis and related
- techniques. Journal of Geophysical Research-Planets, 111, E02S15, 10.1029/2005JE002495.

6	5	6

657	Farrand, W.H., Bell, J.F. III, Johnson, J.R., Jolliff, B.L., Knoll, A.H., McLennan, S.M., Squyres,
658	S.W., Calvin, W.M., Grotzinger, J.P., Morris, R.V. and Soderblom, J. (2007) Visible and
659	near-infrared multispectral analysis of rocks at Meridiani Planum, Mars by the Mars
660	Exploration Rover Opportunity. Journal of Geophysical Research-Planets, 112, E06S02,
661	10.1029/2006JE002773.
662	
663	Farrand, W.H., Bell, J.F. III, Johnson, J.R., Arvidson, R.E., Crumpler, L.S., Hurowitz, J.A., and
664	Schröder, C. (2008) Rock spectral classes observed by the Spirit rover's Pancam on the Gusev
665	crater plains and in the Columbia Hills, Journal of Geophysical Research-Planets. 113,
666	E12S38, doi:10.1029/2008JE003237.
667	
668	Farrand, W.H., Bell, J.F., Johnson, J.R., Rice, M.S., and Hurowitz, J.A. (2013a) VNIR
669	multispectral observations of rocks at Cape York, Endeavour crater, Mars by the Opportunity
670	rover's Pancam. Icarus, 225, 709-725.
671	
672	Farrand, W.H., Ruff, S.W., Rice, M.S., Rice, J.W. Jr., Arvidson, R.E., Jolliff, B.L., Squyres,
673	S.W., Knoll, A.H., Bell, J.F. III, and Johnson, J.R. (2013b) Veins in Matijevic Hill lithologic
674	units observed by Opportunity, 44 th Lunar and Planetary Science Conference, abstract #2482.
675	
676	Farrand, W.H., Bell, J.F. III, Johnson, J.R., Rice, M.S., Jolliff, B.L., and Arvidson, R.E. (2014)
677	Observations of rock spectral classes by the Opportunity rover's Pancam on northern Cape

- 678 York and on Matijevic Hill, Endeavour Crater, Mars. Journal of Geophysical Research-
- 679 Planets, 119, doi:10.1002/2014JE004641.
- 680
- 681 Fox, V.K., Arvidson, R.E., Jolliff, B.L., Carpenter, P.K., Catalano, J.G., Hinkle, M.A.G., and
- 682 Morris, R.V. (2015) Characterization of synthetic and natural manganese oxides as martian

analogues. 46th Lunar and Planetary Science Conference, abstract #2132.

684

- Glotch, T.D., Bandfield, J.L., Christensen, P.R., Calvin, W.M., McLennan, S.M., Clark, B.C.,
- Rogers, A.D., and Squyres, S.W. (2006) Mineralogy of the light-toned outcrop at Meridiani
- 687 Planum as seen by the Miniature Thermal Emission Spectrometer and implications for its
- formation. Journal of Geophysical Research-Planets, 111, E12S03,
- 689 doi:10.1029/2005JE002672.
- 690
- 691 Greeley, R., Kuzmin, R.O., Rafkin, S.C., Michaels, T.I., and Haberle, R. (2003) Wind-related
- features in Gusev crater. Mars, Journal of Geophysical Research-Planets, 108, 8087,
- 693 doi:10.1029/2002JE002006.
- 694
- 695 Grotzinger, J.P., Arvidson, R.E., Bell, J.F., Calvin, W., Clark, B.C., Fike, D.A., Golombek, M.,
- 696 Greeley, R., Haldemann, A., Herkenhoff, K.E., and Jolliff, B.L. (2005) Stratigraphy and
- 697 sedimentology of a dry to wet eolian depositional system, Burns formation, Meridiani
- 698 Planum, Mars. Earth and Planetary Science Letters, 240, 11–72.

700	Haskin, L.A. Wang, A., Jolliff, B.L., McSween, H.Y., Clark, B.C., Des Marais, D.J., McLennan,
701	S.M., Tosca, N.J., Hurowitz, J.A., Farmer, J.D., and Yen, A. (2005) Water alteration of rocks
702	and soils on Mars at the Spirit rover site in Gusev crater. Nature, 436, 66-70.
703	
704	Johnson, J.R., Bell, J.F. III, Cloutis, E., Staid, M., Farrand, W.H., McCoy, T., Rice, M., Wang,
705	A. and Yen, A. (2007) Mineralogic constraints on sulfur-rich soils from Pancam spectra at
706	Gusev crater, Mars. Geophysical Research Letters, 34, L13202,
707	doi:10.1029/2007GL9029894.
708	
709	Kiely, A. and Klimesh, M. (2003) The ICER progressive wavelet image compressor. IPN
710	Progress Report, 42, p.1-46.
711	
712	Klingelhöfer, G., Morris, R.V., Bernhardt, B., Schröder, C., Rodionov, D.S., De Souza, P.A.,
713	Yen, A., Gellert, R., Evlanov, E.N., Zubkov, B., and Foh, J. (2004) Jarosite and Hematite at
714	Meridiani Planum from Opportunity's Mössbauer Spectrometer. Science, 306, 1740-1745.
715	
716	Lanza, N.L., Fischer, W.W., Wiens, R.C., Grotzinger, J., Ollila, A.M., Cousin, A., Anderson,
717	R.B., Clark, B.C., Gellert, R., Mangold, N. and Maurice, S. (2014) High manganese
718	concentrations in rocks at Gale crater, Mars. Geophysical Research Letters, 41, 5755-5763,
719	doi:10.1002/2014GL060329.

721	Lane, M.D., Morris, R.V., and Christensen, P.R. (1999) Spectral behavior of hematite at
722	visible/near infrared and mid-infrared wavelengths, 5 th International Conference on Mars,
723	abstract #6085.
724	
725	Lane, M.D., Bishop, J.L., Dyar, M.D., King, P.L., Parente, M., and Hyde, B.C. (2008)
726	Mineralogy of the Paso Robles soils on Mars. American Mineralogist, 93, 728-739.
727	
728	McLennan, S.M., Bell, J.F. III, Calvin, W.M., Christensen, P.R., Clark, B.D., De Souza, P.A.,
729	Farmer, J., Farrand, W.H., Fike, D.A., Gellert, R. and Ghosh, A. (2005) Provenance and
730	diagenesis of the Burns Formation, Meridiani Planum, Mars. Earth and Planetary Science
731	Letters, 240, 95–121.
732	
733	Ming, D.W., Mittlefehldt, D.W., Morris, R.V., Golden, D.C., Gellert, R., Yen, A., Clark, B.C.,
734	Squyres, S.W., Farrand, W.H., Ruff, S.W., and Arvidson, R.E. (2006), Geochemical and
735	mineralogical indicators for aqueous processes in the Columbia Hills of Gusev crater,
736	Mars. Journal of Geophysical Research-Planets, 111, E02S12, doi:10.1029/2005JE002560.
737	
738	Ming, D.W., Gellert, R., Morris, R.V., Arvidson, R.E., Brueckner, J., Clark, B.C., Cohen, B.A.,
739	d'Uston, C., Economou, T., Fleischer, I., and Klingelhöfer, G. (2008) Geochemical properties
740	of rocks and soils in Gusev Crater, Mars: Results of the Alpha Particle X-Ray Spectrometer
741	from Cumberland Ridge to Home Plate, Journal of Geophysical Research-Planets. 113,
742	E12S39, doi:10.1029/2008JE003195.
743	

744	Morris, R.V., Klingelhöfer, G., Schröder, C., Rodionov, D.S., Yen, A., Ming, D.W., De Souza,
745	P.A., Fleischer, I., Wdowiak, T., Gellert, R., and Bernhardt, B (2006) Mössbauer mineralogy
746	of rock, soil, and dust at Gusev crater, Mars: Spirit's journey through weakly altered olivine
747	basalt on the plains and pervasively altered basalt in the Columbia Hills. Journal of
748	Geophysical Research-Planets. 111, E02S13, doi:10.1029/2005JE002584.
749	
750	Morris, R. V., Klingelhöfer, G., Schröder, C., Fleischer, I., Ming, D.W., Yen, A.S., Gellert, R.,
751	Arvidson, R.E., Rodionov, D.S., Crumpler, L.S., and Clark, B.C. (2008) Iron mineralogy and
752	aqueous alteration from Husband Hill through Home Plate at Gusev Crater, Mars: Results
753	from the Mössbauer instrument on the Spirit Mars Exploration Rover. Journal of Geophysical
754	Research-Planets. 113, E12S42, doi:10.1029/2008JE003201.
755	
756	Nicolau, C., Reich, M., Lynne, B. (2014) Physico-chemical and environmental controls on
757	siliceous sinter formation at the high-altitude El Tatio geothermal field, Chile. Journal of
758	Volcanology and Geothermal Research, 282, 60-76.
759	
760	Noe Dobrea, E.Z., Wray, J.J., Calef, F.J., Parker, T.J., and Murchie, S.L. (2012) Hydrated
761	minerals on Endeavour Crater's rim and interior, and surrounding plains: New insights from
762	CRISM data. Geophysical Research Letters, 39, doi:10.1029/2012GL053180.
763	
764	Potter, R.M. and Rossman, G.R. (1979) Mineralogy of manganese dendrites and coatings.
765	American Mineralogist, 64, 1219-1226.

767	Reid, R.J., Smith, P.H., Lemmon, M., Tanner, R., Burkland, M., Wegryn, E., Weinberg, J.,
768	Marcialis, R., Britt, D.T., Thomas, N., and Kramm, R. (1999) Imager for Mars Pathfinder
769	(IMP) image calibration. Journal of Geophysical Research-Planets, 104, 8907-8926.
770	
771	Rice, M.S., Bell, J.F. III, Cloutis, E.A., Wang, A., Ruff, S.W., Craig, M.A., Bailey, D.T.,
772	Johnson, J.R., de Souza, P.A., and Farrand, W.H. (2010) Silica-rich deposits and hydrated
773	minerals at Gusev Crater, Mars: Vis-NIR spectral characterization and regional mapping.
774	Icarus, 205, 375-395.
775	
776	Rice, M.S., Bell, J.F. III, Cloutis, E.A., Wray, J.J., Herkenhoff, K.E., Sullivan, R., Johnson, J.R.,
777	and Anderson, R.B. (2011) Temporal observations of bright soil exposures at Gusev crater,
778	Mars. Journal of Geophysical Research-Planets, 116, E00F14, doi:10.1029/2010JE003683.
779	
780	Rice, M.S., Cloutis, E.A., Bell, J.F. III, Bish, D.L., Horgan, B.H., Mertzman, S.A., Craig, M.A.,
781	Renaut, R.W., Gautason, B., and Mountain, B. (2013) Reflectance spectra diversity of silica-
782	rich materials: Sensitivity to environment and implications for detections on Mars. Icarus,
783	223, 499–533. doi:10.1016/j.icarus.2012.09.021.
784	
785	Rieder, R., Gellert, R., Anderson, R.C., Brückner, J., Clark, B.C., Dreibus, G., Economou, T.,
786	Klingelhöfer, G., Lugmair, G.W., Ming, D.W., and Squyres, S.W. (2004) Chemistry of Rocks
787	and Soils at Meridiani Planum from the Alpha Particle X-ray Spectrometer. Science,
788	306, 1746-1749.
789	

790	Ruff, S.W., Christensen, P.R., Glotch, T.D., Blaney, D.L., Moersch, J.E., and Wyatt, M.B.
791	(2008) The mineralogy of Gusev crater and Meridiani Planum derived from the Miniature
792	Thermal Emission Spectrometers on the Spirit and Opportunity rovers. In J.F. Bell III, Ed.,
793	The Martian Surface: Composition, Mineralogy, and Physical Properties, p. 315-338.
794	Cambridge University Press, New York.
795	
796	Ruff, S.W., Farmer, J.D., Calvin, W.M., Herkenhoff, K.E., Johnson, J.R., Morris, R.V., Rice,
797	M.S., Arvidson, R.E., Bell, J.F. III, Christensen, P.R., and Squyres, S.W. (2011)
798	Characteristics, distribution, origin, and significance of opaline silica observed by the Spirit
799	rover in Gusev crater, Mars. Journal of Geophysical Research- Planets, 116, no. E7, E00F23,
800	doi:10.1029/2010JE003767.
801	
802	Ruff, S.W. (2015) New observations reveal a former hot spring environment with high
803	habitability and preservation potential in Gusev crater, Mars. 46 th Lunar and Planetary
804	Science Conference, abstract #1613.
805	
806	Schmidt, M.E., Farrand, W.H., Johnson, J.R., Schröder, C., Hurowitz, J.A., McCoy, T.J., Ruff,
807	S.W., Arvidson, R.E., Des Marais, D.J., Lewis, K.W., and Ming, D.W. (2009) Spectral
808	mineralogical, and geochemical variations across Home Plate, Gusev Crater, Mars indicate
809	high and low temperature alteration. Earth and Planetary Science Letters, 281, 258-266.
810	
811	Singer, R.B. (1982) Spectral evidence for the mineralogy of high-albedo soils and dust on Mars.
812	Journal of Geophysical Research, 87, 10159-10168.

0	1	2
0	T	. 0

814	Sohl-Dickstein, J., Johnson, J.R., Grundy, W.M., Guinness, E., Graff, T., Shepard, M.K.,
815	Arvidson, R.E., Bell, J.F. III, Christensen, P.R., and Morris, R.V. (2005) Modeling
816	Visible/Near-Infrared photometric properties of dustfall on a known substrate. Lunar and
817	Planetary Science Conference XXXVI, abstract #2235.
818	
819	Squyres, S.W., Arvidson, R.E., Blaney, D.L., Clark, B.C., Crumpler, L.S., Farrand, W.H.,
820	Gorevan, S., Herkenhoff, K.E., Hurowitz, J., Kusack, A., and others (2006) The Rocks of the
821	Columbia Hills. Journal of Geophysical Research- Planets, 111, E02S11,
822	10.1029/2005JE002562.
823	
824	Squyres, S.W., Aharonson, O., Clark, B.C., Cohen, B.A., Crumpler, L., De Souza, P.A., Farrand,
825	W.H., Gellert, R., Grant, J., Grotzinger, J.P., and Haldemann, A.F.C. (2007) Pyroclastic
826	activity at Home Plate in Gusev Crater, Mars. Science, 316, 738-742.
827	
828	Squyres, S.W., Arvidson, R.E., Ruff, S., Gellert, R., Morris, R.V., Ming, D.W., Crumpler, L.,
829	Farmer, J.D., Des Marais, D.J., Yen, A., and McLennan, S.M. (2008) Detection of silica-rich
830	deposits on Mars. Science, 320, 1063-1067.
831	
832	Squyres, S.W., Arvidson, R.E., Bell, J.F. III, Calef, F., Clark, B.C., Cohen, B.A., Crumpler,
833	L.A., De Souza, P.A., Farrand, W.H., Gellert, R., and Grant, J. (2012) Ancient impact and
834	aqueous processes at Endeavour crater, Mars. Science, 336, 570-576.

835

836	Vaniman, D. T., Bish, D.L., Ming, D.W., Bristow, T.F., Morris, R.V., Blake, D.F., Chipera, S.J.,
837	Morrison, S.M., Treiman, A.H., Rampe, E.B. and Rice, M.S. (2014) Mineralogy of a
838	mudstone at Yellowknife Bay, Gale Crater, Mars. Science, 343, doi:10.1126/science1243480.
839	
840	Wang, A., Haskin, L.A., Squyres, S.W., Jolliff, B.L., Crumpler, L., Gellert, R., Schröder, C.,
841	Herkenhoff, K., Hurowitz, J., Tosca, N.J. ,and Farrand, W.H. (2006) Sulfate deposition in
842	subsurface regolith in Gusev crater, Mars. Journal of Geophysical Research- Planets. 111,
843	E02S17, doi:10.1029/2005JE002513.
844	
845	Wang, A., Bell, J.F. III, Li, R., Johnson, J.R., Farrand, W.H., Cloutis, E.A., Arvidson, R.E.,
846	Crumpler, L., Squyres, S.W., McLennan, S.M., and Herkenhoff, K.E. (2008) Light-toned
847	salty soils and coexisting Si-rich species discovered by the Mars Exploration Rover Spirit in
848	Columbia Hills. Journal of Geophysical Research- Planets, 113, E12S40,
849	doi:10.1029/2008JE003126.
850	
851	Wang, A., and Ling, Z.C. (2011) Ferric sulfates on Mars: A combined mission data analysis of
852	salty soils at Gusev crater and laboratory experimental investigations. Journal of Geophysical
853	Research- Planets, 116, E00F17, doi:10.1029/2010JE003665.
854	
855	Wellington, D.F., Bell, J.F. III, Johnson, J.R., Kinch, K.M., Rice, M.S., and Fraeman, A.A.
856	(2016) Visible and near infrared spectra of select high-interest science targets within Gale
857	Crater, observed by MSL Mastcam. American Mineralogist, in press.

- 859 Wray, J.J., Noe Dobrea, E.Z., Arvidson, R.E., Wiseman, S.M., Squyres, S.W., McEwen, A.S.,
- 860 Mustard, J.F., and Murchie, S.L. (2009) Phyllosilicates and sulfates at Endeavour Crater,
- 861 Meridiani Planum, Mars. Geophysical Research Letters, 36, L21201,
- doi:10.1029/2009GL040734.
- 863
- Yen, A. S., Morris, R.V., Clark, B.C., Gellert, R., Knudson, A.T., Squyres, S., Mittlefehldt,
- 865 D.W., Ming, D.W., Arvidson, R., McCoy, T. and Schmidt, M. (2008) Hydrothermal processes
- at Gusev Crater: An evaluation of Paso Robles Class soil. Journal of Geophysical Research-
- 867 Planets, 113, E06S10, doi:10.1029/2007JE002978
- 868

870	Figure Captions
871	Figure 1. A. L357 (673, 535, 432 nm) enhanced color view of RATed El Capitan from
872	Opportunity sol 37 (sequence P2532). B. Pancam spectrum of RAT grind interior (red) vs. a
873	library spectrum (from the USGS spectral library, Clark et al., 2007) of red hematite (black,
874	reflectance values of library spectrum divided by 2).
875	
876	Figure 2. A. Library reflectance spectra of coarsely crystalline hematite. B. Average of
877	blueberries from scenes P2556 from sol 45 and from P2585 from sol 51.
878	
879	Figure 3. Full spectral resolution library spectra (Clark et al., 2007; PDS spectral library) of red,
880	dark red, and gray hematite over the Pancam spectral range of 430 to 1010 nm.
881	
882	Figure 4. Sol 33 P2589 L357 (673, 535, 432 nm) stretched color composite of target "Cathedral
883	Dome". Blue arrow indicates the buff-colored "HFS" Burns formation color unit of Farrand et al.
884	(2007) and the black arrow indicates the purple-colored "LFS" Burns formation color unit.
885	
886	Figure 5. A. Representative Pancam spectra (denoted by sol number with the prefix of "B" and
887	Pancam sequence number of "P" plus 4 digits) of Burns formation "LFS" (or purple-colored in
888	typically used color composites) surfaces. B. Representative Grasberg formation surface spectra
889	(after Farrand et al., 2014).
890	

- 891 Figure 6. Plots of spectral parameters discriminating Burns and Grasberg formations. A. Fitted
- NIR band minimum vs. 535 nm band depth (after Farrand et al., 2014). B. 754 to 1009 nm slope
 vs. 535 nm band depth.
- 894
- **Figure 7**. Subsection of sol 3567 P2535 L357 (673, 535, 432 nm) composite shows overturned
- rocks Pinnacle Island (inside green circle) and Stuart Island (inside red circle). Both have the
- 897 light and dark-toned coatings.

- **Figure 8. A**. Dark coating on Pinnacle Island. **B**. Desert varnish spectra from USGS spectral
- 900 library (Clark et al., 2007). The ANP90-14 sample is a desert varnish coating on a sandstone and
- 901 GDS78 is desert varnish coating on rhyolite and quartz cobbles.
- 902
- 903 **Figure 9.** A. L357 (673, 535, 432 nm) view of target Monjon (Sol 3419 P2559). Blue coating
- 904 indicated by arrow. **B**. R731 (1009, 803, 436 nm) view of Monjon. **C**. 535 nm band depth view
- 905 of Monjon. White arrow indicates low 535 nm band depth associated with coating.

906

- Figure 10. Spectra of blue coatings on Grasberg formation exposures observed on sols 3739 and3419.
- 909
- 910 Figure 11. A. L357 (673, 535, 432 nm) composite of Spirit sol 721 P2538 view of Arad soils at
- 911 the Dead Sea site. Red polygon and circle indicate spectral extraction region for "yellow" soil in
- 912 spectral plot of **Fig. 11B** and blue polygon and circle indicate spectral extraction region for

- 913 "white" soil in spectral plot of Fig. 11B. B. White and yellow soils from sol 721 P2538 Arad
- observation. Spectra extracted from sites noted in Fig. 11A.
- 915
- 916 Figure 12 A. Sol 471 P2538 Arad white soil. B. Library spectra, convolved to Pancam
- 917 bandpasses of best match (in mixtures) spectra from Johnson et al. (2007).
- 918
- 919 Figure 13. Opportunity sol 2769 P2574 L357 (673, 535, 432 nm) view of gypsum vein
- 920 "Homestake" in Cape York bench.
- 921
- 922 Figure 14. Library spectra (Cloutis et al., 2006; Clark et al., 2007) of calcium sulfate minerals at
- 923 full spectral resolution over the Pancam spectral range (A) and convolved to Pancam bandpasses
- 924 (B).
- 925
- Figure 15. Plot of 754 to 1009 nm slope vs. 535 nm band depth for gypsum veins observed on
- 927 the bench of Cape York vs. those observed in the Matijevic formation on Matijevic Hill.
- 928
- Figure 16. A. Pinnacle Island bright coating spectrum. B. Library spectra (Clark et al., 2007) of
 Mg sulfate minerals epsomite and kieserite.
- 931
- 932 Figure 17. Silica-rich materials in the Inner Basin of the Columbia Hills of Gusev crater,
- discovered by Spirit. A. Pancam L357 (673, 535, 432 nm) composite of the Innocent Bystander
- nodular outcrop (sol 1294, P2581). **B.** Pancam L357 composite of the Gertrude Weise soil (sol
- 1187, P2533), which contains ~98% SiO₂ (Squyres et al., 2008). The width of the wheel track is

936	~16 cm	C. Pancam relative reflectance spectra of silica-rich targets (see Rice et	al 2010 for
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	TO UII.	C. I and an relative reflectance spectra of sinea fren targets (see free of	, an, 2010 ioi

- 937 further discussion). All spectra exhibit a relatively flat near-infrared profile (864 to 934 nm) and
- a characteristic downturn in the longest-wavelength filter (1009 nm) due to H₂O and/or OH
- absorptions near ~1000 nm. Figure modified from Rice et al., (2013).
- 940
- 941 **Figure 18.** A. Sol 3090 P2571 L357 (673, 535, 432 nm) composite of Whitewater Lake outcrop
- 942 showing the gray-toned Azilda RAT grind spot. B. Sol 3098 P2580 L357 view of the RAT-
- 943 brushed Chelmsford dark-toned coatings target. C. Sol 3262 P2579 L357 composite of
- 944 Lihir/Esperance boxwork structure pre-RAT grind. The Esperance target is circled.
- 945
- 946 Figure 19. A. Matijevic formation Whitewater Lake matrix spectra. B. Matijevic formation
- 947 Whitewater Lake dark coating spectra.
- 948
- 949 **Figure 20**. Representative boxwork fracture fill spectra of targets Esperance and Lihir plus a
- 950 piece of boxwork fracture fill broken by the rover's wheels.
- 951
- **Figure 21. A**. 754 to 1009 nm slope vs. 535 nm band depth for gypsum veins and boxwork
- fracture fills. **B**. Fitted reflectance peak positions vs. 535 nm band depth for gypsum veins and

954 boxwork fracture fills.

- 955
- Figure 22. Comparison of spectra of Esperance light-toned "as-is" surface to that of a broken
 Si-rich nodule surface on the Innocent Bystander target.

958

- 959 Figure 23. R6/R7 ratio vs. 754 to 1009 nm slope of Home Plate Eastern Valley silica nodules
- 960 (values from sol 1279 and 1294 views of broken surfaces on Innocent Bystander) compared with

961 Lihir and Esperance (values from sols 3230 (Lihir) and 3262 (Esperance)).

962

963

Tables

964

Name	Center λ (nm)	Bandpass (nm)	Description
L1	739	338	Empty
L2	753	20	Geology, Red stereo left
L3	673	16	Geology
L4	601	17	Geology
L5	535	20	Geology
L6	482	30	Geology
L7	432	32	Geology, Blue stereo left
L8	440	20	Solar neutral density
R1	436	37	Geology, Blue stereo right
R2	754	20	Geology, Red stereo right
R3	803	20	Geology
R4	864	17	Geology
R5	904	26	Geology
R6	934	25	Geology
R7	1009	38	Geology
R8	880	20	Solar neutral density

965 **Table 1**. Pancam Filters

966

Parameter	Formula	Utility
482 to 673 nm	1000*((R673 -R482)/191)	Gauge of Fe oxidation
slope		
535 nm band depth	1-(R535/((0.57*R432)+(0.43*R673)))	Gauge of development of ferric oxides
601 nm band depth	1-(R601/((0.52*R535)+(0.48*R673)))	Assess convexity near 600 nm
803 nm / 904 nm	R803/R904	Indicator of strength of NIR absorption
		band
803 nm / 1009 nm	R803/R1009	Help distinguish between olivine and
		pyroxene dominated lithologies
904 nm band depth	1-(R904/((0.51*R803)+(0.49*R1009)))	Assess depth of NIR absorption band
754 to 1009 nm	1000*((R1009-R754)/255)	Gauge of hematite development;
slope		indicator of pyroxene, olivine.
934 to 1009 nm	1000*((R1009-R934)/75)	Indicator of H ₂ O overtone band
slope		
Fitted reflectance	Maximum of 5 th degree polynomial	Gauge of Fe oxidation
peak position	fitted to bands from 535 to 904 nm	
Fitted NIR band	Minimum of 3 rd degree polynomial	Distinguish between Fe-bearing phases
minimum position	fitted to bands from 864 to 1009 nm	

969 Table 2. Pancam Spectral Parameters (note that the factor of 1000 in slope calculations is only a

970 scaling factor). Notation such as "R673" refers to the reflectance in the 673 nm band.

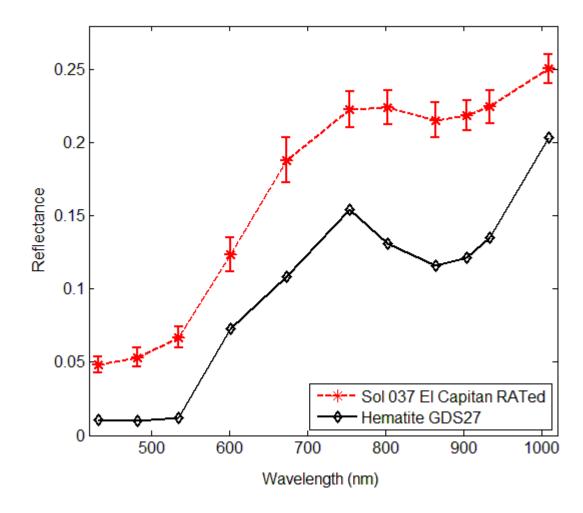
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Figures

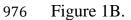


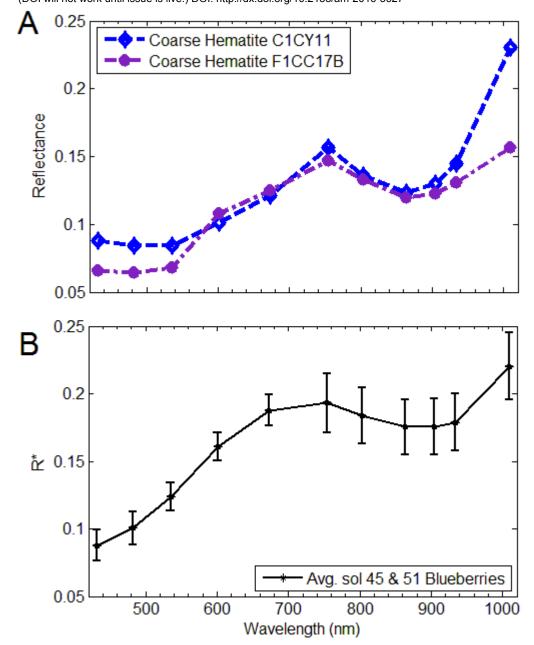
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974 Figure 1A.

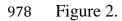


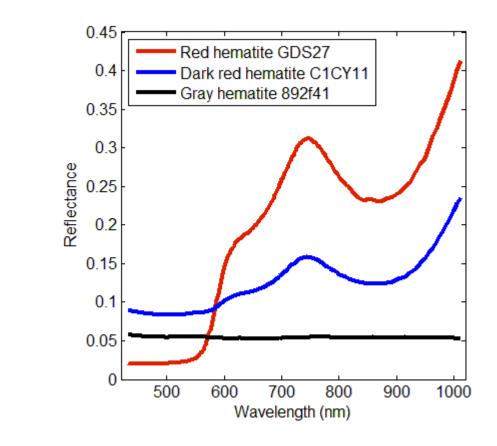




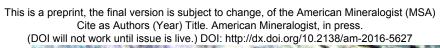


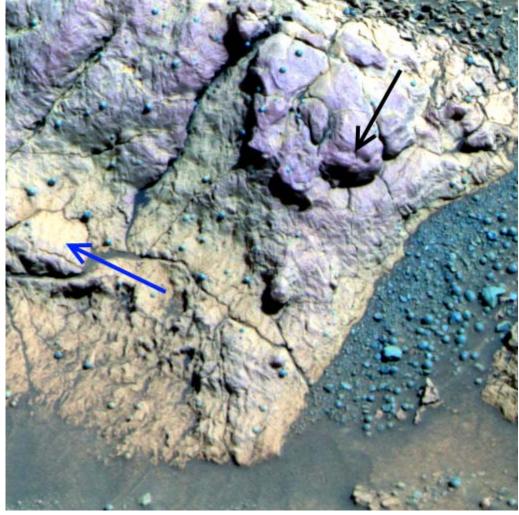




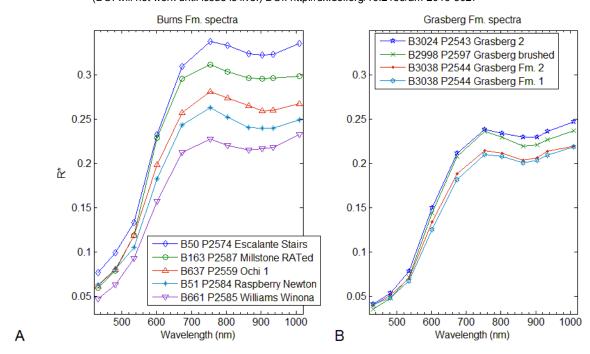


980 Figure 3.



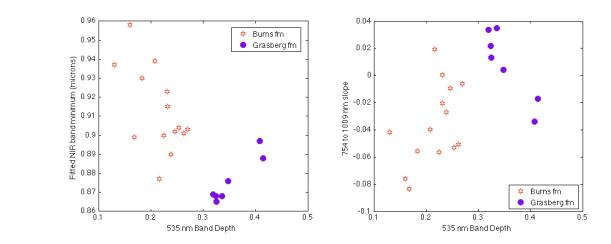


982 Figure 4.



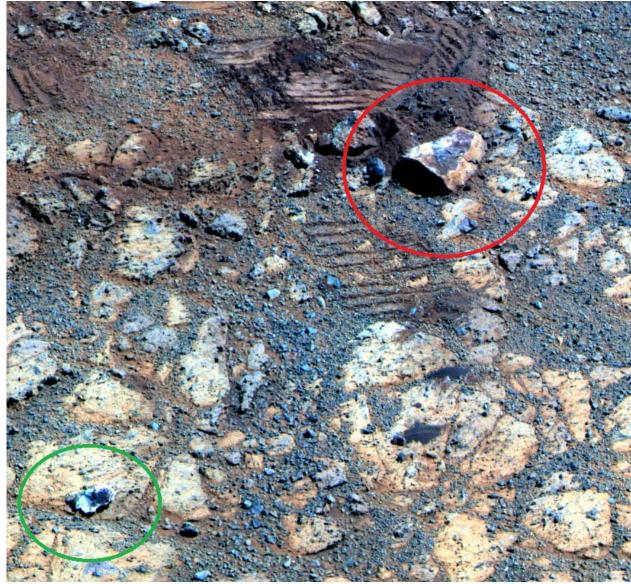


984 Figure 5.





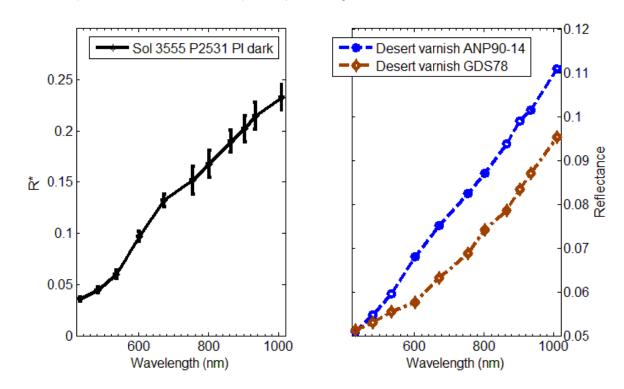
986 Figure 6.



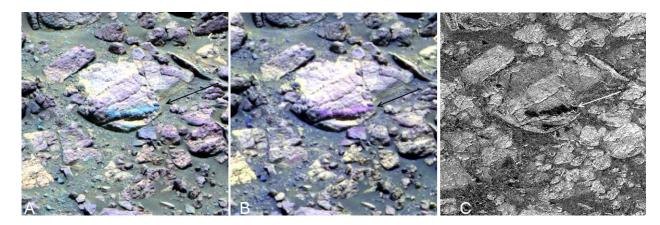
987

988 Figure 7.

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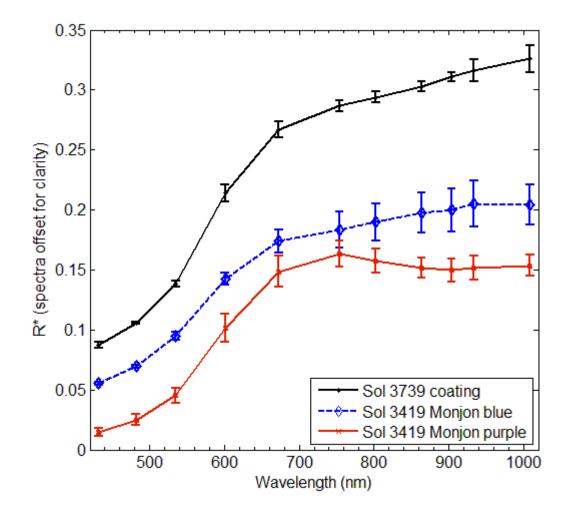


990 Figure 8.



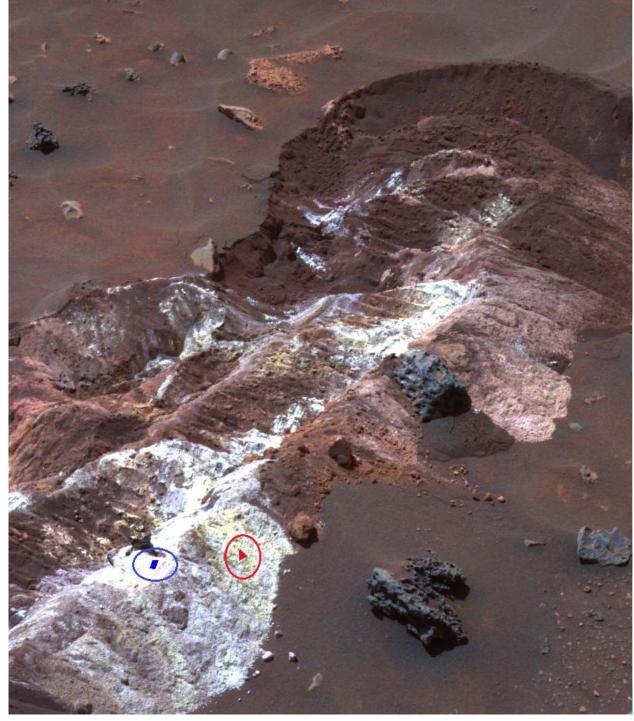
991

992 Figure 9.



993

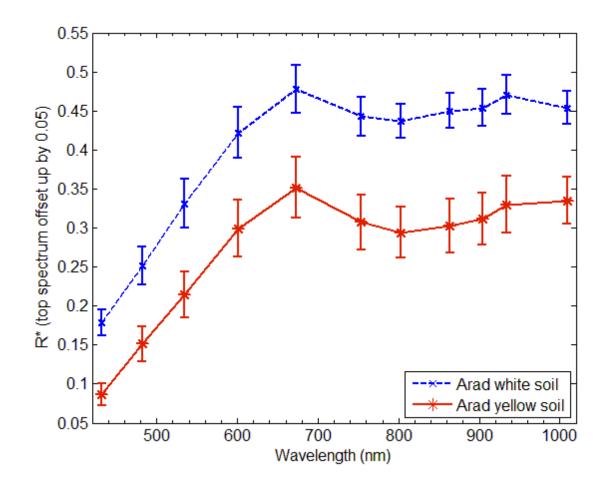
994 Figure 10.

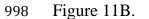


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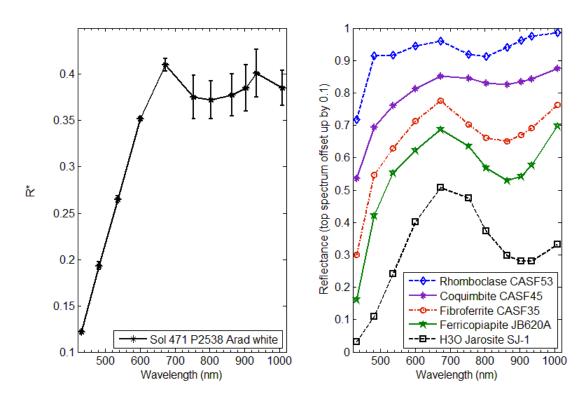
996 Figure 11A.

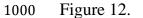
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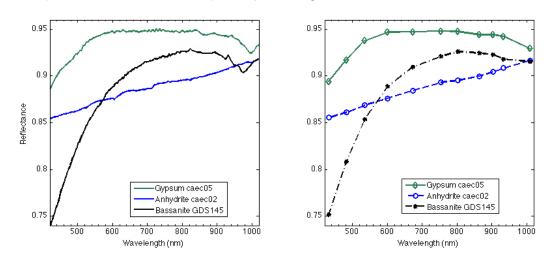




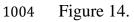


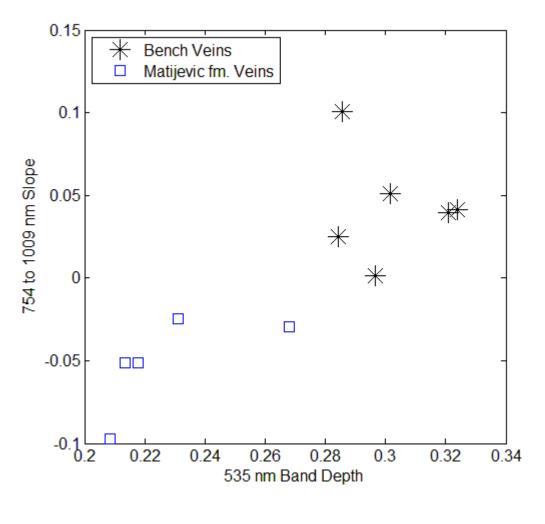
1002 Figure 13.

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1006 Figure 15.

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Figure 16.

A

500

600

700

Wavelength (nm)

800

900

1000

В

500

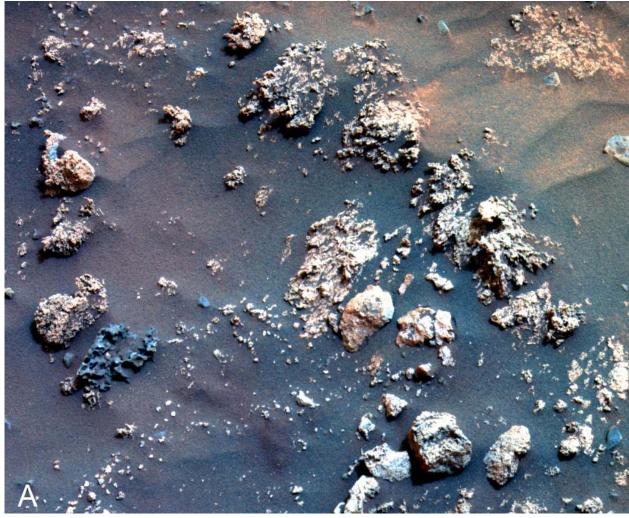
600

700

Wavelength (nm)

800

900



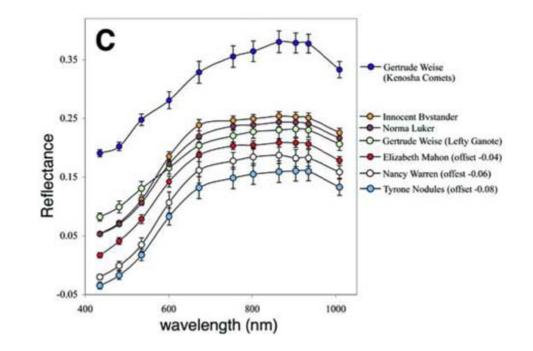
1009

1010 Figure 17A.

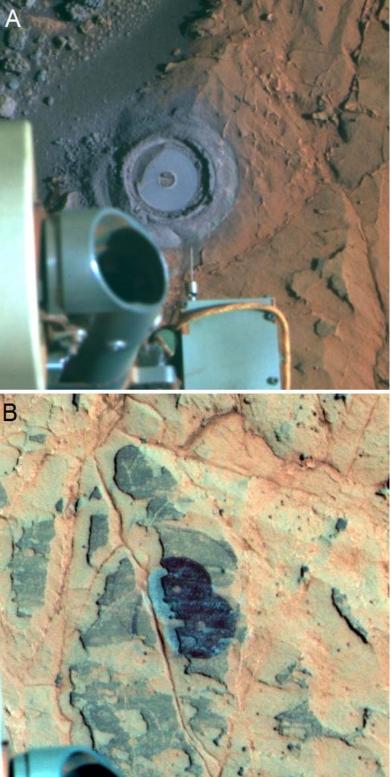


1011

1012 Figure 17B.



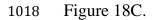


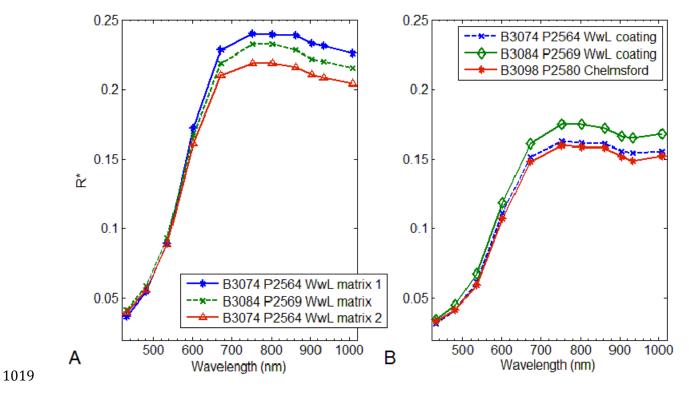


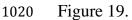
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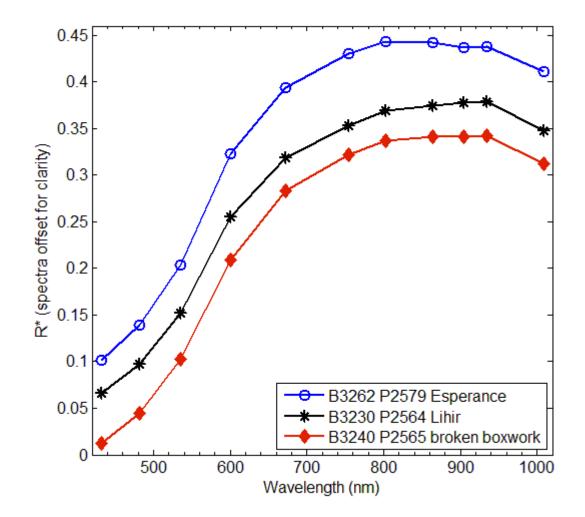
1016 Figure 18 A and B.







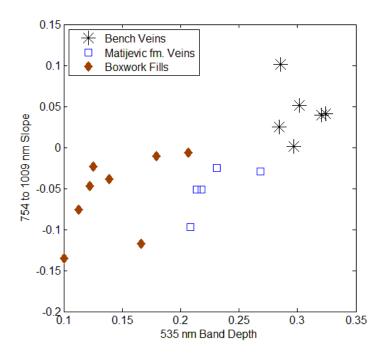


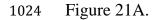


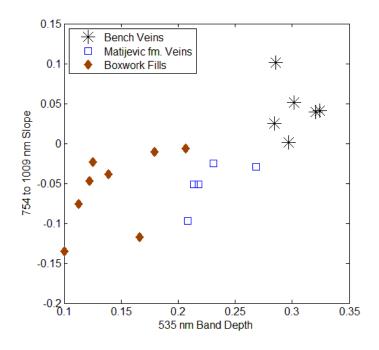


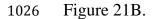
1022 Figure 20.

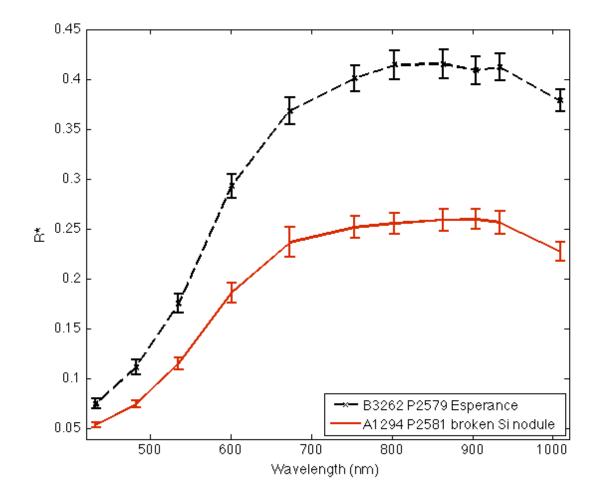
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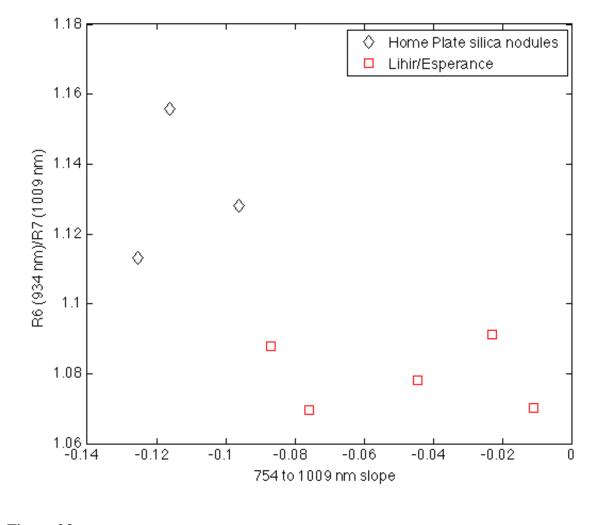






1027

1028 Figure 22.



1030 Figure 23.