

### Mineralogy of the light-toned outcrop at Meridiani Planum as seen by the Miniature Thermal Emission Spectrometer and implications for its formation

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[1] Analysis of Miniature Thermal Emission Spectrometer (Mini-TES) data has led to the recovery of a pure end-member spectral shape related to the light-toned outcrop observed at Meridiani Planum. Data from the MER Mössbauer spectrometer, APXS, and previous Mini-TES measurements were used to constrain a spectral library used to determine the mineralogy of the outcrop from this spectral shape. Linear deconvolution of the outcrop spectral shape suggests that it is composed primarily of Al-rich opaline silica, Mg-, Ca-, and Fe-bearing sulfates, plagioclase feldspar, nontronite, and hematite. Conversion of modeled mineralogy to chemistry shows good agreement with the chemical composition of the outcrops determined by APXS. Details of the analysis procedure and implications for the formation of the outcrop are discussed along with terrestrial analogs of the ancient environment at Meridiani.

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#### 1. Introduction

[2] The detection of gray crystalline hematite by the Mars Global Surveyor Thermal Emission Spectrometer (MGS-TES) [Christensen et al., 2000, 2001] led to the selection of Meridiani Planum as one of the landing sites of the two Mars Exploration Rovers (MERs). The Opportunity rover landed in Eagle Crater in Meridiani Planum on January 24, 2004. Among the first images acquired included a light-toned rock that was the first outcrop observed from the surface of Mars. As seen in Pancam and Microscopic Imager images [Bell et al., 2004; Herkenhoff et al., 2004], the outcrop is a laminated sandstone, with portions that exhibit fine-scale festoon cross lamination indicative of deposition under aqueous flow [Squyres et al., 2004; Grotzinger et al., 2005]. The outcrop is also the source of the nearly ubiquitous hematite-rich spherules, which can be seen eroding out of it [Herkenhoff et al., 2004; Soderblom et al., 2004].

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[3] Initial in situ analyses of the outcrop by the Alpha Particle X-ray Spectrometer (APXS) showed high levels of sulfur correlated with magnesium, suggesting the presence of magnesium sulfates [Rieder et al., 2004]. This result was confirmed by the Miniature Thermal Emission Spectrometer (Mini-TES), which has also seen evidence for calcium sulfates [Christensen et al., 2004]. Additionally, measurements by the Mössbauer spectrometer have indicated that the outcrop is composed of  $\sim 10$  wt.% jarosite, a ferric iron sulfate [Klingelhöfer et al., 2004]. In this work, we expand on the initial Mini-TES analyses of the light-toned outcrop [Christensen et al., 2004; Glotch and Bandfield, 2006], using the results of the APXS and Mössbauer instruments to constrain mineral deconvolution models. We check the results by converting the modeled mineralogy to chemistry and comparing with the average chemical composition of the outcrop determined by the APXS. We also examine Mini-TES spectra of fines derived from the outcrop by application of the Rock Abrasion Tool (RAT) [Gorevan et al., 2003; Bartlett et al., 2005] and compare these spectra to that of the globally homogenous fines (GHF). Finally, we discuss terrestrial analogs to the probable formation environment of the outcrop.

#### 2. Background

# 2.1. Previous Detections of Sulfates From in Situ and Remote Sensing Data

[4] Sulfate minerals have long been suspected to be a key component of the Martian surface materials. The X-Ray Fluorescence (XRF) experiment on the Viking landers detected the presence of S, Cl, and Br in the fines at the Utopia Planitia and Chryse Planitia landing sites. The presence of

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these elements and their correlation with each other implied the presence of salts, including sulfates and chlorides [*Baird et al.*, 1976; *Toulmin et al.*, 1977; *Clark and Van Hart*, 1981; *Clark et al.*, 1982]. Further correlation analysis of the Viking XRF data [*Clark and Van Hart*, 1981] suggested that  $Mg^{2+}$  is the major sulfate cation in the Martian regolith, although Ca and Na were not ruled out.

[5] Sulfates have been suggested in additional regions of Mars by remote sensing observations from both Earth-based telescopes and orbiting spacecraft, covering the visible/near-IR through thermal IR portions of the electromagnetic spectrum. Pollack et al. [1990] observed Mars from the Kuiper Airborne Observatory from 5.4-10.5 µm, and determined that sulfates and carbonates were present in the airborne dust, and that silicates and hydrates were present on the surface. The features that were described as due to carbonates and sulfates, however, have not been seen in TIR data acquired prior to or since the acquisition of these measurements, and fine particulates and water vapor were not properly accounted for in the data calibration. Earth-based telescopic observations covering 4.40 to 5.13 µm showed a spectral feature at 4.5 µm interpreted to be the result of the  $2\nu$ 3 overtone of the SO<sub>4</sub><sup>2-</sup> anion, which may indicate the presence of sulfates [Blaney and McCord, 1995]. In addition to telescopic observations, some evidence for sulfates has come from orbiting spacecraft. Bandfield [2002] reported that several pixels in Acidalia Planitia in 1 pixel per degree (ppd) mineral maps had sulfate concentrations greater than the TES detection limit of  $\sim 10-15\%$ , and Glotch and Christensen [2005] described the tentative detection of sulfates in layered units within Aram Chaos. More conclusive orbital evidence for sulfates has come from the European Mars Express OMEGA instrument, which has found evidence for kieserite (MgSO<sub>4</sub>  $\cdot$  H<sub>2</sub>O), gypsum (CaSO<sub>4</sub>  $\cdot$  2H<sub>2</sub>O), and unidentified polyhydrated sulfates associated with lighttoned layered units in Valles Marineris, equatorial chasmata and chaotic terrains, Terra Meridiani, and Margaritifer Terra [Gendrin et al., 2005].

#### 2.2. Previous Results From the MER Opportunity Rover

[6] Initial results from the MER Opportunity Rover analysis of the soils and outcrops in Eagle crater have shown that they have a high sulfur content primarily in the form of Ca- and Mg-bearing sulfates, with higher concentrations being confined to the outcrops [Rieder et al., 2004; Christensen et al., 2004]. Lane et al. [2004] and Bishop et al. [2005] have analyzed MER Mini-TES, Pancam, and Mössbauer spectra and determined that ferrous sulfates and hydrated iron sulfates may be present in the soil. A primary result of the Opportunity Mössbauer instrument has been the identification of jarosite ((K, Na,  $H_3O$  (Fe<sub>3-x</sub>Al<sub>x</sub>)(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) in the outcrops [Klingelhöfer et al., 2004]. Hematite is the dominant mineral in spherules that erode from the outcrop, and is also present as a separate component within the outcrop matrix [Klingelhöfer et al., 2004]. Hematite-rich spherules have been interpreted as concretions that were formed during groundwater recharge [Squyres et al., 2004; Chan et al., 2004; Ormö et al., 2004; McLennan et al., 2005], as well as volcanic lapilli and impact melt spherules [McCollom and Hynek, 2005; Knauth et al., 2005].

[7] Detailed sedimentological and stratigraphic analyses were also conducted at the outcrops at Eagle and Endurance craters. Seven meters of exposed stratigraphic section, informally termed the Burns formation, have been subdivided into lower, middle and upper units and are interpreted to have been deposited in an aeolian-sand sheet-interdune sedimentary setting [Grotzinger et al., 2005]. The presence of festoon-geometry cross-lamination at the top of the sedimentary sequence [Squyres et al., 2004; Grotzinger et al., 2005] indicates re-working of the original deposits in a subaqueous environment [Harms et al., 1982; Middleton and Southard, 1984; Southard and Boguchwal, 1990]. Stratigraphically lower in the sequence, the outcrops observed in Endurance crater have a variety of cross-bedding and other sedimentological features indicative of aeolian transport [Grotzinger et al., 2005].

[8] All sections of the outcrop are sulfur-rich and there is no indication that the sand grains are composed of volcanic rock fragments or other discernable lithic grains. Accordingly, the sand grains are interpreted to represent reworked sulfate-cemented muds that formed within a desiccating playa lake and were, in turn, derived via chemical alteration of basaltic sources [*McLennan et al.*, 2005]. The rocks also exhibit a variety of microtextural features indicating an extended history of diagenetic alteration involving groundwater recharge and evaporative processes [*Squyres et al.*, 2004; *McLennan et al.*, 2005].

#### 3. Methodology

[9] In this work, we analyze the spectral emissivity of the outcrop and outcrop-derived fines in detail. The outcrop spectral shape was derived by *Glotch and Bandfield* [2006] using factor analysis and target transformation [Malinowski, 1991; Bandfield et al., 2000, 2002]. Glotch and Bandfield [2006] selected ~15,000 Mini-TES spectra for analysis, and they were able to determine the independently varying components of the scene at Meridiani Planum. Thus the outcrop shape used in this work is derived from many Mini-TES observations, and is a spectral end-member of the scene observed by Mini-TES at Meridiani Planum. Use of this shape in determining the mineralogy of the outcrop is necessary because individual Mini-TES observations of the outcrop are often contaminated by dust, hematite-rich spherules, basaltic sand, and downwelling radiance from the atmosphere (Figure 1). It is also important to note that while hematite has been determined to be a component of the outcrops at the  $\sim 6$  wt% level [Klingelhöfer et al., 2004; Clark et al., 2005; McLennan et al., 2005], the factor analysis and target transformation process separated hematite from other components. This is due to the fact that hematite also occurs independently of the outcrop (e.g., as loose spherules mixed with basaltic sand.)

[10] Mineralogical analysis was performed using linear deconvolution [*Ramsey and Christensen*, 1998] on the outcrop spectral shape with a group of mineral end-members listed in Table 1. This end-member library was selected using knowledge of the elemental composition of the outcrop from the APXS [*Rieder et al.*, 2004; *Clark et al.*, 2005, *McLennan et al.*, 2005] as well as mineralogy derived from previous Mössbauer [*Klingelhöfer et al.*, 2004] and Mini-TES [*Christensen et al.*, 2004] spectral analyses. It includes a variety of igneous silicate minerals, Mg-, Ca-, and Fe-bearing

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**Figure 1.** Mini-TES observation of Tamanend Park on MER B Sol 029. (a) Navcam image showing the targeting on Mini-TES. The Navcam source frame for the overlay is 1N130763625FFL0454P1817L0M1, which was acquired on MER B Sol 028. (b) Mini-TES observation of Tamanend Park compared to the target transformation (TT) derived outcrop rock spectral shape scaled for contrast. The spectral emissivity measured by Mini-TES is a combination of outcrop rock, basaltic sand, surface dust, and atmosphere. The high emissivity in the Tamandend Park spectrum between 800 and  $1200 \text{ cm}^{-1}$  is due to a combination of downwelling radiance from the atmosphere and the presence of surface dust. The agreement between the Mini-TES stare on Tamanend Park and the TT-derived outcrop shape is best at long wavelengths, where the effects of the atmosphere and surface dust are negligible. The Tamanend Park spectrum was created by averaging 100 individual spectra from the Mini-TES observation 1T130675141RDR0454P3163N0A1.QUB acquired on MER B Sol 028.

sulfates, amorphous silica and glass, phyllosilicates, and Feoxides/oxyhydroxides.

[11] Although we have selected an end-member library suitable for the mineral deconvolution of the light-toned outcrop at Merdiani Planum, we apply further constraints from previous analyses performed by the Mössbauer, APXS, and Mini-TES instruments. The result should reduce uncertainties in modeled mineralogy compared to an unconstrained deconvolution model. The deconvolution model was applied over the spectral range of  $380-1400 \text{ cm}^{-1}$  using the following constraints: (1) The natrojarosite end-member was forced to be ~10% of the total rock, based on estimates from the Mössbauer and APXS instruments [*Klingelhöfer et al.*, 2004; *Rieder et al.*, 2004; *McLennan et al.*, 2005]. (2) The spectral contrast of Mg- and Ca-bearing sulfates and hematite were adjusted to take into account the amount of Mg<sup>2+</sup> and Ca<sup>2+</sup> available to balance the SO<sub>4</sub><sup>2-</sup> that would be present in sulfates [*McLennan et al.*, 2005; *Clark et al.*, 2005] and

#### Table 1. End-Member Libraries for Linear Deconvolution of Surface Spectral Shapes

Library End-members	Mineral Group
Ouartz BUR-4120	auartz
Anorthite BUR-340	plagioclase feldspars
Bytownite WAR-1384	pragroomoo ronoparo
Labradorite WAR-4524	
Andesine BUR-240	
Oligoclase BUR-060D	
Albite WAR-0244	alkali feldspars
Microcline BUR 3460	
Augite NMNH-9780	clinopyroxenes
Augite NMNH-122302	F
Hedenbergite, manganoan DSM-HED01	
Dionside WAR-6474	
Enstatite HS-9.4B	orthopyroxenes
Bronzite NMNH-93527	15
Forsterite AZ-01	olivines
Favalite WAR-RGFAY01	
Actinolite HS-116.4B	amphibole
Biotite BUR-840	sheet silicates
Muscovite WAR-5474	
Chlorite WAR-1924	
Serpentine HS-8.4B	
Serpentine BUR-1690	
Beidellite SBdl <sup>a</sup>	
Nontronite Nau-1 <sup>a</sup>	
Nontronite Nau-2 <sup>a</sup>	
Hectorite SHCa-1 <sup>a</sup>	
Montmorillinite Swy-1 <sup>a</sup>	
Saponite Eb-1 <sup>a</sup>	
Gypsum ML-S6	Ca-bearing sulfates
Bassanite ML-S7	Ũ
Anhydrite ML-S9	
Glauberite GBYAZ-R1 <sup>b</sup>	
Epsomite <sup>c</sup>	Mg-bearing sulfates
MgSO <sub>4</sub> <sup>c</sup>	
Kieserite KIEDE1 <sup>b</sup>	
Natrojarosite LNVJAR1-R1 perpendicular to lineation <sup>b</sup>	jarosite-alunite
Alunite WD151 <sup>b</sup>	
Natroalunite SLBAZ1 <sup>b</sup>	
Recovered Hematite <sup>d</sup>	iron oxides
Goethite GTS2 <sup>e</sup>	
K-rich glass <sup>f</sup>	high-silica
SiO <sub>2</sub> glass <sup>f</sup>	č
Amorphous silica <sup>g</sup>	
Aluminous opaline silica <sup>h</sup>	
<sup>a</sup> Michalski et al. [2005b].	

<sup>a</sup>Michalski et al. [2005b]. <sup>b</sup>Provided by R. V. Morris. <sup>c</sup>Provided by A. Baldridge. <sup>d</sup>Glotch and Bandfield [2006]. <sup>c</sup>Glotch et al. [2004]. <sup>f</sup>Wyatt et al. [2001]. <sup>b</sup>Provided by M. D. Kraft. <sup>h</sup>Michalski et al. [2005a].

the total FeO present in the outcrop [*Rieder et al.*, 2004; R. Gellert et al., manuscript in preparation, 2006]. This changes the abundances of all minerals reported by the deconvolution model. (3) Carbonates are not included in the library based on Mini-TES observations of outcrop-derived fines (discussed in detail in section 4.4). It is important to note that natrojarosite and Mg- and Ca-bearing sulfates are all used by an unconstrained deconvolution model. Carbonates, when present in the library, are also used at the  $\sim 6-10\%$  level, but misfits caused by their inclusion are clearly present. We also note that the laboratory spectra of the amorphous silica and smectite end-members were acquired as pressed pellets to remove fine particulate spectral features. This process increases the spectral contrast of the end-members compared to how they might be viewed in nature. To account for this, the spectral contrast of the smectite samples, which are not likely to occur as cements in the outcrop were reduced by 50%. On the other hand, the spectral contrast of the amorphous silica samples was not reduced because these end-members would likely occurs as cements in the outcrop rock and would have spectra similar to coarser particulates.

[12] There are potentially important caveats when comparing Mini-TES deconvolutions to APXS mineralogical mass balance or Mössbauer mineral abundance determinations (which rely for absolute concentrations on APXS total iron concentration determinations). Mini-TES results are re-

	Base Model	No Silica/Glass	No Sulfates	No Ca-Sulfates	No Mg-Sulfates	No Nontronite
Silica/glass	25%	_	20%	25%	25%	25%
Nontronite	10%	5%	0%	10%	10%	_
Jarosite	10%	15%	_	0%	10%	5%
Mg-sulfate	20%	0%	_	40%	_	35%
Ca-sulfate	10%	15%	_	_	20%	0%
Plagioclase	15%	15%	55%	20%	20%	20%
Fe-oxides	5%	0%	5%	0%	5%	5%
Other	5%	50%	20%	5%	10%	10%
RMS, %	0.307	0.407	0.425	0.331	0.316	0.342

 Table 2.
 Modal Mineralogy for a Base Deconvolution Model and Several Modified Models Illustrating the Importance of Various

 Mineral Species in the Deconvolution
 Several Modified Models

ported as areal abundance, which can be thought of as volume% (vol.%). APXS elemental abundances and Mössbauer mineral abundances are reported as weight% (wt.%). The differences between the wt.% and vol.% for the reported minerals are not likely to be as large as the errors associated with the various measurements. In addition, the chemical analyses are summed to 100% on an anhydrous basis [*Rieder et al.*, 2004] and thus mineral abundance estimates also assume anhydrous stoichiometry. The presence of structural water and OH<sup>-</sup>, for example in gypsum, hydrated Mg-sulfates or clay minerals, would have the effect of increasing the relative amounts of such minerals at the expense of anhydrous minerals. Mini-TES mineral deconvolutions, on the other hand, take into account the presence of any structural water that is present in the spectral library end-members.

#### 4. Results

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# **4.1.** Constrained Deconvolution of the Outcrop Spectral Shape

[13] The results of the deconvolution of the outcrop spectral shape are listed in Table 2, and the spectral shape with the model fits are shown in Figure 2. Results from the deconvolution indicate that the outcrop is composed primarily of sulfates and amorphous silica/glass/smectite. Amorphous silica and glass are modeled at 25% abundance, with the primary contributor from the spectral library being an X-ray amorphous, Al-rich (12.5 wt% Al<sub>2</sub>O<sub>3</sub>) opaline silica [Michalski et al., 2005a]. In addition, a smectite clay (nontronite) ((Fe<sub>1.92</sub>Mg<sub>0.03</sub>)(Al<sub>0.23</sub>Si<sub>3.76</sub>)O<sub>10</sub>(OH)<sub>2</sub>) [Michalski et al., 2005b] is modeled at 10% abundance. Additional components of plagioclase feldspar (15%) and hematite (5%) are also modeled. The Mg-bearing sulfate used by the deconvolution model is kieserite (MgSO<sub>4</sub>  $\cdot$  H<sub>2</sub>O), which is modeled at an abundance of 20%. The Ca-bearing sulfate is anhydrite (CaSO<sub>4</sub>), which is modeled at 10% abundance, although preliminary tests with a separate simultaneous solution least squares deconvolution model indicates that the Ca-bearing sulfate composition may be composed of both anhydrite and bassanite (CaSO<sub>4</sub>  $\cdot$   $^{1}/_{2}H_{2}O$ ). The 5% "Other" listed in Table 2 is quartz. Both the observed fit and the spectral RMS emissivity errors (0.307%) are better than all of the other model scenarios discussed below.

#### 4.2. Relative Importance of Mineral Components

[14] In order to examine the relative importance of the mineral components present in the deconvolution of the out-

crop spectral shape, a series of tests was performed in which outcrop mineral components were systematically excluded from model fits. The results of these tests give some indication of the sensitivity of Mini-TES in identifying these components, as well as the relative importance of these components in the deconvolution model fits. Model fits with key components eliminated from the end-member library are shown in Figure 2. The resulting modal mineralogies from these fits are shown in Table 2.

[15] The most abundant single component derived in the base model discussed in Section 4.1 is amorphous silica/ glass. When these end-members are eliminated from the spectral library, it results in a somewhat poorer fit than the base model, both in terms of visual appearance (Figure 2b) and spectral RMS emissivity error (0.407%). The fit is degraded especially at ~1150-1200 cm<sup>-1</sup> and 400-500 cm<sup>-1</sup>. In addition to the worse model fit, the modal mineralogy (Table 2) changes drastically. Specifically, the 50% "other" minerals listed in Table 2 are composed of equal parts quartz, potassium feldspar, natroalunite, and serpentine, with smaller amounts of olivine. Mg-bearing sulfates and hematite are absent from the modeled mineralogy, and Ca-bearing sulfate abundance is increased to 20%.

[16] Combined, Ca- and Mg-bearing sulfates make up  $\sim$ 30% of the outcrop in the base deconvolution model described in Section 4.1. When these components, as well as the other sulfates in the end-member library are not used, the fit is worse in terms of visual appearance (Figure 2c) as well as spectral RMS emissivity error (0.425%). In this case, the primary misfit to the outcrop spectral shape is in the 400–600 cm<sup>-1</sup> region, although the fit in the 1000–1200 cm<sup>-1</sup> region is also degraded. The resulting modal mineralogy (Table 2) is dramatically different from the base model, with the largest single component being plagioclase feldspar, with lesser amounts of amorphous silica/glass, quartz, olivine, and iron oxide.

[17] Further testing of the sulfate composition of the outcrop shows that both Ca- and Mg-bearing sulfates are needed to derive the best possible fit to the outcrop spectral shape with a reasonable associated mineralogy. Results of the model fits when Ca- and Mg-bearing sulfates are eliminated individually from the spectral library are shown in Figures 2d and 2e, respectively. When Ca-bearing sulfates are eliminated from the spectral library, the result is a somewhat poorer spectral fit (RMS emissivity error of 0.331%), with an increase in Mg-bearing sulfate content. In addition, jarosite is not identified in the deconvolution model. When Mg-bearing sulfates are excluded, the model fit is good, and



**Figure 2.** Deconvolution models of the outcrop rock spectral shape. (a) Base model using all endmembers listed in Table 1. Spectral RMS = 0.307%. (b) Model excluding all amorphous silica and glass end-members listed in Table 1. Spectral RMS = 0.407%. (c) Model excluding all sulfate end-members listed in Table 1. Spectral RMS = 0.425%. (d) Model excluding all Ca-bearing sulfate end-members listed in Table 1. Spectral RMS = 0.331%. (e) Model excluding all Mg-bearing sulfate end-members listed in Table 1. Spectral RMS = 0.303%. (f) Model excluding nontronite end-members listed in Table 1. Spectral RMS = 0.342%.

the RMS emissivity error (0.316%) is higher only than that of the base model. The concentrations of Ca-bearing sulfates are increased and jarosite abundance is reduced to 5%, which is less that that determined by the Mössbauer spectrometer.

[18] Nontronite is present at the 10% level in the base model, but if it is removed from the end-member library, then

the model fit becomes somewhat worse (Figure 2f), most notably at the long wavelengths. This is also reflected in the spectral RMS emissivity error (0.342%) which is higher than the base model. When nontronite is excluded from the endmember library, it is not replaced by any other phyllosilicates. Instead, the other major components are redistributed. Mgbearing sulfate abundance, in the form of kieserite, increases

Oxide	APXS Range <sup>b</sup>	Base Model	No Am. Silica	No Sulf	No Ca-Sulf	No Mg-Sulf	No Nontronite
SiO <sub>2</sub>	36.2-38.3	39.4	37.9	68.8*	43.9	43.5	41.8
Al <sub>2</sub> O <sub>3</sub>	5.85 - 6.20	6.7	10.4*	13.8*	7.1	8.1*	7.2
FeO(T)	15.3 - 16.5	16.4	11.1*	6.0*	6.4*	17.9	8.0*
MgO	8.00 - 8.45	6.4	7.8	3.7*	13.6*	0*	13.1*
CaO	4.42 - 5.19	5.2	7.3*	1.3*	0.9*	10.6*	1.3*
Na <sub>2</sub> O	1.64 - 1.67	2.4 (2.1)*	3.6 (3.1)*	6.1*	1.9	2.6 (2.3)*	2.5 (2.3)*
$K_2 \tilde{O}$	0.53 - 0.59	0.1 (0.5)	1.7 (2.2)*	0.4*	0.1*	0.1 (0.5)	0.13 (.35)*
$SO_3$	21.31 - 24.91	23.4	20.2	0*	26.1	17.1*	26.1
H <sub>2</sub> O <sup>c</sup>	-	5.5	6.0	0.7	6.1	2.3	6.8

Table 3. Oxide Chemistry Derived From Mini-TES Modeled Mineralogy Compared to Chemistry Determined From APXS Measurements<sup>a</sup>

<sup>a</sup>An entry with an asterisk indicates >20% relative difference between the Mini-TES and APXS chemistry.

<sup>b</sup>All oxide values are normalized to 0% H<sub>2</sub>O and are reported in wt.%.

<sup>c</sup>H<sub>2</sub>O abundances originally determined from Mini-TES mineralogy before normalization.

to 35%, and Ca-bearing sulfates are absent. Other minerals are redistributed at the 5% level. The 5% "other" listed in Table 2 is quartz.

# 4.3. Chemistry of the Outcrop Derived From Mini-TES Mineralogy

[19] Following the method of *Wyatt et al.* [2001] and *Hamilton et al.* [2001], mineralogy derived from the linear deconvolution of the Mini-TES spectra was converted into chemical composition reported as wt.% oxides of major elements. The results for each model, compared to recalibrated APXS data from RATted outcrop observations in Eagle Crater (R. Gellert et al., manuscript in preparation, 2006) are shown in Table 3. Following *Wyatt et al.* [2001] and *Hamilton et al.* [2001], we report modeled oxide abundances to only one significant decimal place. The values derived from Mini-TES are normalized to 0% H<sub>2</sub>O to compare directly to the APXS data. The originally modeled wt% H<sub>2</sub>O from Mini-TES is also shown.

[20] The uncertainties for individual APXS observations for each element are reported by Yen et al. [2005] and R. Gellert et al. (manuscript in preparation, 2006). A general detection limit of 10-15% has been proposed for mineral modes derived from Mini-TES data [Christensen et al., 2004]. These errors are carried forward into the determination of chemical abundances derived from Mini-TES data. In addition, detailed bulk chemistries for all end-members listed in Table 1 are not known, so in some cases, the stoichiometric chemistries of end-members were used, adding additional sources of error. Volume percent standard deviations and relative uncertainties for major oxides determined from 10 cm<sup>-1</sup> spectroscopic data were determined by Hamilton et al. [2001]. These range from 0.4 for Na<sub>2</sub>O and K<sub>2</sub>O to 1.7 vol.% for Al<sub>2</sub>O<sub>3</sub> and 3.5% relative uncertainty for SiO<sub>2</sub> to 95% TiO<sub>2</sub>. These errors were determined from a suite of volcanic rocks that did not contain sulfates or large amounts of other water-bearing minerals. In addition, detailed analyses of this type have not been performed for sedimentary rocks which contain significant cement. For this reason, the errors determined by Hamilton et al. [2001] are not likely to be directly comparable to the derived outcrop chemistry presented here. Instead, to compare with the APXS-derived chemistry, and illustrate the difference between models, for each Mini-TES deconvolution model listed in Table 3, relative differences of greater than 20% between the modeled

oxide abundance from Mini-TES and the abundance derived from APXS data are indicated by an asterisk.

#### 4.4. Observations of Outcrop-Derived Fines

[21] In addition to measuring the spectral emissivity of outcrop, the Mini-TES has also observed fines generated by application of the RAT to the outcrop. About 91% of the fines generated by the RAT have particle sizes ranging from 5-90 µm [Bartlett et al., 2005; D. W. Ming and R. V. Morris, unpublished data, 2005], making them roughly comparable in size (<10  $\mu$ m) to the globally homogenous fines (GHF). A comparison of the GHF spectrum derived from Mini-TES data by Glotch and Bandfield [2006] with RAT-generated outcrop fines is shown in Figure 3c. All three spectra show a broad absorption at >1250 cm<sup>-1</sup>, characteristic of volume scattering of fine particulates [Salisbury and Walter, 1989; Bandfield and Smith, 2003; Ruff, 2004], and emissivity maxima at  $\sim 1630 \text{ cm}^{-1}$ , indicative of bound water [Bandfield et al., 2003; Ruff, 2004]. The Guadalupe spectrum (Figure 3c) also has absorptions at  $\sim 1150 \text{ cm}^$ and  $\sim 500$  cm<sup>-1</sup>, indicating that some coarse-particulate outcrop rock was in the Mini-TES field of view when this spectrum was acquired (Figure 3b). The two outcropderived fines spectra have absorptions centered at 861  $\text{cm}^{-1}$ , while a similar feature in the GHF spectrum is present at 841 cm<sup>-1</sup>. This transparency feature in the GHF spectrum has been attributed to both finely particulate plagioclase feldspar [Bandfield and Smith., 2003] and finely particulate zeolites [Ruff, 2004].

#### 5. Discussion

## 5.1. Mineralogy and Chemistry of the Outcrop at Meridiani Planum

[22] The base deconvolution model described in Section 4.1 is the best model when both the quality of spectral fit and the reasonableness of the derived mineralogy are taken into account. This modeled mineralogy, when converted to chemistry, shows the greatest similarity to the APXS-derived chemistry. Only Na<sub>2</sub>O and K<sub>2</sub>O show a relative difference between the APXS and Mini-TES data of greater than 20% (Table 2). Much of this variation can be accounted for by the composition of the jarosite end-member used in the linear deconvolution, which is assumed to be pure natrojarosite. If the jarosite composition is assumed to be intermediate, with



**Figure 3.** Mini-TES observations of two "ratholes" in outcrop rock at Meridiani Planum. (a) Mini-TES field of view on the McKittrick rathole. Image is Navcam frame 1N131386579FFL0510P1937L0M1. (b) Mini-TES field of view over the Guadalupe rathole. Image is Navcam frame 1N131386579FFL0510P1937L0M1. (c) Mini-TES spectra of outcrop-derived fines from the McKittrick and Guadalupe ratholes compared to a Mini-TES spectrum of the globally homogenous fines (GHF). The outcrop-derived fines lack the structure at >1250 cm<sup>-1</sup> seen in the GHF spectrum, indicating that the carbonate content of the outcrop is  $<\sim 2-5$  wt%. The emissivity maxima at  $\sim 1630$  cm<sup>-1</sup> indicate that the outcrops contain one or more phases with bound water.

half of the cations assumed to be  $K^+$  and half assumed to be Na<sup>+</sup>, then the derived abundance of K<sub>2</sub>O increases and is within the range seen by APXS and the derived abundance of Na<sub>2</sub>O falls significantly, although it is still outside the range seen by APXS. These differences are shown as the set of values in parentheses in Table 3. On the basis of the modal mineralogy of the outcrop described in this model, the outcrop is composed of ~5.5 wt.% H<sub>2</sub>O. Much of this water is bound in kieserite, although both jarosite and nontronite are OH-bearing.

[23] When the largest component group derived in the base model (amorphous silica/glass) is removed, the result

is a poorer model fit (Figure 2b) and a derived mineralogy (Table 2) that is inconsistent with the results of the other instruments on the MER Opportunity rover. The large modeled components of quartz and K-feldspar, natroalunite, and Ca-bearing sulfates, as well as the absence of Mg-bearing sulfates are all inconsistent with the chemical trends observed in the APXS data [*Rieder et al.*, 2004; *Clark et al.*, 2005; *McLennan et al.*, 2005; R. Gellert et al., manuscript in preparation, 2006], as modeled CaO, Na<sub>2</sub>O and K<sub>2</sub>O are too high and FeO(T) is too low (Table 3).

[24] When all of the sulfates are removed from the endmember library, the result is a poor model fit (Figure 2c) and a derived mineralogy that is inconsistent with results of the APXS and Mössbauer spectrometers [Rieder et al., 2004; Klingelhöfer et al., 2004; Clark et al., 2005; McLennan et al., 2005]. The relative differences between the oxide abundances modeled by Mini-TES and those determined by the APXS are all greater than 20% (Table 3). When just the Ca-bearing sulfates are removed from the end-member library, the result is a poorer model fit and (Figure 2d) and a large increase in the Mg-bearing sulfate component. Additionally, jarosite cannot be modeled with positive concentrations in this scenario. All of these results are again inconsistent with the data returned by the APXS and Mössbauer spectrometers [Rieder et al., 2004; Klingelhöfer et al., 2004; Clark et al., 2005; McLennan et al., 2005] (Table 3). When just the Mg-bearing sulfates are removed from the end-member library, the model fit (Figure 2e) is nearly as good as for the base model, although the modeled mineralogy (Table 2) and chemistry (Table 3) indicates that this is not a likely scenario. CaO abundances increase to levels inconsistent with the APXS data, and total SO3 and MgO are low compared to the APXS data (Table 3). This case clearly demonstrates the utility of using data from the other instruments on the MER Opportunity rover to inform the results of Mini-TES deconvolution models.

[25] Although the base model provides a relatively good fit to the outcrop spectral shape (Figure 2a) there is room for improvement. Additional work must be done to identify phases that can improve the fit at long wavelengths as well as the shoulders of the major absorption feature centered at ~1200 cm<sup>-1</sup>. Relatively few sulfates have been included in the end-member library used in this study due to the lack of availability of suitable spectra, and the inclusion of additional probable sulfate phases may improve the fit. The outcrop contains small features at 540 and 580 cm<sup>-1</sup> that are consistent with sulfate  $\nu_4$  bending modes and the shallow feature centered at ~900 cm<sup>-1</sup> is consistent with a vibrational mode of bound water in the sulfate crystal lattice (M. Lane, personal communication, 2005). These features vary in position between the various sulfate species, and may eventually be used to pinpoint the sulfate composition(s).

[26] An additional result worthy of future investigation is the inclusion of both amorphous silica/glass and phyllosilicates, specifically nontronite, in the modeled mineralogy of the outcrop. Due to the short-ordered nature of amorphous silica, glass, and phyllosilicate crystal structures, these minerals/mineraloids have grossly similar spectra [*Wyatt* and McSween, 2002; Kraft et al., 2003]. If either amorphous silica/glass or the nontronite spectra are removed from the end-member library, then the model fit and the modeled chemistry are degraded (Figure 2, Table 3). In addition, recent work [Koeppen and Hamilton, 2005] has shown that glasses and phyllosilicates are statistically separable in linear deconvolution models. This result strengthens the case that both amorphous silica/glass and smectites may be present in the outcrop Meridiani Planum.

[27] Nontronite, an Fe-bearing mineral, is not definitively detected by the Mössbauer spectrometer, but *Klingelhöfer et al.* [2004] report that an unidentified phase referred to as Fe3D3 may be consistent with phyllosilicates. However, the presence of nontronite in the outcrop may also be inconsistent with the low pH chemical environment that allowed jarosite to form in the outcrop because the formation of

jarosites requires acidic conditions [Burns, 1993], whereas the formation of smectites is generally found to be favored by neutral to alkaline conditions [Ross and Hendricks, 1945; Grim and Güven, 1978; Gaines et al., 1997]. The outcrops measured by Opportunity, however, could represent a nonequilibrium evaporite setting that has been reworked [Tosca et al., 2005; McLennan et al., 2005]. It is possible that smectites formed in a moderate- to high-pH environment and were later incorporated into the outcrop. This hypothesis is further supported by the presence of plagioclase in the Mini-TES fits, in the absence of olivine and definitive pyroxene detection by either Mini-TES or the Mössbauer spectrometer. Kinetic models have shown that olivine and pyroxene weather faster than plagioclase over a broad range of moderate pH's. At very low pH's, however, all but the most albitic plagioclase dissolves faster than pyroxene [McAdam et al., 2006; Hurowitz et al., 2006]. In any case, if nontronite is excluded from the end-member library, its absence is not accounted for by other phyllosilicates.

[28] Whether nontronite is present in the outcrop or not, there is significant ( $\sim 25\%$ ) amorphous silica/glass, primarily modeled as Al-rich opaline silica, which is consistent with mineral models produced using the APXS data [*Clark et al.*, 2005; *McLennan et al.*, 2005]. Silica has been predicted to form on Mars from the chemical alteration of mafic minerals [*Gooding et al.*, 1992; *McLennan*, 2003], and has been previously suggested as a component of the outcrop at Meridiani Planum [*Clark et al.*, 2005; *McLennan et al.*, 2005; *McLennan et al.*, 2005; *Squyres and Knoll*, 2005].

[29] The presence of amorphous silica also has implications regarding the formation environment of the outcrop. McCollom and Hynek [2005] have argued that an evaporating brine could not have been responsible for the presence of Fe-, Mg-, and Ca-bearing sulfates in the outcrop because there is no increase in those cation concentrations corresponding the increased sulfur signature observed in the APXS data. They argue that a more likely model is one in which sulfur is added to an ash with a basaltic composition and aqueously weathered over a short period of time in a high-temperature sulfotara-like environment. However, as Bullock [2005] and S. W. Squyres et al. (Response to "A volcanic environment for bedrock diagenesis at Meridiani Planum, Mars," submitted to Nature, 2006) point out, the chemical arguments of McCollom and Hynek [2005] are only relevant if the siliciclastic component of the outcrop is itself unweathered. The cations in the unweathered outcrop precursor material could have been removed prior to the formation of the outcrop itself, as has been argued by Squyres et al. [2004] and Squyres and Knoll [2005]. The base deconvolution model presented in Section 4.1 does include 15% feldspar, in the form of oligoclase, a Na-rich  $(Ab_{70-90})$ plagioclase, but pyroxene and olivine are absent. The other silicic components of the outcrop are 25% aluminous amorphous silica and 10% nontronite. Thus of the 50% of the outcrop composed of silicic minerals, at most 15% could be interpreted as unweathered on the basis of Mini-TES data, and it is possible that the Na-rich nature of even the plagioclase is a result of differential weathering of a more moderate plagioclase. In addition to these arguments, previous work [Glotch et al., 2004, 2006] has shown that a high temperature formation environment is inconsistent with Martian hematite mid-IR spectral signature.

[30] The model mineral assemblage described by *McCollom and Hynek* [2005] also includes components of quartz and alunite which are not observed in the outcrop at levels above the Mini-TES detection limit. The addition of diaspore, also seen in the model of *McCollom and Hynek* [2005], to the end-member library in Table 1 does not alter the derived mineralogy.

[31] Mini-TES observations of the outcrop-derived fines have provided unique insight into the composition of the outcrop and an opportunity to compare the outcrop composition to the GHF. The shift in position of the 841  $\text{cm}^{-1}$ transparency feature between the GHF and the outcropderived fines may be due to the presence of finely particulate sulfates, or alternatively, to different plagioclase compositions in the outcrop and GHF. Previous work has shown that the GHF likely contains a more intermediate  $(An_{30-70})$ plagioclase composition [Bandfield et al., 2003; Hamilton et al., 2005] than the modeled feldspar component of the outcrop. The more sodic plagioclase composition modeled for the outcrop would cause the outcrop fines transparency feature at 841 cm<sup>-1</sup> to shift to higher wave numbers, as is observed [Salisbury et al., 1991]. Milam et al. [2004] have shown that plagioclase compositions are distinguishable in Mini-TES data at the level of +8/-12% of An number. Previous work has shown that Na-rich plagioclase will generally weather at a slower rate than olivine, Ca-rich plagioclase, and pyroxene [Colman, 1982; Eggleton et al., 1987; Michalski et al., 2004]. Thus the presence of a Na-rich plagioclase in the outcrop may indicate that it or its precursor has been thoroughly weathered, although the reaction may not have been carried to completion [e.g., Tosca et al., 2005]. Alternatively, a moderate plagioclase containing Ca- and Narich zones may have weathered in a fashion that preferentially removed the Ca-rich zones and left primarily Na-rich zones (M. Zolotov, personal communication, 2006). Thus there is ample evidence that the silicic portion of the outcrop has been substantially weathered. A caveat to this argument is that the Na<sub>2</sub>O content derived from Mini-TES mineralogy is higher than that determined by the APXS. As has been shown, however, the modeled abundance of Na<sub>2</sub>O can be lowered by adjusting its proportions in the jarosite end-member. In addition, a less albitic plagioclase would also drive up CaO, making it inconsistent with APXS measurements.

[32] The detection of the 15% feldspar component in the outcrop by the Mini-TES corroborates a mineralogical model developed by *Clark et al.* [2005] which uses correlation of Na and K with Al in APXS measurements to suggest that feldspars might be present in the outcrop. In addition to the feldspar detected by Mini-TES, Fe-rich pyroxene has been tentatively detected by the Mössbauer spectrometer. This detection is considered tentative, and could be assigned to glass. [*Klingelhöfer et al.*, 2004]. Analysis of the Mini-TES data (Table 2) indicates that no pyroxene is present in the outcrop rock, lending further indirect evidence that the Mössbauer spectrometer may have detected a phase other than pyroxene.

[33] The results of the Mini-TES analysis of outcropderived fines can also be brought to bear on modeling of APXS data. *Clark et al.* [2005] discuss several mineral models they created to determine mineralogical constraints from the APXS chemical data. The differences among the models include the portion of unaltered rock components within the outcrop, and the partitioning of alkali elements and aluminum (either in the feldspar or alteration products). Case 1a presented by *Clark et al.* [2005] includes 2.3 wt% CaCO<sub>3</sub>. The results of the Mini-TES analysis of the outcrop-derived fines, which takes advantage of the nonlinear addition of fine particulate components, can be used to constrain the carbonate content of the outcrop to below this value, indicating that one of the other models discussed by *Clark et al.* [2005] may be closer to the actual mineralogy of the outcrop rock.

[34] The most noticeable difference between the GHF and the outcrop fines spectra occurs in the region >1250 cm<sup>-1</sup>. The GHF spectrum has an overall increased emissivity compared to the outcrop fines between  $\sim 1300$  and 1600 cm<sup>-1</sup>, with local emissivity minima at 1400 and 1600  $\text{cm}^{-1}$ . This structure has been attributed to the presence of carbonates at the 2-5% level [Bandfield et al., 2003]. An alternative view is that this structure is indicative of the presence of hydrous iron sulfates [Lane et al., 2004]. However, for laboratory samples of two hydrous iron sulfates, the characteristic features at >1250 cm<sup>-1</sup> were absent for the finest particulates tested, which is inconsistent with the presence of these minerals in the loose, finely particulate (<10  $\mu$ m) GHF. Similar features at >1250 cm<sup>-1</sup> have been reported in ferrihydrite samples from Landmannalaugar, Iceland [Bishop and Murad, 2002], and altered volcanic tephra from Haleakala, Maui, which contains hematite, magnetite, maghemtite, alunite-jarosite, phyllosilicates, and some primary glass and silicates [Bishop et al., 2006]. Regardless of the nature of the absorbing material in the GHF, detailed laboratory work [Bandfield et al., 2003] has shown that the presence of 2-5 wt.% carbonate minerals in a plagioclase dust matrix can cause the structure at >1250 cm<sup>-1</sup> seen in the GHF. Thus the lack of this structure in the outcrop-derived fines suggests that the carbonate concentration in the outcrops is less than 2-5 wt.%. Given how the evaporite mineral assemblage is expected to evolve [Tosca and McLennan, 2006], and the iron and sulfate-rich setting at Meridiani Planum, carbonates would not be an expected component of the outcrop.

[35] Mössbauer data indicate that outcrop jarosite is rich in Na and K, and not likely to be of the H<sub>3</sub>O-rich variety [Klingelhöfer et al., 2004]. Analyses of APXS data [Clark et al., 2005] indicate that jarosite abundance does not correlate with Na and K, but the only way to model the proper amount of K<sub>2</sub>O from Mini-TES data is to have a significant amount of K in jarosite. The only available jarosite end-member spectrum, which is used in this work, is a natrojarosite (Na-rich). It is possible that the inclusion of K-rich, or H<sub>3</sub>O-rich jarosite end-member spectra might further improve the results of the deconvolution models presented in Section 4. Because jarosite is modeled at 10% abundance, minor differences in the spectra of specific types of jarosite are not likely to cause major differences in the resulting spectrum, although significant effects on the modeled chemistry may be seen.

# 5.2. Terrestrial Analogs to the Past Acid-Sulfate Environment at Meridiani Planum

[36] Both mineralogy and geochemical modeling of observed bedrock mineralogy is consistent with a low-pH aqueous paleoenvironment at the Meridiani site [*Squyres et al.*, 2004; *Klingelhöfer et al.*, 2004; *Tosca et al.*, 2005; Zolotov and Shock, 2005; Tosca and McLennan, 2006], although a previous period of less acidic weathering may have occurred, as evidenced by the presence of plagioclase, in the absence of pyroxene and olivine, and the suggestion of nontronite. A number of mechanisms have been proposed as models of Martian surface conditions, ranging from water-to-rock ratios from very low water to very high, but recent modeling suggests that the amount of water may be very low and that geochemical reactions did not proceed to completion [Tosca et al., 2005; Elwood Madden et al., 2004; Zolotov and Shock, 2005]. Given the diversity of surface locations on Mars where sulfates have so far been identified, a number of mechanisms may be involved in their deposition. It should also be noted that while the sedimentology of the Meridiani deposits suggests dune/interdune evaporite sequences, on Earth these environments are not typically acidic and so different terrestrial analogs are likely required for the sedimentological observations than for the geochemical and mineralogical ones [Grotzinger et al., 2005].

[37] Among the best studied terrestrial analogs for similar mineralogy are acid sulfate systems commonly associated with pyrite oxidation. Pyrite oxidation has been the subject of recent geochemical studies by King and McSween [2005] and Zolotov and Shock [2005]. Well-studied Mars analog sites include Iron Mountain, California, and the Rio Tinto in Spain. These acid mine drainage locations have received considerable recent attention in the astrobiology community due to the significant microbial diversity in the highly acidic waters as well as several new eukaryotic lineages discovered in this extreme environment [Amaral Zettler et al., 2002; Bishop et al., 2005]. The Rio Tinto region is housed in the Iberian Pyrite belt, a series of volcanogenic deposits of massive pyrite ore often capped by a deep alteration zone, termed a "gossan," rich in hematite and goethite [Guilbert and Park, 1986]. Gossan like deposits were first proposed as an analog to Mars by Burns [1988]. Fernández-Remolar et al. [2003, 2004] proposed the site as an iron formation analog to the hematite at the Meridiani landing site on the basis of the large iron oxide terraces. We now know that the hematite on Mars is in spherical concretions [Soderblom et al., 2004], rather than in layered channel deposits; however, the area still offers a reasonable analog to the diverse sulfate mineralogy found on Mars as well as mineralogical evolution over a long period of terracing, exposure history, seasonal and climate changes. A number of reports on the regional geology, mineralogy and seasonal variability of sulfates in the Rio Tinto region have been published [Hudson-Edwards et al., 1999; Buckby et al., 2003; Fernández-Remolar et al., 2003, 2004, 2005; Ruiz et al., 1998; Braungardt et al., 2003].

[38] Pyrite oxidation is also responsible for the formation of acid brines and groundwater in southern Australia. Lake Tyrell is a 150 km<sup>2</sup> inland salt playa that contains acid salts including alunite, and jarosite as well as iron oxides and oxyhydroxides [*Long et al.*, 1992a, 1992b]. The alunite and jarosite are present as cements in the upper 20 cm of sediments, and are believed to have been deposited as a result of groundwater evaporation [*Long et al.*, 1992b]. The only iron oxide positively identified in the system is goethite, although minor amounts of hematite and lepidocrocite may be present [*Long et al.*, 1992b]. The dominance of goethite over other iron oxides is consistent with oxygen isotope analyses that indicate that salts were deposited at low temperatures [*Alpers et al.*, 1992]. The suitability of southern Australian acid lakes as potential Mars environment analogs has been discussed by *Benison and LaClair* [2003], who also note that similar environments existed in mid-continent North America during the Permian.

[39] Potential sedimentological analogs include the White Sands gypsum dune fields in New Mexico and other winddistributed playa evaporites. White Sands and other desert playas, despite being evaporate playas, are not good chemical analogs to the Meridiani site. They are, however, interesting examples of a possible past environment at Meridiani Planum. They are also often used as test sites for new terrestrial remote sensing instruments due to their bright reflectance in airborne and spaceborne instruments [e.g., Thome, 2001; Crowley, 1993, Crowley and Hook, 1996]. Benison and Bowen [2006] have also argued that lakes in Western Australia (WA) provide an even better Martian analog than lake Tyrell. The pH at the WA lake sites range from 1.5 to 4, and mineral assemblages at these lakes contain gypsum, halite, iron oxides (primarily hematite with secondary geothite), and jarosite. In addition, the WA sites have sedimentary structures including fine planar lamination, cross-bedding, ripple marks, and displacive crystals that may be consistent with the Burns Formation at Meridiani Planum [Benison and Bowen, 2006]. In particular, the White Sands calibration site shows strong sulfate features [e.g., Thome, 2001]. These and other playa evaporate analogs usually show Ca-, Mg-, Na-, and K-bearing sulfate minerals which form the bulk of those modeled from the Mini-TES data in the Meridiani Outcrop. Minerals appearing in playa evaporites depend strongly on the groundwater chemistry, but inland deposits in California and Nevada show a wide variety of borates, gypsum and other sulfates, in addition to halite and other chlorides [Crowley, 1991]. On Earth, many of these regions are periodically wet so that surface mineral signatures are highly variable with local weather conditions and precipitation leading to metastable mineral assemblages.

#### 6. Conclusions

[40] Linear deconvolution of the factor analysis and target transformation-derived Mini-TES outcrop end-member spectrum indicates that the light-toned outcrop at Meridiani Planum is fit best by a mixture of Mg- and Ca-bearing sulfates and Al-rich opaline silica, in addition to jarosite, plagioclase feldspar, hematite, and perhaps nontronite. The linear deconvolution was performed with the benefit of information gained by previous analyses of APXS, Mössbauer, and Mini-TES data, and removal of any major components from the end-member library results in worse model fits and/or unrealistic modeled mineralogy and chemistry of the outcrop.

[41] Mini-TES observations of the outcrop-derived fines have provided valuable information about the mineralogy of the outcrop at Meridiani Planum. The emissivity peak at ~1630 cm<sup>-1</sup> seen in the Mini-TES spectrum of the outcropderived fines (Figure 3b) confirms the presence of an H<sub>2</sub>Obearing phase in the outcrop. Conversion of the modeled outcrop mineralogy to chemistry indicates that the total water content of the outcrop is 5.5 wt.%. The only H<sub>2</sub>O-bearing phase in the base deconvolution model is kieserite, although both jarosite and nontronite are OH-bearing. Mg-sulfates with both more and less  $H_2O$  than kieserite, and  $H_2O$ -bearing Ca-sulfates are not present in the base deconvolution model discussed in Section 4.1, although a separate deconvolution model indicates that bassanite, a hydrated Ca-sulfate may be present in addition to anhydrite. Other water-bearing sulfates absent from the end-member library may also contribute to this bound water detection. In addition to the confirmation of bound water in minerals contained in the outcrop rock, comparison of the outcrop-derived fines spectrum to the GHF spectrum has shown that carbonate concentration in the outcrop rock is close to zero, and that the plagioclase content of the outcrop rock is likely more sodic than that in the GHF.

[42] The modeled mineralogy, including Na-rich plagioclase, amorphous silica, and the Mg/Ca ratio of the sulfates, is consistent with the weathering and diagenesis of an olivine-bearing basaltic rock [*Tosca et al.*, 2004; *McLennan et al.*, 2005]. Chemical weathering products of basalt, rather than unaltered primary igneous minerals, comprise the majority of the silicic components in the outcrop, and thus a volcanic model in which sulfur is added to a basaltic precursor [e.g., *McCollom and Hynek*, 2005] is not needed to explain the outcrop mineralogy and chemistry. Additionally, the presence of Na-rich plagioclase, the absence of pyroxene and olivine, and the suggestion of nontronite may indicate that a previous weathering regime was less acidic than that in which jarosite was formed.

[43] The initial reason for sending the Opportunity rover to Meridiani Planum was the detection of hematite from orbit and its association with a possible aqueous past. Once on the surface, the scene viewed by Opportunity offered several surprises, including the presence of hematite in spherules and the presence of the light-toned silica/sulfaterich outcrop rock. Data from the Athena science payload have strongly pointed to aqueous weathering of an olivine-rich basalt and evaporative deposition of sulfate minerals as the primary mechanisms leading to the formation of the lighttoned outcrop rock.

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