Sulfates in Martian Layered Terrains: The OMEGA/Mars Express View

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The OMEGA/Mars Express hyperspectral imager identified hydrated sulfates on light-toned layered terrains on Mars. Outcrops in Valles Marineris, Margaritifer Sinus, and Terra Meridiani show evidence for kieserite, gypsum, and polyhydrated sulfates. This identification has its basis in vibrational absorptions between 1.3 and 2.5 micrometers. These minerals constitute direct records of the past aqueous activity on Mars.

OMEGA, a visible–near infrared hyperspectral imager (0.35 to 5.1 μm) on board the European Space Agency/Mars Express mission (1), has been performing the surface mapping at a km to sub-km resolution since January 2004 (2). Here, we present the identification and mapping of hydrated sulfates found in geological units exhibiting light-toned layered terrains.

We used wavelengths of 1.3 to 2.5 μm to identify sulfate minerals. In this wavelength range, solar reflected light dominates the spectrum, and the planetary thermal emission is negligible. Consequently, the retrieval of surface and atmospheric contributions is straightforward (3). Although most of the fundamentals of the relevant vibrational absorption signatures lie outside this domain, their overtones and combinations are diagnostic and lead to unambiguous mineralogical identifications through the accurate and combined determination of band position, shape, and depth.

In this wavelength range, the OH and H_2O vibration features dominate. Most hydrated minerals have absorption bands at ~1.4 and ~1.9 μm (Fig. 1). These bands are caused by overtones and combinations of the symmetric H–O–H stretch (v_1), the asymmetric H–O–H stretch (v_3), and the H–O–H bend (v_2) (4). From 2.2 to 2.4 μm, narrow absorptions due to metal–O–H vibrations (4) are present and are diagnostic of mineralogy. S–O bonds also create absorption features in this range when associated with H_2O (Table 1). Spe-

cifically, the $(SO_4)^{2-}$ stretch, with fundamentals near 10 μm, produces overtones from 2.2 to 2.5 μm. Their precise position and shape vary with composition and result in features at 2.2 and 2.4 μm for hydrated sulfates.

The identification in the OMEGA data set of specific combinations of the central position, shape, and depth of absorption bands, with reference to calibration spectra performed on terrestrial analogs, enables us to characterize three spectral types attributed to sulfates as follows.

The first spectral type is characterized by absorptions at 1.6, 2.1, and 2.4 μm (5). The 1.6- and 2.1-μm absorptions correspond to the 1.4-μm and 1.9-μm features shifted to longer wavelengths. Such a shift is observed only in monohydrated sulfates (Fig. 1). It is
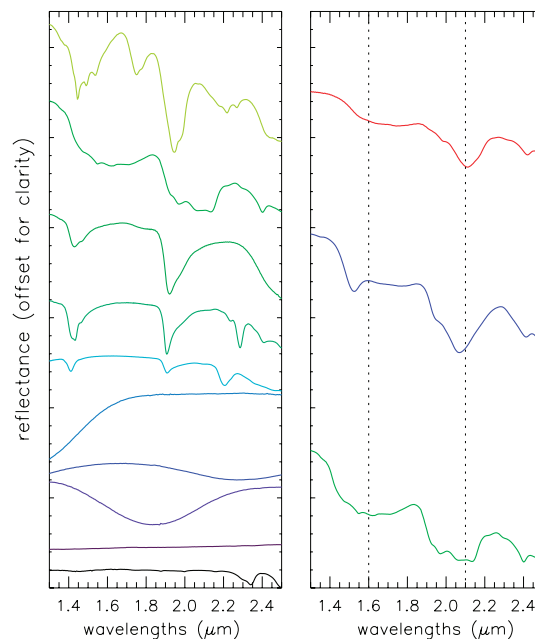

Fig. 1. Laboratory spectra of terrestrial analogs (31). **(Left)** From bottom to top: calcite (carbonate), hematite (oxide), enstatite (orthopyroxene), diopside (clinopyroxene), olivine, montmorillonite (phyllosilicates), nontronite (phyllosilicate), chabazite (zeolite), kieserite (sulfate), and gypsum (sulfate). **(Right)** Monohydrated sulfates, from bottom to top: $MgSO_4\cdot H_2O$ (kieserite), $MnSO_4\cdot H_2O$, and $ZnSO_4\cdot H_2O$.

Table 1. Spectral types identified in the OMEGA data set, corresponding best candidate mineral, and geographic location. Band assignments have their basis in previous studies (29, 30).

Detected absorption bands, position (μm)	Corresponding best candidate mineral	Geographic location
~1.6,* ~2.1,* 2.4†	Kieserite	Ius, Hebes, Capri, Candor, Melas, Juventae Chasma, Aram Chaos, Terra Meridiani
~1.4,* ~1.9,* 2.4† drop	Polyhydrated sulfate	Ius, Hebes, Capri, Candor, Melas, Ophir Chasma, Terra Meridiani
~1.4,* ~1.75, ~1.9,* ~2.2 (2.21‡ and 2.27‡), 2.4† drop	Gypsum	Juventae Chasma, Iani Chaos

*Combinations and overtones of OH^- or H_2O bending and stretching fundamentals.   †$3v_3(SO_4)^{2-}$, H_2O overtone and combinations.   ‡$v + \delta$ (H_2O)

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caused by the strong coupling between the single water molecule and the sulfate ion (6). In hydrated environments, the distinct 2.4-μm band is caused by the $(SO_4)^{2-}$ stretch. These features are diagnostic of monohydrated sulfates. Mg monohydrated sulfate, kieserite ($MgSO_4 \cdot H_2O$), matches the OMEGA spectrum over the 1.4- to 2.5-μm wavelength range (Fig. 2).

The second spectral type is characterized by five absorption bands at 1.4, 1.75, 1.9, 2.2, and 2.4 μm (Fig. 2). The 1.4- and 1.9-μm absorption bands indicate a hydrated mineral. Two humps are observed inside the 1.4-μm band (7). The 2.2-μm absorption band also has a double shape, with two small absorptions at 2.21 and 2.27 μm. The 2.2- and 2.4-μm features are caused by the $(SO_4)^{2-}$ stretch in hydrated environments. This set of absorptions matches the absorptions observed in calcium sulfates, and gypsum ($CaSO_4 \cdot 2H_2O$) or bassanite ($2CaSO_4 \cdot H_2O$) are the best candidates.

The third spectral type has 1.4- and 1.9-μm features characteristic of hydration and a 2.4-μm feature due to the $(SO_4)^{2-}$ stretch in hydrated environment. The features have asymmetrical shapes exhibiting plateau-like right wings. These are diagnostic of polyhydrated sulfates, and sulfates with different cations provide good matches to the OMEGA spectrum. Epsomite ($MgSO_4 \cdot 7H_2O$) fits well the OMEGA spectrum, as does copiapite [$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$] or halotrichite [$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$] (6, 8).

These sulfate minerals (9) are associated with light-toned layered deposits (10–14)
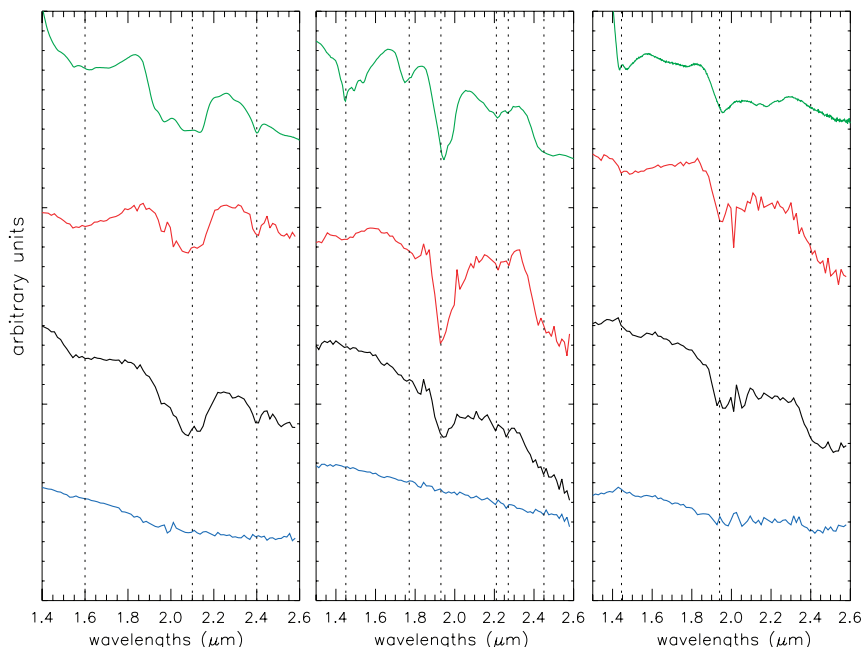

Fig. 2. Sulfate spectra identified in the OMEGA observations. Green, library spectrum; black, OMEGA spectrum; blue, reference spectrum; red, spectral ratio. (**Left**) Kieserite $MgSO_4 \cdot H_2O$(28). (**Center**) Gypsum. (**Right**) Polyhydrated sulfate. The library spectrum corresponds to epsomite ($MgSO_4 \cdot 7H_2O$), but other polyhydrated sulfates are good analogs in this spectral domain.

Fig. 3. Location of the deposits identified in Valles Marineris and surroundings plotted over the MOLA altimetry. (**A**) Red, kieserite type; green, polyhydrated sulfate; blue, spectral class most likely corresponding to gypsum; pink, other hydrated minerals, identified by their absorptions at 1.4 and 1.9 μm. Sulfates are identified over light-toned deposits in (**B**) Ius Chasma floor (orbit 71), (**C**) East Hebes Chasma interior (orbit 360), (**D**) Juventae Chasma interior (orbit 460), Capri Chasma (**E**) crater flank (orbit 61) and (**F**) interior buttes (orbit 363), (**G**) Iani Chaos (orbit 353), and (**H**) Aram Chaos interiors (orbit 401).
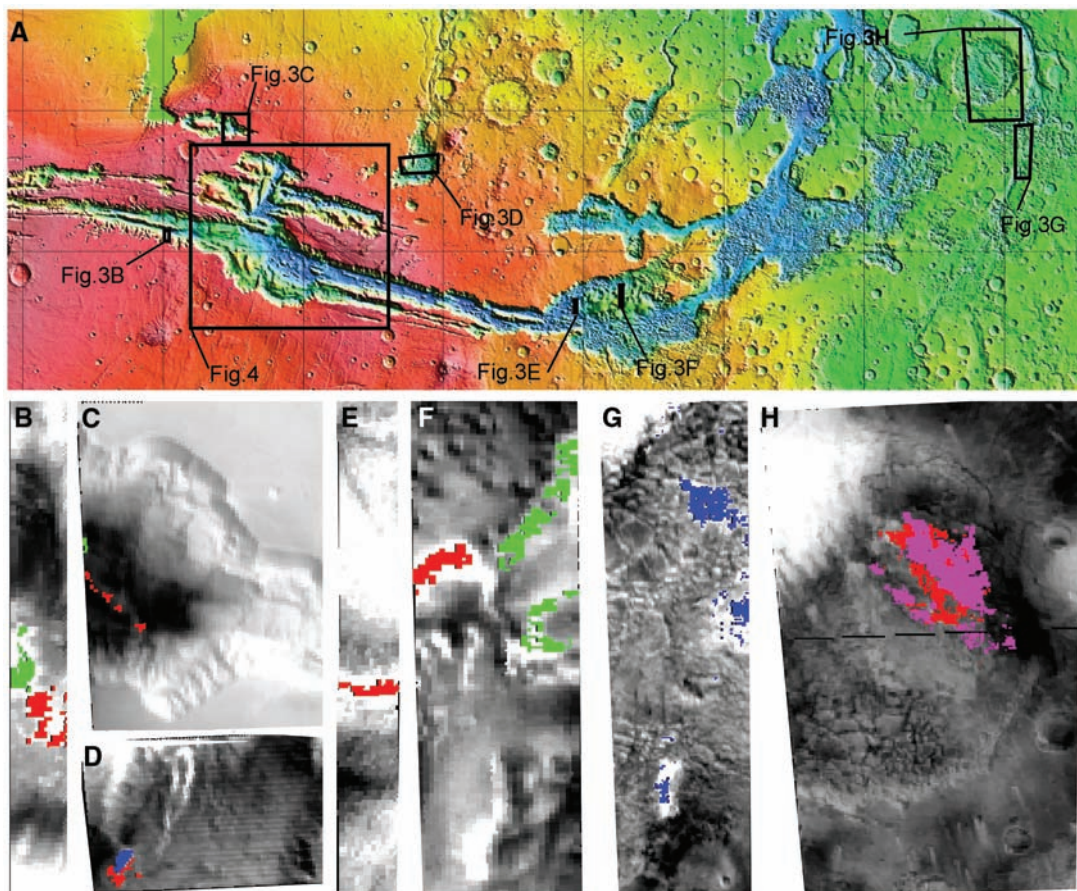
in Valles Marineris, Margaritifer Terra, and Terra Meridiani (Figs. 3 to 6), described as follows.

Fig. 4. Same color code as in Fig. 3 for Melas, Candor, and Ophir Chasmata. We combined orbits numbered 308, 334, 360, 515, 548, and 581 to obtain the mosaic.
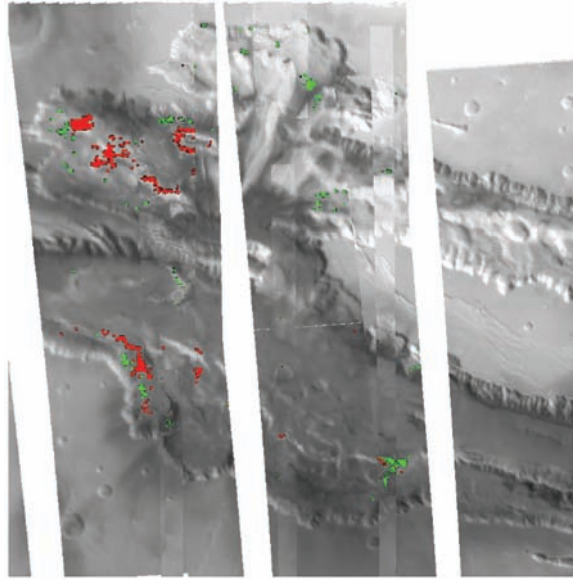
In the main canyons of Valles Marineris, kieserite and polyhydrated sulfates are associated with light-toned deposits (Figs. 3

and 4). Mars Orbiter Camera onboard Mars Global Surveyor images of Candor and Melas indicate that these are layered terrains. In Candor Chasma, kieserite is observed on three sides of a 4-km elevated hill (Fig. 5A); the darker parts of the mesa, corresponding to eolian mantling, have no sulfate signatures. In Melas Chasma, the small buttes at the foot of Valles Marineris flanks display layering; they fit the OMEGA pixels in which polyhydrated sulfates are detected (Fig. 5B). The deposits of Juventae Chasma (Fig. 5C) are peculiar, because gypsum is identified within the horizontal layers some hundred meters in thickness each. Kieserite surrounds gypsum and is associated with a rougher material at lower elevation. The kieserite-rich area slightly extends by a few pixels over the sand dunes surrounding the layered deposits.

In Margaritifer Terra, remnants of layered deposits are scattered in different chaos locations (*14*, *15*). Several deposits inside Iani Chaos (Fig. 3G) appear to be gypsum-rich, with a good correlation with layers observed on high-resolution images (Fig. 5D). Aram Chaos

Fig. 5. Examples of correlation between sulfate deposits identified by OMEGA and layered deposits from Mars Orbiter Camera (MOC) images (Malin Space Science Systems/Jet Propulsion Laboratory/NASA). (**A1** to **D1**) OMEGA classification, see Fig. 3 for color code. (**A2** to **D2**) MOC context images, except (**B2**), THEMIS daytime mosaic. (**A3**) to (**D3**) MOC high-resolution images: (A) Candor Chasma, MOC number E03-01293 (74.5°W, 5.2°S). (B) Melas Chasma, MOC number R09-02972 (74.5°W, 11.8°W). (C) Juventae Chasma, MOC number E23-01035 (62.6°W, 4.5°W). (D) Iani Chaos, MOC number M14-01230, 18.8°W, 4.3°S.
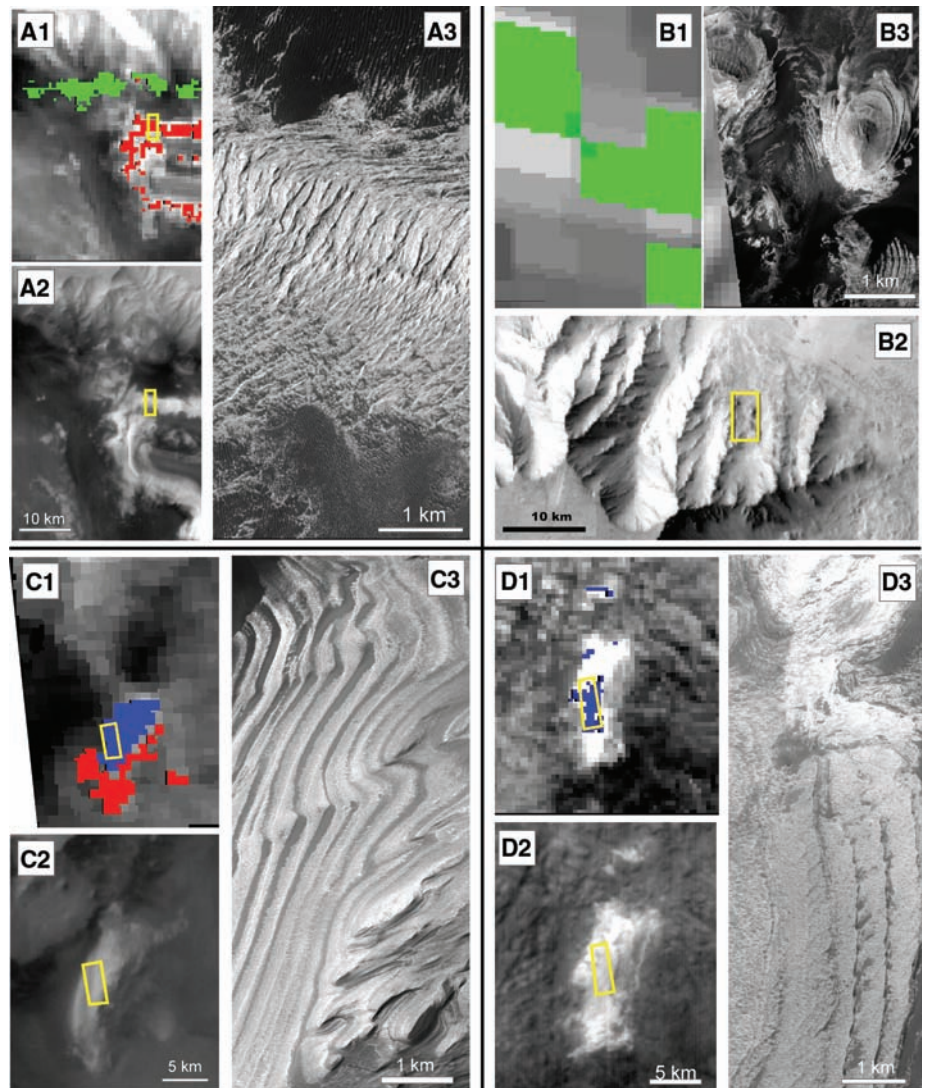
shows a higher spectral diversity (Fig. 3H) where kieserite surrounds other hydrated minerals.

In Terra Meridiani (Fig. 6), sulfates are found associated to a variety of hydrated minerals in different locations over large areas, constituting the so-called etched units, which are composed of light-toned deposits (16). In one specific area, sulfates are abundant (Fig. 6), with kieserite mapped in red and hydrated minerals probably corresponding to polyhydrated sulfates in green. The sulfate-rich unit underlies the crystalline hematite one explored by the Mars Exploration Rover Opportunity: Some of the layers discovered by Opportunity would correspond to the uppermost unit of the etched terrains (17) in which OMEGA locally detects sulfates, indicating that these sulfates are widespread and not restricted to the landing site area.

Not all Martian layered deposits observed by OMEGA exhibit absorption bands typical of hydrated minerals or sulfate minerals. Minerals without spectral signatures in this range, such as halite, might be present in the observed areas.

The stability of kieserite requires specific thermodynamical conditions. Experiments (18) show that kieserite is easily converted to hexahydrite ($MgSO_4 \cdot 6H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$) when exposed to water. However, upon further desiccation, these minerals are not transformed back to kieserite. Therefore, kieserite is not likely to be formed and preserved in deposits that have experienced surface cycles of hydration and desiccation.

The sulfates are a bulk component of the deposits, rather than a soil surface coating.

Magnesium sulfates are known to constitute a substantial component (about 5%) of Martian soils (19). OMEGA observed sulfates in the equatorial regions exclusively in close relation with light-toned layered deposits and not scattered in the surrounding soil. Moreover, most sulfate-rich deposits correspond to fresh exhumed surfaces, as seen by flutes and yardangs typical of eolian erosion, by the lack of small (<100 m) impact craters, and by the thermal signature from THEMIS/Odyssey (19). The formation of these layered deposits is dated to the Noachian and/or Hesperian epochs (12, 13).

By analogy with terrestrial geology, it has been proposed that sulfates would originate from evaporation of standing bodies of water such as shallow lakes (playas) or lagunas connected to the seawater (sabkhas) (20). Large accumulations of gypsum in the terrestrial rock record are common, whereas other sulfates such as kieserite generally exist in much lower amounts (21). However, it is likely that martian brines are more enriched in Fe and Mg relative to terrestrial standards, if they result from the alteration of the mafic crust, leading to a higher content of Mg sulfates and acidic conditions (22, 23) favoring the formation of sulfates relative to carbonates and other salts (24). The formation of evaporites on Mars would require stable liquid water in lakes or seas, which severely constrains the atmospheric properties, even considering that brines can be liquid at temperatures well below 273 K. If deposits in Valles Marineris are interpreted as lacustrine, one must account for sulfates observed over a wide range of elevations (from –4 km

in Ius Chasma to +3 km in Candor Chasma) and not merely as playa deposits in the current bottoms of canyons. It could imply that sediments were formed during the opening of the Valles Marineris canyon and accumulated in shallow water bodies like in terrestrial rift zones (10–13). In Terra Meridiani, the sulfate-rich unit is observed close to the Opportunity landing site, where parts of the layers are interpreted as subaqueous sediments (25).

Sulfates may also form at depths in the presence of sulfur-rich fluids in hydrothermal contexts (20, 26). Layered deposits could have originated as volcanic ash or eolian deposits and could have been altered later to sulfates by acidic groundwater circulation. Possibly hydrothermal conditions would also have favored sulfate deposition by subsurface brine seepage. Such a scenario could also have occurred during the rifting of Valles Marineris (10), favoring sulfur-rich fluid circulation and the alteration of volcanic ashes into sulfates, as well as in chaotic terrains (15) and Terra Meridiani (27). Lastly, sulfates could result from alteration of mafic minerals by rain and/or frost made acidic through volcanic outgassing (2).

References and Notes

1. J.-P. Bibring et al., European Space Agency Spec. Publ. **1240**, 37 (2004).
2. J.-P. Bibring et al., Science **307**, 1576 (2005); published online 17 February 2005 (10.1126/science.1108806).
3. J. F. Mustard et al., Science **307**, 1594 (2005); published online 17 February 2005 (10.1126/science.1109098).
4. R. N. Clark et al., J. Geophys. Res. **95**, 12653 (1990).
5. Band positions are given with an accuracy of 0.1 μm when the absorption bands are broad or their center is in a wavelength range with possible atmospheric residuals, or in a wavelength range with possible remaining instrumental effects. Otherwise, positions are given with an accuracy of 0.01 μm.
6. J. K. Crowley et al., Geochem. Explor. Environ. Anal. **3**, 219 (2003).
7. Y. Langevin et al., Science **307**, 1584 (2005); published online 17 February 2005 (10.1126/science.1109091).
8. M. Lane et al., Geophys. Res. Lett. **31**, L19702 (2004).
9. The sulfates are identified with the use of band ratios. To map the sulfate areas, we used a methodology based on (28). We then checked that each spectrum of the resulting classification presents the absorption bands of interest.
10. J. F. McCauley et al., Icarus **17**, 289 (1972).
11. B. K. Lucchitta et al., NASA Tech. Memo. **85127**, 233 (1982).
12. B. K. Lucchitta et al., J. Geophys. Res. **99**, 3783 (1994).
13. S. S. Nedell et al., Icarus **70**, 409 (1987).
14. M. C. Malin, K. S. Edgett, Science **290**, 1927 (2000).
15. M. G. Chapman, K. L. Tanaka, Icarus **155**, 324 (2002).
16. R. E. Arvidson et al., J. Geophys. Res. **108**, ROV 14-1 (2003).
17. B. M. Hynek, Nature **431**, 156 (2004).
18. D. T. Vaniman et al., Nature **431**, 663 (2004).
19. A. Banin et al., J. Geophys. Res. **102**, 13341 (1997).
20. J. Warren, Evaporites: Their Evolution and Economics (Blackwell Science, Oxford, UK, 1999).
21. Kieserite forms at temperatures typically higher than 40°C, whereas more hydrated phases such as epsomite form at lower temperatures. The association of these minerals of different hydration levels is common on Earth because of diurnal or seasonal temperature variations. Ions and cations present in the body of water control the sequence of formation of evaporitic minerals. The classic terrestrial sequence is dominated by large proportions of halite
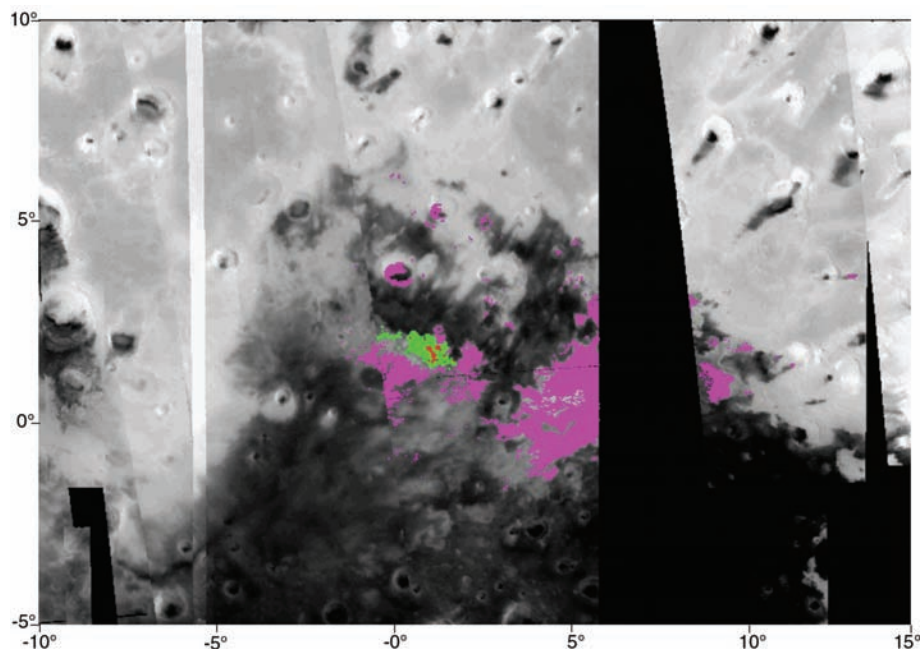
Fig. 6. Same color code as in Fig. 3 for Terra Meridiani. The mosaic is obtained combining orbits 171, 278, 291, 314, 397, 430, 485, 518, 529, and 551.

with underlying gypsum and minor deposits of carbonates at the base. Kieserite and other K or Mg salts are minor components appearing at the top of the sequence. We can outline the large accumulation of kieserite of the Zechstein basin of the Permian epoch and the deposition of magnesium sulfates in the currently drying Aral Sea.

22. M. A. Bullock et al., Icarus 170, 404 (2004).
23. D. C. Catling, J. Geophys. Res. 104, 16453 (1999).
24. A. G. Fairen et al., Nature 431, 423 (2004).
25. S. W. Squyres et al., Science 306, 1698 (2004).
26. D. L. Huston et al., Earth Planet. Sci. Lett. 220, 41 (2004).
27. R. E. Arvidson et al., Science 307, 1591 (2005); published online 17 February 2005 (10.1126/science.119509).
28. Green et al., IEEE Trans. Geosc. Rem. Sens. 26, 65 (1993).
29. G. R. Hunt et al., Mod. Geol. 3, 1 (1971).
30. J. Bishop, E. Murad, Am. Miner., in press.
31. Laboratory reflectance data provided through a cooperation with NASA and the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) team. Reflectance measurements were acquired at the Reflectance Experiment Laboratory (RELAB) at Brown University. Efforts to acquire these data by J. F. Mustard are gratefully acknowledged.

REPORT

Spectral Reflectance and Morphologic Correlations in Eastern Terra Meridiani, Mars

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The Mars Express Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité (OMEGA) hyperspectral image data covering eastern Terra Meridiani indicate the ubiquitous presence of molecular water in etched terrain materials that disconformably overlie heavily cratered terrains and underlie the hematite-bearing plains explored by the Opportunity rover. Identification of crystalline water in kieserite ($MgSO_4 \cdot H_2O$) is linked to materials exposed in a valley and plateau to the north of hematite-bearing plains. The mineralogical similarities between the etched terrain deposits examined with OMEGA data and the layered rocks examined by Opportunity imply that the ancient aqueous environments inferred from analyses of the rover data extend over regional scales.

The Mars Express instrument, OMEGA, has acquired hyperspectral imaging data of the martian atmosphere and surface since January 2004 (1). In this Report, we summarize analyses of OMEGA data from Orbit 485 over Terra Meridiani, acquired on 7 June 2004 at approximately 09:00 Mars local time and a solar incidence angle of ~46°. This Report complements the work on identification and mapping of high-latitude hydrated sulfate minerals (2) and in equatorial to mid-latitude layered deposits (3) from OMEGA data. Our focus is the identification of hydrated phases associated with etched terrain materials exposed to the east and north of the hematite-bearing plains that define Meridiani Planum (4–6).

The geologic setting of Terra Meridiani is among the most complex on Mars and includes exposures of Noachian-aged cratered terrains that have been dissected by channel systems that were carved by water flowing from the southeast to the northwest (7) (Fig. 1). After channeling ceased, several hundred meters of layered materials were disconformably deposited onto the dissected cratered terrains. To the north of Terra Meridiani, the deposits were then buried by the southern edge of a dust mantle that peaks in thickness over Terra Arabia (5). Subsequent wind erosion then exposed the layered deposits in Terra Meridiani and differentially shaped these materials into a set of domes, ridges, plateaus, and other landforms collectively termed etched terrains (5). The hematite-bearing Meridiani Planum surfaces and materials mapped from Mars Global Surveyor (MGS) Thermal Emission Spectra (TES) (8) and explored by the Mars Exploration Rover, Opportunity (9), are at the top of the stratigraphic section of preserved layered materials. Analyses of rover-based data show that the hematite spherules and associated fragments have been concentrated on the surface as a lag deposit as wind erosion has eroded the weak spherule-bearing, sulfate-rich rocks that underlie the plains (10).

OMEGA Orbit 485 data cover portions of the eastern hematite-bearing plains, sections of etched terrains exposed to the east and north of the plains, and extensive areas of dissected and mantled cratered terrains (Fig. 1). Furthermore, the northern exposures of etched terrains include deposits in a valley and plateau oriented to the northwest-southeast and located just to the north of the transition from the hematite-bearing plains to the etched terrains (Figs. 1 and 2). After retrieval of surface Lambert normal albedos (11), standard reduction analyses using principal components techniques (12) were used to extract spectral endmembers. Extractions focused on the wavelength interval from 1.0 to 2.6 μm because interactive inspection of spectra suggested that this region showed the greatest variety of spectral shapes. Five spectral endmembers (Fig. 3) explain 86% of the variance for plains, etched terrains, and surrounding dark cratered terrains: (i) a "bright etched terrain" spectrum typical of the signatures for etched terrain, (ii) a "dark etched plateau" spectrum representative of darker signatures associated with the northwest-southeast–trending valley and plateau (Figs. 1 and 2), (iii) a "bright plains" spectrum, (iv) a "dark plains" spectrum, and (v) a "dark crater floor" spectrum (located in the cratered terrain).

Between 0.4 and 1.0 μm, each of the five endmembers is characterized by an absorption edge between 0.4 and ~0.6 μm, a slope change near 0.6 μm, a relative reflectance maximum at ~0.75 μm, and a band minimum at longer wavelengths. The position of the minimum ranges from ~0.82 μm (feature A, Fig. 3) for the bright etched terrain spectrum to ~1.0 μm (feature B in Fig. 3) for the dark crater floor endmember. The spectral slope between ~0.6 and ~1.5 μm is steep and positive for the bright etched terrain spectrum and slightly negative for the dark crater floor spectrum. All of these spectral features have been detected in previous observations of Mars made at lower spatial resolution as compared to OMEGA data (~2 km for Orbit 485 data versus ~20 km) (13, 14). The spectral features for the bright etched terrain spectrum are consistent with the presence of Fe^{3+}-bearing minerals, interpreted to be a mixture of nanophase ferric iron and hematite (15),

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