

Distribution and formation of chlorides and phyllosilicates in Terra Sirenum, Mars

Timothy D. Glotch,¹ Joshua L. Bandfield,² Livio L. Tornabene,³ Heidi B. Jensen,¹ and Frank P. Seelos⁴

Received 1 July 2010; accepted 15 July 2010; published 24 August 2010.

[1] The Terra Sirenum region of Mars, located in the Noachian southern highlands, is mineralogically diverse, providing unique insight into ancient aqueous processes. Analyses of remote sensing data over the region indicate the presence of both Fe- or Mg-rich phyllosilicates and a spectrally unique deposit interpreted to be rich in chloride salts. The stratigraphic relationships indicate that the phyllosilicates are part of the ancient highland crust and that the salts were deposited at a later time. In some instances, there is clear morphological evidence that salts were mobilized and deposited by near-surface waters.

Citation: Glotch, T. D., J. L. Bandfield, L. L. Tornabene, H. B. Jensen, and F. P. Seelos (2010), Distribution and formation of chlorides and phyllosilicates in Terra Sirenum, Mars, *Geophys. Res. Lett.*, 37, L16202, doi:10.1029/2010GL044557.

1. Introduction

[2] Daytime infrared images from the Mars Odyssey Thermal Emission Imaging System (THEMIS) have been used to infer the presence of multiple occurrences of chloride salts distributed throughout the southern highlands of Mars [Osterloo *et al.*, 2008]. These regions exhibit a featureless blue slope in mid-IR emissivity spectra, which is best explained by the presence of a spectrally neutral material with non-unit emissivity such as chloride salts (referred to hereafter as chlorides). This effect is distinct from slopes that are caused by the effects of anisothermality [Bandfield, 2009]. Chlorides, like sulfates discovered at Meridiani Planum and other regions of Mars [Gendrin *et al.*, 2005; McLennan *et al.*, 2005; Murchie *et al.*, 2009] often form as solute-rich waters or brines evaporate. They are expected to precipitate from SO₄- and HCO₃-poor brines derived from weathering of basaltic rocks [Tosca and McLennan, 2006], but can also be vapor phase deposits from volcanic outgassing [e.g., Naughton *et al.*, 1974]. Halite (NaCl), observed in several SNC meteorites, suggests interactions between water and Martian upper crustal rocks [Gooding *et al.*, 1991; Bridges and Grady, 2000].

[3] This study focuses on the geology of Terra Sirenum, which contains the largest known co-occurrence of chlorides and phyllosilicates on Mars. Based on data from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), phyllosilicates in this region are dominated by Fe- or Mg-rich smectites and are commonly found on Noachian plains, and occasionally on crater floors [Murchie *et al.*, 2009; Wray *et al.*, 2009], as well as channel-fill materials. The presence of smectites and a variety of other aqueous minerals indicates that the Noachian crust, at least in places, was altered by liquid water [Wray *et al.*, 2009].

2. Data and Methods

[4] THEMIS surface emissivity data were generated according to the methods of Bandfield *et al.* [2004] and were used to map chlorides in the study area. CRISM full resolution targeted (FRT), half-resolution long (HRL) and multispectral mapping (MSP) images were used to identify the presence of both clay minerals and chlorides. We used the CRISM D2300 and ISLOPE1 spectral summary parameters described by Pelkey *et al.* [2007] to map the phyllosilicates and chlorides, respectively. We then examined CRISM spectra (corrected for atmospheric gas bands [McGuire *et al.*, 2009]) over each deposit to verify the presence of phyllosilicates or chlorides based on the summary parameters. Decorrelation stretched [Gillespie *et al.*, 1986] CRISM images were created by projecting CRISM bands at 1.15, 2.38, and 1.80 μm as red, green and blue, respectively. Phyllosilicates and chlorides both have low reflectance values at 1.15 μm . Chlorides have high reflectance values at 2.38 μm , which is the position of a phyllosilicate metal-OH band. Finally, the phyllosilicates have relatively high reflectance values at 1.8 μm compared to the chlorides. This combination of spectral properties causes chlorides to appear green and phyllosilicates to appear blue in the Figure 3 images.

[5] Context Camera (CTX) and HiRISE images were used to determine the stratigraphic relationship(s) between the chlorides and phyllosilicates in our study area. A HiRISE digital terrain model (DTM) was created using the methods summarized by Kirk *et al.* [2008] on the PSP_005811_1470 and PSP_006668_1470 stereo pair. A color composite constructed from the CRISM summary parameters was combined with the HiRISE image after the methods of Delamere *et al.* [2010], which was then draped on the HiRISE-derived DTM for 3D analysis.

3. Results

[6] Phyllosilicates and chlorides are closely associated on the intercrater plains (Figure 1). Numerous valley network

¹Department of Geological Sciences, Stony Brook University, Stony Brook, New York, USA.

²Department of Earth and Space Sciences, University of Washington, Seattle, Washington, USA.

³Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona, USA.

⁴Johns Hopkins University Applied Physics Laboratory, Laurel, Maryland, USA.

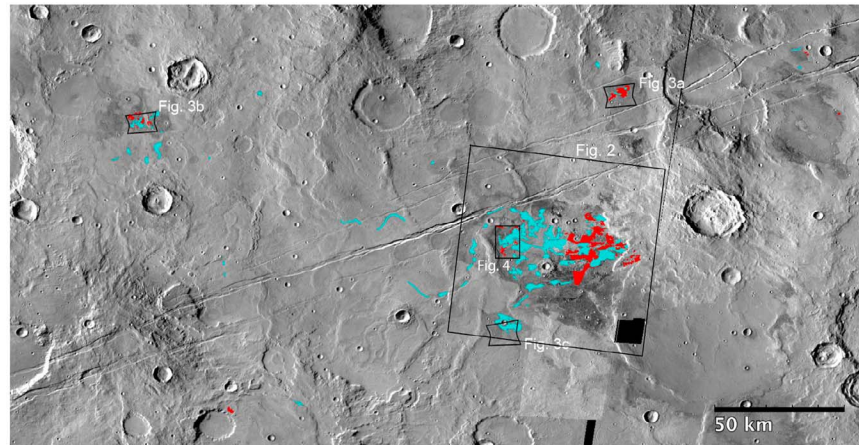


Figure 1. THEMIS band 9 radiance mosaic of the Terra Sirenum region. The mosaic is centered at 205 E, 32.6 S and is sampled at ~ 250 m/pixel. The locations of subsequent figures are shown. Red and blue areas correspond to phyllosilicates and chlorides, respectively.

channels dissect the region and many craters in the area exhibit layered ejecta blankets—a characteristic possibly indicative of the presence of past surface and subsurface water [e.g., Carr *et al.*, 1977; Carr, 2006].

[7] THEMIS data indicate that there are three basic mid-IR spectral types, including the chloride-bearing terrain, the unweathered Noachian surface, and a third spectral type associated with the phyllosilicate-bearing signature detected by CRISM (Figure 2). The spectral shape associated with the chloride-bearing units is similar to those derived by Osterloo *et al.* [2008]. The phyllosilicate-poor Noachian surface has a V-shaped spectrum similar to Thermal Emission Spectrometer (TES) Surface Type 2 or Group 4, while the phyllosilicate-bearing unit displays a shape more similar to TES Type 1 or Group 2 [Bandfield *et al.*, 2000; Rogers and Christensen, 2007]. Surfaces that are chloride or phyllosilicate-bearing have lower 465 cm^{-1} index values [Ruff and Christensen, 2007] than the surrounding terrain. The surface emissivity spectral shapes and spectral index results indicate a paucity of high-Si phases associated with the phyllosilicate and chloride-bearing units (see auxiliary material).¹

[8] Phyllosilicates are observed in CRISM images covering Terra Sirenum, and the phyllosilicates and chlorides both have distinctive and consistent spectral properties in CRISM data (Figure 3). The typical phyllosilicate spectrum is characterized by prominent absorptions at 1.41, 1.93, and $2.31\ \mu\text{m}$ with weaker absorptions at 2.39 and $2.54\ \mu\text{m}$. This spectrum is broadly similar to a range of Fe- or Mg-rich phyllosilicates, with vermiculite or hydrobiotite providing the closest match from the CRISM Spectral Library (ID #700). An additional possibility is a smectite-chlorite mixed-layer clay [Milliken *et al.*, 2010]. The chloride spectrum is characterized by a spectrally featureless red slope (relative to the surrounding terrain) from ~ 1.0 to $2.6\ \mu\text{m}$. This spectrum is replicated with some success in the laboratory by ratioing a mixture of halite and labradorite to a 100% labradorite spectrum (Figure 3d). While this mixture produces a reasonable approximation to the CRISM chloride spectrum, it is not necessarily a unique result. We are cur-

rently investigating a range of salt and silicate compositions at several particle size fractions to determine the uniqueness of the CRISM spectral signature (H. B. Jensen and T. D. Glotch, Near-IR spectra of salt-silicate mixtures: Implications for CRISM observations of chloride salt deposits on Mars, manuscript in preparation, 2010). In addition, as observed by Murchie *et al.* [2009], CRISM ratio spectra of the chloride deposits have a strong positive feature near $3\ \mu\text{m}$, indicative of a lack of structural or bound H_2O in these materials.

[9] Phyllosilicates and chlorides are present in a variety of geologic settings within the Terra Sirenum region. A simple relationship between the relatively unaltered materials, phyllosilicate-bearing materials, and chlorides is observed. The unaltered terrain is topographically the highest standing unit. In places, it gives way to a highly fractured and eroded unit that is phyllosilicate-bearing (Figure 3a) and has an exposed thickness of ~ 10 – 20 m. Below the phyllosilicate-bearing terrain is a phyllosilicate-poor terrain that is spectrally similar to the top unit. Chlorides are confined to local topographic lows, but stratigraphically overlie and embay both the phyllosilicate-poor and -bearing terrains. The chloride-bearing deposits appear to drape the underlying rugged surface topography, suggesting that they are relatively thin. This is supported by several profiles from the DTM, that give a mean minimum exposed thickness of ~ 5 m for the chloride-bearing unit.

[10] Phyllosilicates are confined to rugged knobs that are distinct from the cratered, but relatively level plains of the phyllosilicate-poor terrain (Figure 3b). Embayment relationships are seen throughout the region (Figure 4) and as shown in Figure 3a, the chlorides were deposited after the exposure of the phyllosilicate-bearing crust. The discontinuous nature of the chloride-bearing layer suggests that it was likely more extensive in the past.

[11] Chlorides are present in several channels throughout the region (Figure 3c). A corresponding HiRISE image and stereo-derived anaglyph (auxiliary material) indicates that chloride-bearing material is present as inverted channel-fill material as well as in hills and knobs in surrounding terrain. This suggests that chlorides are present as a cementing agent, making chloride-bearing materials less susceptible to

¹Auxiliary materials are available in the HTML. doi:10.1029/2010GL044557.

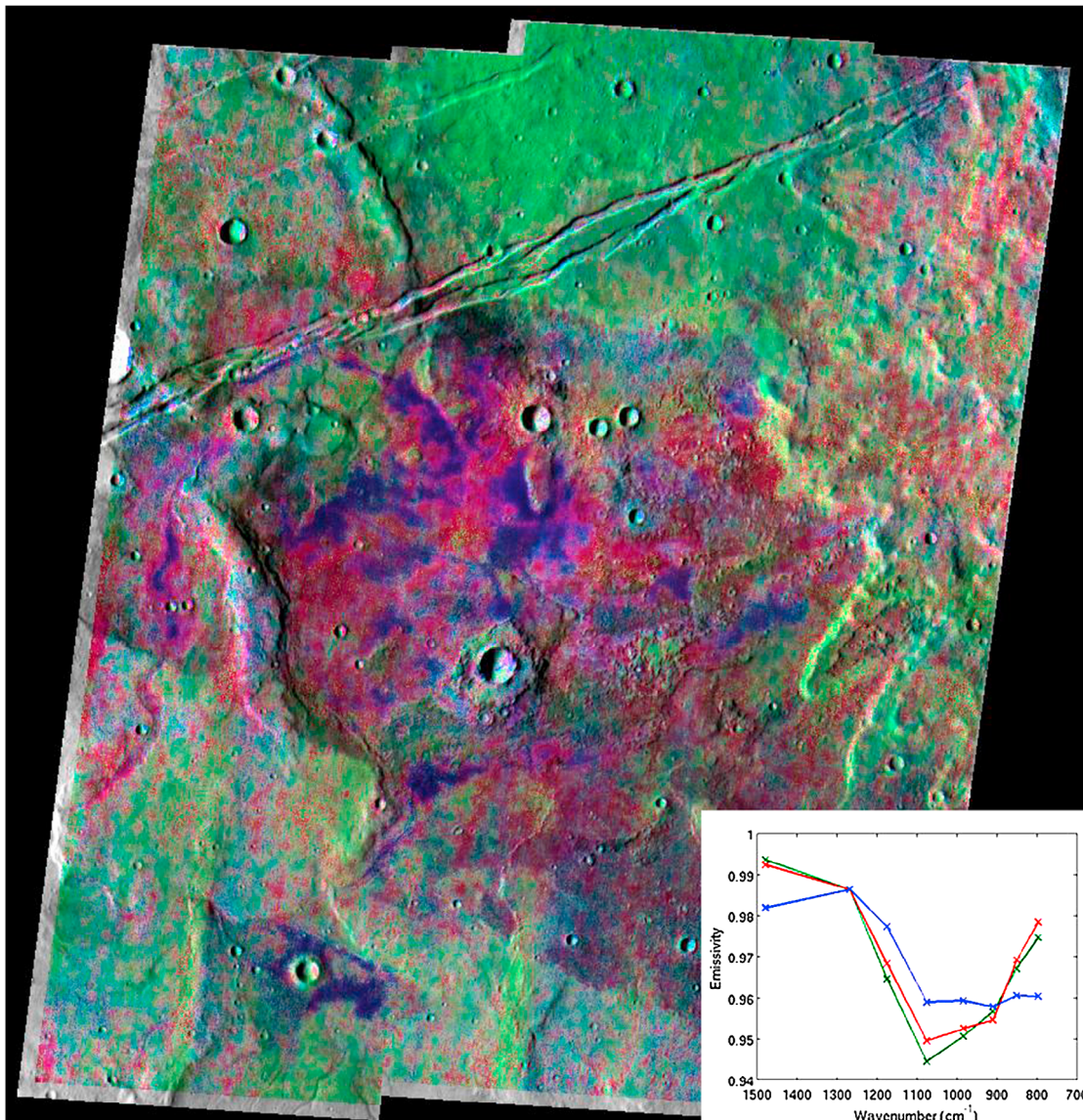


Figure 2. THEMIS composite image of Terra Sirenum. Three spectral end-members were isolated from the THEMIS data. Altered materials corresponding phyllosilicates are shown as red, unaltered materials are shown as green, and chloride-bearing terrain is shown as blue. THEMIS end-member spectra corresponding to each unit are shown in the inset.

erosion in the absence of liquid water at or near the surface since its deposition. This is supported by the observation that chloride-bearing materials tend to have higher thermal inertias than the surrounding terrains, indicating a coarser grain size, induration, or cementation [Osterloo *et al.*, 2008].

[12] The western portion of the main chloride deposit in the region is covered by multiple HiRISE images, including a stereo-pair from which a DTM was derived (Figure 4). This DTM, combined with a false color image created from CRISM image HRL0000860C, provides an additional perspective on the relationship between the three surface units. The phyllosilicates are exposed in rugged knobs throughout the region as well as some crater ejecta. The apparent abundance of phyllosilicates is variable, as some knobs have a distinctly stronger phyllosilicate signature than others. Analysis of the DTM indicates that while much of the surface in this region has this characteristic knobby texture, the

phyllosilicates tend to occur in the higher-standing knobs. This is consistent with apparent confinement of phyllosilicates to a distinct layer. As seen in Figure 4b, the chlorides embay the phyllosilicate-bearing hills, providing strong evidence that they formed subsequent to the formation and exposure of the phyllosilicates.

4. Discussion

[13] Phyllosilicates are not evenly distributed throughout the Terra Sirenum region and are geographically clustered with chloride-bearing deposits. While the stratigraphic relationships suggest that chlorides were deposited some time after the formation of the phyllosilicates, the consistent regional spatial correlation suggests a genetic relationship between the two episodes of mineralization. As a surface component, phyllosilicates are not volumetrically significant

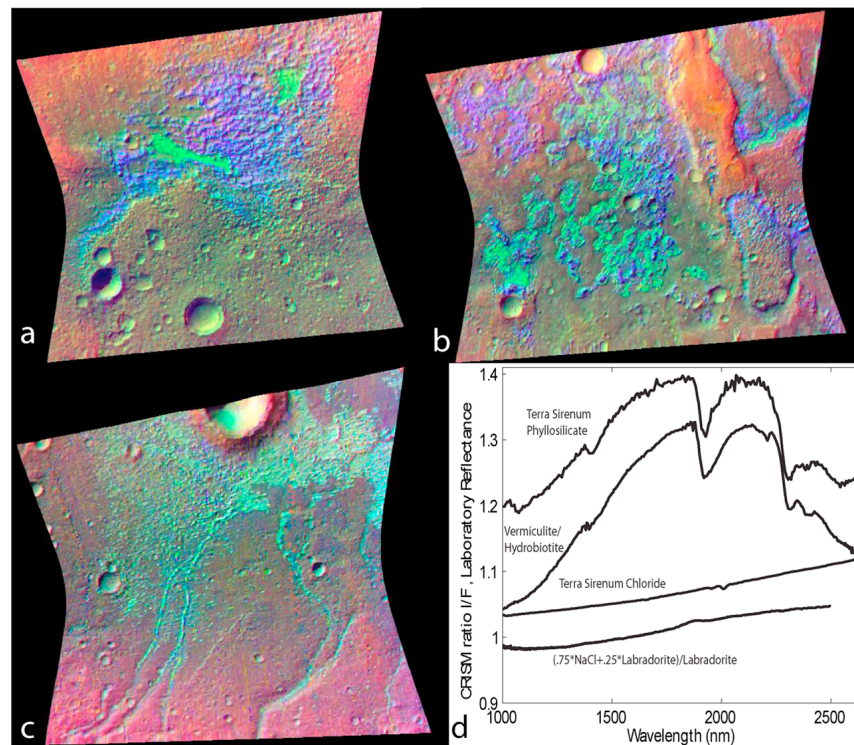


Figure 3. CRISM images revealing the presence of phyllosilicates and chloride salts, and their characteristic NIR spectra. CRISM bands at 1.15, 2.38, and 1.80 μm were chosen as red, green, and blue, to create the color composite DCS images. (a) CRISM image FRT0000AB81. (b) CRISM image FRT0000A253. (c) CRISM image FRT0000BB36. CRISM images are ~ 10 km across. Phyllosilicates appear blue and chlorides appear green. (d) Characteristic ratio spectra of phyllosilicates and chlorides. The phyllosilicate spectrum is matched best by vermiculite/hydrobiotite based on band positions and shapes. The red slope associated with the chloride deposits is reproduced by ratioing a mixture of 75% halite and 25% labradorite to a pure labradorite standard.

where they do occur. THEMIS (Figure 2) spectra from the clay-bearing regions display “box-shaped” spectra broadly similar to TES Type 1 [Bandfield *et al.*, 2000] or Group 2 [Rogers and Christensen, 2007] that are consistent with relatively unaltered basalt. The “V-shaped” mid-IR spectral character of the surrounding surface is consistent with either a glass-rich basalt (or basaltic andesite) [Bandfield *et al.*, 2000] or heavily weathered basalt rich in phyllosilicates [Wyatt and McSween, 2002]. Phyllosilicates are not identified by CRISM in regions displaying this spectral character in THEMIS data, which suggests they may be glass-rich. This view is supported by the high 465 cm^{-1} TES index values that are indicative amorphous silica but not phyllosilicates [Ruff and Christensen, 2007]. The transition from the glassy “V-shaped” spectrum to the “box-shaped” spectrum may have occurred when the crust was chemically weathered, resulting in dissolution of the glass, forming phyllosilicates and perhaps other secondary phases. However, the resulting phyllosilicates make up a relatively minor portion of the weathered crust ($< 10\%$), leading to a THEMIS spectral shape consistent with an unaltered surface.

[14] The best match to the CRISM spectra of the phyllosilicate-bearing unit is vermiculite, hydrobiotite, or perhaps, a smectite-chlorite mixed-layer clay. Vermiculite can form by the alteration of a variety of mafic phases, due to low-temperature weathering, hydrothermal processes, or ground-water percolation [Bassett, 1961]. Hydrobiotite, which consists

of mixed layers of vermiculite and biotite, can form as a high-temperature alteration product, or as a weathering product of biotite [Wilson, 1970; Brindley *et al.*, 1983]. Mixed-layer clays in general result from burial diagenesis in the presence of fluids, and have been suggested to occur on Mars [Milliken *et al.*, 2010]. Thus, the nature of the specific weathering conditions that the crust was subjected to in this region of Mars is difficult to determine. We note, however, that both vermiculite and smectite-chlorite mixed-layer clays would require secondary diagenetic alteration of the initially formed clays. The timing of this alteration is not constrained, but the geographic relationship between the chlorides and the phyllosilicates in Terra Sirenum suggests that the chloride deposition could be related to percolating fluids responsible for this diagenetic event.

5. Conclusions

[15] Terra Sirenum has the largest regional occurrence of chlorides on Mars. The chlorides lie stratigraphically above the ancient Noachian crust, which in some places was aqueously weathered to produce Fe- or Mg-rich phyllosilicates. The chlorides likely formed during the late Noachian-to early Hesperian as a result of groundwater discharge and evaporation. The ancient crust in Terra Sirenum is rich in volcanic and/or impact-generated glasses, making it highly susceptible to weathering by percolating fluids. A later event

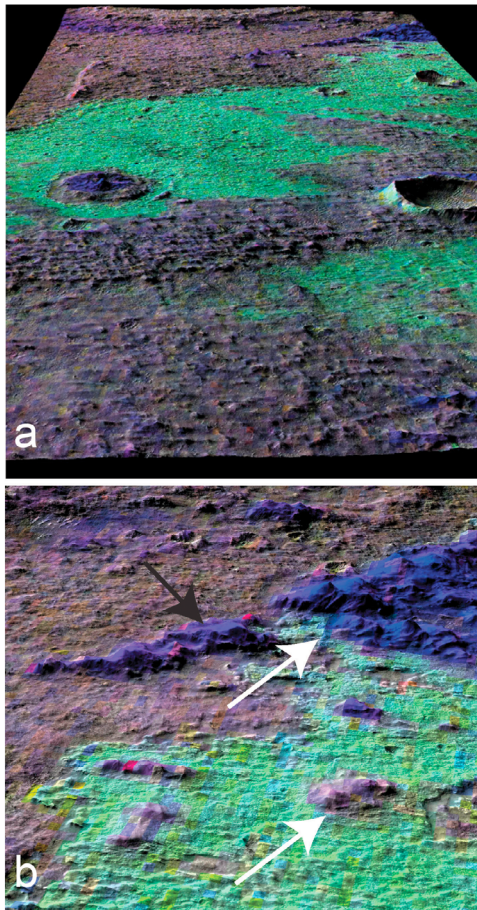


Figure 4. Composite HiRISE DEM and CRISM false color images. Green corresponds to chlorides and blue corresponds to phyllosilicates. Vertical exaggeration is $\sim 3X$. (a) Overview of region showing a thin coating of chloride-rich materials coating the rugged highlands material. (b) Higher knobs are phyllosilicate-bearing (black arrow) while lower terrain is phyllosilicate free. Chlorides embay both phyllosilicate-bearing and phyllosilicate-free hills (white arrows).

involving groundwater, and perhaps surface water, led to the formation of the chloride-bearing units, and potentially, diagenesis of the initially deposited clays.

[16] **Acknowledgments.** TDG, JLB, and HBJ were funded by NASA Mars Data Analysis Program grant NNX08AK93G. We thank two anonymous reviewers who improved the clarity of the manuscript.

References

- Bandfield, J. L. (2009), Effects of surface roughness and graybody emissivity on Martian thermal infrared spectra, *Icarus*, *202*, 414–428, doi:10.1016/j.icarus.2009.03.031.
- Bandfield, J. L., V. E. Hamilton, and P. R. Christensen (2000), A global view of Martian surface compositions from MGS-TES, *Science*, *287*, 1626–1630, doi:10.1126/science.287.5458.1626.
- Bandfield, J. L., D. Rogers, M. D. Smith, and P. R. Christensen (2004), Atmospheric correction and surface spectral unit mapping using Thermal Emission Imaging System data, *J. Geophys. Res.*, *109*, E10008, doi:10.1029/2004JE002289.
- Bassett, W. A. (1961), The geology of vermiculite occurrences, *Clays Clay Miner.*, *10*, 61–69, doi:10.1346/CCMN.1961.0100106.

- Bridges, J. C., and M. M. Grady (2000), Evaporite mineral assemblages in the nakhlite (Martian) meteorites, *Earth Planet. Sci. Lett.*, *176*, 267–279, doi:10.1016/S0012-821X(00)00019-4.
- Brindley, G. W., P. E. Zalba, and C. M. Bethke (1983), Hydrobiotite, a regular 1:1 interstratification of biotite and vermiculite layers, *Am. Mineral.*, *68*, 420–425.
- Carr, M. H. (2006), *The Surface of Mars*, doi:10.1017/CBO9780511536007, Cambridge Univ. Press, New York.
- Carr, M. H., et al. (1977), Martian impact craters and emplacement of ejecta by surface flow, *J. Geophys. Res.*, *82*, 4055–4065, doi:10.1029/JS082i028p04055.
- Delamere, W. A., et al. (2010), Color imaging of Mars by the High Resolution Imaging Science Experiment (HiRISE), *Icarus*, *205*, doi:10.1016/j.icarus.2009.03.012.
- Gendrin, A. N., et al. (2005), Sulfates in Martian layered terrains: The OMEGA/Mars Express view, *Science*, *307*, 1587–1591, doi:10.1126/science.1109087.
- Gillespie, A. R., A. B. Kahle, and R. E. Walker (1986), Color enhancement of highly correlated images: I. Decorrelation and HSI contrast stretches, *Remote Sens. Environ.*, *20*, 209–235, doi:10.1016/0034-4257(86)90044-1.
- Gooding, J. L., S. J. Wentworth, and M. E. Zolensky (1991), Aqueous alteration of the Nakhla meteorite, *Meteoritics*, *26*, 135–143.
- Kirk, R. L., et al. (2008), Ultrahigh resolution topographic mapping of Mars with MRO HiRISE stereo images: Meter-scale slopes of candidate Phoenix landing sites, *J. Geophys. Res.*, *113*, E00A24, doi:10.1029/2007JE003000.
- McGuire, P. C., et al. (2009), An improvement to the volcano-scan algorithm for atmospheric correction of CRISM and OMEGA spectral data, *Planet. Space Sci.*, *57*, 809–815, doi:10.1016/j.pss.2009.03.007.
- McLennan, S. M., et al. (2005), Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars, *Earth Planet. Sci. Lett.*, *240*, 95–121, doi:10.1016/j.epsl.2005.09.041.
- Milliken, R. E., D. L. Bish, T. Bristow, and J. F. Mustard (2010), The case for mixed-layered clays on Mars, *Lunar Planet. Sci.*, *XL1*, Abstract 2030.
- Murchie, S. L., et al. (2009), A synthesis of Martian aqueous mineralogy after 1 Mars year of observations from the Mars Reconnaissance Orbiter, *J. Geophys. Res.*, *114*, E00D06, doi:10.1029/2009JE003342.
- Naughton, J. J., V. A. Lewis, D. Hammond, and D. Nishimoto (1974), The chemistry of sublimates collected directly from Kilauea Volcano, Hawaii, *Geochim. Cosmochim. Acta*, *38*, 1679–1690, doi:10.1016/0016-7037(74)90185-9.
- Osterloo, M. M., V. E. Hamilton, J. L. Bandfield, T. D. Glotch, A. M. Baldrige, P. R. Christensen, L. L. Tornabene, and F. S. Anderson (2008), Chloride-bearing materials in the southern highlands of Mars, *Science*, *319*, 1651–1654, doi:10.1126/science.1150690.
- Pelkey, S. M., et al. (2007), CRISM multispectral summary products: Parameterizing mineral diversity on Mars from reflectance, *J. Geophys. Res.*, *112*, E08S14, doi:10.1029/2006JE002831.
- Rogers, A. D., and P. R. Christensen (2007), Surface mineralogy of Martian low-albedo regions from MGS-TES data: Implications for upper crustal evolution and surface alteration, *J. Geophys. Res.*, *112*, E01003, doi:10.1029/2006JE002727.
- Ruff, S. W., and P. R. Christensen (2007), Basaltic andesite, altered basalt, and a TES-based search for smectite clay minerals on Mars, *Geophys. Res. Lett.*, *34*, L10204, doi:10.1029/2007GL029602.
- Tosca, N. J., and S. M. McLennan (2006), Chemical divides and evaporite assemblages on Mars, *Earth Planet. Sci. Lett.*, *241*, 21–31, doi:10.1016/j.epsl.2005.10.021.
- Wilson, W. J. (1970), A study of weathering in a soil derived from a biotite-hornblende rock: 1. Weathering of biotite, *Clay Miner.*, *8*, 291–303, doi:10.1180/claymin.1970.008.3.07.
- Wray, J. J., S. L. Murchie, S. W. Squyres, F. P. Seelos, and L. L. Tornabene (2009), Diverse aqueous environments on ancient Mars revealed in the southern highlands, *Geology*, *37*, 1043–1046, doi:10.1130/G30331A.1.
- Wyatt, M. B., and H. Y. McSween (2002), Spectral evidence for weathered basalt as an alternative to andesite in the northern lowlands of Mars, *Nature*, *417*, 263–266, doi:10.1038/417263a.