

OUTSIDE IN: CONSTRAINTS ON MARTIAN VOLATILES FROM ORBITAL, IN SITU, AND LABORATORY TIR SPECTROSCOPY. V. E. Hamilton, Southwest Research Institute, 1050 Walnut St. #300, Boulder, CO 80302 USA (hamilton@boulder.swri.edu).

Abstract: Over the last two decades, our knowledge of the mineralogy of Mars' uppermost surface, especially the role of volatile-bearing (or “volatile-involved”) phases, has evolved dramatically. This new information feeds back into not just our understanding of surface processes, but also crustal formation, and ultimately the chemistry of Mars’ interior. The identification of these phases on the “outside” of Mars should be taken into account as we attempt to understand volatiles “inside” the planet.

Background: Our current and still growing knowledge of Martian surface mineralogy literally fills entire volumes [e.g., 1] and can no longer be reasonably summarized in a single abstract or talk. For that reason, I focus here on mineralogical data derived from TIR spectroscopy ($\sim 5 - 50 \mu\text{m}$), which is sensitive to the fundamental vibrational modes of geologic phases that are diagnostic of chemistry and structure (or lack of structure). Because minerals are distinguished by their chemistry and structure, virtually all geologic phases have unique vibrational spectra. Although there are few compositions that do not exhibit any TIR features, there is evidence to suggest that such phases do occur on Mars, as described below.

H₂O: A feature at $\sim 1630 \text{ cm}^{-1}$ in spectra of geologic phases is diagnostic of bound water. [2] noted the presence of this feature in Mars Global Surveyor TES spectra of Martian dust, and [3] identified it in MER Mini-TES outcrop spectra from Meridiani Planum, where they estimate a total of 5.5 wt.% H₂O. [4] created a global map of this feature’s strength and there is a strong correlation with classical high albedo regions, indicating that bound H₂O in some phase(s) is common on Mars. However, this feature is only observable in relatively fine particulate minerals that exhibit transparency in this spectral region, so it is possible that bound water also could be present in low albedo regions comprised of relatively coarser particulates. This feature alone is diagnostic only of the presence of bound water, so the carrier is not well constrained and it could occur in more than one phase unless other diagnostic spectral features are considered.

Zeolites: [4] proposed zeolites as a possible carrier of H₂O in the Martian dust based on the presence of the bound water feature as well as an 830 cm^{-1} transparency feature at that is present in zeolites. The 830 cm^{-1} feature also is present in relatively fine particulate plagioclase feldspars, so although zeolites can account

for both features, they do not provide a unique interpretation.

SiO₂ phases: Quartz and amorphous silica are present on Mars as both primary and secondary phases.

Quartz. TES and THEMIS orbital data exhibit evidence for α -quartz (hereafter, quartz) in limited regions around the Syrtis Major volcanic center [5, 6]. On Earth, quartz is commonly produced from evolved magmas and in cherts. Based on the geological and mineralogical context, the quartz around Syrtis Major has been interpreted by the above investigators as being a component of a quartzofeldspathic (granitoid) composition, indicative of a highly evolved magma.

Amorphous silica. Early orbital observations by TES showed that much of the surface of Mars contains a component ($\sim 25 \text{ vol. \%}$) that is consistent with alkali-bearing amorphous silica. Initially, this component was interpreted to be a primary glass in a basaltic andesitic composition [7], and subsequently proposed as potentially representing smectite phyllosilicates [8], sedimentary silica [9], or leached basaltic glass [10]. The current consensus favors an interpretation that involves some sort of aqueous weathering producing alkali-rich silica over much of Mars. Data from the Mini-TES on *Spirit* identified amorphous silica ($\sim 91 \text{ wt.\% SiO}_2$) in Gusev crater [11, 12], providing additional TIR evidence for the presence of this phase on the surface of Mars. Despite the apparently widespread occurrence of secondary silica on Mars, local occurrences of primary silica glass are present as well, such as at Nili Patera, where there is evidence of primary silica in a dacitic composition based on TES and THEMIS spectral data [13].

Phyllosilicates: As described above, smectite phyllosilicates were proposed as an alternative to the high silica amorphous phase in TES orbital data due to their broad spectral similarities. However, well ordered, dioctahedral smectites have distinctive TIR features that have not been observed in TES data [14, 15]. On the other hand, there is increasing evidence from TIR data for poorly-ordered phyllosilicates on Mars [16, 17]. [18, 19] have shown that heat-induced dehydration or dehydroxylation of dioctahedral phyllosilicates alters the mineral structure leading the diagnostic TIR features to resemble those of amorphous phases.

Carbonates: Anhydrous carbonates and/or their decomposition products have been identified by TIR spectroscopy on Mars. TES data show that carbonate

(dominantly magnesite, $MgCO_3$) is a component of the surface dust at abundances of ~3 - 5 wt.% [20]. This dust is present globally in variable abundance and may represent a large reservoir of CO_2 . Localized occurrences of hydrothermally-produced carbonate have been identified in Gusev crater [20]. Mini-TES TIR spectra of these deposits are consistent with Mg-Fe carbonate comprising approximately 34 vol.% of the outcrop. [22] reported evidence for the interaction of Syrtis Major lavas with subsurface carbonates, or, alternatively, the eruption of carbonate-bearing lavas that were subsequently devolatilized.

Oxides: Crystalline hematite ($\alpha\text{-Fe}_2\text{O}_3$) was observed in early TES orbital observations [23]. The distribution of this phase is limited to regional deposits in Meridiani Terra and Aram Chaos and isolated deposits in the Valles Marineris [24], where the geologic context strongly favors precipitation from aqueous fluids. TES spectra show the hematite to be crystallographically oriented [25]. The Mars Exploration Rover *Opportunity* was sent to Meridiani Planum specifically to investigate these materials. The oriented TIR spectral character was confirmed *in situ* by Mini-TES in association with mm-sized dark spherules thought to have formed as concretions during post depositional diagenesis [26].

Sulfates: Sulfates have been recognized in Mini-TES observations at Meridiani Planum. [27] have identified approximately 30 vol.% Mg-, Ca-, and Fe-bearing sulfates in outcrop materials; these are interpreted to have been evaporatively deposited. [28] found ~10% sulfate in dark sands, with one possible formation mechanism being the formation of sulfate from outgassed H_2SO_4 during volcanism.

Chlorides: As described above, there are very few geologic materials that have no spectral signature at all - chloride salts (e.g., halite) are one of these as a result of their isometric structure and strongly ionic bonding. However, the presence of these spectrally featureless components can be deduced from their effect on the observed spectral properties of the other phases that are present, and this effect has been used to identify chloride salts from TES and THEMIS data in small, but widespread deposits concentrated in the southern highlands of Mars [29, 30]. Most observations of chlorides on Mars are consistent with formation via ponding of surface runoff or groundwater upwelling, although efflorescence and hydrothermal activity may also be possible in some locales. Chlorine is an abundant component of the Martian soil, yet identifying the mineralogical phase from which it is derived has been challenging and chloride salts offer a strong candidate.

Summary: Many geologic phases identified on Mars via TIR spectroscopy are associated with a num-

ber of volatile species (H_2O/OH , CO_2 , Cl , S , O_2) and occur as both primary and secondary phases. Evidence for evolved igneous compositions suggests increased volatiles in magmas, which points to an interior source. Although there is a lack of strong evidence for plate tectonics, processes such as partial melting of basaltic crust can yield evolved compositions. Some volatiles may have originated from volcanic outgassing. The volatiles associated with secondary alteration products (or their production processes) are less easily related to the Martian interior in part due to ambiguities in the ultimate origin of the volatiles (e.g., interior magmatic/outgassing, endogenic atmosphere, exogenic atmosphere). Nonetheless, the presence, compositions, and abundances of volatiles in surface minerals can and should be considered as a constraint on volatiles in the Martian interior.

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