Identification of the Ca-sulfate bassanite in Mawrth Vallis, Mars

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\textbf{Abstract}

The region surrounding the Mawrth Vallis outflow channel on Mars hosts thick layered deposits containing diverse phyllosilicate minerals. Here we report detection of the Ca-sulfate bassanite on the outflow channel floor, requiring a more complex aqueous chemistry than previously inferred for this region. The sulfate-bearing materials underlie phyllosilicate-bearing strata, and provide an opportunity for testing proposed models of martian geochemical evolution with a future landed mission.

1. Introduction

Hydrated minerals on the surface of Mars including sulfates and phyllosilicates attest to a rich planetary history of water–rock interactions (e.g., Squyres et al., 2004; Bibring et al., 2006). There is increasing evidence for diverse conditions of aqueous alteration, which likely varied over time and space (e.g., Mustard et al., 2008; Murchie et al., 2009a; Ehlmann et al., 2009). From the perspective of planetary habitability, perhaps the most intriguing are the Noachian-aged exposures of phyllosilicates, which are inferred to have formed through alteration at weakly acidic to alkaline pH (Chevrier et al., 2007).

The region surrounding Mawrth Vallis contains one of the largest exposures of phyllosilicates on the martian surface (Poulet et al., 2005; Bibring et al., 2006). The phyllosilicates occur in light-toned layered deposits of possible sedimentary or pyroclastic origin (Loizeau et al., 2007, 2010; Michalski and Noe Dobrea, 2007), and exhibit a ubiquitous stratigraphic pattern of Al-rich phyllosilicates including kaolinite and montmorillonite overlying Fe-rich nontroilitite (Wray et al., 2008; Bishop et al., 2008; McKeown et al., 2009). Exposures are scattered across a region $\sim$1000 $\times$ 1000 km in size (Noe Dobrea et al., 2010). Formation of these phyllosilicates must have produced excess cations that were accommodated in complementary salts or oxides (Milliken et al., 2009), yet to date only ferric oxides/hydroxides (Wray et al., 2008; Poulet et al., 2008b; McKeown et al., 2009) and highly localized jarosite ($\text{KFe}_3\text{[SO}_4\text{]}_2\text{[OH]}_6$; Farrand et al., 2009) have been identified in the region. Weak absorptions at $\sim$2.4–2.5 $\mu$m in spectra dominated by phyllosilicates may be consistent with other secondary minerals as a lesser constituent of these rocks (Bishop et al., 2009b), but these spectral features are not yet assigned to specific minerals.

Here we report on a search for locations in the Mawrth Vallis region in which hydrated salts are the spectrally dominant component, for which we used data from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM; Murchie et al., 2007) supplemented by images from the High Resolution Imaging Science Experiment (HiRISE; McEwen et al., 2007), both on NASA's Mars Reconnaissance Orbiter.

2. Methods

We examined browse products (Seelos et al., 2008) for CRISM targeted observations distributed across the region surrounding Mawrth Vallis (Fig. 1). In particular, we searched for spatially contiguous areas highlighted by the BD1900 parameter, which tracks hydrated minerals, but not highlighted by the BD2210 or D2300 parameters that track Al- or Fe/Mg-phyllosilicates, respectively (Pelkey et al., 2007). We took special note of locations highlighted by the SINDEX parameter used to map hydrated sulfates (Roach et al., 2009).
absorptions at 2.2 or 2.3 μm characteristic of phyllosilicates (e.g., nontronite). The overall slope of these spectra from 1 to 2.5 μm is influenced by the choice of spectral denominator, but the positions of the 1.91 and 2.48 μm bands are independent of this choice. The same band positions are also observed in multiple CRISM observations at each site (Full-Resolution Targets 9326, 10424, and 13E49 for sites 1 and 2; FRTs C872, 12D3C, and 12E72 for site 3).

Several different hydrated salts and zeolites have absorptions near 1.9 and 2.4–2.5 μm (Fig. 2a); however, Ca-sulfates provide the best match to our CRISM spectra. The spectrum from site 1 exhibits the strongest absorptions at 1.91 and 2.48 μm and has additional features including a doublet at 1.43 and 1.47 μm and weaker features at 1.77, 2.10, and 2.26 μm. Together these spectral features are most consistent with bassanite (CaSO₄·½H₂O). For comparison, gypsum (CaSO₄·2H₂O) has a similar suite of absorptions at different wavelengths: 1.74, 1.94, 2.21, and 2.41 μm, with a broader triplet at 1.4–1.5 μm and a 1.2 μm band not observed in our spectrum from site 1. Some hydrated chlorides such as carnallite also have similar spectral features, but again their exact wavelengths are distinct from what we observe here (Fig. 2a). Polyhydrated Mg-sulfates lack absorptions at 2.5 or 1.75–1.8 μm and are an even poorer match. Indeed, to our knowledge no measured hydrated salts share the narrow 1.91 μm and strong 2.48 μm absorptions of bassanite (e.g., Crowley, 1991).

Zeolites are also characterized by strong absorptions at ~1.4, 1.9, and 2.4–2.5 μm (Cloutis et al., 2002), and their presence in the Mawrth Vallis region has been suggested on the basis of thermal infrared spectral analysis (Michalski and Fergason, 2009). However, near-IR spectra of most zeolites have no distinct minimum longward of 2.4 μm nor a band in the 1.75–1.8 μm range (Cloutis et al., 2002). A counterexample is analcime, which has these two characteristics and has been identified elsewhere on Mars (Ehlmann et al., 2009; Wray et al., 2009), but its band centers at 1.79 μm and 2.52 μm are distinct from those in our site 1 spectrum (Fig. 2a). No other mineral or combination of minerals in our spectral libraries has all the features in the observed spectrum; therefore, we conclude that the spectrum of site 1 indicates bassanite as the spectrally dominant component, although additional minerals that are featureless in this spectral range (e.g., anhydrous sulfates) could also be present. Spectra from site 2 and the noisier observations of site 3 are also consistent with—though less diagnostic of—bassanite, possibly in mixtures with Fe-bearing phases that could be responsible for the spectral curvature from 1 to 1.5 μm and the obscuration of the 1.4 μm absorption (Fig. 2a).

Comparing the mapped distribution of the probable bassanite to imaging and topographic data reveals that it is found in topographic depressions (e.g., Fig. 2d) that are surrounded by exposures of Fe/Mg-smectite (Fig. 2b and c). Although some of the bassanite could be erosional debris accumulating in these depressions, HiRISE images show that it also occurs in distinct layers (Fig. 3a) that stratigraphically underlie the adjacent Fe/Mg-smectites (Fig. 3b and c). Stratigraphic boundaries between the smectite and sulfate range from gradual (Fig. 3a) to sharp (Fig. 3c) relative to CRISM resolution. Color images show that the areas with the strongest sulfate signatures are bluer than adjacent Fe/Mg-smectite-bearing materials (e.g., Fig. 3b), consistent with a lower Fe³⁺ content in the spectrally dominant mineral (Delamere et al., 2010). The sulfate-bearing materials exhibit varying fracture patterns at scales of a few meters (Fig. 3a–c), and appear texturally distinct from the overlying smectite-bearing materials, suggesting different physical or chemical properties and/or a different modification history. The base of the sulfate-bearing strata is not observed, but exposures such as that in Fig. 3a suggest a thickness of at least a few meters, based on the scarp geometry and assuming the beds are approximately horizontal.

3. Results

We identify three locations with spectra dominated by a non-phyllosilicate hydrated phase, all of which occur on the floor of Mawrth Vallis (Fig. 1). Spectra from these sites share strong bands at 1.91 and 2.48 μm (Fig. 2a), and they do not have the distinct
On the basis of their distribution across terrains of different ages, Bibring et al. (2006) proposed that martian sulfates generally formed later than phyllosilicates. This hypothesis can be tested by observations of places where these two minerals are found in contact. Here we have shown that sulfate-bearing beds in Mawrth Vallis underlie Fe/Mg-smectite-bearing beds, which had previously been identified as the lowest stratigraphic unit exposed in the region (Wray et al., 2008; McKeown et al., 2009). Although the timing and location of smectite formation are unknown, the principle of superposition implies that the beds hosting the sulfates predate those hosting the phyllosilicates. Taken together with stratigraphic analyses of several other regions where phyllosilicates and sulfates are interbedded or intimately mixed (Poulet et al., 2008a; Wray et al., 2009; Milliken et al., 2010; Weitz et al., 2010), our results suggest that the alteration history of at least several regions on Mars may have been different or more complex than the model of Bibring et al. (2006) suggests.

However, an alternative explanation at Mawrth Vallis could be that sulfates formed in the subsurface coevally with (or after) phyllosilicates. Specifically, if at least some of the region’s phyllosilicates formed via top-down weathering that leached monovalent and divalent cations (Na, Ca, Mg) from the upper horizons (e.g.,

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McKeown et al., 2009; Noe Dobrea et al., 2010), then these should have precipitated elsewhere in salts or oxides (Milliken et al., 2009). Especially on Mars, Ca-sulfate is the least soluble of the expected salts (Tosca et al., 2008) and therefore could have precipitated in the lower horizons at Mawrth Vallis while more soluble salts—including the Mg/Fe sulfates that appear to dominate many equatorial layered deposits (e.g., Gendrin et al., 2005; Roach et al., 2009; Bishop et al., 2009a)—were transported elsewhere either initially or after subsequent dissolution (Milliken et al., 2009). Even if bassanite in Mawrth Vallis formed only from the Ca liberated from smectite interlayer sites, leaching of the uppermost ~50 m (Wray et al., 2008; McKeown et al., 2009) of layered deposits ~50% nontronite by volume (Poulet et al., 2008b) could have formed a ~meter-thick layer of pure bassanite. If additional Ca was leached from primary silicates and/or other minerals are present in the bassanite-bearing unit (both likely), then its thickness could be greater. This hypothesis could be tested by future in situ observations of the Al-clay, Fe/Mg-clay, and sulfate-bearing layers; in particular, major element chemistry and microscopic textures would constrain whether the Al-clay horizons could have been the source of cations that combined with sulfate in solution to form the observed salts.

The detection of bassanite (CaSO$_4$\(\frac{1}{2}\)H$_2$O) in Mawrth Vallis (23°N) is of interest to global studies of Ca-sulfates on Mars. Previously, gypsum (CaSO$_4$\(\frac{1}{2}\)H$_2$O) has been found in circumpolar dunes at ~80°N (Langevin et al., 2005) and in Columbus crater at 29°S (Wray et al., 2009); preliminary reports of gypsum in equatorial layered deposits (e.g., Gendrin et al., 2005) have been refuted by subsequent analyses (Noe Dobrea et al., 2008; Kuzmin et al., 2009; Bishop et al., 2009a), although Ca-sulfates may be present in one portion of Noctis Labyrinthus (Mangold et al., 2010). Both Mars Exploration Rovers have also found evidence for Ca-sulfates, for which the orbital and surface remote sensing data are most consistent with anhydrite (CaSO$_4$) in both the rocks of Meridiani Planum at 2°S (Clark et al., 2005; Glotch et al., 2006) and the bright soils of the Columbia Hills at 15°S (Johnson et al., 2007; Lane et al., 2008). Collectively, these observations suggest a general trend of increasing Ca-sulfate hydration with latitude, as might be expected if relative humidity and/or surface temperature are controlling the hydration state. However, the slow kinetics of Ca-sulfate hydration state changes under Mars-like conditions may prevent equilibration with the atmosphere (e.g., Vaniman et al., 2008, 2009), as appears to be the case for martian Mg-sulfates (Roach et al., 2009).

![Fig. 3. Meter-scale textures of probable sulfate-bearing layers and overlying smectite-bearing layers.](image)
Bassanite could instead have formed via dehydration from gypsum under a warmer paleoclimate (Vaniman et al., 2009). Other alternatives proposed by Vaniman et al. (2008) include bassanite formation under hydrothermal conditions, via burial diagenesis of gypsum, or from acid-sulfate alteration of preexisting calcium carbonates. The range of hydration states observed across the planet may therefore reflect differences in precursor mineralogy and/or conditions of sulfate formation or diagenetic history. For example, Ca-sulfates were likely buried to hundreds of meters depth at Meridiani Planum (Hynek et al., 2002) and Mawrth Vallis (Loizeau et al., 2007, 2010; Noe Dobrea et al., 2010), which may not have occurred in Columbus crater or the polar sand sea. In situ study of the minerals accompanying bassanite at Mawrth Vallis would help to distinguish between the diagenetic, hydrothermal, and acid alteration hypotheses for its origin. Once formed, bassanite may persist longer at the surface of Mars than it does on Earth because of the colder, more arid martian conditions (Vaniman et al., 2009).

Together with the jarosite identified by Farrand et al. (2009), our detection of bassanite adds to the already considerable mineralogical diversity of the Mawrth Vallis region (Loizeau et al., 2007; Wray et al., 2008; Bishop et al., 2009a; McKeown et al., 2009; Noe Dobrea et al., 2010). Mawrth Vallis is one of the final candidate landing sites for the Mars Science Laboratory mission, for which it has been argued that an ideal site would provide access to both phyllosilicates and sulfates (Grotzinger, 2009). Relative to the currently favored landing ellipse, Farrand et al.'s (2009) jarosite lies ~95 km from its northwest edge, whereas our site 3 discussed above is ~30 km to the northeast (Fig. 1). Additional CRISM coverage of the channel floor should be acquired to search for other sulfate exposures even nearer the ellipse. If the way is trafficable, driving eastward and down into Mawrth Vallis would also enable a direct test of whether some or all of the region's phyllosilicates and layered deposits predate the outflow channel (Poulet et al., 2005; Loizeau et al., 2007, 2010; Michalski and Noe Dobrea, 2007) or constitute a younger drape deposit (Howard and Moore, 2007; Wray et al., 2008), with significant implications for when and how these deposits formed. Mawrth Vallis remains an intriguing and geologically diverse region for future surface exploration.

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References


Clark, R.N., Swayze, G.A., Wise, R.A., Livo, K.E., Hoefen, T.M., Kokaly, R.F., Sutley, S.J., 2007. USGS digital spectral library splib06a. US Geol. Surv., Digital Data Series 30 km to the northeast (Fig. 1). Additional CRISM coverage of the channel floor should be acquired to search for other sulfate exposures even nearer the ellipse. If the way is trafficable, driving eastward and down into Mawrth Vallis would also enable a direct test of whether some or all of the region's phyllosilicates and layered deposits predate the outflow channel (Poulet et al., 2005; Loizeau et al., 2007, 2010; Michalski and Noe Dobrea, 2007) or constitute a younger drape deposit (Howard and Moore, 2007; Wray et al., 2008), with significant implications for when and how these deposits formed. Mawrth Vallis remains an intriguing and geologically diverse region for future surface exploration.

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