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Testing evidence of recent hydration state change in sulfates on Mars

L. H. Roach,¹ J. F. Mustard,¹ S. L. Murchie,² J.-P. Bibring,³ F. Forget,⁴ K. W. Lewis,⁵ O. Aharonson,⁵ M. Vincendon,¹ and J. L. Bishop⁶

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[1] The East Candor Interior Layered Deposit (ILD) has signatures of mono- and polyhydrated sulfate in alternating layers that give insight into the processes which formed these layered deposits and on the environmental conditions acting on them since then. We use orbital data to explore multiple hypotheses for how these deposits formed: (1) sulfate-bearing ILDs experience hydration changes on seasonal to a few years timescales under current Mars environmental conditions; (2) the deposits experience hydration under recent Mars conditions but require the wetter climate of high obliquity; and (3) the kieserite could be an original or diagenetic part of a complex evaporite mineral assemblage. Modeled climatology shows recent Mars environmental conditions might pass between multiple sulfate fields. However, comparison of Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) and Compact Reconnaissance Imaging Spectrometer (CRISM) observations of the same ILD do not show changes in hydration over 2 Mars years. Low temperatures might slow the kinetics of that transition; it is likely that more clement conditions during periods of high obliquity are needed to overcome mineral metastability and hydrate kieserite-bearing deposits. We find the alternate model, that the deposit is a cyclic evaporite sequence of mono- and polyhydrated sulfates, also plausible but with an unexplained dearth of Fe sulfates.

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1. Introduction

[2] Sulfates are important secondary minerals produced from the evaporation of fluids involved in the aqueous alteration of Mars' primary lithology [Tosca *et al.*, 2005]. They indicate an interaction of volcanic SO₂, in the form of gas or sulfide, with crustal materials in the presence of water and may be the mineral remnants of an early wetter and acidic climate on Mars. Sulfates can form as evaporites in standing bodies of water, by precipitation from saturated groundwater, or by acid fog alteration of primary minerals [Schreiber and El Tabakh, 2000; Spencer, 2000; Settle, 1979]. The layered sediments at Meridiani Planum, investigated in detail by the Mars Exploration Rover (MER) *Opportunity*, is one significant sulfate deposit. The Burns formation at Meridiani Planum consists of a sedimentary

sequence of sand-sized evaporitic and basaltic grains, transported by wind and cemented by multiple fluctuations in groundwater level [McLennan *et al.*, 2005]. Syndepositional evaporite minerals and hematite concretions indicate several episodes of chemically distinct groundwater flow [McLennan *et al.*, 2005]. This interaction of acidic groundwater with basaltic material produced considerable Mg, Fe, and Ca sulfates [Clark *et al.*, 2005; Tosca *et al.*, 2005]. The bright subsurface sulfate soils exposed in Gusev crater at Paso Robles and other sites indicate the presence of acidic aqueous processes here as well [Johnson *et al.*, 2007; Lane *et al.*, 2008]. Acid sulfate alteration processes may have been widespread across Mars.

[3] A recent model of Mars mineralogic history posited three distinct alteration periods — eras of phyllosilicate, sulfate, and anhydrous ferric oxide formation as Mars cooled and water was increasingly sequestered in the frozen subsurface [Bibring *et al.*, 2006]. In this model, sulfate formation predominantly occurred after a global climate change from an alkaline, wet environment to an acidic, drying environment. This climate change could have been triggered by extensive Tharsis volcanism and SO₂ outgassing and/or by loss of the atmosphere from sputtering after the internal dynamo weakened [Bibring *et al.*, 2006]. After volcanism subsided and the atmosphere was sufficiently depleted, sulfate formation ceased and anhydrous ferric oxides coated the now cold and dry surface of Mars. Currently on Mars, the dominant active phases of water

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are frost and atmospheric water vapor. However, the lack of liquid water might not prevent ongoing alteration. Understanding the potential for sulfates to change hydration states under current conditions could help constrain how active groundwater, frost, and atmospheric vapor have been in the most recent period on Mars.

[4] Significant sulfate deposits on Mars occur in two main regions: within and near the equatorial Valles Marineris canyon system and in dunes around the north polar ice cap. Sulfates are found throughout Valles Marineris, in related outflow channels such as Aram Chaos, and in areas east of Valles Marineris such as Meridiani Planum. The reason for the association of sulfates with Valles Marineris is uncertain but could be due to a combination of SO_2 gas sourced from nearby Tharsis volcanism, deep basins to concentrate or retain sulfate-rich brines, and hydrothermal or groundwater circulation of sulfur-rich fluids [Gendrin *et al.*, 2005]. One explanation for the concentration of sulfates near Valles Marineris comes from modeling the effect of Tharsis volcano building on the Martian global hydrology [Andrews-Hanna *et al.*, 2007]. The model shows that Valles Marineris and its outflow channels and Meridiani Planum are locations of prolonged groundwater upwelling and subsequent evaporation would result in accumulation of significant evaporite deposits [Andrews-Hanna *et al.*, 2007; S. L. Murchie *et al.*, Compositional evidence for the origin of layered deposits in Valles Marineris, submitted to *Journal of Geophysical Research*, 2009]. It is difficult to tie the genesis of the gypsum near the North Pole to near Valles Marineris events. The gypsum-bearing late Amazonian-aged circumpolar dunes are enigmatic as no source of the gypsum has been identified [Langevin *et al.*, 2005]. The gypsum might be formed by local ice cap meltwater altering basaltic sand grains or by modern reexposure and reworking of the Polar Basal Unit, which may contain variable amounts of gypsum [Langevin *et al.*, 2005; Fishbaugh *et al.*, 2007].

[5] The presence of sulfates in a location does not imply they were formed there, since the relatively high solubility of sulfates and their mobility in solution complicates our ability to tie sulfate formation to specific volcanic or geologic processes. Present sulfate locations and abundances on the Martian surface are likely a function of how they have been transported, altered or recycled, and preserved since formation. For example, the sulfate deposits at Meridiani Planum are interpreted as transported sulfate grains, recemented by local groundwater fluctuations [McLennan *et al.*, 2005]. However, regional similarities in the lithology, mineralogy, and relative stratigraphy of sulfate exposures in the Valles Marineris system indicate that similar processes may have formed or modified many sulfate deposits in this region.

[6] The Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) spectrometer aboard the Mars Express (MEx) spacecraft has revealed the monohydrate, kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), and a polyhydrated sulfate of unknown cation in many light toned layered units (Interior Layered Deposits or ILDs) in Valles Marineris [Bibring *et al.*, 2005; Gendrin *et al.*, 2005; Mangold *et al.*, 2008]. The term "polyhydrated sulfate" is unsatisfactory and can include a variety of sulfates. Many sulfates with 3+ water molecules show similar deep absorption features near 1.4,

1.9, and 2.4 μm [Cloutis *et al.*, 2006]. Originally suggested polyhydrated sulfates include epsomite, copiapite, or halotrichite [Gendrin *et al.*, 2005], but can include many other non-Fe-bearing sulfates. The ILDs consist of finely or massively bedded light-toned materials that weather into mesas and mounds and have been proposed to be either lacustrine, aeolian, subglacial or air fall ash deposits [Lucchitta *et al.*, 1992; Nedell *et al.*, 1987; Beyer *et al.*, 2000; Chapman and Tanaka, 2001; Komatsu *et al.*, 2004]. There is debate as to whether some ILDs formed before Valles Marineris opened or if all postdate the canyon formation [Malin and Edgett, 2000; Lucchitta *et al.*, 1994; Komatsu *et al.*, 1993]. Resolving this point has important implications for the timing of sulfate formation within the Martian geologic timeline.

[7] Subsequent measurements by Compact Reconnaissance Imaging Spectrometer (CRISM) on the Mars Reconnaissance Orbiter (MRO) has elaborated on the distribution and type of sulfate found within the ILDs [Murchie *et al.*, 2007b; Bishop *et al.*, 2007; Parente *et al.*, 2007; Roach *et al.*, 2007; S. L. Murchie *et al.*, submitted manuscript, 2009]. CRISM targeted observations show kieserite and polyhydrated sulfate occasionally alternate by layer within an ILD [Roach *et al.*, 2008]. It is not common to find a locale on Earth with alternating occurrences of multiple hydration states of a sulfate with a single common cation (such as gypsum, bassanite, and anhydrite in alternating layers) since the mineral rapidly converts to the thermodynamically stable phase, which is often kieserite or anhydrite (CaSO_4), with burial diagenesis (e.g., Permian evaporite [Lowenstein, 1988] and Messinian evaporite [Testa and Lugli, 2000]). However, slower kinetics on Mars could preserve metastable assemblages [Chipera and Vaniman, 2007]. If the polyhydrated sulfate identified on Mars has some Mg sulfate component, then the presence of both mono- and polyhydrated forms of Mg sulfate in an outcrop raises questions about environmental conditions since deposition in light of the mineral's thermodynamic stability.

[8] Experimental work on the stability fields of Mg sulfates [e.g., Chipera and Vaniman, 2007] finds the range of environmental conditions on Mars potentially encompasses several fields in a Mg sulfate phase diagram. It also reveals that Mg sulfates exhibit strong metastable behavior, which affects the kinetics of hydration or dehydration. Relevant findings are discussed more in section 2. Investigating deposits with alternating exposure of monohydrated Mg sulfate and polyhydrated sulfates (possibly Mg-bearing), is one way to better understand hydrated sulfate behavior on Mars and to develop hypotheses for formation and subsequent alteration of these sulfate layers.

[9] The hydration state of a sulfate deposit is a function of its formation process, possible diagenesis or alteration, and subsequent reexposure to the environment. This paper focuses on an ILD in East Candor Chasma (Figure 1) with a multiple sulfate assemblage in order to look for evidence of changing hydration state. The presence of multiple hydration states of Mg sulfate in a layered deposit is challenging, since Mg sulfate readily changes hydration state on Earth. Martian conditions vary in RH and T over diurnal, seasonal, and millennial timescales. A given Mg sulfate phase, such as kieserite, is not within its stability field at all Martian conditions. What is important is how

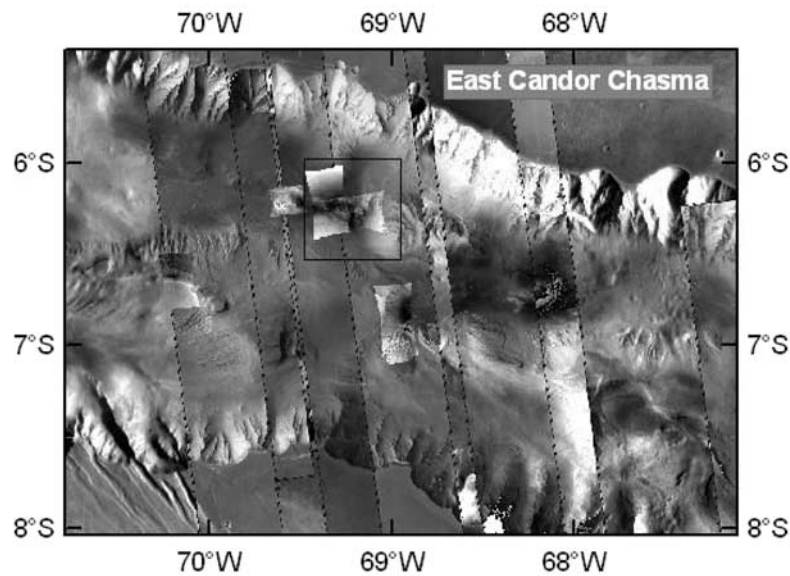


Figure 1. Context map of East Candor Chasma. Box indicates extent of Interior Layered Deposit study area, as shown in Figure 5.

long it is outside those boundaries and if that is sufficient for hydration to occur. Mangold was the first to suggest kieserite in ILDs might be weathering to polyhydrated sulfate with exposure to the atmosphere [Mangold *et al.*, 2008]. In an effort to explain the presence of kieserite and of a multisulfate suite in Valles Marineris, we put our mineralogic and geomorphic findings in context with experimental stability data and temporal studies. We consider experimental data on the stability of Mg sulfates in various temperature and humidity conditions, which provides constraints to expected phases under current Valles Marineris environments. We also compare OMEGA and CRISM observations of the sulfate deposit spaced 1 and 2 Mars years apart to assess sulfate stability and whether seasonal and annual environmental changes in hydration state occur.

2. Stability of Hydrated Mg Sulfates on Mars

[10] Much work has been done on the stability of Mg sulfates with respect to hydration and dehydration [Vaniman *et al.*, 2004; Chipera *et al.*, 2005; Marion and Kargel, 2005; Vaniman *et al.*, 2005; Vaniman and Chipera, 2006; Chipera and Vaniman, 2007], summarized in Figure 2. In order to speed reaction rates, this wealth of experimental data can only partially imitate the temperature (T), pressure (P), and RH (relative humidity) conditions of modern Mars. Nonetheless, there is an abundance of data that foremost, speaks forcefully to the complex behavior of Mg sulfates and second, gives indications about sulfate stability on Mars. The Mg sulfate system has extensive metastability fields when kinetic limitations prevent phase changes. An example of where Mg sulfate metastable conditions overstep a stability field before they can overcome an activation energy barrier is the possibility of hydrating kieserite to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ without first forming $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$. Metastability is especially persistent in conditions of rapid crystallization at low RH in concentrated brines [Vaniman *et al.*, 2004]. The recent discovery of a kieserite pseudomorph that may form

under different conditions than typical kieserite [Wang *et al.*, 2008] raises questions about Mg sulfate stability that will require more investigation.

[11] While the most extensive studies on kinetics and stability have been run at temperatures above 273 K, some have been performed under Martian conditions. Vaniman *et al.* [2006] have shown that under Martian temperature conditions (constant 243 K trials) but ~ 1 bar pressure, kieserite hydrates to hexahydrate in ~ 1000 h at 100% RH. At 100% RH in lower temperatures (193 K), the water vapor does not hydrate kieserite, but accumulates as surface frost on the mineral [Vaniman *et al.*, 2006]. The rate of hydration on Mars is not necessarily on the same order of magnitude as on Earth, since the experiments were run under terrestrial pressures, and the kinetics of the reaction are likely to be slower under the thinner Martian pressures. While water ice is not currently present for extended periods today in Valles Marineris, during periods of higher obliquity (conditions of 100% RH and temperatures of at least 243 K), ice was likely stable [Vaniman *et al.*, 2006; Vaniman and Chipera, 2006]. A location with stable ice in the subsurface would more likely produce a microclimate for possible kieserite hydration [Forget *et al.*, 2006; J.-B. Madeleine *et al.*, Amazonian mid-latitude glaciation on Mars: A proposed climate scenario, submitted to *Icarus*, 2009]. The experimental results demonstrate that kieserite is not stable anywhere on Mars where water ice is present for long periods of time. While the speed of hydration cannot be constrained, the reaction of kieserite to polyhydrated Mg sulfate in the presence of ice is favorable.

[12] While kieserite is not stable under all of Mars' surface conditions, we should consider kieserite's extensive metastability field, as its actual hydration rate under Martian conditions is unknown. Diurnal fluctuations in temperature and RH on Mars mean kieserite is not held at 100% RH and sufficiently high temperatures for long periods of time, so its hydration rate may be retarded. Additionally, diurnal temperature and RH cycles in equatorial regions may cause

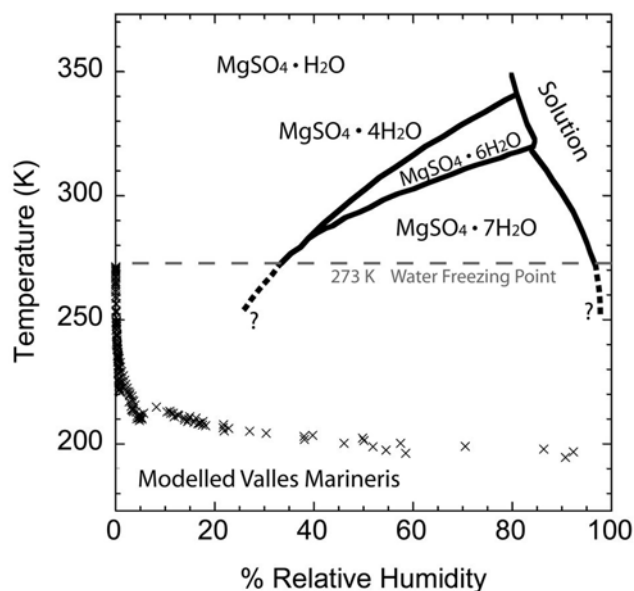


Figure 2. Experimental temperature (in K)-%RH phase diagram for Mg sulfates. Modeled Mars environmental conditions are also plotted as “x”. Modeled T , %RH at Capri Chasma serves as proxy for the environmental conditions in Valles Marineris. Dashed gray line delineates the freezing point of pure water at 1 atm pressure. The extension of Mg sulfate stability fields below freezing is uncertain. The boundary between kieserite and $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ is not well defined so the black dotted line is an approximation of that boundary. The current environment in Valles Marineris might pass between multiple sulfate fields, although the low temperatures would slow the kinetics of that transition.

polyhydrated Mg sulfate to vary between polyhydrated states or to and from an amorphous, slightly hydrated, state [Vaniman and Chipera, 2006; Chou and Seal, 2007]. The speed of this dynamic response to atmospheric water vapor is not well defined, but could occur daily or seasonally. Figure 2 shows experimentally determined stability fields for the Mg sulfate system at temperatures >273 K; metastability can complicate extrapolation to subfreezing temperatures. Further experimental data is needed at subfreezing temperatures to bracket Mg sulfate stability.

3. T , P , and RH at Vallis Marineris

[13] Pathfinder, Viking, and MER lander data confirm that equatorial regions get warm enough for hours a day in the summer to promote hydration (Figure 2) [e.g., Savijärvi, 1995; Spanovich et al., 2006]. The Thermal Emission Spectrometer (MiniTES) instrument on Opportunity in Meridiani Planum measured a maximum surface temperature of 295 K in early afternoon, $L_s = 339^\circ$, with surface temperature above freezing for ~ 5 h [Spanovich et al., 2006]. While no RH measurements exist from landed missions, modeled RH at the Viking 1 landing site (22°N) ranges from 100% at night to $<1\%$ in the afternoon [Savijärvi, 1995]. To better understand the environmental conditions in Valles Marineris and how they differ from

those at the landing sites, we modeled T and RH values in Capri Chasma throughout the year using a tuned global climate model described in [Forget et al., 1999]. Capri Chasma was chosen because its large size covered more than one 3.75° latitude \times 5.625° longitude pixel in the model. Model results from Capri Chasma were considered to confidently represent Valles Marineris conditions with minimal contribution from the surrounding plateaus and can be extrapolated to represent East Candor Chasma. The model’s 2 h temporal resolution allows sensitive tracking of daily variation in RH. While consistent with the extreme T and estimated RH values of the Viking 1 lander, it additionally shows the rapidity of RH decrease with increasing T . The modeled Martian conditions do not pass through experimentally measured Mg sulfate stability fields, and the location of those stability fields under Mars conditions is currently unknown. Yet, the RH and T conditions for an entire diurnal cycle do not remain within the kieserite stability field. The amount of time outside the kieserite stability field is unknown, but may be long enough to promote phase transition under certain conditions.

[14] The reverse transformation (dehydration) of polyhydrated Mg sulfate to kieserite cannot happen in the ILDs under current Martian surface conditions. In experimental studies at all T , kieserite converts to more hydrated Mg sulfates as humidity increases but does not revert to kieserite on desiccation; instead it becomes amorphous and remains more hydrated than kieserite [Vaniman et al., 2004]. Wang et al. [2008] formed kieserite by direct high-temperature precipitation (~ 368 K), but kieserite cannot form at Martian temperatures (near freezing) from a polyhydrated Mg sulfate [Freeman et al., 2007]. Crystallization of amorphous Mg sulfate to kieserite occurs at 323 K, but not at 293 or 273 K, in experiments run for several months [Freeman et al., 2007]. Colder, Mars-like temperatures are unlikely to crystallize kieserite. Conversion of polyhydrated Mg sulfates to kieserite is favored under elevated temperatures [e.g., Wang et al., 2008], so penecontemporaneous diagenesis is possible. Exhumation after diagenesis is necessary to reexpose the kieserite. Thus, the presence of dominantly kieserite on fresh surfaces indicates that they have not changed hydration state since exposure and that they are either original evaporites or a diagenetic phase after $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ and other sulfates. Mars surface conditions are too cold for dehydration of epsomite to kieserite.

[15] The Mg sulfate hydration state depends on not just the appropriate T and RH conditions, but also the time spent at those conditions. On Mars, strong kinetic limitations on Mg sulfate equilibrium may prevent kieserite hydration [Vaniman and Chipera, 2006].

4. Visible and Near-Infrared Spectra

[16] Visible and Near-Infrared (VNIR) spectra are used to identify sulfates and their hydration state. In targeted hyperspectral mode, CRISM acquires observations at 544 wavelengths from 0.392 to 3.92 μm at ~ 20 m/pixel [Murchie et al., 2007a]. OMEGA observations have 352 wavelengths from 0.35 to 5.1 μm and a spatial sampling that varies from 300 m to 4.8 km/pixel [Bibring et al., 2004]. Both data sets are calibrated to radiance and divided by the solar spectrum, yielding I/F. An empirical atmospheric correction is

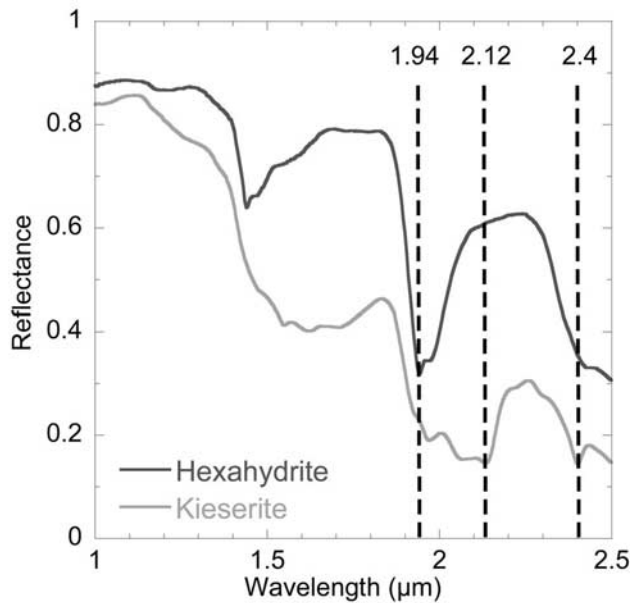


Figure 3. Compact Reconnaissance Imaging Spectrometer (CRISM) wavelength-resampled RELAB library sulfate spectra with central wavelength locations for 1.9, 2.1, and 2.4 μm band depth parameters.

performed by division of I/F spectra by an atmospheric transmission spectrum derived over Olympus Mons as in [Pelkey *et al.*, 2007]. The atmospheric transmission spectrum is scaled each OMEGA and CRISM observation by the strength of the 2.0 μm CO_2 absorption. This approximately removes the atmospheric spectral absorptions due to gas bands, but does not account for aerosol effects.

[17] CRISM observations can also be corrected for aerosols using the gimbaled observations [Murchie *et al.*, 2007a] to solve for the aerosol phase function as in the work of Vincendon *et al.* [2007]. After gas band removal, the emission phase function is modeled for mean surface Lambert albedo and aerosol optical depth as a function of wavelength. A smoothed model of aerosol optical depth with wavelength and albedo is then removed from the central CRISM observation. Large differences in topography across the scene can affect optical depth results because there is a change in the relative magnitude of the surface contribution with changing phase angle. Aerosol removal accuracy is also affected by variation in surface illumination due to slopes, since the model assumes a flat, constant albedo surface. These caveats are relevant to the observations in East Candor Chasma, as the ILD covers ~ 450 m in elevation and is steep-sided.

[18] The 1.0–2.6 μm VNIR wavelength region of the OMEGA and CRISM detectors is suited to identifying hydrated sulfates. Example library reflectance spectra are shown in Figure 3. Spectral band depths for each pixel in a scene are calculated for both OMEGA and CRISM observations to capture spectral features related to both sulfate mineralogy and atmospheric constituents and to map surface mineralogic units [Pelkey *et al.*, 2007]. CRISM ratioed reflectance spectra of the spectral variability of the East Candor ILD are shown in Figure 4. CRISM spectra of interest are ratioed to spectra of nearby spectrally neutral

materials with similar albedo to accentuate mineral absorption bands and to remove instrumental artifacts and residual calibration effects.

[19] Polyhydrated sulfates, and other hydrated minerals, have an absorption near 1.9 μm due to a combination of water molecule bending and stretching vibrations [Cloutis *et al.*, 2006]. The 1.9 μm band strength measures the average absorption depth within the ~ 1.9 μm water absorption, compared to the reflectance just outside the absorption at 1.857 μm and 2.067 μm , weighted by their distance from the center of the absorption (equation (1), where R_{1930} is the reflectance at 1.930 μm) [Pelkey *et al.*, 2007]. Amorphous polyhydrated Mg sulfates are spectrally very similar to their crystalline counterparts [Wang *et al.*, 2008]. Monohydrated sulfates as a class have an absorption near 2.1 μm due to water vibrational combinations, with the exact minimum varying by cation [Cloutis *et al.*, 2006]. The 2.1 μm band strength measures the average absorption depth within the ~ 2.13 μm absorption compared to the reflectance on either side outside the absorption (at 1.93 μm and 2.25 μm) (equation (2)) [Pelkey *et al.*, 2007]. We identify hydrated sulfates by combining these band depth parameters with a parameter (SINDEX) to measure the spectral shape near the 2.4 μm band, which is due to sulfate and water combinations and/or overtones [Cloutis *et al.*, 2006]. The 2.4 μm parameter gauges the convexity at 2.29 μm due to sulfate absorptions at 1.9 or 2.1 μm and 2.4 μm (equation (3)) and is modification of BD2400 in the work of Pelkey *et al.* [2007].

$$BD_{1900} = 1 - \frac{(R_{1930} + R_{1985}) \times 0.5}{0.52 \times R_{1857} + 0.48 \times R_{2067}} \quad (1)$$

$$BD_{2100} = 1 - \frac{(R_{2120} + R_{2140}) \times 0.5}{0.38 \times R_{1930} + 0.62 \times R_{2250}} \quad (2)$$

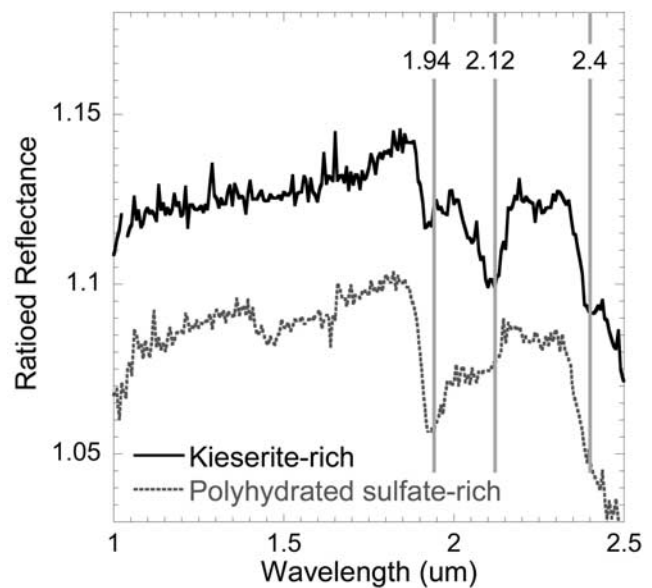


Figure 4. Representative kieserite-rich and polyhydrated sulfate-rich spectral ratios from the East Candor Chasma Interior Layered Deposit (ILD) from CRISM observation HRS00002FAF.

$$SINDEX = 1 - \frac{R2100 + R2400}{2 \times R2290} \quad (3)$$

[20] The East Candor Chasma ILD hosts a multisulfate assemblage, several types of which can be identified by their VNIR spectra. A monohydrated sulfate is identified as kieserite, rather than other monohydrated sulfates, on the basis of its 2.13 μm reflectance minimum, and 2.4 μm absorption. The mineral determination “polyhydrated sulfate” from OMEGA and CRISM spectra does not refer to a specific cation, as many polyhydrated sulfates have similar VNIR spectral shapes due to their very hydrated state. Possible mineral matches for the OMEGA detection include polyhydrated Mg sulfates such as epsomite, hexahydrite or starkeyite, Fe^{2+} sulfates such as halotrichite, Fe^{3+} sulfates such as botryogen, and mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ sulfates including copiapite group minerals [Gendrin *et al.*, 2005; Mangold *et al.*, 2008]. Other possible mineral matches include the bloedite [$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$], kainite [$\text{KMg}(\text{SO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$], and bischofite [$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$], which are all diagenetic salts often found with kieserite in terrestrial deposits. Fe-bearing sulfates are unlikely matches in this deposit since the ferrous absorption corresponds to the loose pyroxene-bearing dunes overlying the deposit, and not to specific layers within the deposit. Both OMEGA and CRISM data sets also indicate minor phases such as hydrated silicate or gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] may be present on the basis of weak absorptions in the 2.21–2.26 μm region. This identification is uncertain because of the weak bands, and would correspond to very trace amounts of gypsum, since only a few weight % gypsum is necessary to have discernible bands [Bonello *et al.*, 2004]. Other possible but less satisfactory mineral matches to the ~ 2.2 μm region include jarosite group minerals, polyhalite [$\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$], and a clay mineral such as montmorillonite.

5. Geologic Setting of East Candor ILD

[21] The study area (Figures 1 and 5) is a ~ 450 m high finely layered (meters scale) light-toned deposit exposed below a dusty ridge in the middle of East Candor Chasma. The East Candor Chasma ILD is surrounded to the north, east, and west by wall rock landslides and chaotic terrains [Le Deit *et al.*, 2007]. This obscures the ILD’s relationship to chasma wall rock and thus its age relative to Valles Marineris formation. Small bedrock and possibly aeolian drift outcrops of bright mono- and polyhydrated sulfate extend to the south. The regional extent of sulfate-bearing materials is ~ 250 km^2 . The ILD appears to be eroding along layers on its relatively flat top and along one exposed side. Talus and significant landslide material are shedding off the ILD.

[22] A HiRISE stereo-derived digital elevation model (DEM) with 1 m post spacing was produced for this region using the method of Kirk *et al.* [2008] (Figure 7). HiRISE paired observations PSP_002076_1735 and PSP_002498_1735 were used in this analysis. Structural measurements were made by fitting planar surfaces to elevation profiles using linear regression. Efforts were made to ensure these measurements adequately constrained a unique orientation

by selecting outcrops with natural curvature. The measurements shown in Figure 7a all had errors less than 5 degrees in azimuth and 0.5 degrees in dip. The layering within the ILD is subparallel with a $\sim 10^\circ$ westerly dip toward the western edge and a $\sim 15^\circ$ dip to the south in the exposed southern flank. The layering is a relatively constant thickness across the ILD, attesting to a lack of slumping during deposition. A schematic cross section (Figure 7b) shows gentle folding of the sulfate-bearing layers.

[23] The HiRISE-derived topographic model, used in conjunction with overlapping CRISM spectral data, shows kieserite-rich material is found on cliff-forming units and polyhydrated sulfate-rich material is more common on flat units. This is consistent with the broader finding of kieserite being more common on steep slopes elsewhere in Valles Marineris, which are interpreted to be more recently exposed by erosion than flat units [Mangold *et al.*, 2008].

[24] The layers are not mineralogically pure: generally speaking, regions identified as spectrally kieserite-rich also have strong 1.9 μm absorptions consistent with a polyhydrated sulfate, and taken all together, there is a continuum of kieserite/polyhydrated sulfate spectral strengths across the scene. Spectra in Figure 4 show the presence of varying amounts of sulfates with mixed hydration phases. There are two interpretations for these spectral findings. The first interpretation is a difference in the relative amounts of polyhydrated/monohydrated sulfates between layers, which may also have different physiochemical properties that affect their weathering appearance. Kieserite-bearing layers may be better cemented, making them stronger and more likely to form cliffs than the polyhydrated sulfate-bearing layers. Formation of polyhydrated sulfate from kieserite or cyclic hydration and dehydration of polyhydrated sulfates may cause expansion and fracturing, thus weakening polyhydrated sulfate-bearing layers, making them less resistant to erosion than their monohydrated counterparts. The second interpretation is that surfaces with different exposure ages may show varying progress in conversion of kieserite to polyhydrated sulfate. Steeper surfaces, which are undergoing more rapid erosion, would have fresher exposures of kieserite. Flatter surfaces that have been exposed to the atmosphere for longer would have had time to convert to mostly polyhydrated sulfate.

[25] The geologic context under which these sulfates are found is important evidence to argue whether the hydration is recent. Sulfate is restricted to ILD bedrock and bright dunes at the base of the ILD, a distribution in line with previous studies across Valles Marineris [Gendrin *et al.*, 2005; S. L. Murchie *et al.*, submitted manuscript, 2009]. Dark, pyroxene-bearing dunes collect at the bases of cliffs between layers of the sulfate deposit. CRISM spectra allow a more detailed correspondence of mineralogy with geologic context and indicate that the sulfate mineralogy is relatively uniform within a layer and that it changes between layers (as delineated by morphology). This is easily seen in Figure 8, where layers with different relative amounts of polyhydrated and monohydrated sulfates appear as different colors on a spectral band depth parameter image. Within a layer, the consistent mineralogy is reflected in the fairly uniform strength of the band depth parameter. Slight variation in band strength within a layer could be attributed to differences in surface exposure or layer geometry. Hydrated silica

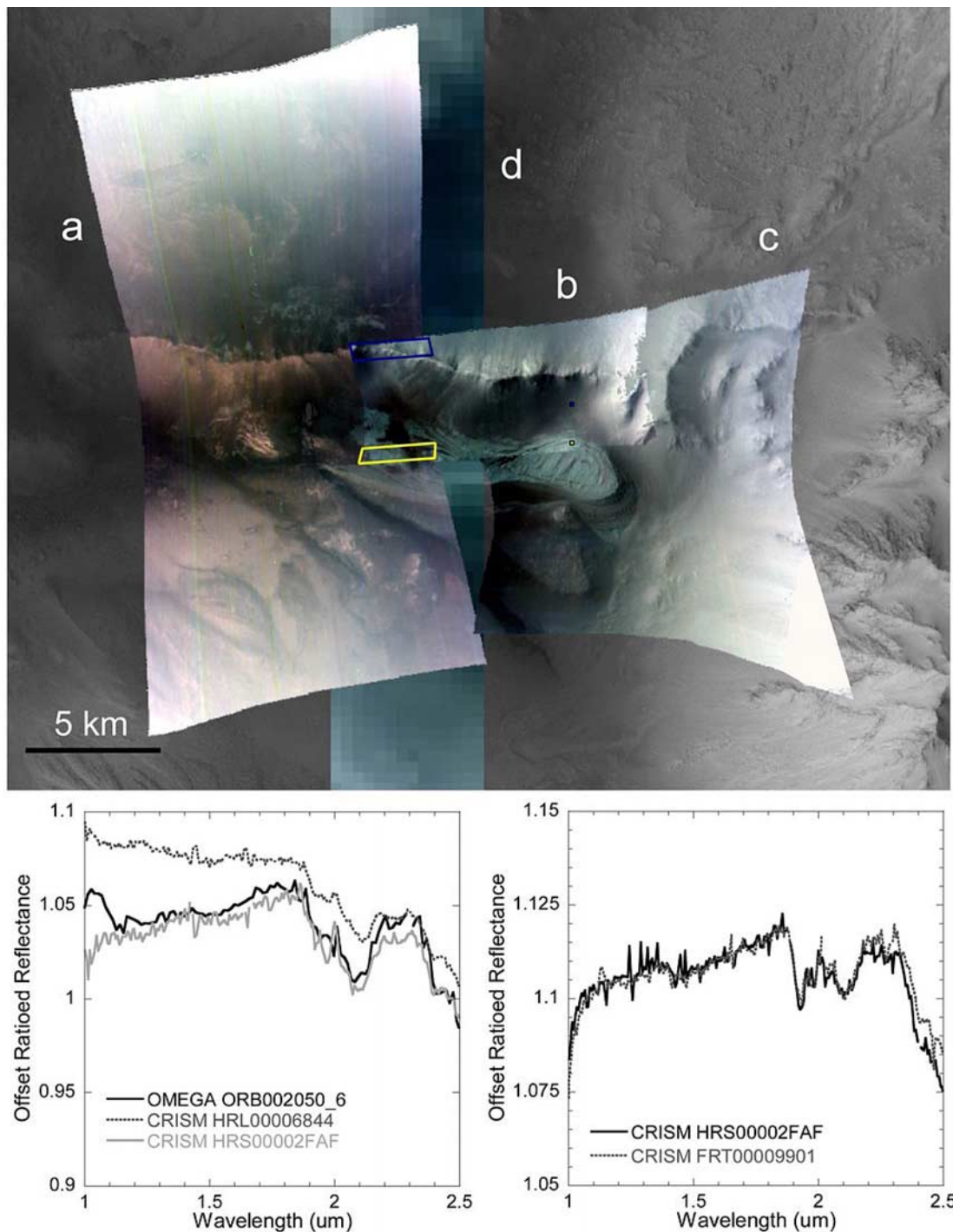


Figure 5. (top) CRISM observations HRL00006844 (region a), HRS00002FAF (region b), and FRT00009901 (region c) over Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) observation ORB002050_6 (region d, background). Coaligned sulfate spectra were collected from yellow boxes, and the corresponding bland denominators for spectral ratioing were collected from blue boxes. The larger polygons indicate locations of coaligned spectra from regions a, b, and d, and the small squares indicate locations from regions b and c. (bottom left) Comparison of OMEGA ORB002050_6 spectral ratio with aerosol-removed CRISM HRS00002FAF and HRL00006844 spectral ratios of location shown as large polygon. HRS00002FAF spectrum is offset by +0.25, and interpreted as a mixed monohydrated/polyhydrated sulfate assemblage. The relative band depths of mono- and polyhydrated sulfate are similar for all three observations. (bottom right) Comparison of CRISM HRS00002FAF and FRT00009901 spectral ratios of location shown as small square. HRS00002FAF spectrum is offset by -0.055 . Similar relative band depths of mono- and polyhydrated sulfate in the two observations show no evidence for yearly sulfate hydration state change.

Table 1. Targeted Observations of East Candor Chasma ILD^a

Instrument	Date	L_s	Observation	Spatial Resolution
OMEGA	21 August 2005	273°	ORB002050_6	~560 m/pixel
CRISM	12 November 2006	134°	HRS00002FAF	~21 m/pixel
CRISM	6 July 2007	271°	HRL00006844	~35 m/pixel
CRISM	20 January 2008	20°	FRT00009901	~33 m/pixel

^aILD, Interior Layered Deposit; OMEGA, Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité; CRISM, Compact Reconnaissance Imaging Spectrometer.

or gypsum is additionally identified in the ILD on the basis of an absorption at 2.21–2.26 μm . This feature is very weak and thus not able to be constrained to specific layers. Dark sulfate-bearing dunes (with strong sulfate signatures) are commonly associated with ILDs in nearby West Candor Chasma (S. L. Murchie et al., submitted manuscript, 2009), but are not seen here.

6. Temporal Observations of Sulfates

[26] CRISM has imaged an ILD in East Candor Chasma three times since OMEGA first detected kieserite there (Table 1). The images span over 1 Mars year and are all of sufficient spatial resolution to resolve the ILD and show variation in the relative amounts of polyhydrated and monohydrated sulfate across layering. Correcting for the aerosol loading in the CRISM observations is important as one observation (HRL00006844) was acquired in the build-up to a global dust storm and had significant aerosol contribution.

[27] We perform two spectral comparisons of the East Candor Chasma ILD. The first comparison is of OMEGA spectra from Northern hemisphere winter (L_s 273°) and coaligned CRISM spectra from the following late Northern summer and winter (HRS00002FAF (L_s 134°) and HRL00006844 (L_s 271°), respectively) (Figure 5). They cover the same ~ 3.7 km² location. The spectra from the observations are quite similar and show both a 1.9 μm and a relatively deeper 2.1 μm absorption. The observations were acquired over a range of L_s yet are not significantly different. The second comparison is of CRISM observations HRS00002FAF and FRT00009901 (L_s 20°), taken late Northern summer and the following spring. The OMEGA observation does not overlap this pair. Comparing only CRISM data allows us to compare smaller areas that are likely more homogeneous. Three comparisons of 7000 m² regions, one location of which is shown in Figure 5, record similar sulfate hydration states.

[28] Additionally, two other paired OMEGA and CRISM observations spaced over 2 Mars years have consistent spectra. The first OMEGA and CRISM pair is located in Ius Chasma (ORB0071_2 and FRT0000A91C, respectively), and were acquired 1 February 2004 (L_s 343°) and 23 April 2008 (L_s 62°), respectively. Figure 9 shows region of overlap and paired OMEGA and CRISM spectra of the kieserite deposit. The second pair is over a Capri Chasma kieserite deposit (ORB0061_3 and FRT0000A23F, respectively), acquired 29 January 2004 (L_s 341°) and 27 February 2008 (L_s 37°), respectively. These two locations are the first two where OMEGA discovered kieserite, and both show similar kieserite band depths in OMEGA and CRISM pairs.

Multiple paired OMEGA and CRISM spectra have similarities in the relative band depths of the 1.9 μm and 2.1 μm absorptions.

7. Implications and Conclusions

[29] There are three plausible hypotheses for the finding of polyhydrated sulfate and kieserite in the same deposits: (1) kieserite is converting to a polyhydrated state upon exposure to the surface environment under current environmental conditions; (2) kieserite conversion cannot progress under current environmental conditions and requires a warmer and wetter climate, such as periods of high obliquity; and (3) a multisulfate evaporite assemblage created by changing brine chemistry during evaporation, altered by diagenesis. There are complications to these three sulfate formation and alteration mechanisms that should be considered, such as the presence of other phases that are spectrally neutral in the VNIR and the unknown kinetics of sulfate phase change under Martian conditions.

[30] Another hypothesis, that the kieserite and polyhydrated sulfate could have formed elsewhere and been transported by aeolian processes to the ILD, is unlikely since the cementing process would probably affect or homogenize the sulfate hydration state and it is implausible that this process occurred at least six or seven times (six alternations in sulfate mineralogy visible in Figure 6). Additionally, dehydration of a polyhydrated Mg sulfate to kieserite at Martian surface conditions is not plausible, since the dehydration product would be an amorphous phase, not crystalline kieserite [Freeman et al., 2007].

7.1. Active Hydration of Kieserite Hypothesis

[31] The presence of significant talus at the base of the East Candor Chasma ILD and other ILDs is evidence that they are easily weathered. Steeper surfaces undergo more continual erosion, continually refreshing the surface exposure of kieserite in these strata, which creates layering with the flatter polyhydrated strata, which have been exposed longer at the surface.

[32] The similarity of paired orbital observations indicate the proportionate amounts of polyhydrated sulfate and kieserite have not changed within the resolving capability of these instruments over at least 2 Mars years, but several other factors must be considered. Differences in shadows may explain some of the offset in ratioed reflectance. Slight inaccuracies in data coaligning and differences in instrumental atmospheric calibrations may account for some differences in spectral shape, especially <1.3 μm . It is possible that there is a slight seasonal or yearly variation in hydration state, but that it is less than CRISM's detection limit. However, CRISM has a signal-to-noise of ~ 400 around 2 μm , which corresponds to a 3- σ detection of a 1% band depth [Murchie et al., 2007a], so nondetection of a real change in hydration state is improbable.

7.2. High-Obliquity Hydration of Kieserite Hypothesis

[33] If the hydration is not occurring under current conditions, it could be provoked during obliquity oscillations that bring warmer or more humid conditions to Valles Marineris [Vaniman et al., 2004; Vaniman et al., 2006]. Numerical models of Martian climate with obliquities of up

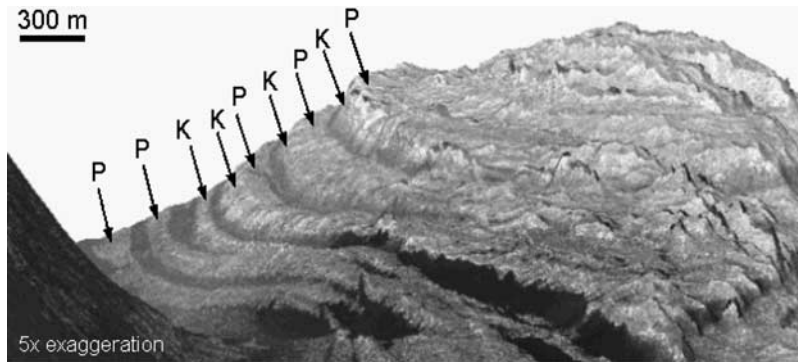


Figure 6. Looking east along top of East Candor Chasma ILD in HiRISE PSP_2076_1735 orthographically projected and draped on HiRISE-derived digital elevation model. Slope up to ridge is just visible on left. Kieserite-dominated units, labeled K, occur as steeper slopes than polyhydrated sulfate-dominated units, labeled P. Six alternations between kieserite and polyhydrated sulfate are visible.

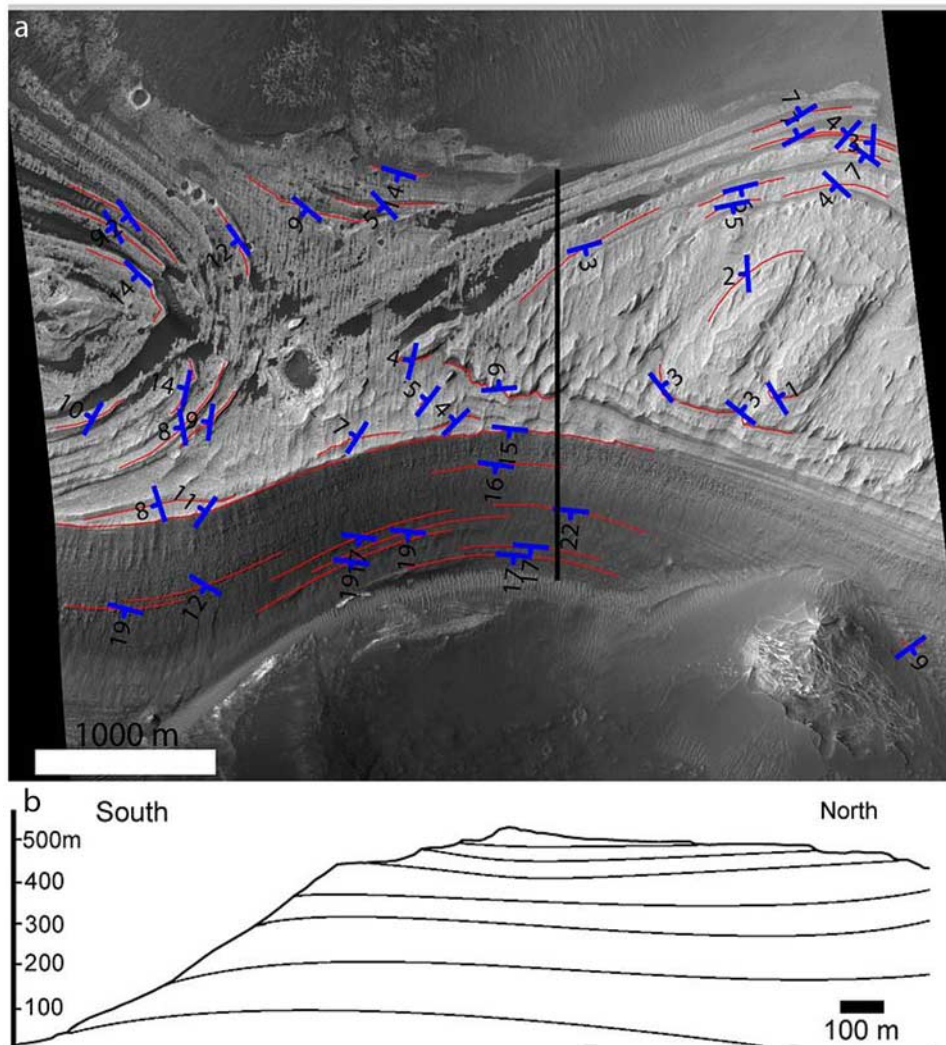


Figure 7. (a) Strike and dip measurements of layers in East Candor Chasma ILD. The red lines indicate the portion of the layer used to calculate the strike and dip. (b) Schematic N-S cross section through middle of ILD showing deformed layering.

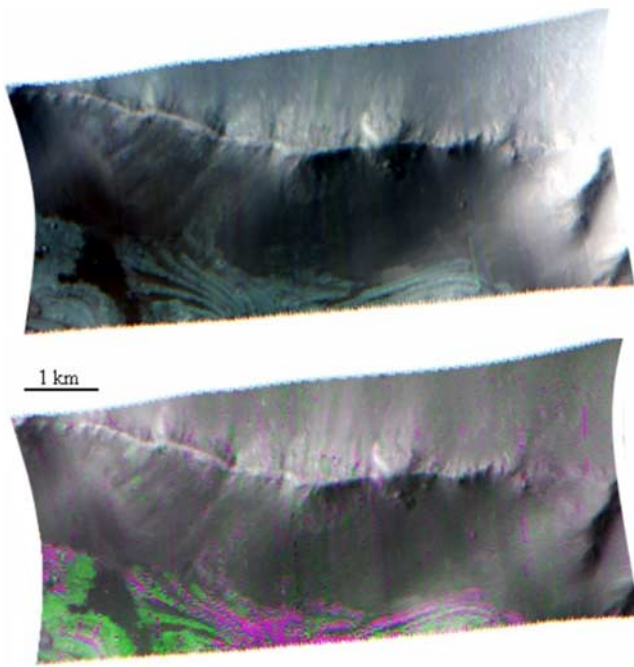


Figure 8. (top) CRISM HRS00002FAF false color IR (RGB: 2.5, 1.5, 1.08 μm). Dusty ridge to north with exposed layering from ILD to south. (bottom) Spectral band depth parameter image (magenta: 1.9 μm band depth, green: 2.1 μm band depth) overlain on false color IR albedo. Magenta areas indicate presence of dominantly polyhydrated sulfates; green areas are mostly kieserite.

to 45° show significant seasonal water ice precipitation in Valles Marineris [Forget *et al.*, 2006; J.-B. Madeleine *et al.*, submitted manuscript, 2009]. The ease with which these models can create ice in the equatorial regions with a variety of parameters and a high obliquity indicates that kieserite hydration during high-obliquity periods is credible. The obliquity of Mars is well constrained for the past 10 million years and during this period there were multiple occurrences of obliquity $>40^\circ$ [Laskar *et al.*, 2004]. These periods of increased surface and subsurface ice stability seasonally established conditions for kieserite to hydrate to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ [Vaniman *et al.*, 2006]. The continued presence of kieserite on Mars in conditions outside of its stability field suggests kieserite behaves metastably and that periods of kieserite hydration to polyhydrated sulfate would be episodic and incomplete.

7.3. Multisulfate Evaporite Deposit Hypothesis

[34] A third hypothesis for the multisulfate assemblage is alternating mono- and polyhydrated sulfate-rich layers that are metastable under current conditions. These alternating sulfate layers could have been laid down as basinal evaporites from a brine of cyclically changing composition.

[35] Cyclic evaporite sequences have multiple salts precipitated as the brine concentrates and passes through chemical divides [e.g., Hardie and Eugster, 1970; Tosca *et al.*, 2005]. Evaporites derived from weathering of Martian basalts would produce multiple phases, depending of relative amount of HCO_3^- to SO_4^{2-} and degree of evaporative

concentration, and include the sulfates gypsum, epsomite, and melanterite [Tosca and McLennan, 2006]. Total evaporation of the brine in a closed system results in relative proportions of 44% epsomite, 43% Fe sulfates, and 13% gypsum [Tosca and McLennan, 2006]. Fe sulfates do not appear in this deposit, and gypsum (or alternatively hydrated silica) does not appear in large concentrations. Multiple cation chemistries for the polyhydrated sulfate are possible, including bloedite [$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$], kainite [$\text{KMg}(\text{SO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$], and bischofite [$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$]. Other phases common in massive evaporites, such as anhydrite, halite, or sylvite, may also be present in this deposit, but are not detected because they are either completely dehydrated or otherwise lack bands in the VNIR wavelength region.

[36] Possible formation mechanisms for cyclically alternating sulfate layers include groundwater interaction or original evaporite deposition. Groundwater interaction is less favorable than evaporitic deposition since the layers are on the order of meters thick, and are unlikely to form repeated oscillations between mono- and polyhydrated sulfate over such a small distance. An evaporating closed basin with changing brine chemistry could precipitate first a polyhydrated sulfate, then epsomite or another Mg sulfate as the brine concentrates, then a different polyhydrated sulfate again when fresher water dilutes the brine [Hardie, 1991]. Kieserite could be formed by syndepositional diagenesis of epsomite, and the polyhydrated sulfate currently observed could be converted to bloedite, kainite, and bischofite from the original evaporite. At least six changes in sulfate mineralogy are visible in CRISM imagery of the East Candor Chasma ILD where dust and landslides do not obscure layering (Figure 7). If these layers are evaporitic, it points to a reservoir of relatively concentrated brine in East Candor Chasma that was frequently recharged.

[37] The sulfate composition of the layers could also be related to material properties, such as grain size, porosity, and induration; that is, the kieserite-bearing units are more resistant units and the softer units are enriched in polyhydrated sulfate. Polyhydrated sulfate-bearing units in West Candor Chasma have generally higher thermal inertia than kieserite-bearing units, arising from their more hydrated state and probably also differences in material properties of each unit [Mangold *et al.*, 2008]. The additional water in polyhydrated sulfate-rich material might make it structurally weaker and more likely to form slopes.

7.4. Discussion

[38] An alternative hydration scenario is that anhydrous but slowly hydrating sulfates are mixed as a minor phase with the kieserite. A complex mineral assemblage in the ILD of kieserite with other, non-Mg-bearing sulfates is possible. These anhydrous sulfates would have no distinguishing VNIR spectral shape as they lack bonded OH and HOH to form vibrational features [Hunt, 1977]. However, with hydration, these anhydrous sulfates can impart their spectral character to the resulting mixed spectrum. Thus, the steeper slopes could contain kieserite and an anhydrous sulfate while the flatter slopes contain kieserite and a now polyhydrated sulfate that spectrally dominates.

[39] If the polyhydrated sulfate is Mg-bearing, then finding both monohydrated and polyhydrated Mg sulfate

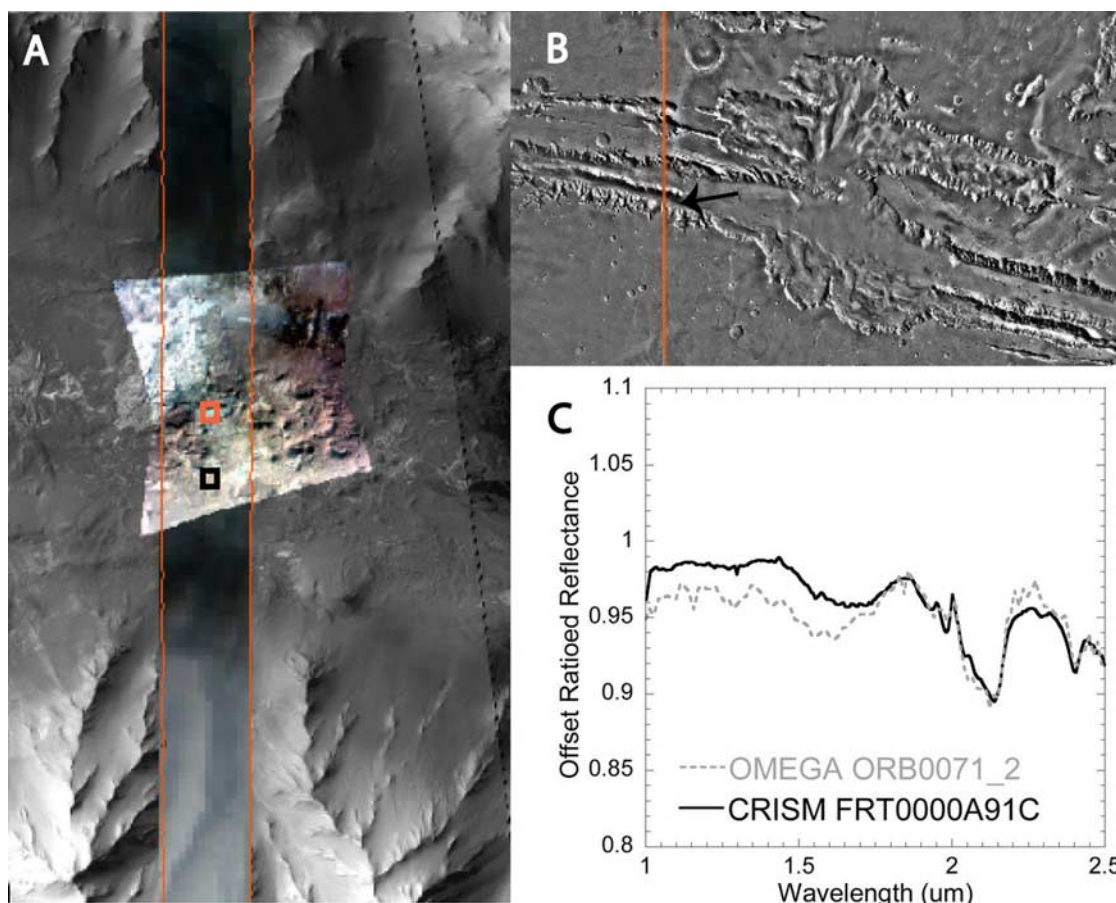


Figure 9. (a) Overlapping observations OMEGA ORB0071_2 (between orange lines) and CRISM FRT0000A91C (hourglass shape) with CTX mosaic in background. Numerators located at orange box; denominators located at black box. (b) Context map of central Valles Marineris. Arrow points to paired observations, located in Ius Chasma. The orange line is the outline of the very narrow OMEGA ORB0071_2. (c) Comparison of ratioed reflectance spectra, showing similarity of 2.1 μm band depths due to kieserite. OMEGA spectrum offset by -0.22 .

on the Martian surface raises questions about the relative stability of the various phases. Kieserite and lower hydrated crystalline and amorphous Mg sulfates are the most stable forms in the warmer areas of the Martian surface, such as Valles Marineris [Chipera and Vaniman, 2007]. Kieserite and a polyhydrated Mg sulfate might exist together metastably in Valles Marineris; active conversion between Mg sulfate phases could be limited because excursions into the hexahydrate T -RH stability field are on the order of hours a day in the summer and might not be for long enough to overcome the kinetic limitations.

[40] In the Martian chemical divide model, epsomite is expected to precipitate from brine that has previously precipitated gypsum and melanterite and/or a carbonate [Tosca and McLennan, 2006]. The brine resulting from weathering a Martian basalt results in subequal amounts of Mg and Fe sulfates with the bulk of the Mg sulfates precipitated last, so it is unrealistic to expect a closed evaporite sequence to contain no appreciable Fe^{2+} while showing strong spectral evidence for monohydrated Mg sulfate. Even if the Fe^{2+} precipitated as an iron oxide instead of a ferrous or ferric sulfate, the strong Fe charge transfer bands in the VNIR wavelength region [e.g., Hunt et al.,

1971] would allow confident detection at low abundances. The lack of a ferrous (or ferric) sulfate detection unfortunately does not allow us to make a strong case for a cyclic evaporite model or to constrain the original brine chemistry. Thus, if this deposit is an evaporite, it precipitated from an evolved brine saturated with only Mg sulfate or experienced significant postdepositional groundwater alteration.

[41] The speed of the proposed active hydration of kieserite to a polyhydrated sulfate in a complex assemblage is not well constrained. Having complex sulfate mixtures may affect sulfate stability fields by creating microenvironments with conditions different from the ambient environment [Freeman et al., 2007]. Paired OMEGA and CRISM observations over 1+ Martian year do not indicate a change in the assemblage's hydration state, and another similar ILD shows no change over more than 2 Mars years. However, the hydration reaction must have progressed at some point in the past to produce both mono- and polyhydrated sulfates in the same assemblage. Hydration may only be possible during periods of high obliquity and is not presently progressing. Furthermore, the CRISM observations span multiple seasons yet are spectrally similar, which contravenes seasonal changes in hydration.

[42] While we discard the hypothesis that sulfates are hydrating on a seasonal or several year period, we cannot decide between either hydration under periods of high obliquity or exposure of metastable cyclic evaporite sequences as the preferred explanation for the multisulfate assemblage at the East Candor ILLD. Experimental sulfate stability studies and modeled Mars climate data suggest sulfate hydration is possible and likely rapid under certain (wetter) conditions. The evaporite model is consistent with other sulfate-bearing ILLDs, especially those in nearby West Candor Chasma. Both possibilities offer exciting implications for the formation and alteration of layered deposits within Valles Marineris, and future MRO and MEx monitoring of this and similar sites within Valles Marineris will continue to test the two hypotheses.

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