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1 Sulfates and Iron Oxides in Ophir Chasma, Mars, based on OMEGA and CRISM

2 observations

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We investigate the sulfate and iron oxide deposits in Ophir Chasma, Mars, based on short-wave infrared data from the Compact Reconnaissance Imaging Spectrometer for Mars CRISM and from the Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité OMEGA. Sulfates are detected mainly in two locations. In the valley between Ophir Mensa and the southern wall of Ophir Chasma, kieserite is found both within the slope of Ophir Mensa, and superposed on the basaltic wall of the chasm. Here, kieserite is unconformably overlain by polyhydrated sulfate deposits and iron oxides. Locally, jarosite and unidentified phases with absorptions at 2.21 μm or 2.23 μm are detected, which could be mixtures of jarosite and amorphous silica or other poorly crystalline phases.

The second large sulfate-rich outcrop is found on the floor of the central valley. Although the same minerals are found here, polyhydrated sulfates, kieserite, iron oxides, and locally a possibly jarosite-bearing phase, this deposit is very distinct. It is not layered, almost horizontal, and located at a much lower elevation of below -4250 m. Kieserite superposes polyhydrated sulfate-rich deposits, and iron oxides form lags.

The facies of sulfate formation remains unclear, and could be different for the two locations. A formation in a lake, playa or under a glacier is consistent with the mineralogy of the central valley and its flat, low-lying topography. This is not conceivable for the kieserite deposits observed south of Ophir Mensa. These deposits are observed over several thousands of meters of elevation, which would require a standing body of water several thousands of meters deep. This would have lead to much more pervasive sulfate deposits than observed. These deposits are therefore more consistent with evaporation of groundwater infiltrating into previously sulfate-free light-toned

deposits. The overlying polyhydrated sulfates and other mineral phases are observed in outcrops on ridges along the slopes of the southern chasm wall, which are too exposed to be reached by groundwater. Here, a water supply from the atmosphere by rain, snow, fog or frost is more conceivable.

Keywords: Mars, Surface, Spectroscopy

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Sulfates and Iron Oxides in Ophir Chasma, Mars

1 Introduction

The Light-Toned Deposits [LTD] or Interior Layered Deposits [ILD] (Lucchitta *et al.*, 1992) within the chasmata of Valles Marineris are some of the most intensely studied geological features on Mars. Many theories for their formation have been put forward, including subaerial fluvial deposition or volcanism (Lucchitta *et al.*, 1992), accumulation of eolian dust or sand (Peterson, 1981), evaporite precipitation in lakes (McKay and Nedell, 1988) or from groundwater (Murchie *et al.*, 2009a), subaqueous (Nedell *et al.*, 1987) or sub-ice volcanism (Chapman and Tanaka, 2001), or the formation as spring deposits (Rossi *et al.*, 2008), but a conclusive theory combining all implications suggested by the composition, structure and stratigraphic position of these deposits is still missing. A detailed discussion of the shortcomings of each of the formation theories is provided by Lucchitta, 2009a; 2009b. One major constraint on these theories is the role of liquid water, evidenced by the presence of ferric oxides and sulfates, which are the subject of this study.

The mineralogy of the LTD's has been studied on a regional scale by Gendrin *et al.*, 2005 and Mangold *et al.*, 2007, based on short-wave infrared (SWIR) data from the Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité OMEGA (Bibring *et al.*, 2004), and by Weitz *et al.*, 2008, based on thermal infrared data from the Thermal Emission Spectrometer TES (Christensen *et al.*, 1992). A comparative study on the geological context of the individual outcrops of aqueous minerals in Valles Marineris by Chojnacki and Hynek, 2008, showed that the LTDs are much more diverse than previously thought, which makes a single formation process explaining all depositions by the same mechanism less likely, and which raises the need for individual, detailed mineralogic and geologic studies for each of the basins of Valles Marineris. In this paper, we analyze SWIR data from OMEGA and the Compact Reconnaissance Imaging

Spectrometer for Mars CRISM (Murchie *et al.*, 2007) in combination with multispectral imagery, digital elevation models and stereo images from the High Resolution Stereo Camera HRSC (Neukum and Jaumann, 2004), and panchromatic images from HRSC, the Context Imager CTX (Malin *et al.*, 2007) and the High Resolution Imaging Science Experiment HiRISE (McEwen *et al.*, 2007) acquired over Ophir Chasma in order to understand the mineralogy and local stratigraphy and layering characteristics of the water-related minerals found here, mainly sulfates and iron oxides. Similar studies on neighboring chasmata include the work of Mangold *et al.*, 2008, and Murchie *et al.*, 2009a, on West Candor Chasma, Le Deit *et al.*, 2008, on East Candor Chasma, and Roach *et al.*, 2010b, on Ius Chasma.

[INSERT FIGURE 1 HERE]

Ophir Chasma is the northernmost depression of central Valles Marineris. It extends approximately 270 km in East-West direction and 90 km in North-South direction (Fig. 1). The floor of the chasma lies at elevations between 4200 and 4800 m below datum, its rim is at elevations between 3400 and 4500 m above datum. Most of the western part of Ophir Chasma is covered by a mound of LTDs, Ophir Mensa, which rises up to an elevation of 3200 m above datum. This results in a total thickness of (at least) 7-8 km of deposits, assuming that the floor below Ophir Mensa is approximately horizontal at an elevation close to the deepest points of the chasm. Ophir Mensa is surrounded on all sides by depressions, which separate these deposits from the chasm walls. For convenience, we informally named the depression to the north as the "northern moat", the depression to the south as "mineral bowl", following Chojnacki and Hynek,

2008, and the depression to the east as the "central valley" (Fig. 1A). A second mound of light-toned deposits is located between the central valley and the south-eastern rim of Ophir Chasma. The geology of the LTDs was investigated by Nedell *et al.*, 1987 and Komatsu *et al.*, 1993, and a geological map based on Viking imagery was provided by Lucchitta, 1999. According to these authors, the chasmata of Valles Marineris probably formed as collapse structures along faults that later widened to grabens into the surrounding Noachian to Hesperian aged plains, which are built up by Tharsis-derived lava. By the time of the deposition of the LTDs, the chasm walls were already eroded to the spur-and-gully morphology observable today, which indicates that the deposition was clearly post-tectonic. Subsequently, the LTDs were heavily eroded by wind and/or water action. The walls of the chasmata receded from the remaining LTD platforms, and the resulting "moat" surrounding them was partly covered by landslides.

2 Datasets and Methods

2.1 Hyperspectral data

OMEGA and CRISM are both visible-short wave infrared imaging spectrometers. OMEGA (Bibring *et al.*, 2004) is the mapping infrared spectrometer onboard ESA's Mars Express spacecraft. It covers the wavelength range from 0.38 μm to 5.1 μm in 352 contiguous bands. The data is acquired by three different channels, one for the visible to near infrared spectrum (0.38-1.05 μm), a second for the spectral range from 0.93 to 2.73 μm and a third covering the range from 2.55 to 5.1 μm . We used mostly data from 0.93 to 2.73 μm , as this range covers electronic transition absorptions due to olivine and pyroxene (Adams, 1974, Cloutis and Gaffey, 1991, Sherman *et al.*, 1982, Sunshine and Pieters, 1990), and vibrational absorptions in H_2O and/or hydroxyl-bearing minerals such as phyllosilicates, hydrated sulfates and oxyhydroxides (Burns,

1993, Clark *et al.*, 1990). The spectral resolution of OMEGA is 20 nm in this wavelength range.

Due to Mars Express' highly elliptical orbit, the spatial resolution of OMEGA varies between

300 m and 3-4 km per ground element. Most of the OMEGA data used in this study have a

spatial resolution in the order of 600 to 700 m per ground element.

CRISM (Murchie *et al.*, 2007; 2009c) onboard NASA's Mars Reconnaissance Orbiter (MRO)

features a similar spectral range from 0.4 to 3.9 μm in 544 bands at a spectral resolution of 6.55

nm, recorded by two distinct detectors, the "S"-detector in the range of 0.39 to 1.02 μm , and the

"L" detector in the range of 1.02 to 3.92 μm wavelength. The data are acquired in several modes,

including the targeted mode at a spatial resolution of 18 m (FRT mode) or 36 m/pixel (HRL

mode) using all bands, or in multispectral mapping (MSP) mode at a spatial resolution of 200 m

per pixel using a subset of 72 selected spectral bands. We mostly used the data in the range of 1

to 2.6 μm , as this is the range where absorption bands of sulfates occur, but included the visible

range for the confirmation of the presence of ferric oxides. Table 1 provides the observation

numbers used here.

[INSERT TABLE 1 HERE]

The OMEGA and CRISM data were converted to I/F, divided by the cosine of the solar

incidence angle, and the CO₂ absorption features around 2 μm caused by the Martian atmosphere

were removed using the improved volcano-scan technique provided by McGuire *et al.*, 2009.

Noise in CRISM data was reduced using various filtering procedures (Parente, 2008). We used

the spectral indices or "summary products" (Bishop *et al.*, 2009; Murchie *et al.*, 2009b; Pelkey *et*

al., 2007) on OMEGA and CRISM data to identify spectral features characteristic for specific

minerals or groups of minerals. Out of these, the index for a band at 1.9 μm due to combinations of H_2O bending and stretching vibrations (BD1900), the 2.1 μm band depth (BD2100) the band depth at 2.21-2.26 μm due to Si-OH vibrations (BD2210) and the index quantifying the spectral convexity around 2.3 μm caused by H_2O absorptions (SINDEX) were particularly useful to identify regions that required detailed spectral analysis.

Ferric oxide was identified by its strong increase in reflection between 1 and 1.3 μm , which we calculated as the ratio between the reflectance at 1.2767 μm and the reflectance at 1.080 μm for CRISM data and the ratio between reflectance at 1.2705 μm and 1.0837 μm for OMEGA data, similar to Le Deit *et al.*, 2008; Mangold *et al.*, 2008. This index is sensitive to ferric oxides or oxyhydroxides like hematite and goethite or mixtures containing these minerals, but also to iron bearing sulfates, like, for example, copiapite. We therefore corroborated the presence of ferric oxides using the spectral data in the visible-near infrared range from the CRISM S detector. To this end, we excluded the spectral data shortward of 0.41 μm and longward of 0.97 μm as well as the range between 0.64 and 0.69 μm due to known calibration problems in these regions of the detector (Murchie *et al.*, 2009c). Spectra of Mars in the visible wavelength range are dominated by the presence of nanophase ferric oxides. The detection of coarse-grained red hematite, goethite or other ferric phase therefore requires the calculation of spectral ratios to a reference spectrum in the same observation, which is spectrally unobscured and dominated only by dust. These reference spectra were calculated as average spectra over a few hundreds or thousands of pixels. The spectral bands of ferric oxides, ~ 0.53 and 0.86 μm for red hematite and ~ 0.5 and 0.9 μm for other ferric phases, were then made visible by removing the continuum separately in the range of 0.41 to 0.64 μm and 0.69 to 0.97 μm (Clark *et al.*, 1987). Further evidence for the presence of ferric oxides in Ophir Chasma is the independent identification of

grey hematite in the thermal infrared by TES (Weitz *et al.*, 2008). Spectra in the range of 1 to 2.6 μm were averaged over regions of interest and either compared directly to laboratory spectra or likewise ratioed to spectrally bland (dusty) regions. We used laboratory spectra of pure minerals from the RELAB spectral library provided with the CRISM Analysis Tool (CAT).

An absorption band near 1.9 μm is found in various types of minerals: Hydrated silica, hydrated sulfates, phyllosilicates and also carbonates show this spectral feature, which makes further absorptions necessary to distinguish between these groups of minerals. Monohydrated sulfates show an absorption near 2.1 μm , which is detected by the BD2100 index. The exact location of this absorption band is at 2.13 μm for the magnesium-rich kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and at 2.09 μm for the iron-rich szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$). Both minerals also show an absorption at 2.4 μm (Cloutis *et al.*, 2006). A distinction between these two minerals was only attempted for OMEGA and CRISM data at full spectral resolution. and not the multispectral data from CRISM, as the generally higher noise level prevented an analysis to this detail.

Polyhydrated sulfates are identified by absorption bands at 1.45 and 1.95 μm and a drop-off in reflectance near 2.4 μm . Absorptions in the 2.2-2.3- μm -region are indicative for hydrated silica, phyllosilicates, or jarosite, and are attributed to OH-stretching and Si-OH bending. Hydrated silica such as opal show a broad absorption band between 2.20 and 2.26 μm due to overlapping bands caused by hydroxyl-groups and water molecules in the hydrate sphere. Jarosite is identified by absorptions at 1.47, 1.85 and a doublet at 2.21 and 2.26 μm . Phyllosilicates show a narrow absorption band in the wavelength region between 2.2 and 2.31 μm . Its exact position allows a distinction between aluminum-rich clays like montmorillonite (2.20 μm), iron-rich nontronite (2.28 μm), and magnesium-rich saponite (2.31 μm).

2.2 Panchromatic and multispectral imagery

The High Resolution Stereo Camera HRSC (Neukum and Jaumann, 2004) combines nine CCD line detectors behind a common optics. The viewing directions of the detectors are oriented at angles between -18.9 and $+18.9^\circ$ with respect to the nadir view, and four of the sensors are equipped with broadband color filters for the red, green, blue and near infrared sections of the spectrum. This design allows for the simultaneous acquisition of panchromatic images with a map-projected ground resolution of up to 12.5 m per pixel, multispectral/color images and panchromatic multiple stereo ground coverage to produce digital terrain models (DTM). The resolutions of the color channels and the off-nadir panchromatic channels is usually reduced onboard by a factor of two or four with respect to the nadir channel to reduce the amount of data to be transferred to Earth (McCord *et al.*, 2007).

The HRSC color images have been beneficial for the mapping of the dark, basaltic sand dunes and deposits (McCord *et al.*, 2007; Williams *et al.*, 2009), which have a bluish hue in color-stretched RGB representations of the red, green and blue HRSC channels, and for the distinction between Al- and Mg/Fe-rich clay minerals in Mawrth Vallis (Loizeau *et al.*, 2007). Although a direct correlation between HRSC color spectra and specific minerals or rock types in other cases is difficult, the subtle color variations in HRSC images can and should be used to distinguish geologic units visually. We therefore used HRSC RGB representations of the red, green and blue HRSC channel, pansharpened with the higher resolved panchromatic, nadir-viewing HRSC channel or with CTX (Malin *et al.*, 2007) images in several occasions in this study.

We investigated the geometry of the LTDs based on digital elevation models (DTM) with spatial resolutions of 50 or 100 m cell size, which were derived from individual HRSC orbits (Gwinner *et al.*, 2000). We also used a regional DTM of the entire Valles Marineris at a resolution of 150 m cell size, which was produced from several bundle-block-adjusted HRSC orbits (Dumke *et al.*,

2010). We estimated the attitude of observed layers by fitting a plane through three or more points selected in the HRSC DTMs along the outcrop of the layering observed in the co-registered imagery (similar to Zegers *et al.*, 2006) using the software tool developed by Kneissl *et al.*, 2010. In addition to this, anaglyphs were produced directly from the HRSC nadir channel and one of the stereo channels, as these products provide more topographical detail than a DTM produced from the same data.

We also used panchromatic imagery from the Context Imager CTX (Malin *et al.*, 2007) with a spatial resolution of approx. 6 m per pixel, and panchromatic and color images from the HiRISE experiment (McEwen *et al.*, 2007) with a spatial resolution of up to 25 cm per pixel.

3 Results

3.1 Overview

Figure 1A shows Ophir Chasma as a false color mosaic of the red, green and blue channel of HRSC. Figure 1B shows the mineral indices for iron oxides, sulfates (SINDEX) and monohydrated sulfates (BD2100) calculated from OMEGA and CRISM data as a RGB image overlain on a panchromatic HRSC mosaic. In this visualization, monohydrated sulfates appear in a blue-green hue, polyhydrated sulfates have a green hue, and iron oxides are shown in red. In the HRSC color image, dark, basaltic material appears with a bluish hue. It is found as a dune-forming aeolian deposit in the central valley, the "mineral bowl", in wind traps along the northern of Ophir Mensa and on top of the ILD east of the central valley. The basaltic sand covers ILDs and landslides, its deposition therefore occurred after sulfate formation. The dark material shows a spectral signature of pyroxenes and in the central valley of pyroxenes and monohydrated (kieserite) deposits. Possible sources of the basaltic material are the eroding

chasm walls and landslide material, and a possible late-stage volcanism (Lucchitta, 2002). In nearby western Candor Chasma, dark, basaltic material shows a spectral signature of monohydrated sulfates, and HiRISE images show distinct, friable layers within the ILDs, from which the basaltic sands are released by erosion (Murchie *et al.*, 2009a). Similar layers are not found in Ophir Chasma. The ILDs appear to be mostly massive, without showing a layering structure. Locally, dark bands are observed, e. g., east of the central valley. At close inspection, these bands appear to be superficial, aeolian deposits on terraces caused by differential erosion along layering in the ILDs, but not basalt-bearing layers *within* the ILDs. The fact that the basaltic sand in the central valley shows spectral features of monohydrated sulfates does not imply an origin of the basalts from within the ILDs, as suggested for western Candor Chasma, as the sulfate signature is likely caused by the light toned kieserite deposits peeking through the loose, dark sand cover. On the other hand, erosion of the chasm walls inevitably continued during deposition of the ILDs independent of the depositional environment in the basin: therefore, an incorporation of basaltic material into the ILDs most likely took place, but the lack of distinct, dark layers suggests that this process played only a minor role. Consequently, the co-occurrence of pyroxenes and sulfates does not imply a genetic relationship between the two groups of minerals, which would allow a reconstruction of a common deposition. Spectral signatures of iron oxides and sulfates are found only on a small fraction of the deposits in Ophir Chasma, while most of the deposits are spectrally bland. Mangold *et al.*, 2008, Chojnacki and Hynek, 2008, and LeDeit, 2008, observed, that sulfates are found only in consolidated rocks with an elevated thermal inertia in TES data, and concluded that sulfates might be much more pervasive within the LTDs, but undetectable due to a cover of unconsolidated dust. This general trend is correct, but many locations are spectrally bland despite

relatively high thermal inertia values (Chojnacki *et al.*, 2006). This is the case for the ILD material on the northern flank of Ophir Mensa, which shows an elevated thermal inertia, but is nevertheless spectrally featureless in CRISM and OMEGA data. Although optically thick dust deposits could mask spectral features in the visible and near infrared region and at the same time hardly affect the thermal radiation, these locations are on steep flanks with deep erosional rills and free of dunes in high-resolution imagery, which does not suggest a dust cover.

The locations of sulfate and ferric oxide detections can be divided into three groups based on their stratigraphy with respect to Ophir Mensa. The observations in the west of Ophir Mensa (Fig. 2) and on the northern side of the "mineral bowl" suggest the presence of sulfates within the deposits of Ophir Mensa. On the southern wall of the "mineral bowl" (and Ophir Chasma), the stratigraphic relationship to Ophir Mensa is not completely clear. The outcrops in the "moat" north of Ophir Mensa and in the central valley form the third group of deposits, as they appear to overlay, and thus postdate the formation and erosion of the bulk of the light-toned deposits making up Ophir Mensa. All outcrops will be discussed in detail in the following text.

Figure 1A also shows the location of a prominent marker horizon within Ophir Mensa as a dashed, red line. This horizon shows several curves and can be traced from the western end of Ophir Mensa up to its base at the eastern end of the "mineral bowl" valley. It mostly forms a steep cliff approx. 500 m high (Fig. 2). Layer attitude measurements along this horizon indicate that the layering generally dips outward, following the topography of Ophir Mensa (compare to Zegers *et al.*, 2006). In the west of Ophir Mensa, the horizon is located stratigraphically near the top of the mound and dips approximately horizontally. In the center of Ophir Mensa, the horizon appears to plunge at angles in the order of 5° underneath the stratigraphically higher deposits of

the eastern Ophir Mensa. Towards the flanks, dip angles increase to around 20° . A kink in the slope is observed in the "mineral bowl", changing from 17° directly above the marker horizon to values around 10° below it. Interestingly, the sulfate deposits within Ophir Mensa are only found in the section beneath this horizon.

INSERT FIGURE 2 HERE

3.2 Western Ophir Mensa

Figure 3 shows a subset of the CRISM targeted observation FRT0000B27B in the western part of Ophir Mensa. In this location, the LTDs show layering in the order of a few tens of meters in thickness, which dip westward at moderate angles around 7° . Absorption bands near $1.6\ \mu\text{m}$, $2.1\ \mu\text{m}$ and at $2.4\ \mu\text{m}$ suggest the presence of monohydrated sulfates such as kieserite. The slightly lower albedo and the presence of small dunes in the region showing a presence of polyhydrated sulfates (green) in the HiRISE image PSP_008458_1760 (Fig. 3B) suggests that the boundary of kieserite detection, which does not coincide with the layering, is caused by the thin dust coverage, and not by a change of the mineralogy of the rocks in these layers. This suggests that the ILDs of Ophir Mensa above the marker horizon are sulfate-free, whereas the detection below this horizon is controlled by the presence or absence of a masking dust cover. Thus, in the lower part sulfates might be much more abundant, despite only limited detections in orbital data.

3.3 The "mineral bowl"

[INSERT FIGURE 4 HERE]

The "mineral bowl" is the depression between Ophir Mensa and the southern wall of Ophir Chasma. It extends approximately 70 km in East-West-direction and is up to 20 km wide (Fig. 4). It owns its informal name due to the complex relationship between spectrally bland ILDs of Ophir Mensa and sulfates and crystalline ferric oxide detections within Ophir Mensa, on the southern wall, and on the valley floor (Chojnacki and Hynek, 2008). The southern wall itself is built up from layers of basaltic rocks (Lucchitta, 1999). The spatial and spectral resolution of the CRISM and OMEGA data of this valley is very diverse. Therefore, the mineralogy of this complex outcrop region can only locally be assessed in detail. We will provide an overview of the mineral phases observed, before discussing the relationship between Ophir Mensa and the southern chasm wall (Fig. 5) and between the southern chasm wall and the overlying LTDs (Fig. 6).

Starting in the eastern part of the northern slope of the valley, CRISM detects absorption bands at 1.6, 2.13 and 2.4 μm consistent with kieserite at the base of Ophir Mensa and an erosional remnant of Ophir Mensa approx. one km towards the center of the valley. These outcrops show layering of tens of meters in thickness, and HiRISE imagery reveals even thinner internal layering in the meters scale. The layers were interpreted as the source of crystalline ferric oxides found in the dark material covering the floor of the valley (Weitz *et al.*, 2008). The sulfate and hematite-bearing rocks form a bench, which is evidenced by a break in dip angles from approx. 17° in the sulfate-free ILDs above to 10° within the sulfate-bearing rocks. The floor of the "mineral bowl" drops towards the south and is covered by dark material, which appears to be a

mixture of basaltic, pyroxene rich sand and crystalline ferric oxides, as evidenced by TES (Weitz et al., 2008) and CRISM data. Several light-toned patches with a spectral signature of monohydrated sulfates are found underneath this blanket. This suggests that the bench of sulfate-rich material extends further south underneath the dark cover to the opposite slope of the valley. In the center of the northern slope of the "mineral bowl", the sulfate-bearing bench forms a cliff about 400 meters high. Polyhydrated sulfate deposits are observed near the top of the cliff, monohydrated sulfate-rich deposits are found at the base and on the valley floor below. In the western part of the "mineral bowl", the base of Ophir Mensa is heavily eroded and forms a deep embayment towards the north, bound by steep flanks. OMEGA and CRISM data show kieserite spectra on these walls up to an elevation of approximately +250 m. The observation of kieserite spectra despite the heavy erosion suggests that fresh sulfates from within Ophir Mensa are exposed, rather than being a thin surface coating on the Ophir Mensa slopes. On the valley floor, layering of smooth, dark-toned, basaltic material and lighter-toned material with intermixed sulfates and iron oxides can be observed. Locally, light-toned, sulfate-rich dunes are found.

[INSERT FIGURE 5 HERE]

The relationship between Ophir Mensa and the southern chasm wall is shown in Fig. 5. Monohydrated sulfates are observed within the eroded base of Ophir Mensa and overlying the spur-and-gully morphology of the southern chasm wall ("MHS in situ" in Fig. 5A), where they are found from the foot of the slope at an elevation of ~-2200 m up to ~+800 m. The thickness of the light-toned cover of the southern wall appears to increase from the top to the bottom of the southern slope, suggesting downslope movement of material. Several light-toned ridges are

observed (white arrows in Fig. 5) covering the kieserite deposits, which have been described as "pasted on" the underlying basaltic basement (Chojnacki and Hynek, 2008; Weitz *et al.*, 2008) based on MOC imagery (Malin *et al.*, 1992). They are too small to be resolved in the CRISM MSP data available here, but are very similar in texture to light-toned ridges further to the east, (Fig. 6 and 7), showing a distinct mineralogy (see below). The kieserite on the southern slope of the "mineral bowl" is overlain by rough-textured polyhydrated sulfates and locally ferric oxides. The sulfate deposits on the southern wall end abruptly along an east-west-trending lineament we interpret as a normal fault. Together with a parallel feature approx. two to three km northward it forms a graben in the floor of the "mineral bowl" (center of Fig. 5A). The graben can be traced further eastward as a depression with angular boundaries (top of Fig. 5B). The graben is filled with smooth layers of monohydrated sulfates eroded from Ophir Mensa and the southern chasm wall ("MHS, redeposited" in Fig. 5A). Partly, these monohydrated sulfate outcrops are covered by spectrally bland material from further up the slope of Ophir Mensa.

The black arrows in Fig. 5 mark a "tongue shaped" deposit that bridges the gap between the southern slope of Ophir Chasma and Ophir Mensa. It starts below the top of Ophir Mensa at approx. 0 m elevation, stretches down the slope of Ophir Mensa to an elevation of ~-400 m, and rises again to ~0 m on the southern wall of Ophir Chasma. This outcrop is covered only by OMEGA data at a spatial resolution of 2.5 km/pixel and is partly overlain by smooth material, but the textural similarity to outcrops further to the east suggests that it consists of kieserite and is the westward prolongation of the kieserite deposits on the southern chasm wall ("MHS, in situ" Fig. 5). If this is the case, this suggests that (1) at the time when light-toned deposits of Ophir Mensa extended further to the south, as suggested by the monohydrated sulfates on the southern wall and the southward continuation of the light-toned deposits underneath a basaltic

cover described in the eastern part of the "mineral bowl" (Fig. 5), these light-toned deposits never filled up the "mineral bowl" to the top of Ophir Mensa, but instead, a valley existed at the location of the "tongue-shaped" deposit between Ophir Mensa and the southern wall. It also suggests, that (2) the polyhydrated sulfate deposits on the southern wall discordantly superpose the kieserite deposits ("MHS in situ", Fig. 5) on the southern chasm wall. Further high resolution HiRISE and CRISM observations of this part of the "mineral bowl" would help to solve this case.

The diverse mineralogy and complex depositional pattern of the LTDs on the southern wall are observed at the highest spectral and spatial resolution in the CRISM observation FRT0000A86A in Fig. 6. It shows ridges of kieserite in the valley cut into the chasm wall (center of Fig. 6A). These ridges, which could correspond to "MHS in situ" in Fig. 5, are overlain by a sequence of smooth layers corresponding to "MHS, redeposited" in Fig. 5. The smooth layers dip downslope at an angle of approx. 14° . Polyhydrated sulfates are found concordantly on the top of the smooth layers, but at the foot of the slope, they discordantly superpose and embay a massive outcrop of kieserite (Fig. 7A, C). Iron oxides are mostly associated with polyhydrated sulfates, but they also occur directly on top of kieserite. We analyzed the ferric oxides further using the CRISM data in the visible spectrum, as described in section 2. The regions appearing red in Fig. 5A show very similar spectral characteristics with a broad absorption band at $0.86\ \mu\text{m}$ and two minor bands at 0.5 and $0.58\ \mu\text{m}$, resembling the spectrum of red hematite (Fig. 6G).

[INSERT FIGURE 6 HERE]

Three other mineral phases are detected in this CRISM observation as well. Phase one displays spectral bands at 1.85 and 2.27 μm , diagnostic for jarosite, with the Fe-depleted H_3O -jarosite (Milliken *et al.*, 2008) being the best match (blue in Fig. 6B). It is found in several locations close to polyhydrated sulfates, both in the narrow valley and near the base of the slope. In the visible spectral range, this material displays an asymmetric absorption band at 0.45 μm , which fits to an absorption feature of jarosite at 0.44 μm . A second phase is characterized by absorptions near 1.93 and 2.21 μm and a shoulder near 2.32 μm (2.21-phase). Its spectrum does not match any of the laboratory spectra available from RELAB. Laboratory spectra with an absorption near 2.2 μm include amorphous SiO_2 and Al-rich phyllosilicates like montmorillonite (Fig. 5). However, amorphous SiO_2 shows a broad absorption band around 2.22 μm and no shoulder towards longer wavelengths, while montmorillonite has a narrow absorption band at 2.21 μm and shoulder near 2.27 μm , which makes both minerals unlikely matches. Similar spectra have been reported by Roach *et al.*, 2010b from Ius Chasma and elsewhere in Valles Marineris, and have been interpreted as hydrated silica phases or mixtures of phyllosilicates, amorphous silica and/or jarosite. A third phase has a very similar spectrum as the 2.21- μm -phase, but shows an absorption band at 2.23 μm . This spectrum is similar to spectra observed in Aram Chaos and interpreted as a ferric hydroxysulfate (Lichtenberg *et al.*, 2010), which was produced in the laboratory by desiccation of synthetic melanterite ($\text{Fe}^{2+}\text{SO}_4 \cdot 7(\text{H}_2\text{O})$). Unlike any other spectra in this observation, this material displays an absorption band at 0.76 μm (Fig. 5G). The polyhydrated ferric sulfate coquimbite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$, not shown) has a similar band near 0.76 μm , but its spectrum does not match in the short wave infrared range. The 2.21- μm -

phase and the 2.23- μ m-phase occur in similar stratigraphic positions. They superpose kieserite deposits as a thin, very light-toned coating, and are covered by basaltic debris, as shown in Fig. 7 and the schematic cross-sections therein. The outcrop of the 2.23- μ m-phase in Fig. 7A appears to be more deeply eroded than the 2.21- μ m-phase. It therefore is interpreted as underlying the 2.21- μ m-phase in the cross section in Fig. 7C. Polyhydrated sulfates are found in a similar stratigraphic position overlying kieserite units. The basalts at the top of the ridge in Fig. 7B appear blocky and layered, and thus resemble remnants of basaltic lava flows underlying the sulfates rather than aeolian deposits on top of them. This ridge is very similar to ridges in the west of the "mineral bowl" (white arrow in Fig. 5), suggesting that its mineralogy is present elsewhere in this part of Ophir Chasma, but not detected due to the lack of high-resolution spectral data.

[INSERT FIGURE 7 HERE]

3.4 The "northern moat"

The "northern moat" is the west-east-trending valley between Ophir Mensa and the northern rim of Ophir Chasma. Its floor is mostly covered by landslides eroding the chasm wall. In a few places, patches of light-toned material appear through windows in the landslide material cover (Fig. 8). The two outcrops in Fig. 8 A and B have a texture similar to Ophir Mensa, which suggests that Ophir Mensa once extended further northward. The two patches show no spectral signature of sulfates, and are located at elevations of -3100 m and -3300 m, whereas a third patch of light-toned material is found at -4600 m. This third patch is similar in texture to the floor of the central valley. Ratioed CRISM MSP and OMEGA spectra show an absorption band at

1.4 μm , a broad feature at 1.9 μm and a drop-off in reflectance longward of 2.3 μm , consistent with polyhydrated sulfate. The similar elevation, mineralogy and texture of this outcrop and the deposits in the central valley suggests that unlike the two outcrops in Fig. 8A and B, this outcrop is not a remnant of Ophir Mensa, but rather an infill of the basin between Ophir Mensa and the northern chasm wall, similar to the central valley fill.

[INSERT FIGURE 8 HERE]

Sulfates are also found within the deposits of a landslide in Fig. 9. It shows sulfate-rich material at the tip of a landslide fan that was deposited against the LTDs of Ophir Mensa. Since the time of deposition of this landslide, the slope of Ophir Mensa has been eroded backward 1.2 to 2.5 km by wind, leaving behind a flat, dune-covered plain between the landslide deposit and the slope of Ophir Mensa. The HRSC anaglyph in Fig. 9B suggests that the landslide deposit and the sulfate material therein overlay the light-toned deposits of Ophir Mensa, as shown in the cross-section in Fig. 9C. Theoretically, the sulfates could have formed prior to the landslide event, or by water released by the landslide event itself. Lucchitta, 1987, argued that the landslides in the central valley of Ophir Chasma released large quantities of water, which caused the collapse of the mountain barrier between Ophir and Candor Chasmata, and deepened the central valley. However, Quantin *et al.*, 2004, observed, that landslides in Valles Marineris occurred at all times between 3.5 Ga and 50 Ma before present, and that they always show the same characteristics. This suggests that no water was involved in the formation of the landslides, as the atmospheric conditions during this period did not allow a sustained existence of liquid water. The topographic elevation of the sulfates of -3450 m is also much higher than the -4500 m of the closest sulfate

deposits in the "northern moat" (Fig. 8C). We therefore conclude that the sulfates in Fig. 9 were formed prior to the landslide events. The ages of the landslides in Ophir Chasma range between 80 Ma and 1 Ga (Quantin *et al.*, 2004) and provide no constraint on ILD formation and water-related activity, which ended at 3 to 3.5 Ga (Quantin *et al.*, 2010).

[INSERT FIGURE 9 HERE]

3.5 The central valley

The floor of the central valley is partly covered by sulfate-rich deposits, as shown in Fig. 10. Its surface gently drops from -4250 m in the south-west to -4900 m in the north-east, resulting in a dip of approximately 1° (Chojnacki and Hynek, 2008; Gendrin *et al.*, 2005; Mangold *et al.*, 2007). The deposits are at least 270 m thick, and are easily recognized by a distinct hue in HRSC false color images (fig. 10D). The CRISM observations of this area generally confirm the mineralogy derived from OMEGA data. The top of the deposit is dominated by the monohydrated sulfate kieserite, that is partly covered by dunes of dark-toned, basaltic material. It has a rough, fluted texture with curved ridges trending approximately perpendicular to the valley axis (Fig 10E, F and G). An increase of the spectral slope between 1 and 1.3 μm in CRISM and OMEGA spectra in the southern part of the valley indicates that the smooth material with an intermediate albedo found in this part of the valley is rich in ferric oxides (fig. 10F). Directly south of landslide deposits in the north of the central valley, the valley floor deposits display spectra of polyhydrated sulfates. They show a fluted, wind-eroded topography (fig 10E), but are devoid of the ridges found in the monohydrated sulfates (fig. 10F) and are not covered by dark, basaltic dunes. The patch is topographically lower than the neighboring monohydrated-

sulfate rich deposits. This suggests that monohydrated sulfates overlay polyhydrated sulfates, as shown in the cross-section in Fig. 10C. The superposition of monohydrated sulfates on top of polyhydrated sulfates is contrary to sulfates in the "mineral bowl" and other chasmata of Valles Marineris, such as Juventae Chasma (Bishop *et al.*, 2009; Gendrin *et al.*, 2005) and West Candor Chasma (Murchie *et al.*, 2009a). The boundary between poly- and monohydrated sulfates is gradational and coincides with a decrease in albedo from the brighter poly- to the slightly darker monohydrated sulfates. However, it also coincides with an increase in the abundance of dark dunes. Therefore, the albedo difference between the brighter polyhydrated sulfates and the darker monohydrated (kieserite-dominated) sulfates (Chojnacki and Hynek, 2008), might be caused by the presence of basaltic dunes and iron oxides in the area of the monohydrated sulfates, and not by a color variation between the two sulfate species. Both sulfate species are not layered. The deposit ends abruptly near the remains of the mountain barrier between Ophir and Candor Chasma at 72° E, 5° S.

[INSERT FIGURE 10 HERE]

Light-toned, often subcircular patches with a diameter of a few hundred meters are observed in the northern part of the central valley, where polyhydrated minerals are found (fig. 11). They show bands at 1.93 μm , 2.21 μm and 2.27 μm and shoulder at 2.32 μm in CRISM targeted observations, which is very similar to the 2.21- μm -phase observed in the "mineral bowl" (Fig. 6) and Ius Chasma (Roach *et al.*, 2010b). Again, a mixture of jarosite (possibly H_3O -jarosite) and amorphous silica or montmorillonite is the best spectral match. A phase with a band at 2.23 μm is not observed here. Unlike the deposits in the "mineral bowl", the deposits in the central valley

are not layered, and almost indistinguishable from the surrounding deposits by their texture alone.

[INSERT FIGURE 11 HERE]

4 Discussion

4.1 Mineral detections

Roach *et al.*, 2010b suggested four hypotheses for the minerals showing absorption bands at 2.21 μm observed in Ius Chasma, which are spectrally very similar to the 2.21- μm -phase observed in Ophir Chasma: (1) a sulfate mineral structurally similar to jarosite, (2) amorphous silica mixed with Fe-Mg-smectite, (3) a mixture of Al- and Fe-Mg-smectite, or (4) poorly crystalline mixed Al-Fe clay formed either by acid alteration of clay minerals or as a direct formation from dissolved basalt.

Library spectra of the three most common jarosite minerals, Na-jarosite, K-jarosite and H_3O -jarosite, are very similar to the 2.21- μm -phase, but no perfect spectral match. Like the unknown phase, they display absorptions at 1.93 μm and a shoulder near 2.32 μm , but the band at 1.85 μm , characteristic for jarosites, is not observed in the unknown phase. An absorption band at 2.21 μm is observed in K-jarosite, but this mineral shows a second, deeper absorption near 2.27 μm , which is absent or only weakly expressed in the unknown phases. Therefore, if a jarosite mineral is present in these phases, it is probably mixed with a different mineral.

Amorphous silica displays a broad spectral band at 2.21 μm , and a shoulder at 2.26 μm . In contrast, the absorption band at 2.21 μm of the unknown phase is narrow, and its right shoulder

is located at longer wavelengths at 2.32 μm , which makes pure amorphous silica a bad spectral match. A mixture of Al-rich and Mg/Fe-rich clay minerals or of clay minerals and jarosite could reproduce the absorption bands observed here. However, clays form under circum-neutral pH-conditions, whereas the clear identification of jarosite in neighboring locations, and partly in similar stratigraphic positions, points towards acidic conditions (pH < 3-4, Papike *et al.*, 2006), which makes the presence of clay minerals unlikely. A theoretical alternative would be the formation of clay minerals at a different location than the jarosite minerals and subsequent transport to this place, but the location of the 2.21- μm -phase high on the slopes just below the crests of fresh basaltic wall rock effectively rules out this option, as it suggests a formation of this phase *in situ*.

The last hypothesis is the formation as a poorly crystalline Fe-SiO₂-phase by acidic to neutral leaching of nontronite, which would produce Si-OH vibrations due to the formation of amorphous silica as in clay-rich material exposed to acidic vapors at Mauna Kea (Swayze, unpublished data in Roach *et al.*, 2010b). This mechanism would also explain the observed 2.23 μm band observed locally during this study due to FeAlOH vibrations. Alternatively, Tosca *et al.*, 2008, report the formation of a poorly crystalline Fe-SiO₂-phase as a precipitate from dissolved basalt by addition of S and Cl under oxidizing conditions at a pH of 5-7 in laboratory tests, which would possibly display similar spectral bands between 2.21 and 2.26 μm .

Of the proposed mineralogies of the unknown 2.21- μm -phase, we favor a mixture of jarosite and amorphous silica or jarosite and a newly formed, poorly crystalline Fe-SiO₂- phase, and a mixture of jarosite and a poorly crystalline Fe-Al-SiO₂-phase for the locations showing a 2.23 μm absorption, rather than mixtures of different phyllosilicate minerals or phyllosilicate minerals and jarosite. In the "mineral bowl" (fig. 6), the clear identification of H₃O-jarosite

suggests acidic conditions, which are inconsistent with clay formation. Amorphous silica in combination with jarosite has also been identified by CRISM on the plateau above Juventae Chasma (Bishop *et al.*, 2009; Milliken *et al.*, 2008) and in Melas Chasma (Metz *et al.*, 2009), where they are interpreted as the product of acidic alteration of basalts.

On Earth, jarosite and amorphous silica are known from acid mine drainage deposits, for example in Spain (i.e., Sánchez España *et al.*, 2005) and Greece (Triantafyllidis and Skarpelis, 2006), where the oxidation of sulfides produces sulfuric acid, which in turn dissolves olivines, pyroxenes and feldspars in the basaltic rocks to form jarosite, leaving behind amorphous silica and kaolinite as the least soluble minerals. A similar mechanism has been proposed for Mars (Burns, 1987; Burns and Fisher, 1990; Poulet *et al.*, 2008). Investigations on a Martian meteorite show that a part of the jarosite and amorphous silica on Mars formed under hydrothermal conditions (McCubbin *et al.*, 2009), but the H₃O-jarosite best matching the spectra from Ophir, Melas and Juventae Chasma indicates temperatures below 100°C (Milliken *et al.*, 2008). All jarosite species indicate a limited water supply and short time for the chemical alteration, as the acidity is not neutralized by the decomposition of feldspars (Höller, 1967; Madden *et al.*, 2004). H₃O-jarosite forms at even lower water/rock ratios, when sulfide minerals dissolve more rapidly than rock forming minerals, resulting in a lack of Na and K with respect to Fe in the solution, which prevents the formation of K- and Na-jarosite (Brophy and Sheridan, 1965). At rising pH, H₃O-jarosite becomes unstable, and goethite (FeOOH) forms, while the sulfate ions go back into solution (Burns and Fisher, 1990). At the same time, poorly crystalline Fe- or FeAl-SiO₂-phases can form (Tosca *et al.*, 2008), which can be considered precursors to clay minerals. Goethite can later transform into hematite, while the sulfate ions could precipitate as polyhydrated sulfates upon evaporation of the brine. An alternative source for the acidity required for the jarosite

formation other than weathering of sulfides are volcanic, SO₂-rich exhalations as observed at the Kilauea volcano (Schiffman *et al.*, 2006).

The mineral assemblage observed on the southern wall of Ophir Chasma (fig. 6 and 7) is consistent with an acidic alteration of basaltic rock: jarosite and the unidentified, possibly jarosite-amorphous silica bearing phases are almost always observed at the top of the hillsides, just below the crest, locations that would have received very little water. They are covered by basaltic debris, which would be the source rock. They are topographically higher than iron oxide detections and polyhydrated sulfates, which would represent the more developed alteration products. On the northern side of the mineral bowl, where the slopes are lacking a basaltic cover, no 2.21- μ m-phase or jarosite are found. In the central valley, the relationship between the abundant polyhydrated sulfates and the patchy outcrops of the 2.21- μ m-phase is not clear and gives no hint on the formation history. A possible source rock for the sulfatic alteration products cannot be identified.

4.2 Stratigraphic relationships

Any hypothesis for the formation of the light-toned deposits and the role of water therein has to meet the constraints imposed by the stratigraphic relationships within the LTD units and between the LTDs and the wall rocks. They are visualized in Fig. 12 and summarized as follows:

(1) All light-toned deposits in Ophir Chasma superpose the spur-and-gully morphology of the canyon walls. Their deposition therefore postdates the formation of the chasm (Chojnacki and Hynek, 2008).

(2) The LTDs of Ophir Mensa can be divided into two units based on layer boundaries and mineralogy. A marker horizon (fig. 1) separates the two units. Its dip roughly follows the local topography, with steep ($\sim 20^\circ$) slopes at the flanks of Ophir Mensa and approx. horizontal

layering in the center. This implies that the eastern part of Ophir Mensa is younger than the western part.

(3) The lower unit of Ophir Mensa is kieserite-bearing. The strong erosion of Ophir Mensa in the "mineral bowl" suggests that the kieserite signature is not a superficial deposit draped over a sulfate-free rock, but that the entire lower unit contains kieserite sulfate.

(4) The monohydrated sulfates on the southern wall of the "mineral bowl" are connected to Ophir Mensa by a "tongue" of light-toned, sulfate-rich material. This suggests that these deposits are of the same age. The monohydrated sulfates in the "mineral bowl" therefore formed, when Ophir Mensa extended further southward up to the southern wall of the chasm. The top of the LTDs along the southern wall of Ophir Chasma dropped from west to east, as shown by remnants of light-toned material on the chasm wall.

(5) However, at the time of sulfate formation, a precursor valley of the "mineral bowl" already existed, which formed a depression between the center of Ophir Mensa and the southern wall. This is shown by the (likely) sulfate-bearing "tongue" between the southern wall and Ophir Mensa: It starts near the top of Ophir Mensa, drops down at its center and raises again towards the southern wall (fig. 5B).

(6) Polyhydrated sulfates in the "mineral bowl" are found near the top of the light-toned material. The transition between kieserite and polyhydrated sulfates appears concordant on the upper slope of the southern wall (fig. 6 and 7), but discordant in the lower parts, where polyhydrated sulfates embay an eroded remnant of kieserite-rich rock. Further westward, the polyhydrated sulfates appear to discordantly overlay parts of the "tongue" between Ophir Mensa and the southern wall. This implies that polyhydrated sulfates formed after the deposition and partial erosion of the kieserite-rich rocks.

(7) It is not clear if the polyhydrated sulfates precipitated directly in their current form, or if they formed by hydration of the underlying kieserite-rich material. The presence of jarosite and poorly constrained, probably amorphous silica-rich material underneath a cover of basaltic debris is consistent with an acid alteration of the basaltic cover caused by the decomposition of sulfides, as suggested by Burns, 1987. This would require the presence of water, which could also have transformed monohydrated kieserite to polyhydrated sulfates. An alteration from kieserite to polyhydrated sulfates has also been suggested for Ius Chasma (Roach *et al.*, 2010b), whereas the variation in sulfate mineralogy in Candor and Juventae Chasma has been interpreted to be caused by changes of the composition of the evaporating brine (Murchie *et al.*, 2009a, Bishop *et al.*, 2009).

(8) Ferric oxides contained within the sulfate-rich deposits in Ophir Mensa (Bibring *et al.*, 2007) accumulate on the floor of the "mineral bowl", where they form a partly indurated lag deposit together with sulfates and basaltic debris from the south wall.

(9) The sulfates of the central valley and the "northern moat" show distinct characteristics. They formed after the incision of the central valley, and therefore post-date Ophir Mensa.

(10) All sulfate deposits in the central valley are found below -4250 m, approx. 1450 m below the lowest sulfate detections in the "mineral bowl". Only the sulfates underneath a landslide in the "northern moat" are found at higher elevations (fig. 8), but it is not clear if they formed *in situ* or have been transported to this elevation by the landslide.

(11) In the central valley, monohydrated kieserite apparently stratigraphically superposes polyhydrated sulfates, unlike in Candor Chasma, Aram Chaos and Juventae Chasma, where monohydrated sulfates are stratigraphically below polyhydrated sulfates (Bishop *et al.*, 2009; Lichtenberg *et al.*, 2010; Murchie *et al.*, 2009a), but similar to Ius Chasma (Roach *et al.*, 2010b).

[INSERT FIGURE 12 HERE]

4.3 Implications for formation hypotheses

The presence of sulfates within the ILDs of Ophir Mensa indicate, that water played a role in their formation. On the other hand, large parts of the ILDs are spectrally bland although they are likely not covered by dust, as indicated by elevated TI values around 500 thermal inertia units (Chojnacki and Hynek, 2008, fig. 2a), steep slopes and no visible small dunes in HiRISE images. Therefore, these parts of the LTDs must either have formed under dry conditions that did not involve water, or they are cemented by minerals that are not detectable from orbit, such as halite (NaCl) or anhydrite (CaSO₄). In the following paragraphs, we will discuss the formation of the ILDs in the light of our observations, before we investigate, whether the sulfates in Ophir Chasma precipitated from evaporating groundwater (Roach *et al.*, 2010b; Rossi *et al.*, 2008) or lakes (Lucchitta, 2009a; 2009b; McKay and Nedell, 1988) or meteoric water, or a combination of these processes.

Some authors suggested that the LTDs were exhumed light-toned material from the chasm walls (Adams *et al.*, 2009; Malin and Edgett, 2000). This idea can be rejected, as the light-toned material clearly overlays the spur-and-gully morphology of the chasm walls as elsewhere in Valles Marineris (Blasius *et al.*, 1977; Lucchitta *et al.*, 1992; Nedell *et al.*, 1987). The idea that the LTDs are subice volcanoes was proposed by Chapman and Tanaka, 2001. This theory explains the outward dipping layers of the LTDs and the fact that most LTDs form free-standing mounds, separated from the chasm walls by depressions. However, it implies that the LTDs are

volcanic strata. This is contradictory to the lack of a basaltic spectral signature of these rocks and the missing of clear volcanic morphologies such as craters or lava flows.

If the LTDs were eolian or pyroclastic deposits (Chapman and Tanaka, 2001; Peterson, 1981), we would expect similar deposits outside Valles Marineris (Glotch and Rogers, 2007). Layered deposits are found on the plains surrounding Valles Marineris (Bishop *et al.*, 2009, Milliken *et al.*, 2008, Le Deit *et al.*, 2010), which are interpreted as airfall deposits (Le Deit *et al.*, 2010). These deposits are much thinner (<100 m) than the deposits within the chasmata.

Thus, an origin of the spectrally bland material in the LTDs by airfall, either as volcanic clasts or windblown dust, is conceivable, but an additional mechanism to trap and lithify these deposits is required to explain the observed thickness of the deposits (Lucchitta, 2009a, 2009b).

Regardless of the origin of the spectrally bland LTDs, the sulfates within them are formed by water. The stratigraphic relationships described in section 4.2 require at least two phases of sulfate formation. In a first phase, sulfates formed within Ophir Mensa and in a second phase the in the central valley. The monohydrated sulfates on the southern wall of Ophir Chasma appear to be remnants of the sulfates of Ophir Mensa, which once extended further southward. The polyhydrated sulfates possibly formed later, either by alteration of the previous monohydrated sulfate, or by acid weathering of the overlying basaltic debris. The timing of this alteration phase is poorly constrained. It can be contemporaneous with the sulfate formation in the central valley and the northern moat, or might also have taken place independently from that event. For nearby Capri Chasma, Roach *et al.*, 2010a advocated the concept that the monohydrated kieserite was not the sulfate phase that initially precipitated, but was formed later during diagenesis from previously polyhydrated sulfates under the overburden of several kilometers of sediments on top. The LTDs of Ophir Mensa are several kilometers thick, therefore, diagenetic processes or

intrusions of brines that altered an initial mineralogy to the mineralogy now observed is possible, but an assessment of their role is difficult and remains an open question.

The idea that the sulfates formed in lakes (Lucchitta, 2009a; 2009b; Peterson, 1981) implies that the lakes acted as a trap for clastic deposits. The sulfates therefore would have formed at the same time as the spectrally bland clasts hosting them. If this was the case, we would expect horizontal layering and a constant upper elevation of the sulfate detection, which would resemble the water level in the lake. The upper part of the LTDs, which is sulfate-free, would have been formed by a different process. Therefore, the elevation variations of the upper sulfate detection limit in the "mineral bowl" and the lack of sulfate detections in the LTDs at similar elevations on the northern and eastern flank of Ophir Mensa are better explained by a formation by groundwater (Murchie *et al.*, 2009a) that entered the LTD mound after its deposition. In this case, the variations in elevation of the sulfate detections and the coexistence of sulfate-bearing and sulfate-free LTDs at the same elevation would reflect the initial morphology of the hosting sediments in the chasm, or variations of their permeability.

The deposits in the central valley are almost horizontal, which is consistent with a formation in a lake as well as a playa, similar to the mechanism proposed for Meridiani Planum (Arvidson *et al.*, 2003). The slight dip towards the north would either imply a dip of the sediments after deposition, possibly by downfaulting of the entire chasm floor along the northern rim, or simply deposition on an inclined chasm floor. The remnants of the collapsed mountain ridge between Ophir and Candor Chasma could have acted as a barrier to form a lake behind it. The low elevation of the sulfate deposit, implied by sulfate detections restricted to elevations below -4250 m, is consistent with the proposed lake in central Valles Marineris/Coprates Chasma with a maximum ponding level at -3560 m proposed by Harrison and Chapman, 2008. The flanks of the

central valley show rills on both sides. Similar structures in Candor have been interpreted by Murchie *et al.*, 2009a, as braided channels formed by flowing water. If this was the case in Ophir Chasma, they could have acted as pathways for water entering the suggested lake. The rills have also been interpreted to be formed by glacial scouring (Chapman and Smellie, 2007; Roach, 2009), which would also be consistent with a (frozen) lake in the central valley. However, the rills may also have formed by wind erosion: Many of them are not perfectly perpendicular to the slope of the hillsides they form in, but curve southward. This is a strong indication for wind erosion rather than flowing water or ice.

Like in the central valley, polyhydrated sulfates are found topographically below monohydrated sulfates in western Candor Chasma and Aram Chaos (Lichtenberg *et al.*, 2010; Murchie *et al.*, 2009a). In these locations, the polyhydrated sulfates have been interpreted as late-stage sediments that were deposited discordantly in low-lying areas after erosion of the monohydrated sulfates, so they would be stratigraphically above the monohydrated sulfate-rich deposits. In the central valley, we do not see evidence for this interpretation. The boundary between mono- and polyhydrated sulfates is transitional, and no unconformity is observed. We therefore interpret that the topographically low polyhydrated sulfates are also stratigraphically below the monohydrated sulfates. This stratigraphy has also been inferred for mono- and polyhydrated sulfates in Ius Chasma (Roach *et al.*, 2010b).

The sulfates on the southern wall of the "mineral bowl" are spread over a wide range of elevations, and dip downslope. This, and the "tongue" between Ophir Mensa and the southern wall, implies that the "mineral bowl" depression existed already at the time of the deposition of these sulfates. Even if Ophir Mensa once extended further southward, it would already have been eroded away at least partly, as otherwise the layering of the deposits on the southern wall would

be more horizontal. If the sulfates were formed in a lake, this lake would have to have been deep enough to form sulfates very high on the slope. In this case, other parts of this valley would have been submerged at the same time, and should therefore show sulfate deposits too, which have not been observed. The formation by evaporating groundwater would require that a groundwater discharge from the entire slope of the chasm wall: water leaking from the top of the wall would not have reached the debris deposits below the basaltic rocks on the "spurs" of the wall, where some of the sulfates are found (fig. 7). The presence of high water tables in the narrow mountain ridge between Ophir and Candor Chasma is also not likely. Therefore, if these deposits are indeed acid alteration products of basalt, which is consistent with the spectral observations of jarosite, amorphous silica, ferric oxides, polyhydrated sulfates and possibly poorly crystalline Fe-SiO₂- or Fe-Al-SiO₂-phases (the 2.21- μ m-phase and the 2.23- μ m-phase), the best way to explain the supply of water to the locations where these minerals are found, would be rain, snow or frost.

Glaciers in Valles Marineris, which could provide the required water, and could also explain the variable range of elevations where water has been present, have been proposed in previous studies (Chapman and Smellie, 2007; Chapman and Tanaka, 2001; Chapman and Tanaka, 2002; Mège and Bourgeois, 2010), but in this particular location, associated landforms such as U-shaped valleys are missing. A second source for water could be the fog clouds in Valles Marineris (i.e., Moehlmann *et al.*, 2009). If the Martian soil contains perchlorates, as suggested by results from the Phoenix lander (Zorzano *et al.*, 2009), these hygroscopic minerals would attract water from the fog clouds in Valles Marineris and allow liquid water at temperatures as low as 225°K. However, if this is indeed the process responsible for the alteration, it remains

unclear why it would be constrained to this part of Ophir Chasma only, as other parts of the LTDs in the same chasm at similar elevations did not develop a spectral hydration signature.

5 Conclusions

Our study confirms and refines, based on OMEGA and CRISM data, previous studies based on OMEGA data alone (Chojnacki and Hynek, 2008; Gendrin *et al.*, 2005; Mangold *et al.*, 2007). Water-related minerals in Ophir Chasma are found mainly in two locations: In the "mineral bowl" valley between Ophir Mensa and the southern wall, and on the central valley floor. The same minerals are observed in these two locations, kieserite, polyhydrated sulfates, iron oxides and newly discovered phases that are consistent with mixtures of jarosite and amorphous silica or other poorly crystalline phases, but the two deposits are very distinct (Chojnacki and Hynek, 2008). In the "mineral bowl", kieserite is found in the bulk material of Ophir Mensa and on the southern wall, where it could represent remnants of Ophir Mensa, which once extended further southward. The variations in elevation of these sulfates are best explained by a post-depositional alteration of clastic material of unknown origin, possibly airfall deposits, by ground water rather than an open water body. On the southern wall, kieserite is superposed by H₃O-jarosite, and/or possible jarosite-amorphous-silica mixtures with spectral bands at 2.21 μm or 2.23 μm , polyhydrated sulfates and iron oxides. This sulfate deposit is layered, dips downslope, is stretched over a wide range of elevations, and could be stratigraphically discordant to the underlying bulk LTDs. Its formation therefore possibly took place after the excavation of the "mineral bowl" valley. A similar succession of polyhydrated sulfates discordantly on top of monohydrated sulfates in local depositional traps has been observed in western Candor Chasma and Aram Chaos (Lichtenberg *et al.*, 2010; Murchie *et al.*, 2009a). In Candor Chasma, rills that

show similarities to braided river beds on the slopes of LTD mounds have been interpreted as evidence of springs relatively high up the slopes of the chasm, which would have supplied the water that eventually deposited the polyhydrated sulfates. In Ophir Chasma, locations of the polyhydrated sulfates and the phases with absorptions at 2.21 or 2.23 μm on ridges of the underlying basaltic material is neither consistent with a water supply scenario nor with an open lake: therefore, meteoric water in the form of snow, frost or fog might have played a role. Debris from the LTDs, including iron oxides, are found as lag deposits on the floor of the valley, where they mix with basaltic material (Bibring *et al.*, 2007; Chojnacki and Hynek, 2008; Weitz *et al.*, 2008). On the northern side, the lack of CRISM targeted observations prevents a detailed spectral analysis.

The sulfates in the central valley form a flat deposit at low elevations (< -4250 m), but appear to be stratigraphically higher than Ophir Mensa's LTDs. These deposits are not layered, show ridges or joints, and kieserite superposes polyhydrated sulfates. The polyhydrated sulfates contain outcrops a few hundred meters in diameter of an unidentified mineral phase spectrally consistent with a jarosite-amorphous-silica mixture. A deposition of these deposits in a lake, possibly behind a mountain barrier that once separated Candor and Ophir Chasma, or in a playa-like environment as in Meridiani Planum is conceivable.

The proposed succession of events is very similar to the suggested history of western Candor Chasma, where the bulk of the sulfates in the LTDs is formed by intruding groundwater, and a lesser amount of sulfates is formed by fluvial processes after excavation of the valleys cross-cutting the ILDs by outflow events (Murchie *et al.*, 2009a, Fig. 9). However, in Ophir Chasma, the excavation of the central valley is not necessarily an outflow event, but possibly caused by glaciers. We do not observe convincing evidence for fluvial activity.

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[TABLES]

Table 1: List of CRISM and OMEGA observations used in this study

CRISM targeted observations ^a	CRISM Multispectral Mapping Strips ^a	OMEGA observations ^b
FRT000082C5_07	MSP000031C3_05	0548_3
FRT000096E6_07	MSP000032FE_05	1180_5
FRT0000A86A_07	MSP000033F3_07	1202_1
FRT0000AD8D_07	MSP000034E0_05	1213_2
FRT0000B27B_07	MSP00003899_01	3228_3
FRT0000B994_07	MSP00003A47_01	4358_3
FRT0000BB63_07	MSP00003EA9_05	4380_3
FRT000109E5_07	MSP00004044_07	
HRL0000508A_07	MSP0000416B_05	
HRL00005B82_07	MSP000046F2_07	
HRL00007468_07	MSP00004825_01	
HRL000075E7_07	MSP00004AA1_01	
HRL00007E21_07	MSP00005575_03	
HRL0000A432_07	MSP000059A0_05	
HRL0000B7D4_07	MSP00006CCB_01	
HRL0000BF5E_07	MSP0000CB50_01	
HRL0000C30D_07		
HRL0000C59C_07		

^aThe first three characters of the CRISM file names designate the type of observation: full(FRT) or half resolution targeted (HRL) observation or multispectral mapping strip (MSP). The next characters are unique hexadecimal identifiers for each observation. The last two figures indicate the component image used from that observation.

^b OMEGA observations are identified by the four-digit orbit number followed by the sequence number within that orbit

1077 [FIGURE CAPTIONS]

1078

1079 Figure 1

1080 A: Color mosaic of HRSC orbits 334 and 3127 of Ophir Chasma with location names and
1081 simplified geologic units. Contour lines every 500 m from HRSC DTM with 150 m post spacing.

1082 Dashed red line: Prominent marker horizon in Ophir Mensa, separating it in a lower and upper
1083 unit. Local layer strike and dip measurements. Compare to Zegers et al., 2006.

1084 B: HRSC nadir mosaic with contour lines for orientation, overlain with 'ratio of reflectance at 1
1085 and 1.3 μm ', SINDEX and BD2100 as RGB image from OMEGA and CRISM multispectral and
1086 targeted observations, and resulting mineralogic units (white lines). Iron oxides appear red,
1087 polyhydrated sulfates green, monohydrated sulfates blue.

1088

1089 Figure 2

1090 Details of the horizon marked red in Fig. 1. In the west of Ophir Mensa, it forms a steep cliff
1091 near the top of the mound (A). In the center of Ophir Mensa, it plunges at angles around 4° under
1092 the overlying LTDs further east and north (B). CTX images P02_002208_1748,
1093 P12_005676_1746, P15_006955_1746.

1094

1095 Figure 3

1096 A: CTX observation P20_008893_1762 from western Ophir Mensa, overlain with spectral
1097 indices from CRISM FRT0000B27B as in Fig. 1, showing presence of kieserite (blue) and a
1098 weak presence of polyhydrated sulfates (green). The red stripe is an artifact.

1099 B: Detail of HiRISE observation PSP_008458_1760. MHS: monohydrated sulfates. The kieserite
1100 detection boundary is controlled by dust cover and oblique to layering, suggesting that kieserite

is abundant in this part of Ophir Mensa despite spatially limited detections, whereas the area showing the PHS signature is stronger affected by dust.

Figure 4

A: HRSC orbit 334 of the "mineral bowl" overlain with HRSC contours and spectral indices as in fig. 1. Red dashed line: Prominent horizon in Ophir Mensa. Sulfate detections are restricted to units below this horizon.

B: Interpreted mineralogic map of same region. MHS: monohydrated sulfates. PHS: Polyhydrated sulfates.

Figure 5

A: Detail of fig 4 showing the complex stratigraphic relationship between Ophir Mensa, LTDs on southern chasm wall and basaltic wall rock (CTX P12_005676_1746 and P13_006243_1746 overlain on HRSC color image orbit 3127) North is left. Mineralogy as in Fig. 4, combined with geomorphologic interpretation. MHS: monohydrated sulfates. PHS: polyhydrated sulfates. White arrow: Light-toned material on ridge of southern wall. Black arrow: "Tongue" of LTD bridging a valley between Ophir Mensa and southern wall. This implies that a depression already existed at this location at the time of sulfate deposition (see text). B: Anaglyph from HRSC orbit 3127 of the same area.

Figure 6

A: CTX observation P03_002208_1748 and P12_005676_1746 of LTDs on southern chasm wall overlain with spectral indices from FRT0000A86A as in fig. 1. Contours from HRSC DTM. LTDs form deposits on top of basaltic wall rock. Layered kieserite is superposed by polyhydrated sulfates and iron oxides. Layers dip downslope. At base of slope, polyhydrated

1125 sulfates embay kieserite, suggesting discordant deposition. B: Same as A, but spectral indices
1126 BD2210, BD2230 and ratio between reflectance at 2.33 μm and 2.28 μm as red, green and blue
1127 color planes. C: locations, where average spectra were taken. Spectra were averaged over tens to
1128 thousands of pixels to reduce noise, and divided by a spectrally inconspicuous reference region
1129 (black). D: Average reflectance spectra of monohydrated sulfates, polyhydrated sulfates, iron
1130 oxides and reference. E: Same spectra as D, ratioed to reflectance spectrum, and matching library
1131 spectra from RELAB. F: Average reflectance spectra of the three spectrally distinct regions in B,
1132 in the range of 0.41 μm to 2.6 μm , together with ferric oxide spectrum and reference for
1133 comparison. Three phases are observed: A phase with absorption band at 2.21 μm (magenta),
1134 one with a band at 2.23 μm (green) jarosite (cyan). G: Ratioed reflectance spectra in the range of
1135 0.41 to 0.64 μm and 0.69 to 0.97 μm with separately removed continuum, and resembling
1136 laboratory spectra. H: Same spectra as in F and G (except ferric oxide), in the spectral range 1 -
1137 2.6 μm , ratioed to reference region spectrum. Spectra resemble jarosite/H₃O-jarosite mixed with
1138 amorphous silica or Al-rich clays (montmorillonite). Library spectra from RELAB, except H₃O-
1139 jarosite from Milliken et al., 2008.

1140

1141 Figure 7

1142 A: Details of LTD at the foot of southern chasm wall (HiRISE anaglyph of ESP_011662_1750
1143 and ESP_011807_1750). B: Detail of ridge in Fig. 6. The 2.21-micron-phase overlays kieserite
1144 as a thin, very bright coating. Its occurrence is restricted to the talus deposit underneath fresh
1145 basaltic ridge. A water supply to this location from groundwater or by a lake is inconsistent.
1146 Instead, water might have precipitated as rain, frost or snow from above. (HiRISE
1147 ESP_011807_1750_COLOR). C: Interpretative cross-sections to A and B (not to scale). The

2.21- μ m-phase, the 2.23- μ m-phase and the polyhydrated sulfates are found in similar positions discordantly superposing MHS. The relationship among these phases is unclear due to basaltic cover. Ferric oxides are found in association with PHS.

Figure 8

Outcrops of light-toned material underneath landslide deposit cover in "northern moat". A and B: Sulfate-free LTDs at elevations of 3100 and 3300 m below datum. C: Sulfate-bearing LTD at elevation -4600 m. Possible floor of "northern moat" prior to landslides. (CTX images P12_005676_1746, P03_002208_1748, P18_007891_1742; contours: HRSC).

Figure 9

A: Sulfate deposits in landslide superposed on now partly eroded LTD of Ophir Mensa (CTX P03_002208_1748; spectral indices as in fig. 1). B: Anaglyph from HRSC orbit 2083 visualizing the stratigraphy. C Interpretative cross-section of landslide based on HRSC DTM showing sulfates overlaying Ophir Mensa LTD.

Figure 10

A: HRSC nadir (orbit 334) and contours of the central valley of Ophir Chasma overlain with spectral indices as in fig. 1. B: HRSC color image with interpreted mineralogy. MHS: Monohydrated sulfates. Polyhydrated sulfates are found in north of central valley. They are overlain by monohydrated sulfates (kieserite), iron oxides accumulating in the southern part of the valley, and basaltic dunes.

1171 C: Interpretative longitudinal profile of central valley. Monohydrated sulfates superpose
1172 polyhydrated sulfates.

1173 D: Sulfates are revealed in HRSC color data by their distinct hue.

1174 E: Fluted surface texture of polyhydrated sulfates. (HiRISE PSP_007535_1755_RED)

1175 F: Ridged surface texture of kieserite-bearing valley floor, covered by basaltic dunes (SE of
1176 figure) and iron-oxide rich deposits (SW of figure; CTX P20_008972_1756).

1177 G: Example of curvilinear, sulfate-bearing ridges. Spectral indices from CRISM HRL0000B7D4
1178 as in fig. 1 on HiRISE PSP_009183_1750

1179

1180 Figure 11

1181 A: Spectral index BD2210 of two CRISM HRL observations overlain on CTX images of the
1182 northern central valley (CTX P05_003131_1747, P20_008972_1756), and exemplary spectra.
1183 Spectra resemble jarosite with additional phases mixed in (compare fig. 6).

1184 B and C: Outcrops of the 2.21 μm phase here are subcircular and almost indistinguishable in
1185 texture from the surrounding sulfate-rich rock

1186

1187 Figure 12

1188 Suggested succession of events in Ophir Chasma. 1: Opening of Valles Marineris. 2: Deposition
1189 of the LTDs such as Ophir Mensa, possibly as airfall deposits or ash. 3: Formation of kieserite in
1190 Ophir Mensa by intruding groundwater. 4: Excavation of the "mineral bowl", "central valley"
1191 and "northern moat". 5: Deposition and/or alteration to form polyhydrated sulfates and other
1192 phases in "mineral bowl", possibly by precipitation water. Deposition of PHS and MHS (6) in
1193 "central valley", possibly in lake or underneath a glacier. The relative timing of these events is

1194 not constrained and could coincide with deposition of layered deposits with similar mineralogy
1195 on the plateau above Valles Marineris. 7: Landslides enlarge the chasm and partly cover the
1196 floor.

1197

1198

1199 [Figures]

1200 [Figure 1]

[Figure 2]

[Figure 3]

[Figure 4]

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1211 [Figure 5]

[Figure 6]

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1217 [Figure 7]

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1220 [Figure 8]

[Figure 9]

[Figure 10]

[Figure 11]

[Figure 12]

Sulfates and Iron Oxides in Ophir Chasma based on OMEGA and CRISM Observations**by Wendt et al.****Research highlights:**

- Detection of jarosite and hydroxylated phases, kieserite, polyhydrated sulfates and hematite
- Interpretation of mineralogy together with digital elevation models and anaglyphs
- Discussion of formation theories
- comparison to light-toned deposits elsewhere on Mars