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Occurrences of possible hydrated sulfates in the southern high latitudes of Mars

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A B S T R A C T

Hydrated sulfate minerals record the history of water and habitable environments on Mars, yet prior studies of them have neglected a vast region surrounding the planet's south pole. Some of the few sulfates reported there are localized to putative ancient volcanoes that may have erupted under an ice sheet, possibly forming sulfates via hydrothermal alteration. Alternatively, sulfates may have formed more recently from sunlight causing minor melting of polar ices and the weathering of embedded dust particles, a process thought to explain the sulfates found near Mars' north pole. To test these hypotheses, we searched for southern high-latitude sulfates using the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on the Mars Reconnaissance Orbiter (MRO), focusing on regions that include putative volcanoes or geologically similar landforms. In 217 targeted images, we used spectral parameters to identify regions of interest from which we extracted spectra. The spectra were then visually compared to laboratory spectra to identify possible hydrated mineral constituents. In this paper, we present spectra from 16 of the images and statistics derived from the full set of 217, along with spectra from one mapping tile. We find that hydrated sulfates are found throughout the southern high latitudes suggesting a ubiquitous process for hydrated mineral formation and/or the relocation of hydrated minerals due to a long history of impacts, aeolian transport, weathering and periglacial processes.

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1. Introduction

Sulfates, and in particular the Ca-sulfate gypsum, are widespread on the Earth. They are often found in large marine sedimentary beds where they precipitated from saline waters. One of the most important reasons to study Mars is to find the missing links in Earth's history, where plate tectonics have left large gaps in the terrestrial geologic timeline. Mars experienced little or no plate tectonics, and so could have preserved a ''snapshot'' of sedimentary beds from the era when life was evolving on Earth. Sulfates occur in some of the most ancient sedimentary rocks studied on Mars, and act as a marker for a wide variety of aqueous processes.

On Mars, sulfate salts are found throughout the geologic record ([Ehlmann and Edwards, 2014](#page--1-0)), and are interpreted as indicating environments that were once aqueously active. They are hypothesized to reflect a transition from a wet, neutral-pH early Mars to a

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hyper-arid world where fluids are saline, acidic, and rare [\(Bibring](#page--1-0) [et al., 2006](#page--1-0)). Investigating the composition of the sulfates and their mineral assemblages in more detail will help to determine the types of aqueous environments that occurred on Mars and their potential habitability (pH, water activity, etc.). Their detailed characterization has been essential for choosing rover landing sites ([Wray, 2013](#page--1-0)), and will continue to drive site selection for future missions (e.g., [Mars Mid-Range Rover Science Analysis Group](#page--1-0) [\(MRR-SAG\), 2010](#page--1-0)).

A high sulfur content in martian soils was first measured by the Viking landers and attributed to widespread sulfate salts [\(Clark](#page--1-0) [et al., 1976\)](#page--1-0). Similar measurements were made at all subsequent landing sites, from the near-equatorial terrains explored by the Sojourner, Spirit and Opportunity rovers [\(Vaniman et al., 2004\)](#page--1-0) to the Phoenix landing site at 68° N latitude [\(Kounaves et al.,](#page--1-0) [2010](#page--1-0)). Direct evidence that this sulfur occurs in sulfates came first from minor abundances of these minerals found in martian meteorites (e.g., [Bridges et al., 2001\)](#page--1-0) and from Earth-based remote sensing ([Blaney and McCord, 1995; Pollack et al., 1990\)](#page--1-0). While correlated Mg and S abundances suggest that much of this soil sulfur occurs in Mg-sulfates (e.g., [Vaniman et al., 2004; Kounaves et al.,](#page--1-0)

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[2010\)](#page--1-0), localized soils rich in Fe- and Ca-sulfates have also been found, with spatial distributions reflecting both their original formation under high-temperature acidic conditions (hydrothermal or fumarolic alteration) and more recent dissolution and reprecipitation by minor snowmelt-derived fluids [\(Arvidson et al., 2010;](#page--1-0) [Yen et al., 2008\)](#page--1-0). Recent analyses of sand in Gale crater by the Curiosity rover suggest that multiple sulfate species are present there too, including minor anhydrite $(CaSO₄)$ definitively identified via X-ray diffraction ([Bish et al., 2013\)](#page--1-0) and other amorphous or minor crystalline species that may include Fe-sulfates and/or sulfate ions adsorbed onto mineral grains [\(McAdam et al., 2014](#page--1-0)). Orbital constraints on elemental chemistry imply that the majority of soil H2O may be stored in sulfate phases across vast swaths of the planet ([Karunatillake et al., 2013\)](#page--1-0).

In addition to soils, sedimentary rocks at equatorial and middle latitudes have now been found to contain sulfates, which—along with other aqueously altered minerals—have been detected on Mars by several orbiting spectrometers. The Thermal Emission Spectrometer (TES) on the Mars Global Surveyor mapped thermal emission spectra globally in 143 wavelengths from 6 to 50 μ m at pixel scales of ${\sim}3$ ${\times}$ 6 km ([Christensen et al., 2001\)](#page--1-0). Mineral maps derived from the linear deconvolution of TES data showed that sulfates were an allowable low-abundance component, although there was no definitive evidence for them on the surface ([Bandfield, 2002\)](#page--1-0). TES did find gray hematite associated with Hesperian-aged layered sedimentary deposits [\(Christensen et al., 2000,](#page--1-0) [2001\)](#page--1-0). With the arrival of the Mars Exploration Rover Opportunity, hematite was found to be associated with eroded sulfate- and silica-rich outcrops [\(McLennan et al., 2005; Squyres et al., 2004\)](#page--1-0), including a definitive identification of the acid Fe-sulfate jarosite ([Klingelhöfer et al., 2004](#page--1-0)). Gypsum veins have been found crosscutting older rocks at the Opportunity rover site, potentially resulting from upwelling groundwater at relatively low temperatures and/or post-impact hydrothermal fluid circulation [\(Arvidson](#page--1-0) [et al., 2014; Squyres et al., 2012\)](#page--1-0). Sedimentary rocks explored by Curiosity contain similar gypsum veins, as well as the less hydrous Ca-sulfates bassanite and anhydrite, as part of a lacustrine mudstone assemblage that experienced limited late diagenesis ([Vaniman et al., 2014](#page--1-0)).

THEMIS (Thermal Emission Imaging Spectrometer), a multispectral thermal infrared imager that detects the same vibrational absorptions as TES ([Christensen et al., 2004\)](#page--1-0), covers wavelengths from 6.8 to 14.9 μ m at 100 m/pixel. In terms of alteration minerals, THEMIS has detected chloride ([Osterloo et al., 2008\)](#page--1-0) and, using recently developed techniques, can map phyllosilicate detections by OMEGA (Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activite) or CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) into THEMIS data ([Viviano and Moersch, 2012\)](#page--1-0). Recent analyses of THEMIS data acquired under the most ideal conditions do reveal sulfates in the layered deposits of Columbus crater [\(Baldridge et al., 2013\)](#page--1-0).

It was when OMEGA began operation that widespread occurrences of sulfates and phyllosilicates were first detected definitively on the planet [\(Bibring et al., 2005](#page--1-0)). OMEGA, a spectrometer on Mars Express, measures the surface from \sim 0.3 to 5 μ m $-$ similar to the CRISM spectral range but extending to longer wavelengths. Analysis of OMEGA data motivated the hypothesis of a shift from a neutral and wet environment forming phyllosilicates to a dry and acidic one forming sulfates [\(Bibring et al., 2006\)](#page--1-0), with many of the sulfate-bearing outcrops occurring in a narrow equatorial zone and attributed to a common formation process during a specific period in martian history ([Bibring et al., 2007; Gendrin et al.,](#page--1-0) [2005\)](#page--1-0). Yet sulfates have now been found in rock units spanning a wider range of latitudes ([Wray et al., 2009, 2011a](#page--1-0)) and dating from the Early or Mid-Noachian [\(Wray et al., 2010\)](#page--1-0) through the Late Amazonian ([Mangold et al., 2010\)](#page--1-0), so they have likely formed throughout martian history via multiple processes in diverse settings.

Using the combination of OMEGA and CRISM, sulfates in Amazonian sand dunes around the north polar cap have been detected ([Langevin et al., 2005\)](#page--1-0) and investigated in detail [\(Calvin et al.,](#page--1-0) [2009\)](#page--1-0). The dunes within the Olympia Undae region are estimated to contain \sim 900 km³ volume of sediment [\(Lancaster and Greeley,](#page--1-0) [1990\)](#page--1-0). Since their discovery, the gypsum-rich materials of the northern high latitudes have seemed anomalous relative to other major aqueous deposits on Mars, due to their relatively late formation ages ([Murchie et al., 2009](#page--1-0)a) and concentration at the highest latitudes not covered in ice. The origin of the large gypsum (CaSO₄₋ 2H2O) concentrations (up to 40 wt.%; [Fishbaugh et al., 2007;](#page--1-0) [Horgan et al., 2009](#page--1-0)) in those dunes is not well understood, but may be related to gypsum that is actively being eroded from the Planum Boreum Cavi unit, the basal stratigraphic unit of the north polar layered deposits [\(Calvin et al., 2009; Horgan et al., 2009;](#page--1-0) [Massé et al., 2010, 2012\)](#page--1-0). Gypsum may have formed in those icerich layers when sunlight caused minor melting and weathering of embedded dust [\(Niles and Michalski, 2009](#page--1-0)). Alternatively, these sulfates might have formed via volcanic hydrothermal ([Settle,](#page--1-0) [1979; Tanaka, 2006](#page--1-0)) or acidic snow or fog alteration ([Langevin](#page--1-0) [et al., 2005](#page--1-0)). Because known volcanoes are distant from these regions, sulfates have also been hypothesized to have originated from subglacial melting and impact features where subglacial melting would have caused a concentration of sulfate deposition after discharge ([Fishbaugh et al., 2007; Langevin et al., 2005](#page--1-0)). The ultimate source(s) of sulfur remain poorly constrained, but may include volcanic exhalations and other atmospheric processes (e.g., [Smith et al., 2014\)](#page--1-0) and/or weathering of primary crustal sul-fides [\(Burns, 1987](#page--1-0)). The reason(s) for Ca-rich salts in the north polar region—in contrast to Mg/Fe-rich sulfates that likely predominate at lower latitudes ([Gendrin et al., 2005](#page--1-0))—are also poorly understood.

Similar to the north, non-ice hydration is detected from \sim 60 $^{\circ}$ latitude to the edge of the southern residual ice cap, with regional variations [\(Poulet et al., 2008\)](#page--1-0). In some cases the orbital spectra are consistent with sulfates specifically ([Michalski et al., 2010\)](#page--1-0), but no analog to the northern hemisphere's gypsum-rich dunes ([Fishbaugh et al., 2007; Horgan et al., 2009](#page--1-0)) has been reported. A few localized sulfate exposures in the southern high latitudes have been suggested to be concentrated on the mountains of the Sisyphi Montes region ([Wray et al., 2009](#page--1-0)), which have been interpreted as volcanoes that erupted under a Hesperian ice sheet [\(Ghatan and](#page--1-0) [Head, 2002a\)](#page--1-0). Alternatively, the icy weathering mechanism proposed for the north polar gypsum [\(Niles and Michalski, 2009](#page--1-0)) could have also occurred in the south polar layered deposits when the southern permanent cap was more extensive, producing a broad distribution of southern sulfates.

We have sought to find new examples of hydrated sulfates at high southern latitudes in order to test the volcanic vs. ice weathering hypotheses based on the mineralogy and spatial distribution of sulfates. Our study regions to date include the Sisyphi Montes and other mountainous areas near the Thyles Rupes, the Ulyxis Rupes, and the Chamberlin Crater ([Fig. 1](#page--1-0)).

After describing our spectral analysis techniques (Section [2\)](#page--1-0) and approach to classifying sulfates (Section [3\)](#page--1-0), we discuss the distribution of hydrated sulfates in the Sisyphi Montes region and corresponding morphology (Section [4\)](#page--1-0). In particular, we focus on the correlation between hydrated sulfates and putative volcanoes in this region. In Section [5](#page--1-0) we discuss three other sections of the southern high latitudes, relating the distribution of hydrated sulfates to putative volcanoes and to excavation in and around craters. Discussion of how the hydrated sulfates could have formed occupies Section [6](#page--1-0), and we conclude the paper with a summary of our results (Section [7](#page--1-0)).

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