

SULFATE-RICH DEPOSITS ON MARS: A REVIEW OF THEIR OCCURRENCES AND GEOCHEMICAL IMPLICATIONS. J. Flahaut¹, M. Massé², L. Le Deit³, P. Thollot⁴, J.-P. Bibring², F. Poulet², C. Quantin⁴, N. Mangold³, J. Michalski⁵ and J. L. Bishop⁶. ¹Faculty of Earth and Life Science, VU University Amsterdam, De Boelelaan 1085, 1081HV Amsterdam, The Netherlands (jessica.flahaut@ens-lyon.org). ²Institut d'Astrophysique Spatiale (IAS), CNRS/Université Paris Sud, 91405 Orsay Cedex, France (m.masse@ias.u-psud.fr). ³Laboratoire de Planétologie et Géodynamique de Nantes (LPGN), CNRS/Université Nantes, 44322 Nantes Cedex, France. ⁴Laboratoire de Géologie de Lyon (LGL-TPE), CNRS/Université Lyon 1, 69622 Villeurbanne Cedex, France. ⁵Earth Sciences Department, Natural History Museum, London SW7 5BD, UK. ⁶SETI Institute/NASA-ARC, Mountain View, CA, 94043.

Introduction: Remote sensing and *in situ* data from recent European and US Martian orbital and landed missions have provided extensive evidence for the former presence of water-lain sedimentary rocks on Mars [e.g.,1,2]. In addition, spectral-imager instruments have detected hydrated minerals such as sulfates on the Martian surface [3-6]. These water-rich outcrops are key to the evolution of the Martian surface and its past habitability; however, little is known about their origin. The present study presents a comprehensive review of the spatial distribution and geological context of sulfate detections on Mars.

Identification of sulfates in the VNIR (Visible Near InfraRed): The presence of sulfates was suspected from the Viking and the MER (Mars Exploration Rover) Opportunity *in situ* analyses of S-rich soils and rocks [7,8]. However, the first unambiguous detection of sulfates was made in 2004 by the imaging spectrometer OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité) onboard ESA's Mars Express orbiter. Sulfates are identified in the VNIR from their absorptions in the 1.3 to 2.5 μm wavelength range [3,4]. Although most of the fundamentals of the relevant vibrational absorption signatures lie outside this domain, their overtones and combinations are diagnostic and lead to precise mineralogical identifications through the accurate and combined determination of band position, shape, and depth. In this wavelength range, most hydrated minerals have absorption bands at 1.4 and 1.9 μm from the H₂O molecule vibrations, except for monohydrated sulfates which are characterized by the shift of the 1.9 μm absorption to 2.1 μm . S-O bonds also create absorption features in this range when associated with H₂O, which result in features at 2.2 and 2.4 μm for hydrated sulfates. The combination of all these absorptions generally allows for distinction between monohydrated and polyhydrated sulfates, and between different cationic compositions (Ca vs Mg vs Fe/Al).

Sulfates are particularly abundant in Valles Marineris, Margaritifer Terra, near the northern cap in the cricumpolar dune field, and in the Terra Meridiani plains [3-6,9]. They have also been detected as smaller outcrops in some intra-crater deposits [6,11] (e.g., in

Gale crater) or as plateau deposits [10,12] (e.g., in Mawrth Vallis) by the higher resolution CRISM (MRO) spectral imager. The presence of sulfates has also been detected by the *in situ* investigations of the MER rover Spirit in Gusev Crater [13] and recently by the Mars Science Laboratory rover in Gale Crater [14].

Sulfates in the equatorial region of Mars:

Valles Marineris and Margaritifer Terra sulfates: Both Mg-rich monohydrated (kieserite) and Mg/Fe-rich polyhydrated sulfates have been detected by OMEGA, in association with ferric oxide minerals, in the Valles Marineris and Margaritifer Terra areas [4,15,16]. These detections are usually associated with kilometer-thick remnants of layered deposits and are scattered in different canyons or chaos locations and stratigraphically distributed [16-22]. CRISM data have enabled high resolution analyses focused on some of the deposits and showed that the mineralogic assemblages present in these layered deposits are even more diverse with halloysite/kaolinite, Fe-smectite, Si-OH bearing phases and hydroxylated Fe-sulfates including jarosite and unidentified 2.2 μm -band bearing phases being locally detected [20-27].

Terra Meridiani sulfates: In Terra Meridiani, sulfates are found associated with the so-called etched units, which are composed of kilometer-thick light-toned deposits [9,28-30]. Both remote sensing and *in situ* analyses show that Fe-rich sulfates and gypsum are detected in the upper part of the etched terrains, in association with hematite and Fe+Al-rich phyllosilicates. Kieserite is detected at low elevation with the lowest part of the stratigraphic section dominated by Mg and/or Fe-rich polyhydrated sulfates.

Gale crater sulfates: Sulfates are detected within the 300 m thick lower formation of Gale crater's central mound whereas the upper formation, which is younger, is spectrally bland [11]. The lower formation is further divided into three members with distinct morphologic characteristics and mineralogies, similar to that observed at Terra Meridiani [30]: the lower member shows signatures of both polyhydrated sulfates and monohydrated sulfates, likely magnesian in composition. This lower member is overlain by fine layers of sulfates and phyllosilicates, most consistent with Fe-

smectites. The upper part of this middle member and the upper member show strong sulfate signatures, sometimes associated with hematite [11].

Terra Sirenum sulfates: Sulfates (gypsum, polyhydrated and monohydrated Mg/Fe-sulfates, jarosite, alunite) were detected together with Al- phyllosilicates (kaolinite, montmorillonite), Fe/Mg-phyllosilicates, and crystalline ferric oxide or hydroxide in the layered deposits of Columbus and Cross craters. Surrounding plains and adjacent craters in northwest Terra Sirenum contain more exposures of Al + Fe/Mg phyllosilicates associated to chlorides (plains) [31].

Sulfates in the north polar region of Mars: Calcium-rich sulfates, most likely gypsum were detected early in the OMEGA investigations around the northern polar cap, in the Amazonian-aged Olympia Undae dune field [5]. Further studies have shown that these detections extend to the whole circumpolar dune field and are associated to a dark, sandy material likely derived from part of the polar basal unit [32,33].

Associated detections, formation mechanisms and future work: The OMEGA discovery of discrete deposits of sulfate-bearing, layered rocks that are typically younger than, and sometimes overlying, clay-bearing crustal outcrops raises the question of the nature and evolution of past environments on Mars. A wealth of spectral data at higher spatial resolution from CRISM is now available to focus on specific deposits and show a wide assemblage of minerals detected together with sulfates. Although their distribution is less pervasive than phyllosilicates, they are observed in various contexts. The detection of jarosite was used early to advocate for the formation of Mars sulfates in highly acidic conditions ($\text{pH} < 3$, [34]), but these environments might have been spatially restricted. Indeed the recent multiple detections of intermingled clays and sulfates [e.g., 9,11,30] could indicate that most sulfates likely formed at more neutral pH, as smectite should be destroyed by complex chemical processes such as acidolysis at low pHs [35]. The recent detections of chlorides [36], which possess eutectic temperatures lower than sulfates, reinforce the hypothesis that brines existed at the surface of Mars and the dominance of sulfate over chlorine in the martian regolith suggests precipitation of salts at temperatures higher than the minimum [37].

Multiple working hypotheses for the origin of sulfates are being explored: 1) formation as evaporites in association with groundwater surge and/or transient surface waters [e.g.,3,16,28] 2) acidic weathering of ash and clastic sediments [38], 3) hydrothermalism [24] and/or alteration of sulfur-rich bedrock [39], 4)

aqueous cementation in a snowmelt area [40], 5) formation of sulfates through weathering of dust within massive, ancient ice deposits [32,41]. This last mechanism has been favored for the gypsum-rich deposits of the northern polar plains. In regions where various sulfates and high concentrations of iron oxides are associated, this mineralogical assemblage is similar to that observed by Opportunity at Meridiani Planum. *In situ* data provided a ground-truth that helped to develop some of these formation hypotheses [42]. Given the wide range of mineralogic assemblages observed it is likely that sulfate-rich deposits on Mars originate from different or multiple formation mechanisms, and likely imply different sources of sulfur.

References: [1] Malin, M. C., & Edgett, K. S. (2000), *Science*, 290, 1927-1937. [2] Carr, M. H., & Head III, J. W. (2010), *EPSL*, 294(3), 185-203. [3] Bibring J.-P. et al. (2006), *Science*, 312,400-404 [4] Gendrin A. et al. (2005), *Science*, 11, 1584-1586 [5] Langevin Y. et al. (2005), *Science*, 11, 1581-1584 [6] Murchie S.M. (2009), *JGR*, 114, E00D06 [7] Banin, A. et al. (1992), Physical and Chemical Weathering, Mars, U of Ariz. Press, 594-625 [8] P. R. Christensen et al. (2004), *Science*, 306(5702), 1733-1739 [9] Poulet F. et al. (2008), *Icarus*, 195 (1), 106-130 [10] Poulet F. et al. (2007), *JGR*, 112, E8 [11] Milliken R.E. et al. (2010), *GRL*, 37,4 [12] Loizeau D. et al. (2007), *JGR* 112. [13] P. R. Christensen et al. (2004), *Science* 305, 837 [14] Nachon M. et al. (2014) LPSC 45th, #1777 [15] Bibring J. P. & al. (2007), *Science*, 1206-1210 [16] Mangold N. et al. (2008), *JGR*, 113(E8) [17] Quantin C. et al. (2005), *LPSC 36th*, #1789 [18] Le Deit L. et al. (2010), *Icarus*, 208 [19] Bishop J. L. (2009), *JGR*, 114. [20] Flahaut J. et al. (2010), *JGR*, 115 [21] Massé M. et al. (2008), *JGR*, 113.E12 [22] Sowe M. et al. (2011), *Geol.Soc., London, Spec. Pub.*, 356(1), 281-300. [23] Roach L.H. et al. (2010), *Icarus*, 206, 253-268. [24] Thollot P. et al. (2012), *JGR*, 117(E11). [25] Wendt L. et al. (2011), *Icarus*, 213(1), 86-103. [26] Thollot P. et al., *this meeting* [27] Flahaut J. et al., *this meeting* [28] Arvidson R.E. et al. (2005), *Science*, 307, 1591-93. [29] Wiseman S. (2009), *JGR*, 115, E00D18. [30] Flahaut J. et al. (2014), *accepted to Icarus* [31] Wray J.J. et al. (2011), *JGR*, 116, E1 [32] Massé et al. (2010), *Icarus*, 209(2), 434-451 [33] Massé et al. (2012), *EPSL*, 317-318, 44-55. [34] Klingelhöfer, G. et al. (2004), *Science*, 306, 1740-1745 [35] Altheide T. S. et al. (2010), *Geochim. Cosmochim. Acta*, 74, 6232-6248 [36] Oosterloo M.M. et al. (2008), *Science*, 319, 1651-1654 [37] Brass G. W. (1980), *Icarus*, 42(1), 20-28 [38] McCollom, T.M. and B.M. Hynek (2005), *Nature*, 438, 1129-1131 [39] Dehouck E. et al. (2012), *Geochim. Cosmochim. Acta*, 90, 47-63 [40] Kite, E. S. et al. (2013), *Icarus*, 223(1), 181-210 [41] Niles, P. B., & Michalski, J. (2009), *Nature Geosc.*, 2(3), 215-220 [42] Poulet et al., *this meeting*.