

A New Hypothesis for the Origin and Redistribution of Sulfates in the Equatorial Region of Western Mars.

Chaojun Fan¹, Dirk Schulze-Makuch¹, Alberto G. Fairén², and John A. Wolff¹, ¹SEES at Washington State University, Pullman, WA 99163, USA (cfan1@wsu.edu, dirksm@wsu.edu, jawolff@mail.wsu.edu), ²Space Science and Astrobiology Division, Ames Research Center, Moffett Field, CA 94035, USA (afairen@arc.nasa.gov).

Introduction: The formation of sulfates on Mars has been under debate since they were identified in situ by landers and rovers, and by hyperspectral imaging starting from the 1970s. Here we propose that prior to uplift of the Tharsis rise, sulfates initially formed as sequences of evaporites [1, 2] from enclosed standing bodies of water in the Valles Marineris region. Phyllosilicate weathering of basaltic crust [3, 4] provided soluble cations such as K, Na, Ca, Mg [5], while S was released by volcanic degassing [6, 7] and oxidized in hydrous environments to SO_4^{2-} . Sulfate evaporites were then elevated and mobilized during and after uplift of the Tharsis rise. Beginning in the late Noachian or the early Hesperian [8], periodic outbursts of water transported sulfates together with fragments of basaltic rocks and pyroclastic materials to Meridiani Planum, where they were deposited as fluvial or alluvial sedimentary deposits [9, 10].

Origin of sulfates in the Tharsis area: Sulfate formation by evaporation of standing bodies of acidic and salty water is well-known from Earth [11], although other processes cannot be ruled out. Formation of sulfate evaporites in Valles Marineris followed phyllosilicate alteration of basaltic crust [3] before uplift of the Tharsis rise. Before the Tharsis rise, the area of Valles Marineris was located around the dichotomy boundary of Mars [12] with the lower depressions forming ideal sites for the accumulation of soluble elements leaching out from the phyllosilicate altered basaltic crust. The Tharsis uplift destroyed these depressions, but not before they had become filled with sulfate evaporites.

The basaltic rocks surrounding Valles Marineris were subjected to long-term intensive alteration by rock-water interactions and formed widely distributed phyllosilicates [3, 4]. Less soluble elements like iron, aluminium and silica in basalts remained to form phyllosilicates while soluble ions such as K^+ , Na^+ , Ca^{2+} and Mg^{2+} were leached out [5] and dissolved in fluids. Sulfur sources could be hydrothermal fluids which could release sulfur into the surface environment via hot springs [6] and syn-eruptive degassing of basaltic magma [7]. Martian basaltic magmas had oxygen fugacities similar to or lower than their modern counterparts on Earth that release sulfur dominantly as SO_2 , with lesser amounts of H_2S and S_2 . In the absence of a strongly oxidizing atmosphere such as on early Mars, SO_2 and more reduced sulfur species are nonetheless converted to SO_3 via photochemical reactions [13],

and SO_3 in turn converts to H_2SO_4 upon contact with water. Martian meteorites carry S isotopic evidence of such a photochemical oxidation sequence [14].

Evaporation oversaturated the salty water with solutes and led to the precipitation of sulfate salts, which is thought to be the most likely mechanism of the reported layered occurrences of kieserite, gypsum and other as yet unidentified polyhydrated sulfates [1]. An alternation of sulfate evaporites and the deposition of volcanic materials is supported by the systematic correlation of sulfate occurrences with Interior Layered Deposits (ILDs) in West Candor Chasma [1] and the interbedding of the darker layered units with light-toned deposits as recently observed on High Resolution Imaging Science Experiment images. Sulfates distributed in the chasmas of Valles Marineris and mainly located on the flanks of massive deposits and on several isolated ILDs [15] were exposed by later erosion.

Erosion and migration of sulfate evaporites: After the formation of sulfate evaporites, Tharsis started to rise. The uplift was probably the result of mantle processes [16] during the late Noachian and early Hesperian [8], and may have continued into the late Hesperian [17]. The light-tone layered sulfates are covered unconformably by dark-tone blocky layers, which are thought to be Hesperian-age lava flows based on Mars Orbiter Camera images. The uplift of Tharsis elevated the layered sulfate evaporites and triggered the formation of Valles Marineris [18]. Large amounts of water were sporadically discharged from the subsurface aquifer due to the change in the hydraulic head of groundwater [12] and released from the Martian interior due to contemporaneous volcanic activity [19]. Repeated catastrophic releases of groundwater were discharged towards the east along Valles Marineris because its elevation is generally several kilometers higher than the Chryse outflow region.

We propose that sulfate evaporites were eroded and carried away from Valles Marineris to Meridiani Planum and Chryse Planitia along with volcanic debris and fragments of basaltic crust by discharges of water, because sulfates are soft and easily re-dissolved. Exhumation of layered sulfates was accompanied with the formation of chasmas in Valles Marineris. The vertical distribution of sulfates in different chasmas supports the formation of sulfates before the coalescence of the Valles Marineris canyon. Sulfate layers more than 2.5 km thick [2] observed over a wide range

of elevations from -4 km in Ius Chasma to $+3$ km in Candor Chasma [1] could be explained by differential elevation and different cutting depths. Sedimentary deposition also likely happened in the remaining water bodies when the flooding was close to ceasing.

Deposition of sulfates in Meridiani Planum: Sulfate evaporites, together with basaltic debris and pyroclastics in Valles Marineris, were transported to Meridiani Planum and Chryse Planitia, and deposited as alluvial or fluvial sedimentary deposits when turbulent flow conditions became reduced. Sulfates in solution and perhaps in tiny granulates such as colloids were deposited as inter-granular cement in siliciclastic material. The environmental conditions in Meridiani Planum involved episodic inundation, evaporation and desiccation [9, 10, 19]. Each wash-out of sulfates and associated materials from Valles Marineris formed a cross-bedded layer of deposits around Meridiani Planum. The altitude of the cross-bedding indicates flow from west to east [20], consistent with the flooding from Valles Marineris into Meridiani Planum. The planar laminae are usually on a millimeter scale with single grain thicknesses ranging from 0.3 mm to 1 mm with a maximum stratigraphic thickness exposed at Eagle crater being about 30 to 50 cm [9].

The sediments in Meridiani Planum are composed of (by weight) $\sim 40\%$ sulfate minerals, $\sim 50\%$ siliciclastic fine-grains and $\sim 10\%$ hematite [9]. The outcrops of finely layered sandstone in the wall of Eagle crater contain nearly 40% by weight sulfate salts, including magnesium sulfate, calcium sulfate, and the iron sulfate jarosite [3]. Two types of lithic particles, subangular to irregular at 1.5 to 5.0 mm and rounded at 0.5 to 2.0 mm in diameter [20], are likely deposits from materials that were transported along Valles Marineris. They are thought to be basalt clasts exhibiting vesicles from two different types of sources of basalt [21].

Shallow standing bodies of water have been suggested [9] as a possible source of sulfate deposits and weathered siliciclastic components in Meridiani Planum. But sulfate formation by evaporation in shallow water bodies fails to explain 1) extensive sulfate distribution in the absence of a topographic basin [12], 2) mixture of sulfates and basaltic particles with sulfates as cement, 3) the wide extent of etched terrains in this region, 4) the observation that the most soluble salts (halides, Mg-sulfate) coexist with the least soluble salts (Ca-sulfate, jarosite) [22], and 5) the 1 km thickness of deposits in Meridiani Planum [23]. On the contrary, the transport of significant amounts of sulfates to the Meridiani region adequately explains 1) why sulfates are widely scattered in Meridiani, and the thickness of the deposits, because it is the natural eastern gravitational destination for materials derived from

the Tharis uplift; 2) why materials are mixed and cemented with sulfates, including the mixing of salts with very different solubilities (see Appendix), as a result of a spatially and temporally long transport process resulting in homogenization of materials previously differentiated; and 3) the presence of etched terrains as a consequence of differential deposition processes resulting in uneven topographies, not expected after prolonged sedimentation sequences. However, it is possible for shallow water bodies to be present during intervals of sporadic catastrophic flooding. Formation of thin liquid film evaporites in these water ponds is also possible.

Sulfates in both Valles Marineris and Meridiani Planum have been subjected to later (Amazonian) secondary alteration and aeolian relocation after the earlier (Noachian to Hesperian) processes of erosion and sedimentary deposition ceased.

Summary: Our hypothesis links together all forms of sulfates identified near the equator in the western Martian hemisphere based on the evolution of the Martian surface, distribution, textures and compositions of sulfates, and the geomorphology of sulfate occurrences. Sulfates were also identified by MER Spirit in Gusev crater [24], and by OMEGA/MEX in the dark dunes of the northern polar region of Mars [25]. These sulfates occur in subsurface regolith or sand dunes, and their setting may have involved analogous relocation processes to those of sulfates near the equator in the Martian Western hemisphere.

Appendix: The solubility of MgSO_4 is 2.8 mol/l, CaSO_4 0.015 mol/l, NaCl 6.1 mol/l, and jarosite 10^{-11} mol/l.

References: [1] Gendrin et al. (2005), *Science* 307,1587-1591. [2] Bibring et al. (2005), *Science* 307,1576-1581. [3] Bibring et al. (2006), *Science* 312, 400-404. [4] Poulet et al. (2005), *Nature* 438, 623-627. [5] Eggleton et al. (1987), *Clay & Clay Mineral* 35, 161-169. [6] Schoen and Rye (1970), *Science* 170, 1082-1084. [7] Thordarson and Self (1996), *J. Volcanol. Geotherm. Res.* 74, 49-73. [8] Robinson (1995), *Earth, Moon and Planets* 69, 249-269. [9] Squyres et al. (2004), *Science* 306, 1709-1714. [10] Squyres et al. (2004), *Science* 306, 1698-1703. [11] Tucker (2001), Sedimentary petrology. [12] Andrews-Hanna et al. (2007), *Nature* 446, 163-166. [13] Okabe (1978), Photochemistry of Small Molecules. [14] Farquhar et al. (2000), *Nature* 404, 50-52. [15] Quantin et al. (2006), MSRAFR, LPI. [16] Janle and Erkul (1991), *Earth, Moon and Planets* 53, 217-232. [17] Dohm et al. (2001), *J. Geophys. Res.* 106, 32943-32958. [18] Peulvast et al. (2001), *Geomorphology* 37, 329-352. [19] Fairén et al. (2003), *Icarus* 165, 53-67. [20] Klingelhöfer et al. (2004), *Science* 306, 1740-1745. [21] Soderblom et al. (2004), *Science* 306, 1723-1726. [22] Knauth et al. (2005), *Nature* 438, 1123-1128. [23] Christensen and Ruff (2004), *J. Geophys. Res.* 109, EO8003. [24] Squyres et al. (2004), *Science* 305, 794-799. [25] Langevin et al. (2005), *Science* 307, 1584-1586.