

SULFATES ON MARS: A PYROCLASTIC AIRFALL MODEL FOR ORIGIN, EMPLACEMENT, AND INITIAL ALTERATION OF VALLES MARINERIS INTERIOR LAYERED DEPOSITS (ILD). James W. Head¹ & Lionel Wilson^{1,2} ¹Dept. Earth, Environ. & Planet. Sci., Brown Univ., Providence RI 02912 USA. ²Lancaster Environ. Centre, Lancaster Univ., Lancaster LA1 4YQ UK. (James.Head@brown.edu) (l.wilson@lancaster.ac.uk)

Introduction: Sulfur is both ubiquitous and locally concentrated on the surface of Mars and the martian sulfur cycle [1] is of intense interest due to the information it provides about: 1) mantle composition, source regions and differentiation processes, 2) magmatic eruptive processes, environments of sulfur exsolution and retention in effusive and explosive eruptions, sulfur speciation during eruptions and interaction with the atmosphere and surface, 3) atmospheric evolution and effects and constraints on climate, 4) surface sedimentary deposition, aqueous and eolian transport, concentration and diagenesis, implications for climate evolution, 5) groundwater processes (solution, leaching from bedrock, transport, evaporative concentration and deposition, 6) post-depositional diagenesis and implications for the hydrological cycle, 7) host rock characteristics, sources, environments of emplacement, and 8) the role of sulfur in environmental conditions, liquid water acidity/alkalinity, and creation and maintenance of environments conducive or restrictive to formation and evolution of life.

The past several decades of Mars exploration have shown that sulfur-related surface deposits are concentrated in time and space on Mars. Pioneering orbital remote sensing data [2] demonstrated that a period favoring non-acidic aqueous alteration and formation of phyllosilicates was followed by an acidic aqueous alteration environment in the Late Noachian-Early Hesperian which resulted in the emplacement of sulfate deposits, and was coincident with a period of significant volcanism. This acidic aqueous alteration environment was followed by the “atmospheric aqueous-free alteration” period of anhydrous ferric oxide formation during the Amazonian [2]. Subsequent and complementary orbital remote sensing data [3] provided insight into the locations of the sulfate-rich environments and the stratigraphic relationships between phyllosilicates and sulfates. Sulfates were concentrated in several distinctive environments (e.g., Meridiani-type and Valles Marineris-type layered deposits, intracrater clay-sulfates, polar gypsum deposits) and were often interbedded with phyllosilicates (particularly in Valles-type interior layered deposits, ILDs [3-6]) showing that the change in surface environments from non-acidic to acidic [3] may have been transitional.

What are the necessary requirements for the formation, evolution and preservation of sulfates? These conditions are highly specific due to high sulfate solubility and the environmental sensitivity of sulfates to phase transitions (temperature and humidity) [1] and include: 1) sources of S, 2) sources of liquid water and climates conducive to the derivation (leaching) and/or transport of S, 3) acidic environments resulting from S concentration in aqueous

solutions, 4) sufficiently warm conditions to collect S-rich waters, and then to evaporate water and concentrate and deposit sulfates, 5) oscillating climate conditions to permit the interbedding of phyllosilicates and sulfates, 6) environments to explain their concentration in certain locations/settings, & 7) subsequent dry/cold climates necessary to preserve ancient sulfate deposits to the present.

Surface exploration of the *Meridiani-type layered deposits* by *Opportunity* showed that the Burns formation consisted of 18-25 wt% S, mixtures of Mg and Ca sulfates, and about 10% jarosite [7]. Together with sedimentary structures and stratigraphic relationships, these data were interpreted to indicate that it was emplaced in an eolian environment in which the sulfates formed in a groundwater upwelling low-pH aqueous evaporative environment, and underwent subsequent diagenesis. The process was envisioned to involve repeated upwellings of groundwater, periodically recharging local subaqueous depositional settings, and evaporating to concentrate the S and create the sulfate-rich deposits [7]. Pioneering theoretical and laboratory work [8-9] has shown that surface water and groundwater interactions with basalts can leach and concentrate S in solution, a primary prerequisite for further evaporative concentration and sulfate deposition. Modelling of the martian hydrological cycle [10] showed that an episodic evaporative environment at Meridiani could be formed by rainfall and infiltration in equatorial regions, lateral groundwater migration and leaching of sulfur during transport, and upwelling and evaporation at Meridiani, a general interpretation adopted to account for the *Opportunity* data [11].

Remote sensing characterization of the Valles Marineris ILDs [3-6] showed that: 1) sulfate deposits were distinctly layered, 2) monohydrated sulfates were overlain by polyhydrated sulfates, 3) phyllosilicate and sulfate layers were interbedded, and 4) ILDs occur in kms-thick deposits exposed in eroded plateaus on the floors of Valles Marineris. While the origin and age of the ILDs are controversial [12], the formation of the sulfates is generally attributed to the same groundwater upwelling and evaporative deposition model as invoked at Meridiani [10]. Sulfur was concentrated by groundwater leaching from basaltic rocks, and further concentrated and deposited in sulfates by evaporative processes [3, 10].

While the groundwater concentration and evaporation scenario successfully accounts for a large number of requirements imposed by observations, it may not account for all documented environments of sulfate emplacement and preservation [3] on Mars. It also requires stringent sulfur mass-balance relations [12] and long-duration global warm and wet environmental conditions at the

time of formation, conditions that have been difficult to reconcile with climate models [13]. We explore the role of magmatic processes [14] as an additional model for formation, evolution & preservation of sulfates on Mars.

Generation, Ascent & Eruption of Magma on Mars: As a basis for understanding the character and nature of volcanic eruptions in the martian environment (e.g., low gravity, currently low and historically evolving atmospheric pressure, presence of groundwater and ground ice) we have developed a theoretical and predictive framework for the generation, ascent and eruption of magma on Mars [14]. We have shown that basaltic plinian eruptions are highly favored (relative to Earth) [14-15] and explored the characteristics and dispersal of tephra [16] and gases from such eruptions in different locations and under different P_{atm} conditions, and how this might lead to the observed distribution of fine-grained deposits [16]. The potential behavior and fate of S species during volcanic eruptions has also been investigated [17], including the role of H_2SO_4 precipitates in surface melting & creation of aqueous acidic environments [18].

Discussion: On the basis of these considerations, we address the question: Can volcanic eruptions under martian conditions account for the characteristics of units in the Valles Marineris Interior Layered Deposits? Observations consistent with such an hypothesis include: 1) The Tharsis region is the most significant focus of volcanism on Mars, beginning in the Noachian and continuing through the Amazonian, with peak regional resurfacing in the Late Noachian-Early Hesperian [19]. 2) Explosive plinian basaltic volcanism is favored on Mars in general, and with increasing altitude (Tharsis) and decreasing P_{atm} . 3) Any interaction of rising magma and groundwater/ground ice can contribute to explosivity [14]. 4) The martian environment favors the production of finer ash relative to Earth ($\sim 22 \mu\text{m}$ geometric mean for Mars), enhancing dispersal. 5) The presence and dominance of fine ash creates a profusion of readily available nucleation sites for condensation of co-erupted H_2O and S species. 6) Airfall products are predicted to consist of tephra coated with condensed H_2O and S species, producing extensive layered and graded deposits, and possible lapilli beds [15]. 7) The distribution of eruptive products is predicted to be focused latitudinally (equatorial in the case of Tharsis sources), with decreasing grainsize as a function of distance from the vent [16]. 8) Rapid formation of aerosols is predicted to occur, with global warming due to erupted S species being very short-lived, and global cooling ensuing until ambient conditions return [17]. 9) On the basis of calculated tephra dispersal and cooling times, temperatures of deposited tephra will decrease with distance from the vent, with the majority of deposit temperatures being close to that of the ambient atmosphere. 10) Magmatic exsolution of sulfur is favored by lower P_{atm} and enhanced by higher altitude eruption sites (Tharsis). 11) Petrogenetic relations favor

the co-exsolution of H_2O and S species under these conditions. 12) Sulfur speciation and atmospheric chemistry predictions favor H_2SO_4 formation and widespread dispersal during and immediately following eruptions [18]. 13) Condensation and ensuing precipitation of H_2SO_4 is predicted to melt any existing surface snow and ice, and to provide acidic aqueous surface environments favoring sulfate precipitation [18]. 14) Estimates of eruption duration and continuity readily predict deposit accumulations in excess of hundreds of meters to kilometers. 15) Oscillation of eruption conditions and S speciation may lead to alternate water-rich and sulfur-rich depositional conditions and interbedding of phyllosilicates and sulfates.

Conclusions: The characteristics of martian volcanism in the Tharsis region appear to meet the necessary requirements for the formation, evolution and preservation of sulfates in the ILD, including: 1) sources of sulfur (*magmatic exsolution and precipitation*), 2) sources of liquid water (*co-precipitated and surface H_2O melted by H_2SO_4*) and climates conducive to the derivation and/or transport of sulfur (*operates in a cold and icy climate; concentration by groundwater leaching of basaltic bedrock is not required*), 3) acidic environments resulting from sulfur concentration in aqueous solutions (*provided by H_2SO_4 precipitation and melting*), 4) sufficiently warm conditions to collect S-rich waters (*ponding of acidic meltwater created by H_2SO_4 precipitation*), and then to evaporate water and concentrate and deposit sulfates (*dry evaporative environments following eruptive phases*), 5) oscillating climate conditions to permit the interbedding of phyllosilicates and sulfates (*oscillatory conditions very plausible in the transition to lower P_{atm}*), 6) environments to explain their concentration in certain locations and settings on Mars (*adjacent to long-lived Tharsis volcanic sources*), and 7) subsequent dry and cold climatic conditions necessary to preserve the ancient sulfate deposits to the present (*cold and icy conditions remain as P_{atm} evolves to present conditions*).

In order to test this hypothesis further, we are currently developing predictive eruption and tephra/volatile dispersal models that can serve as an interpretative framework to compare to the detailed characteristics and trends observed in the Valles Marineris ILDs [e.g. 3-6].

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