

Acid Sulfate Alteration on Mars

Ming, D. W. and Morris, R. V.

NASA Johnson Space Center, Houston, Texas, 77058, USA

A variety of mineralogical and geochemical indicators for aqueous alteration on Mars have been identified by a combination of surface and orbital robotic missions, telescopic observations, characterization of Martian meteorites, and laboratory and terrestrial analog studies. Acid sulfate alteration has been identified at all three landing sites visited by NASA rover missions (*Spirit*, *Opportunity*, and *Curiosity*). *Spirit* landed in Gusev crater in 2004 and discovered Fe-sulfates and materials that have been extensively leached by acid sulfate solutions [1]. *Opportunity* landing on the plains of Meridiani Planum also in 2004 where the rover encountered large abundances of jarosite and hematite in sedimentary rocks [2]. *Curiosity* landed in Gale crater in 2012 and has characterized fluvial, deltaic, and lacustrine sediments. Jarosite and hematite were discovered in some of the lacustrine sediments [3].

The high elemental abundance of sulfur in surface materials is obvious evidence that sulfate has played a major role in aqueous processes at all landing sites on Mars. The sulfate-rich outcrop at Meridiani Planum has an SO₃ content of up to 25 wt.% [4]. The interiors of rocks and outcrops on the Columbia Hills within Gusev crater have up to 8 wt.% SO₃ [5]. Soils at both sites generally have between 5 to 14 wt.% SO₃ [6], and several soils in Gusev crater contain around 30 wt.% SO₃ [7]. After normalization of major element compositions to a SO₃-free basis, the bulk compositions of these materials are basaltic, with a few exceptions in Gusev crater and in lacustrine mudstones in Gale crater. These observations suggest that materials encountered by the rovers were derived from basaltic precursors by acid sulfate alteration under nearly isochemical conditions (i.e., minimal leaching). There are several cases, however, where acid sulfate alteration minerals (jarosite and hematite) formed in open hydrologic systems, e.g., in Gale crater lacustrine mudstones [8]. Several hypotheses have been suggested for the aqueous formation of sulfate-bearing phases under acidic conditions on the surface of Mars including (1) sulfuric acid weathering of basaltic materials; (2) oxidative weathering of ultramafic igneous rocks containing sulfides; (3) acid fog weathering of basaltic materials, and (4) near-neutral pH subsurface solutions rich in Fe²⁺ that were rapidly oxidized to Fe³⁺, which produced excess acidity as iron was oxidized on exposure to O₂ or photo-oxidized by ultraviolet radiation at the martian surface [9,10]. Next, we briefly describe evidence for these hypothesis.

Sulfuric Acid Solutions from Volcanic Processes: The formation of jarosite in Meridiani Planum outcrops is strong evidence for the aqueous alteration of basaltic materials under acid sulfate conditions and may be analogous to the formation of jarosite in basaltic materials on Mauna Kea volcano in Hawaii under oxidizing, hydrothermal conditions [11]. The Mauna Kea sulfuric acid solutions are the result of interactions of SO₂-rich volcanic gases with water. Acid sulfate solutions percolated up through the basaltic tephra, dissolved Fe and other cations, and precipitated jarosite when environmental conditions permitted its formation. The pH of the system plays a major role in defining the stability field between jarosite and hematite (or goethite) formation. The composition of Meridiani sediments was basaltic on a SO₃- and Cl-free basis, suggesting that sulfuric (and possibly hydrochloric) solutions permeated the sediments with minimal leaching (i.e., closed hydrologic system). The sulfuric acid solutions in Meridiani were apparently not sufficiently “neutralized” by the basaltic sediments, and thus the pH was low enough to favor precipitation of jarosite. Similar trends were observed in Gusev crater and described in detail elsewhere [11].

Sulfuric Acid Solutions from Sulfides: Acid-sulfate weathering on Earth, in general, results from processes that release sulfuric acid into a soil or sediment. Nearly all of the occurrences of acid sulfate soils and sediments on Earth have resulted from the oxidative weathering of sulphidic materials and are often the culmination of complex biogeochemical processes. Burns [12] suggested that oxidative weathering of sulfides might be a significant process on the surface of Mars. In his model, iron-rich ultramafic igneous rocks containing pyrrhotite-pentlandite contacted aerated groundwater, generating strongly acidic, sulfate-rich solutions. In the oxidized section above the groundwater table, sulfates (e.g., jarosite) and hydrated ferric oxides are precipitated from solution by the oxidation of the sulfide and dissolution of Fe. The recent discovery of jarosite and hematite in a lacustrine mudstone in Gale crater suggests authigenic or diagenetic acid sulfate alteration; however, it is not clear if the acid sulfate environment resulted from oxidative, aqueous alteration of Fe-sulfides or via sulfuric acid fluids migrating through the sediments [3].

Acid fog on Rock/Soil Surfaces: Acid fog alteration on rock and soil surfaces has been suggested as an acid sulfate weathering process for surface materials [13,14,15,16]. The acid sulfate reactions are driven by acidic volatiles (e.g., SO₂, HCl) deposited from the atmosphere and then reacted with the mineral surfaces in the dry Mars environment. Laboratory simulated acid weathering of palagonitic tephra by Banin *et al.* [14] resulted in the formation of gypsum and alunogen; those authors hypothesized that the top layer of Mars “soil” may have formed by extremely slow ongoing weathering interactions at the atmosphere-rock interfaces. Golden *et al.* [15] subjected basaltic tephra materials to acid fog conditions in the laboratory and found that Al, Fe, and Ca sulfates and amorphous silica formed

from plagioclase-rich tephra, and Mg and Ca sulfates and amorphous silica formed from the olivine-rich sand. Hurowitz *et al.* [16] have presented evidence for very low pH (pH = 0 to 1) alteration at rock and outcrop surfaces in Gusev crater based upon laboratory experiments. They suggest that there is a leached layer where outcrops and rocks are depleted in Mg and Fe at their surfaces compared to their interiors, probably as a result of pyroxene and/or basaltic glass dissolution by acidic fluids (*e.g.*, sulfuric acid fog). Under this process, acidic vapors reacted only at the surfaces of rocks and outcrops, leaching some elements (*i.e.*, Fe and Mg) and resulting in the observed depletion trends of Mg and Fe from the rock's interior.

Rapid oxidization of Fe²⁺ to Fe³⁺: Hurowitz *et al.* [10] have hypothesized that jarosite and hematite in Meridiani Planum sedimentary rocks formed via a two stage process. First, water was brought to the surface by groundwater upwelling and may represent the last vestiges of the widespread occurrence of liquid water on Mars. The groundwater transported Fe²⁺ from basaltic dissolution to the surface where the Fe was rapidly acidified during oxidized on exposure to O₂ or photo-oxidized by ultraviolet radiation at the martian surface. Oxidized Fe under acidic conditions then reacted with SO₄²⁻ also brought to the surface by groundwater upwelling to produce jarosite and hematite in the Meridiani sediments.

Summary: Acid sulfate weathering was an important aqueous alteration environment on ancient Mars. Key indicator minerals such as jarosite and other Fe-sulfates provide evidence for these environments. The type of acid sulfate environment, *i.e.*, “sulfidization” vs. sulfuricization, is more problematic to identify because the mineralogical/geochemical properties of the “host” materials may be unknown (*e.g.*, presence of Fe-sulfides). However, Mars had extensive volcanism early in its history and almost certainly sulfuric acid fluids have interacted with basaltic materials.

References:

- [1] Morris, R. V. *et al.* 2016. Acid sulfate alteration in Gusev crater, Mars. *This conference*.
- [2] Klingelhöfer, G., *et al.* 2004. Jarosite and hematite at Meridiani Planum from the Mössbauer Spectrometer on the Opportunity Rover, *Sci.*, **306**, 1740-1745.
- [3] Rampe, E. B., *et al.* 2016. Diagenesis in the Murray Formation, Gale Crater, Mars. *LPSC, Abst. #2200*, The Woodlands, TX, March 21-25, LPI, Houston, TX.
- [4] Clark, B. C., *et al.* 2005. Chemistry and mineralogy of outcrops at Meridiani Planum. *Earth Planet. Sci. Lett.*, **240**, 73-94.
- [5] Ming, D. W., *et al.* 2006. Geochemical and mineralogical indicators for aqueous processes in the Columbia Hills of Gusev crater, Mars. *J. Geophys. Res.*, **111**, E02S12, doi:10.1029/2005JE002560.
- [6] Gellert, R., *et al.* 2006. Alpha Particle X-Ray Spectrometer (APXS): Results from Gusev crater and calibration report. *J. Geophys. Res.*, **111**, E02S05, doi:10.1029/2005JE002555.
- [7] Ming, D. W., *et al.* 2008. Geochemical Properties of Rocks and Soils in Gusev crater, Mars: Results of the Alpha-Particle X-ray Spectrometer from Cumberland Ridge to Home Plate. *J. Geophys. Res.*, **Vol. 113**, E12S39, doi:10.1029/2008JE003195, 28 pp.
- [8] Ming, D. W., *et al.* 2014. Authigenesis/diagenesis of the Murray formation mudstone in Gale crater, Mars. *53rd Meeting of the Clay Minerals Society*, June 6-8, Georgia Tech University, Atlanta, GA.
- [9] Ming, D. W., *et al.* 2008. Chapter 23: Aqueous alteration on Mars. In J. F. Bell, III (ed), *The Martian Surface: Composition, Mineralogy, and Physical Properties*, pp. 519-540, Cambridge University Press, Cambridge, UK.
- [10] Hurowitz J.A. *et al.* 2010. Origin of acidic surface waters and the evolution of atmospheric chemistry on early Mars. *Nat. Geo.*, **3**, 323-326.
- [11] Morris, R. V., *et al.* 2000. Mineralogy, composition, and alteration of Mars Pathfinder rocks and soils: Evidence from multispectral, elemental, and magnetic data on terrestrial analogue, SNC meteorite, and Pathfinder samples *J. Geophys. Res.*, **105**:1757-1817.
- [12] Burns, R.G. 1988. Gossans on Mars. *Proc. Lunar Planet. Sci.*, **XVIII**, pp. 713-721.
- [13] Clark, B.C. and Baird, A.K. (1979). Is the Martian Lithosphere Sulfur Rich? *J. Geophys. Res.* **84**, 8395-8402.
- [14] Banin, A., *et al.* 1997. Acidic volatiles and the Mars soil. *J. Geophys. Res.*, **102**, 13,341-13,156.
- [15] Golden, D. C., *et al.* 2005. Laboratory simulated acid-sulfate weathering of basaltic materials: Implications for formation of sulfates at Meridiani Planum and Gusev Crater, Mars. *J. Geophys. Res.*, **Vol. 110**, E12S07, doi:10.1029/2005JE002451, 15 pp.
- [16] Hurowitz, J. A., *et al.* 2006. In-situ and experimental evidence for acidic weathering of rocks and soils on Mars. *J. Geophys. Res.*, **111**, E02S19, doi:10.1029/2005JE002515, 16 pp.