Acid Sulfate Alteration in Gusev Crater, Mars

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The Mars Exploration Rover (MER) Spirit landed on the Gusev Crater plains west of the Columbia Hills in January, 2004, during the martian summer (sol 0; sol = 1 martian day = 24 hr 40 min). Spirit explored the Columbia Hills of Gusev Crater in the vicinity of Home Plate at the onset on its second winter (sol ~900) until the onset of its fourth winter (sol ~2170) At that time, Spirit became mired in a deposit of fine-grained and sulfate-rich soil with dust-covered solar panels and unfavorable pointing of the solar arrays toward the sun. Spirit has not communicated with the Earth since sol 2210 (January, 2011) [1]. Like its twin rover Opportunity, which landed on the opposite side of Mars at Meridiani Planum, Spirit has an Alpha Particle X-Ray Spectrometer (APXS) instrument for chemical analyses and a Mössbauer spectrometer (MB) for measurement of iron redox state, mineralogical speciation, and quantitative distribution among oxidation (Fe³⁺/ΣFe) and coordination (octahedral versus tetrahedral) states and mineralogical speciation (e.g., olivine, pyroxene, ilmenite, carbonate, and sulfate) [2].

The concentration of SO₃ in Gusev rocks and soils varies from ~1 to ~34 wt% (Fig. 1a) [3,4,5]. Because the APXS instrument does not detect low atomic number elements (e.g., H and C), major-element oxide concentrations are normalized to sum to 100 wt%, i.e., contributions of H₂O, CO₂, NO₂, etc. to the bulk composition care not considered. The majority of Gusev samples have ~ 6 ± 5 wt% SO₃, but there is a group of samples with high SO₃ concentrations (~30 wt%) and high total iron concentrations (~20 wt%). There is also a group with low total Fe and SO₃ concentrations that is also characterized by high SiO₂ concentrations (>70 wt%) (Fig. 1a). The trend labeled “Basaltic Soil” is interpreted as mixtures in variable proportions between unaltered igneous material and oxidized and SO₃-rich basaltic dust. The Mössbauer parameters are not definitive for mineralogical speciation (other than octahedrally-coordinated Fe³⁺ but are consistent with a schwertmannite-like phase (i.e., a nanophase ferric oxide).

The high oxidation state (Fig. 1b) and values of Mössbauer parameters (center shift and quadrupole splitting) for the high-SO₃ samples imply ferric sulfate (i.e., oxidized sulfur), although the hydration state cannot be constrained. In no case is there an excess of SO₃ over available cations (i.e., no evidence for elemental sulfur), and Fe sulfide (pyrite) has been detected in only one Gusev sample. The presence of both high-SiO₂ (and low total iron and SO₃) and high SO₃ (and high total iron as ferric sulfate) can be accommodated by a two-step geochemical model developed with the Geochemist’s Workbench. (1) Step 1 is anoxic acid sulfate leaching of martian basalt at high water-to-rock ratios (>70). The result is a high-SiO₂ residue (Fig 1a), and anoxic conditions are required to solubilize Fe as Fe²⁺. (2) Step 2 is the oxic precipitation of sulfate salts from the leachate. Oxic conditions are required to produce the high concentrations of ferric sulfate with minor Mg-sulfates and no detectable Fe²⁺-sulfates.