ACID-SULFATE ALTERATION AT GUSEV CRATER AND ACROSS MARS: HIGH-SIO₂ RESIDUES AND FERRIC SULFATE PRECIPITATES.

R.V. Morris[1], J.G. Catalano[2], G. Klingelhöfer[3], C. Schröder[4], R. Gellert[5], B.C. Clark[6], D.W. Ming[1], A.S. Yen[7], R.E. Arvidson[2], B.A. Cohen[8], I. Fleischer[3], T.J. McCoy[9], D.W. Mittlefehldt[1], and S.W. Squyres[10]. [1]NASA JSC (richard.v.morris@nasa.gov), [2]Washington U. St. Louis, [3]Johannes Gutenberg U., [4]U. Stirling, [5]U. Guelph, [6]SSI, [7]JPL/Caltech, [8]NASA MSFC, [9]Smithsonian Inst., [10]Cornell U.
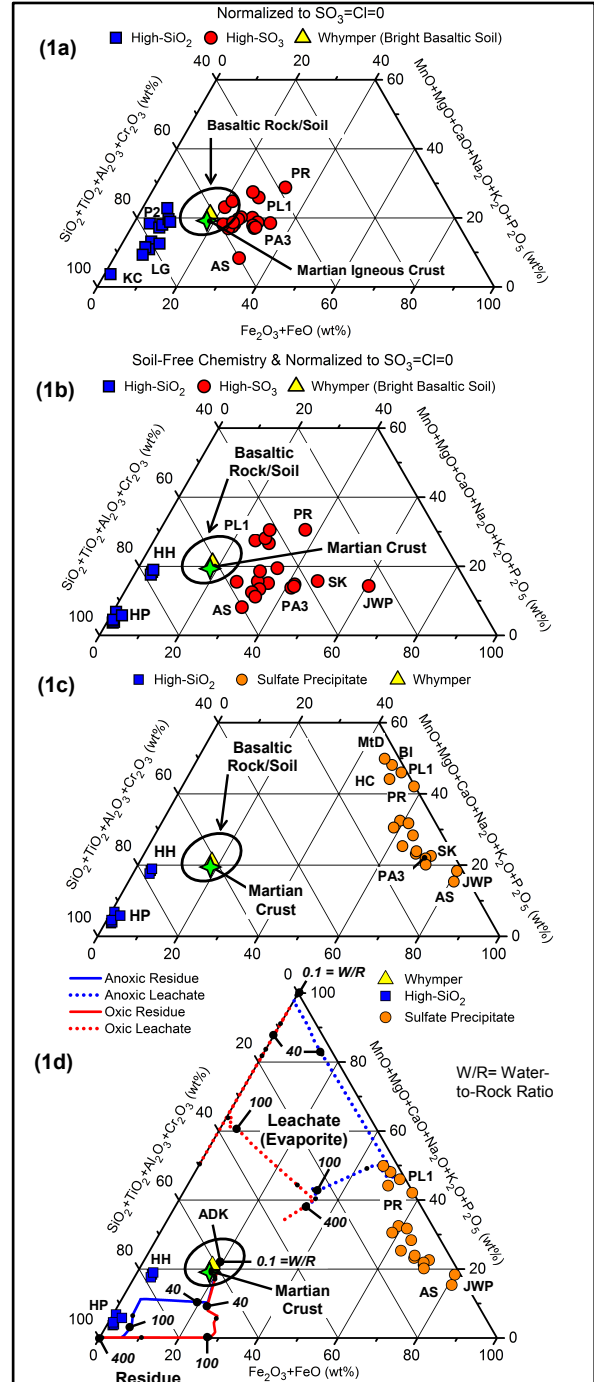
Introduction. The Mars Exploration Rover *Spirit* ended its mission in Gusev crater on sol 2210 after it had become stuck in a deposit of fined-grained and sulfate rich soil with dust covered solar panels unfavorably pointed toward the sun [1]. Final analysis of remaining data from *Spirit's* Mössbauer spectrometer (Fe redox and mineralogy) for sols 1529 through 2071 is now complete [2]. We focus here on chemical (APXS) and MB data for targets having high-SiO₂ or high-SO₃ and process link the targets through mixing and geochemical modelling to an acid-sulfate system centered at Home Plate, which is considered to be a hydrovolcanic complex [3,4].

Methods. Weighted least squares mixing calculations [5,6] on APXS chemistry were performed using 9 lithologic endmembers: KenoshaComets (KC) and Penn2* (P2; Ca-apatite-free Penn2) as high SiO₂ compositions; basaltic soil Whymper; anhydrous binary sulfates of Fe^{3+} (Fe^{2+} sulfate not detected by MB), Mg, Ca, and Al; Fe_2O_3; and Ca-apatite. Geochemical modelling of acid-sulfate weathering of Adirondack-composition basalt was done with Geochemist's Workbench (v. 9.0.9) [7]. Select fluid oxidation and evaporation calculations were performed using a Pitzer-style activity model. All calculations were done at 25°C because reliable thermodynamic data for requisite phases are available only at this temperature.

Mixing Model. The APXS compositions (normalized to SO₃=Cl=0 wt.%) of high-SiO₂ and high-SO₃ targets are plotted in Fig. 1a. Also plotted are compositions for average upper martian igneous crust [8], bright soil Whymper, and the region (ellipse) for Gusev crater basaltic rocks and soils. Virtually all analyses are "contaminated" by admixtures of basaltic soil, and this component was mathematically removed using the results of the chemical mixing model in Fig 1b. Note that the high-SiO₂ and high-SO₃ targets plot outside the ellipse and are thus not isochemical alteration products of basaltic progenitors and that the high-SiO₂ targets fall into a group spatially associated with Home Plate (HP) and a group having higher Al₂O₃ concentrations associated with Husband Hill (HH).
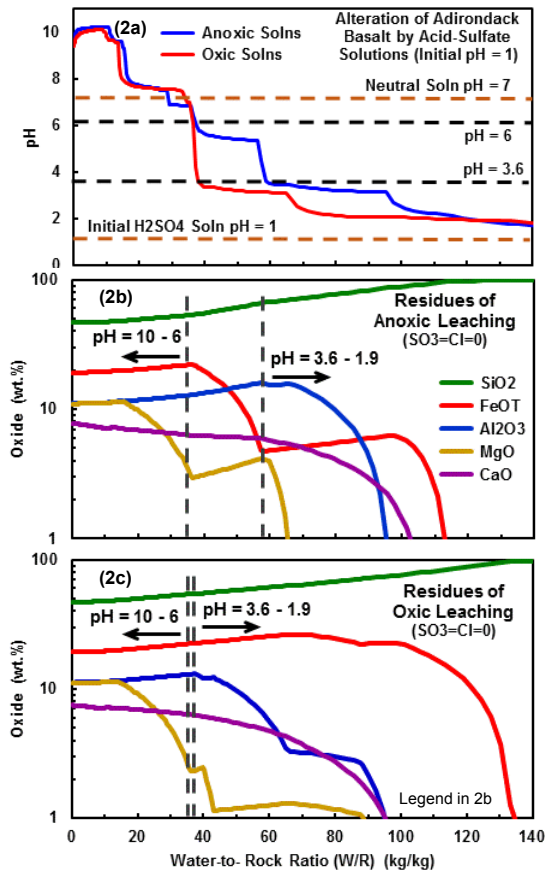
The chemical mixing model also shows that the high-SO₃ targets are chemical mixtures of mixed cation sulfates and a high-SiO₂ components (KC or P2*). In Fig. 1c, the high-SiO₂ component was mathematically removed from the soil-free high-SO₃ composition to give the Fe^{3+}-rich sulfate precipitates (>50 wt% Fe₂O₃).

Geochemical Models. The plots in Fig. 2 show model solution pH and residue oxide concentration as a function of water-to-rock ratio (W/R) for Adirondack composition basalt and for anoxic and oxic acid-sulfate solutions with

initial pH=1. At low W/R (<20) basalt dissolution controls pH, and leachate solutions are alkaline (>8). At high W/R (>100) the initial solution pH dominates, and leachate solutions remain strongly acidic (<2).
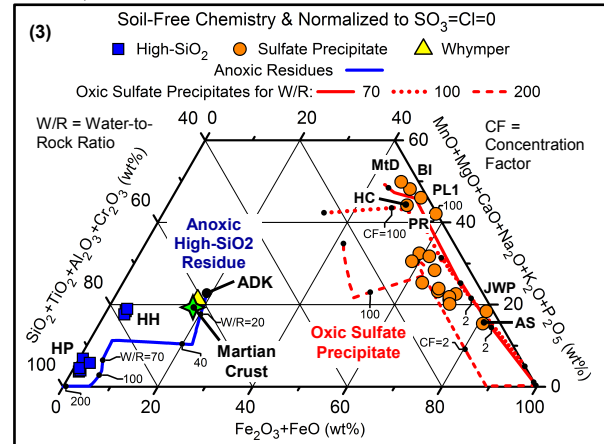
The residue chemical composition is strongly dependent on redox state because of differences in the solubility of Fe^{2+} and Fe^{3+} in sulfate solutions. For anoxic leaching (Fe^{2+}), the residue compositions has $SiO_2 > Al_2O_3 > Fe_2O_3$ only for the interval defined by $3.6<pH<5.0$ and $30<W/R<90$ (Fig. 2b). For oxic leaching, $SiO_2 > Fe_2O_3 > Al_2O_3$ for all pH and W/R (Fig. 2c). Comparison with Fig. 1c shows that the compositions for both HP and HH compositions are accommodated by the anoxic leaching model with physical separation of residue and leachate solutions. However, precipitated leachate solutions (by evaporation or freezing) are not compatible with this simple model (Fig. 2c).

The observed precipitate compositions are modelled (Fig. 3) by incomplete precipitation (concentration factor CF ~2 to ~200) of solutions with initial chemical compositions equivalent to the anoxic leachates for W/R = 70, 100, and 200 (Fig. 2b) but are now oxic (i.e., all Fe as Fe^{3+}) after physical separation from their corresponding residues. The red lines (Fig. 3) denote precipitate compositions as a function of CF for these three oxic solutions, and the mixed-cation sulfate precipitates are Fe^{3+}-rich ($Fe_2O_3 >50$ wt.%). Movement of Fe^{3+}-depleted residual solutions to different locations and subsequent precipitation there produces sulfate precipitates and residual solutions whose compositions depend on CF and prevailing environmental conditions. Precipitation will continue

(with or without movement of residual solutions) until no fluid remains.

To explain the SiO_2 component (chemically equivalent to HP or HH high-SiO_2 targets) of the soil-free compositions of high-SO_3 targets (Fig. 1b), the onset of oxic sulfate precipitation took place as solutions moved through pre-existing (and chemically inert) high-SiO_2 material. That is, the compositions of the high-SO_3 targets are on mixing lines between the precipitate and HP or HH compositions (compare Figs 1b and 1c).

Acid Sulfate Alteration Across Mars. Geochemical calculations reported here and by [9] provide a model basis that martian aqueous alteration by acid-sulfate process was widespread in space and time. The alteration assemblage at Gusev is consistent with this view and so are many rover- and orbital-based observations across Mars. The high-SO_3 outcrop at Meridiani Planum has precipitated jarosite and a SiO_2 component [10,11], and HH-like high-SiO_2 material has also been reported [12]. Jarosite and high-SiO_2 deposits are detected at Gale crater [13,14] and Valles Marineris [15]. Orbital detections of high-SiO_2 deposits with and without sulfates or clay minerals are summarized by [16]. Circum-neutral to alkaline pH, conducive to clay mineral precipitation, is consistent with Noachian acid-sulfate processes both theoretically (Fig. 2a and [9]) and experimentally [17].

References: [1] Arvidson *et al.* (2010) *JGR 115*, E00F03. [2] Morris *et al.* (2017) to be submitted. [3] Yen *et al.* (2008) *JGR 113*, E06S10. [4] Squyres *et al.* (2008) *Science 320*, 1063. [5] Korotev (1981) *PLPSC12*, 557. [6] Korotev *et al.* (1995) *JGR 100*, 144,403. [7] Bethke (2007). [8] McLennan (2012) *Sed. Geol Mars*, 102, 119. [9] Zolotov and Mironenko (2016) *Icarus 275*, 203. [10] Morris *et al.* (2008) *JGR 111*, E12S15. [11] Clark *et al.* (2006) *EPSL 240*, 73. [12] Clark *et al.* (2016) *AmMin 101*, 1515. [13] Rampe *et al.*, (2017) in revision *EPSL*. [14] Frydenvang *et al.* (2016) *LPSC47*, #2349. [15] Milliken *et al.* (2008) *Geology 36*, 847. [16] Ehlmann and Edwards (2014) *AnRevEPS 42*, 291. [17] Peretyashko *et al.* (2017) *This Volume*, 2017.