PHOSPHORUS GEOCHEMISTRY OF MARTIAN ROCKS AND SOILS: EVIDENCE FOR ACIDIC WEATHERING AT GUSEV AND MERIDIANI. J. P. Greenwood[1] and R. E. Blake[2], [1]Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459 (jgreenwood@wesleyan.edu), [2]Dept. of Geology & Geophysics, Yale University, New Haven, CT 06520.

Introduction: Phosphorus appears to be strongly correlated with sulfur in Martian soils, and also in sulfur-rich rocks (e.g. Meridiani outcrops; Paso Robles, Gusev) (Fig. 1: [1-3]). Phosphorus is also positively correlated with chlorine and nano-phase oxide abundances in Martian soils (Fig. 2: [4,5]). We show that this is strong evidence for acidic weathering processes on ancient Mars.

Origin of S, Cl, and P correlations: The high sulfur contents of Martian soils have been previously ascribed to volcanic degassing [6], hydrothermal alteration by volcanic acid-sulfate fluids [7], and aqueous oxidation of sulfides [8]. High chlorine has been suggested to arise from either volcanic degassing [6] or alteration by neutral-chloride fluids [7]. It has recently been shown that mass-independent sulfur isotope signatures in SNC's are indicative of atmospherically-processed sulfur, such as volcanogenic SO_2 [9], which delineates an unambiguous contribution of atmospheric sulfur to the Martian surface. In light of evidence from SNC's, an origin of Martian surface sulfur via volcanic degassing of SO_2 seems likely. This rules out models that explain high sulfur abundances in Martian soils as being due to volcanic fluids [7] or weathering of sulfides [8,10].

Phosphorus is not predicted to form volumetrically significant gaseous species during magmatic degassing under reasonable estimates of fO_2 for SNC or terrestrial magmas [11]. An origin of high phosphorus in Martian soils as a result of volcanic degassing is untenable. Phosphorus additions to the Martian salt component must ultimately be as a result of weathering of igneous rock phosphate minerals, such as merrillite and chlor-apatite. Dreibus et al. [12] have shown that SNC phosphates are easily dissolved in acidic fluids, and even circum-neutral fluids can extract phosphates readily from SNC meteorites [13].

Rieder et al. [2] have favored weathering of rocky material by acidic fluids to form acidic brines, including the dissolution of phosphate minerals, at Meridiani. This is a reasonable explanation for the Meridiani outcrops. This explanation does not explain high and constant P/S of Martian soils, or high P/S in rocks at Gusev.

Phosphorus aqueous geochemistry:

Solubility and Dissolution rates. Phosphate minerals are generally highly insoluble under neutral to basic pH fluids. Calcium-phosphate minerals display log-linear increases in solubility with decreasing pH at pH < 7 [9]. Apatite dissolution rates follow a similar relationship with pH; dissolution rates increase logarithmically with pH < 6, but change little in the circum-neutral to basic range [9]. Experimental apatite dissolution rates at low pH can be orders of magnitude faster than dissolution rates of silicates under similar conditions, and are very similar to dissolution rates of magnesite ($MgCO_3$). This suggests that the low amounts of carbonate on the Martian surface, if due to acidic weathering, should correlate with low abundances of Ca-phosphate minerals.

Sorption. The correlation of phosphorus and nano-phase oxide in Martian soils is suggestive of adsorbed phosphate. The similar correlation of chlorine with nano-phase oxide argues against adsorption, as chlorine should not adsorb strongly to iron oxides, due to its forming outer-sphere complexes on iron 'oxide' surfaces, rather than the much more strongly bonded inner-sphere complexes formed by phosphate and possibly sulfate. If phosphate is not concentrated on nano-phase oxides in Martian soils due to adsorption, then the P/S ratios of Martian soils are likely indicative of these ratios in Martian fluids [9].

P in Martian soils: The high phosphorus contents of Martian soils, and its correlation with sulfur and chlorine, rather than the rock-forming elements [1,2], is strong evidence that phosphorus behaved as a soluble element in Martian fluids. If P/S ratios of Martian soils are indicative of these ratios in Martian fluids, these aqueous fluids must have been acidic. The soils at Gusev and Meridiani both display this behavior, thus, a global phenomenom of weathering of Ca-phosphate minerals from igneous rocks must have occurred, or be occurring. The BIG question is: Did the weathering of phosphate minerals occur long, long ago, when Mars was warm and wet, or is it a process that has been slowly building up P contents of Martian soils for the last 2-4 Ga? Two possible mechanisms present themselves: 1) An acidic hydrosphere was active on ancient Mars, which led to large-scale weathering processes, and the addition of phosphate to Martian fluids occurred readily over much of the planet. 2) The formation of Martian bright soils (which are enriched in the nano-phase

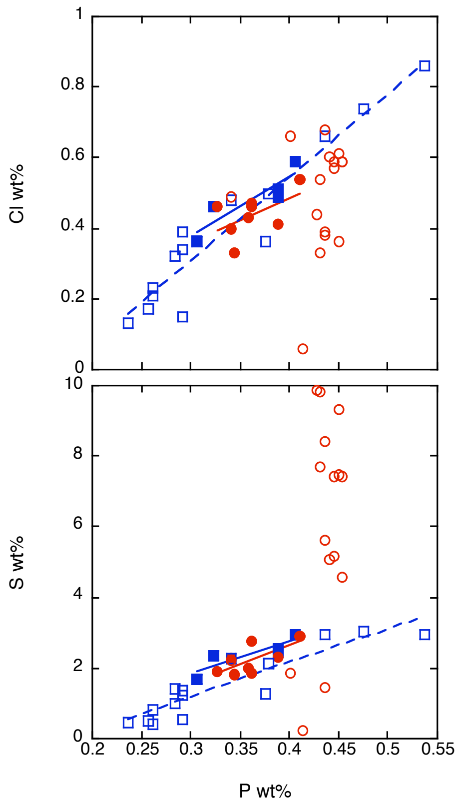

Figure 1. Chlorine (upper panel) and sulfur (lower panel) vs. phosphorus in Martian soils (closed symbols) and rocks (open symbols) at Gusev Crater (blue) and Meridiani Planum (red). Linear regressions are shown for Gusev soil (solid blue; Cl vs. P: R=0.90; S vs. P: R=0.87), Gusev rocks (dashed blue; Cl vs. P: R=0.95; S vs. P: R=0.91) and Meridiani soils (solid red; Cl vs. P: R=0.53; S vs. P: R=0.69). All values shown in weight percent.

oxide-, sulfur-, chlorine-, phosphorus-rich component) has been a slow, but highly acidic process, which has led to the preferential leaching of phosphates (relative to other minerals) and their enrichment in the bright soil component. Clearly, both are reasonable hypotheses. Model 1) is favored though, because of two facts: High P/S is not just a characteristic of Martian soils, but ALSO of putatively ancient sulfate-rich rocks at Meridiani, AS WELL AS sulfur-rich rocks in the Columbia Hills (Paso Robles being the most obvious example). Thus, while option 2) above cannot be ruled out, and may indeed play a role, an acidic hydrosphere, capable of mobilizing Ca-phosphate minerals out of igneous rocks and into sulfur-rich rocks (or more likely the fluids that precipitated rocks such as Paso Robles) must have occurred on ancient Mars.

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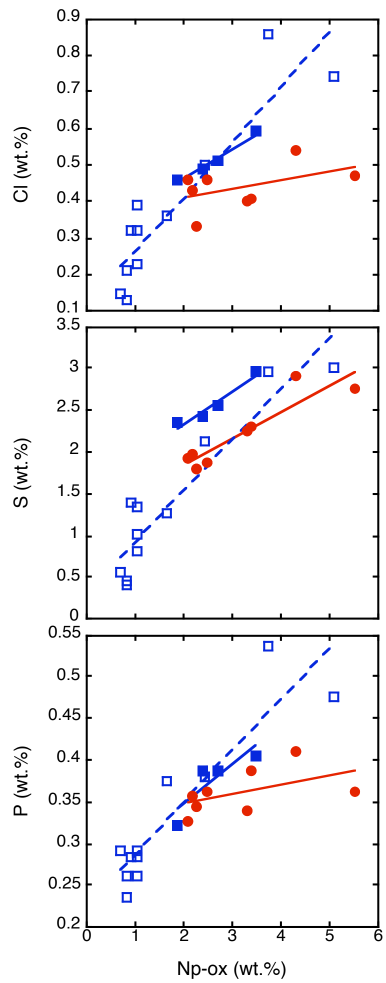

Figure 2. Chlorine (top panel), sulfur (middle panel), and phosphorus (bottom panel) vs. nano-phase iron oxide (Np-ox). Same symbols as Fig. 1.