

Evidence for an acidic ocean on Mars from phosphorus geochemistry of Martian soils and rocks

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ABSTRACT

Recent analyses of elemental concentrations and mineralogy of iron-bearing compounds of Martian soils and rocks by the Mars Exploration Rovers at Meridiani Planum and Gusev Crater demonstrate that phosphorus concentration is correlated with sulfur and chlorine. The positive correlation of these three elements with each other in soils at both sites argues for a globally homogeneous soil component. Sulfur, and possibly chlorine, in Martian soils and Meridiani Planum outcrop rocks is likely derived from volcanic exhalations, but phosphorus must be derived from the weathering of igneous rocks. Here we show that the similar concentration of phosphorus in soils at the two Mars Exploration Rover sites, coupled with positive correlations to chlorine and sulfur, is best explained as resulting from mixing and homogenization of phosphate, sulfate, and chloride in a large acidic aqueous reservoir, such as an acidic ocean. Acidic thin-film or acid-fog weathering cannot readily produce the similar P/S and P/Cl ratios of soils measured on Mars, and more important, cannot explain the high phosphorus content of ancient (ca. 3–4 Ga) sulfate-rich rocks in outcrop at Meridiani. The existence of a global acidic hydrosphere or ocean at some time in early Martian history can also explain the lack of extensive carbonate deposits on the Martian surface.

Keywords: Mars, Martian soil, acid weathering.

INTRODUCTION

The origin of the Martian soils has been debated since the first measurements by the Viking landers in 1976 found them to be rich in sulfur and chlorine (Clark et al., 1976). Basalt-water-type interactions (Singer, 1982; Wyatt and McSween, 2002), acidic groundwaters (Burns, 1987; Benison and LaClair, 2003), and acid-fog alteration (Settle, 1979; Banin et al., 1997) are the leading hypotheses that have emerged to explain these observations. The close spectral match between weathered basalt and Martian surface materials has led to the suggestion of hydrothermal (Wyatt and McSween, 2002) or hydrolytic (Singer, 1982) alteration of basalt on Mars. An alternative model to explain the origin of Martian soils is that volcanic gases rich in SO₂ and Cl formed H₂SO₄ and HCl on basaltic rock and mineral surfaces, and altered the Martian igneous bedrock and ultimately led to the formation of the Martian soils (Banin et al., 1997). Based on Mars Exploration Rover (MER) observations at the Gusev Crater landing site, Yen et al. (2005) proposed a new variation of the acid-fog weathering model, in which diurnal or seasonal thermal variations lead to the formation of thin films of acidic fluid on rock and mineral surfaces, which they invoked to explain heterogeneities in soil Br abundances.

Hurowitz et al. (2006) suggested that acid-fog or acid thin-film weathering resulted in leached alteration zones several millimeters thick on float rocks in the Columbia Hills, Gusev Crater, which led to phosphate mineral dissolution in this alteration layer and ultimately contributed to the formation of the global soils. Acidic waters have been implicated in the formation of the Meridiani sulfate-rich outcrop rocks, due to the identification of jarosite (Klingelhöfer et al., 2004). The first high-precision measurements of phosphorus on the Martian surface (Rieder et al., 2004; Gellert et al., 2006) allow us to reassess these alternative models for the formation of Martian soils.

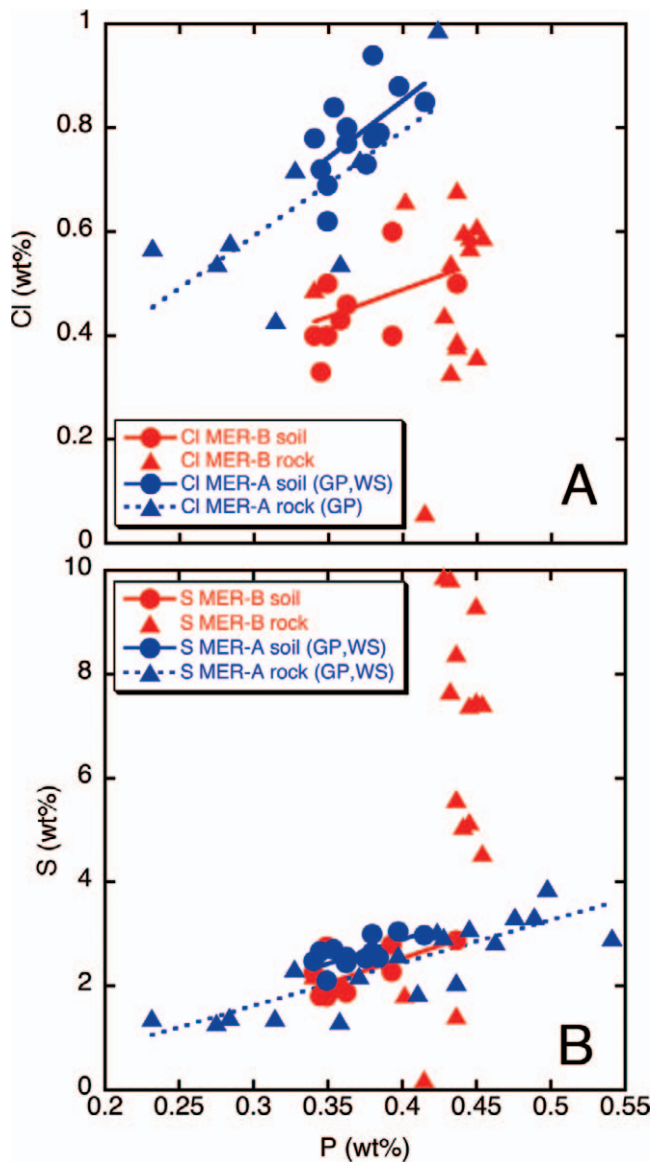
All the major rock-forming elements measured in the soils on Mars show a negative correlation with sulfur and chlorine at both MER sites, with the notable exception of phosphorus (Rieder et al., 2004; Gellert et al., 2006). A positive correlation of phosphorus with sulfur and chlorine in soils at the two MER sites (Fig. 1) has led to the suggestion that phosphorus was an aqueous species, rather than a rock component, where phosphorus was derived by the local weathering of rocky material by acidic brines (Rieder et al., 2004). This is unlike most waters on Earth, where dissolved phosphorus concentrations are gen-

erally low, due to the important role of the biosphere in the uptake of dissolved phosphate in global phosphorus geochemistry (Compton et al., 2000). Mössbauer determination of the nano-phase ferric oxide (Np-ox) component of Martian soils, believed to be a weathering product of mafic silicate minerals (Morris et al., 2004; Klingelhöfer et al., 2004), shows a highly significant correlation with sulfur (Fig. 2). The similar systematics of phosphorus, sulfur, chlorine, and possibly Np-ox suggests that this component of the Martian soil is present at both Gusev Crater and Meridiani Planum, which are thousands of kilometers from each other, and argues for a globally homogeneous soil component. A globally homogeneous soil component was argued for from the similar S/Cl of soils measured at the two Viking landing sites, Mars Pathfinder landing site, and the two Mars Exploration Rover sites (Clark et al., 1976; Wänke et al., 2001; Rieder et al., 2004; Gellert et al., 2006). Pancam spectra show that the high-sulfur, high Np-ox-bearing soils at the two MER sites are similar to bright dust measured at Mars Pathfinder and by telescopic observations at the same wavelengths (Yen et al., 2005). Dark soils are low-sulfur end members, which contain significant amounts of basaltic materials, and are also present at both MER landing sites (Yen et al., 2005). Most soil analyses at the two MER sites plot on a mixing line between high-sulfur and low-sulfur end members, consistent with a contribution from the ubiquitous sulfur-rich bright dust to the majority of soil alpha particle X-ray spectrometer analyses (Yen et al., 2005). We are concerned here with the origin of the sulfur-rich, chlorine-rich, phosphorus-rich, Np-ox-rich soils, which are a significant component of the bright dust and bright undisturbed soils on the Martian surface.

ORIGIN OF HIGH SULFUR, CHLORINE, AND PHOSPHORUS IN MARTIAN SOILS

The origin of the high sulfur concentrations in Martian soils is likely volcanic SO₂ rather than oxidative weathering of sulfide minerals (Burns, 1987), based on the presence of mass-independent sulfur isotope signatures in sulfate and sulfide phases in young Martian me-

Figure 1. Chlorine vs. phosphorus (wt%) and sulfur vs. phosphorus (wt%) in Martian soils (circles) and rocks (triangles) at Meridiani Planum (red) and Gusev Crater (blue). A: Cl vs. P: linear regressions are shown for undisturbed Gusev soils from Gusev Plains (GP) and West Spur, Columbia Hills (WS) (solid blue: $y = -0.03 + 2.21x$, $R = 0.58$, $N = 13$), Gusev Plains rocks (dashed blue: $y = -0.01 + 2.01x$, $R = 0.70$, $N = 8$) and Meridiani soils (solid red: $y = 0.07 + 1.04x$, $R = 0.41$, $N = 12$). Chlorine and phosphorus are not significantly correlated in Meridiani soils. B: S vs. P: linear regressions are shown for undisturbed Gusev soils (GP and WS) (solid blue: $y = -0.81 + 9.27x$, $R = 0.69$, $N = 13$), Gusev rocks (GP and WS) (dashed blue: $y = -0.84 + 8.21x$, $R = 0.84$, $N = 19$), and Meridiani soils (solid red: $y = -1.31 + 9.62x$, $R = 0.67$, $N = 12$). Undisturbed GP and WS rock analyses are included because high sulfur and chlorine contents are likely due to air-fall bright dust. High phosphorus contents of Husband Hills rocks have likely contributed to local soils and are not representative of global soils, and are not included in this regression. Chlorine and phosphorus show negative correlation in WS rocks and are not included. Rocks at Meridiani have probably undergone multiple aqueous processes, which have led to differences from global soils. See text for data sources. MER—Mars Exploration Rover.



teorites (Farquhar et al., 2000) (shergottites and nakhlites) and sulfide phases in an ancient Martian meteorite, ALH84001 (Greenwood et al., 2000). Mass-independent sulfur isotope effects are believed to result from reactions of sulfur-bearing gases with ultraviolet light in planetary atmospheres (Thiemens, 1999). The high sulfur concentration of Martian soils, as well as high S/Cl (relative to chondritic meteorites or the Earth's oceans), is likely derived by volcanic degassing. The high chlorine may be due to high Cl in volcanic gases, but Cl/Br ratios of some Martian soils are near chondritic (Rieder et al., 2004), allowing the possibility for a contribution from original chondritic salts from a late chondritic veneer.

Phosphorus is unlikely to have been an important volatile element on Mars, as it forms calcium phosphate minerals in both terrestrial

and Martian basalts, and is not considered to have been an important volatile species on the Earth (Holland, 1984). Fugacities of plausible phosphorus containing gas species are very low, even under reducing conditions (Holland, 1984). Concentrations of oxidized phosphorus gas species at active volcanoes are also predicted to be very low (Mambo et al., 1991). The ultimate source of phosphate in Martian fluids is likely from the weathering of calcium-phosphate minerals in igneous rocks. A similar analogy has been made for the early prebiotic Earth (Holland, 1984), and preindustrial inputs of phosphorus to the Earth's oceans are also likely dominated by weathering of phosphate minerals on the continents (Holland, 1984). Rieder et al. (2004) ascribed high phosphorus in Meridiani outcrop rocks to alteration of local igneous rocks by acidic

brines; they did not speculate on the origin of the high phosphorus concentrations in Martian soils. It is believed that phosphorus has an approximate tenfold enrichment in the Martian mantle over the Earth's mantle (Wänke and Dreibus, 1988). Thus, phosphorus concentrations in Martian soils are not extraordinarily high. The geochemical behavior of phosphorus, which appears to be behaving as a soluble element in the Martian soils (due to positive correlations with sulfur and chlorine), renders phosphorus a unique chemical fingerprint for understanding Martian soils.

AQUEOUS GEOCHEMISTRY OF PHOSPHORUS ON MARS

Calcium-phosphate minerals have low solubilities in neutral to alkaline pH fluids, but display a log-linear relationship of increasing solubility with decreasing pH in the acidic range (Stumm and Morgan, 1996). Aqueous dissolution rates of Ca-phosphate minerals also display a log-linear relationship of increasing dissolution rate with decreasing pH in the acidic range (Valsami-Jones et al., 1998; Guidry and Mackenzie, 2000). Thus, high concentrations of phosphorus in Martian aqueous fluids would likely be a product of increased weathering rates of igneous calcium-phosphate minerals in acidic environments, or higher solubilities of phosphate minerals in acidic waters, or both. Circum-neutral pH waters on Mars would likely have low phosphorus concentrations, due to low solubilities of calcium-phosphate minerals (Stumm and Morgan, 1996). The P/S and P/Cl ratios of Martian fluids, if indicative of these ratios in Martian soils, would likely necessitate orders of magnitude higher solubilities for phosphate minerals than are possible in circum-neutral pH fluids. This can probably only be achieved for acidic fluids. Alternatively, phosphorus could be concentrated in Martian soils, relative to sulfur and chlorine. A possible mechanism for concentrating phosphorus could be as adsorbed phosphate on ferric-oxide particles. Phosphate adsorbed onto poorly crystalline iron oxyhydroxide particles at hydrothermal vents in the Earth's ocean is an important reservoir in the global phosphorus cycle, with estimates of 15%–50% of oceanic phosphate being involved in this process (Berner, 1973; Wheat et al., 1996). The lack of significant positive correlation of phosphorus with Np-ox (Fig. 2) in Martian soils, coupled with the significant correlation of sulfur and Np-ox in Meridiani soils (Fig. 2), suggests that phosphate has not been concentrated in Martian soils due to adsorption onto iron oxides. Phosphate should outcompete sulfate during adsorption on iron oxides (Parfitt, 1982). Dissolved phosphate concentrations in Earth's

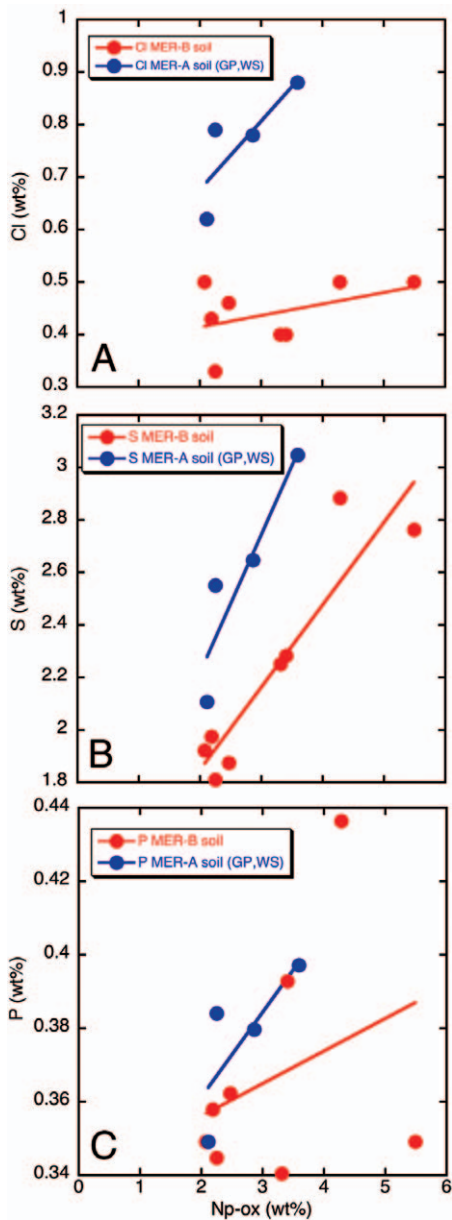


Figure 2. Chlorine, sulfur, and phosphorus vs. nano-phase iron oxide (Np-ox) (wt%). A: Cl vs. Np-ox: linear regressions are shown for Gusev soil from Gusev Plains (GP) and West Spur, Columbia Hills (WS) (blue) ($y = 0.41 + 0.13x$, $R = 0.82$, $N = 4$) and Meridiani soils (red) ($y = 0.37 + 0.02x$, $R = 0.43$, $N = 8$). Chlorine is not significantly correlated with Np-ox in soils at either site. **B: S vs. Np-ox:** linear regressions are shown for Gusev soils (blue) (GP and WS) ($y = 1.16 + 0.53x$, $R = 0.92$, $N = 4$) and Meridiani soils (red) ($y = 1.22 + 0.31x$, $R = 0.92$, $N = 8$). Sulfur shows highly significant correlation with Np-ox in Meridiani soils. **C: P vs. Np-ox:** linear regressions are shown for Gusev soils (blue) (GP and WS) ($y = 0.31 + 0.02x$, $R = 0.77$, $N = 4$), and Meridiani soils (red) ($y = 0.34 + 0.01x$, $R = 0.33$, $N = 8$). Phosphorus is not significantly correlated with Np-ox in soils at either site. Weight percent Np-ox is fraction of Np-ox determined by Mössbauer multiplied by total iron measured by alpha particle X-ray spectrometer. See text for data sources. MER—Mars Exploration Rover.

present-day ocean are generally low and ultimately controlled by biological cycling. In a prebiotic ocean, dissolved phosphate concentrations would likely be controlled by phosphate mineral solubilities and riverine phosphate input from weathering of igneous rocks. If the high P/S and P/Cl ratios measured in the Martian soils are indicative of these ratios in Martian water, an acidic and abiotic hydrosphere would be indicated. The similarity in the elevated ratios of P/S and P/Cl in Gusev and Meridiani soils argues for large acidic bodies of water, such as regional groundwater systems, lakes, or an ocean.

Phosphorus and sulfur should be decoupled during magmatic degassing and in neutral to alkaline waters. A high P/S ratio in Martian fluids can likely only be attained under acidic conditions. Due to the different sources of phosphorus (weathering) and sulfur (volcanic), attaining a similar P/S ratio at both landing sites requires a global mechanism for the attainment of a near-constant P/S ratio. Mixing of dissolved phosphate and dissolved sulfate in an acidic ocean on Mars could be very efficient at homogenizing P/S. The Earth's deep ocean waters have mixing times of ~ 1 k.y. (Broecker and Peng, 1982); this suggests that an ocean on Mars may have been acidic for only a short period of time.

ACID THIN-FILM OR ACID-FOG WEATHERING VS. EARLY ACIDIC HYDROSPHERE

High, near-constant P/S and P/Cl ratios of Martian soils cannot be easily explained by acid-fog weathering. Acid-fog weathering models call for the formation of thin or thick films of acidic water on rock and mineral surfaces, where the acid is either derived from deposition of H_2SO_4 and HCl acid aerosols (Banin et al., 1997) or from the hydrolysis of ions in salts by diurnal or seasonal cycling of water in the present Martian environment (Yen et al., 2005). Phosphorus enrichment due to acid-fog weathering would arise from enhanced dissolution of phosphate minerals in these films. Leached alteration zones several millimeters in thickness on float rocks of the Columbia Hills, Gusev Crater, show evidence for calcium-phosphate mineral depletion and may have been affected by this process (Hurowitz et al., 2006). These acidic weathering films would likely yield heterogeneous P/S and P/Cl ratios, as phosphorus concentration in these weathering products would depend on the total amount of calcium-phosphate minerals in the protolith, and mineral dissolution rates in these films. Mineral dissolution rates will likely be dependent on a number of factors, such as temperature, time, and pH, which cannot be expected to be constant on a plan-

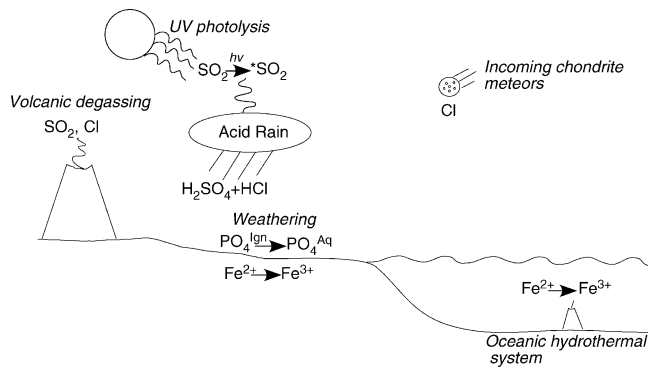
etary scale. Martian igneous meteorites show a range of phosphorus concentrations (0.006–1.5 wt%; Meyer, 1998), suggesting that igneous rocks on the Martian surface will have a range of phosphorus contents. A large variation in phosphorus content has been found for rocks of indeterminate origin in the Husband Hills, Gusev Crater, consistent with widely varying phosphorus contents of Martian rocks (Gellert et al., 2006). The acidic thin films proposed by Yen et al. (2005) are responsible for heterogeneities in Br concentrations in Martian soil. Thus, acidic thin films in the present Martian environment should lead to soil heterogeneities in mobile elements (such as S, Cl, P, and Br), not homogeneities. This evidence suggests that aqueous alteration processes that may occur in the current Martian environment are unlikely to be responsible for the chemically homogeneous global bright dust. It is possible that eolian homogenization of planet-wide acid-fog alteration products could lead to the chemically homogeneous global soils, but this style of alteration cannot explain the uniformly high phosphorus contents of ancient (ca. 3–4 Ga) sulfate-rich outcrop rocks at Meridiani Planum (Squyres and Knoll, 2005). The ancient aqueous environment at Meridiani Planum was permeated with phosphorus, chlorine, and sulfur-rich fluids during its formation. There is no need to invoke acidic thin films or acid-fog alteration to explain enhanced phosphorus concentrations in Martian soils, because phosphorus was probably released from igneous rocks in ancient Martian weathering environments.

SUMMARY

The high phosphorus contents associated with the S-rich and Cl⁻-rich bright soils, as well as the S-rich, Cl⁻-rich, Meridiani Planum outcrop rocks, likely results from weathering of Ca-phosphate minerals in a global acidic hydrosphere. Evaporation of a global acidic ocean could lead to Np-ox particles with constant S, Cl, and P, as seen in the Martian bright soils. Acidic thin-film or acid-fog weathering will result in heterogeneous P/S and P/Cl in Martian soils, and are unlikely processes to have led to high phosphorus in ancient Meridiani Planum sulfate-rich outcrop rocks. The chemically homogeneous bright soils argue for a global acidic ocean, though eolian homogenization of the evaporated salts of a number of acidic water bodies cannot be ruled out. Regardless, high phosphorus in the ancient (ca. 3–4 Ga) Meridiani Planum rocks, as well as soils at both landing sites, argues for an early acidic hydrosphere on Mars.

An acidic ocean or hydrosphere can also explain the lack of carbonate rock exposures on the Martian surface, as pointed out by Fairén

Figure 3. Idealized phosphorus, sulfur, and chlorine cycle for early Mars. Sulfur is derived from volcanic degassing primarily as SO₂. SO₂ undergoes ultraviolet (UV) photolysis in Martian atmosphere. Chlorine is derived from volcanic degassing and possibly incoming chondritic meteors. Atmospheric sulfur and chlorine can help promote acid rain, which will lead to weathering of Ca-phosphate minerals in igneous rocks. P is derived primarily by weathering, which leads to riverine input of phosphorus to Martian ocean. Nano-phase iron oxide (Np-ox) particles are formed where oxidized surface fluids react with Fe²⁺ in igneous rocks, and possibly at areas of submarine volcanism, where reduced iron in solution undergoes oxidation.



et al. (2004). Carbonate minerals can only form in an acidic ocean or lake at a location where the Martian bedrock is able to neutralize the acidic waters. The acidic ocean may have been short-lived, as mixing times are <1 k.y. in the Earth's deep oceans. A schematic of the Martian phosphorus, chlorine, and sulfur cycle is shown in Figure 3. High concentrations of phosphorus in a Martian ocean would not be expected if Mars had an active biosphere during the ocean's existence.

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