

## GEOCHEMICAL CONSTRAINTS ON THE SURFACE (SEDIMENTARY) MINERALOGY OF MARS.

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**Introduction:** Any insight into Martian surface mineralogy is of interest because it helps to constrain surficial chemical processes. Among the approaches to the problem are imaging, spectroscopy, magnetics, and chemical analyses. Geochemical constraints, considered here, come from analyses of soils and rocks at the Viking and Pathfinder sites, gamma-ray spectroscopy, and analyses of SNC meteorites.

There have been several attempts to constrain Martian soil mineralogy by a combination of thermodynamic considerations and chemical mass balance [1-4]. However, thermodynamic insight into mineralogy requires a variety of assumptions about surficial conditions (e.g.,  $pH$ ,  $pO_2$ ,  $pCO_2$ , etc.) and multi-component mixing models are typically non-unique. An alternative approach (also see [4,5]) is to use geochemical variations among soils and rocks to constrain possible involvement of various minerals during sedimentary processes.

**Complex Mixing and “Soil-Free Rock”:** For the most part, chemical variations among soils and rocks from the Pathfinder site have been explained by a two component mixing model where variable amounts of soil adhere to rocks of essentially identical composition (so-called “soil-free rock”) [6,7]. Although such a model appears to explain much of the variation among several elements, various ratio-element and ratio-ratio diagrams indicate that in detail the mixing is significantly more complex [5]. Accordingly, linear extrapolations to a “soil-free rock” based on two component mixing may not have geological significance for some elements.

**Heavy Mineral Fractionation:** There is growing evidence for variable grain sizes, including sand, within Martian soils and for fluvial and aeolian transport on the Martian surface (including deflation surfaces). An obvious sedimentological process to test is fractionation of heavy minerals. In basaltic sediment (and SNC meteorites), various titanium oxides (ilmenite, titanomagnetite) are likely to be the dominant heavy minerals with specific gravity about 20-70% higher than the most abundant major minerals (pyroxene, olivine, plagioclase). Possible fractionation of titanium oxides (ilmenite, titanomagnetite) can be evaluated on a plot of  $TiO_2$  vs.  $SiO_2/SO_3$  (Fig. 1). Using extreme Pathfinder soil (A4) and rock (A17) compositions as mixing end members, the Pathfinder and Viking soils are consistent with up to about 1.5% fractionation of ilmenite, well within the levels found in SNC meteorites.

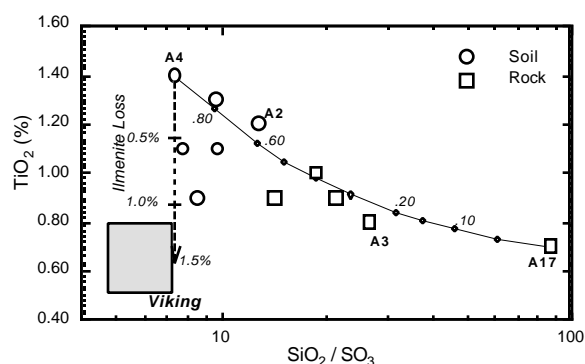


Fig. 1. Plot of  $TiO_2$  vs.  $SiO_2/SO_3$  for Pathfinder and Viking samples. Shown is a mixing line between soil A4 and rock A17 and effects of removing up to 1.5% ilmenite from A4.

**Iron Oxide ( $\pm$ Sulfate?) Fractionation:** Although there remains much controversy regarding the nature of the magnetic mineral in Martian dust and soil, some form of iron oxide (e.g. maghemite) is commonly cited. If so, one might expect fractionation of iron from other cations within soils and rocks during transport. Fig. 2 plots  $FeO_T$  vs.  $SiO_2/SO_3$  using Pathfinder samples A4 and A17 as mixing end members. The mixing line between these samples forms a lower  $FeO_T$  bound for all samples and Viking and Pathfinder soils (and Pathfinder rocks) are consistent with up to about 6% addition of iron oxide (as  $Fe_2O_3$ ).

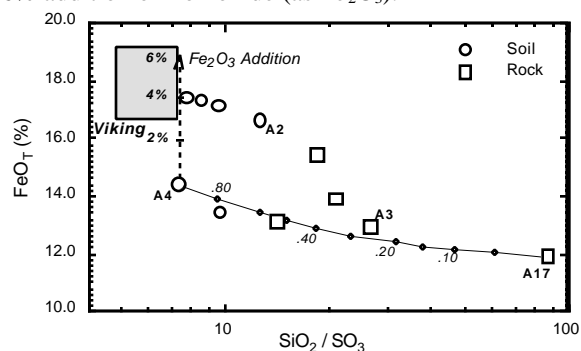


Fig. 2. Plot of  $FeO_T$  vs.  $SiO_2/SO_3$  for Pathfinder and Viking samples. Results are consistent with addition of an iron phase (up to 6%  $Fe_2O_3$ ) to most soils and some rocks.

Such material could be intrinsic components of the soils as well as fine dust adhered to the surfaces of boulders and other fragments. Iron enrichment would not be restricted to iron oxide but could include any phase where iron is significantly enriched. One obvious example is an iron sulfate phase (e.g. jarosite,

schwertmannite), minerals commonly cited as possible constituents of the soil.

**Sulfur Mineralogy:** The high S content found in Martian soil has led to a variety of sulfur minerals being proposed. Included are calcium sulfates (gypsum, anhydrite), iron sulfates (jarosite, schwertmannite), and magnesium sulfates (kieserite, bloedite) [8,9]. Elemental sulfur is another possibility. The correlation between MgO and SO<sub>3</sub> for Pathfinder soils and rocks has been taken as evidence for the presence of Mg-sulfate. However, it is notable that Viking soils have significantly lower Mg than predicted by the Pathfinder correlation line suggesting that another non-magnesian phase could play a role. On a ternary plot of mole proportions SO<sub>3</sub> - MgO - FeO<sub>T</sub> (Fig. 3) Pathfinder soils and rocks align along a straight line consistent with a mixing line where MgSO<sub>4</sub> (plus a small amount of excess Mg, perhaps as magnesium chloride) is one endmember. Viking soils are offset towards the SO<sub>3</sub> - FeO<sub>T</sub> edge consistent with (but not necessarily requiring) a component of iron sulfate. None of the systematics on this diagram requires a role for calcium or sodium sulfates.

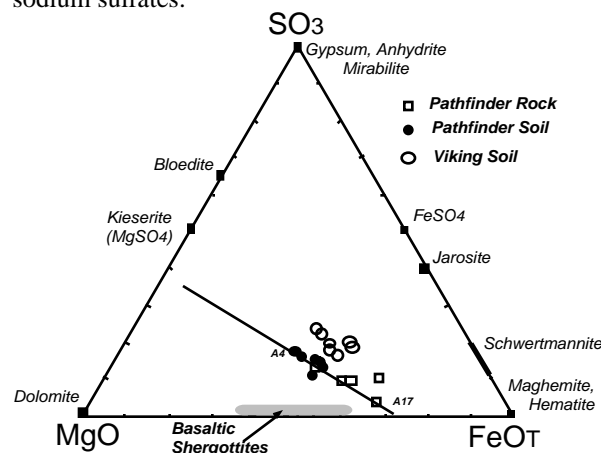
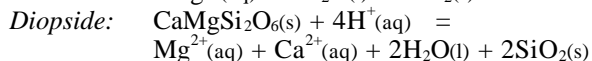
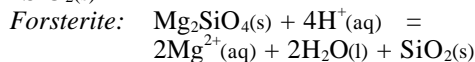
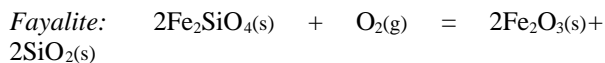


Fig. 3. Ternary diagram of molecular proportions SO<sub>3</sub>-MgO-FeO<sub>T</sub> for Pathfinder and Viking samples. Also shown are idealized mineral compositions and extrapolated A4 - A17 mixing line.

**A Case for Sedimentary Silica:** The likely occurrence of magnesium (and possibly iron) sulfate and iron oxide at the Martian surface indicates alteration of basalt. Assuming that SNC mineralogy is generally representative of Martian basalt the most readily altered phases would be olivine, pyroxene, plagioclase, and glass [10]. An obvious question is what happens to silica derived from alteration of basalt (especially olivine and pyroxene)? The possibility of significant amounts of sedimentary silica near the Martian surface is of importance, especially considering the unexpected occurrence of silica-rich rocks at the Pathfinder site [6].

During terrestrial weathering of basalt under acidic and oxidizing conditions, silica is mobile and up to >50% can be lost from weathering profiles [10]. Simi-

larly, during low temperature palagonitization of basalt, silica is also mobile [11]. Idealized weathering reactions include [12]:



In nature, amorphous silica dissolves in water as silicic acid (H<sub>4</sub>SiO<sub>4</sub>) [13]. Note that 1-2 moles of silica are released for every mole of mineral that reacts.

There are several possible fates for any liberated silica. Near the alteration zone, some may combine with aluminum (derived from plagioclase) and various cations to form palagonite and clay minerals. However silica that is lost from the alteration zone (i.e., open-system behavior) could be transported considerable distance and be precipitated as a separate silica phase (e.g., amorphous silica, chalcedony, quartz, etc.). Thus silica could be found in a variety of settings, including veins, fracture fillings, overgrowths, encrustations on rock surfaces, discrete mineral grains, or dust coatings.

Spectral identification of silica on the Martian surface would be difficult in that spectroscopic properties are largely determined by trace elements [14], however, some of the spectroscopic observations do appear to be consistent with the presence of silica [7].

**References:** [1] Toulmin III, P., *et al.* (1977) *JGR*, 82, 4625-4634. [2] Banin, A. *et al.* (1993) In: *Mars* (eds. H. H. Kieffer *et al.*), 594-625, U. Ariz. Press. [3] Burns, R.G. (1993) *GCA*, 57, 4555-4574. [4] Clark, B.C. (1993) *GCA*, 57, 4574-4581. [5] McLennan, S.M. (1999) *LPS XXX*, Abst. #1700. [6] Rieder, R. *et al.* (1997) *Science*, 278, 1771-1774. [7] McSween Jr., H.Y. *et al.* (1999) *JGR*, 104, 8679-8715. [8] Bell III, J.F. (1996) *Geochem. Soc. Spec. Publ.* 5, 359-380. [9] McSween Jr., H.Y. & Treiman, A.H. (1998) *Rev. Mineral.*, 36, 6/1-6/53. [10] Nesbitt, H.W. & Wilson, R.E. (1992) *AJS*, 292, 740-777. [11] Daux, V. *et al.* (1994) *GCA*, 58, 4941-4954. [12] Curtis, C.D. (1976) *Earth Surf. Proc.*, 1, 63-70. [13] Dove, P.M. & Rimstidt, J.D. (1995) *Rev. Mineral.*, 29, 259-308. [14] Rossman, G.R. (1995) *Rev. Mineral.*, 29, 433-467.