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SULFIDE MINERALIZATION: ITS ROLE IN CHEMICAL WEATHERING OF MARS

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Summary. Pyrrhotite-pentlandite assemblages in mafic and ultramafic igneous rocks may have contributed significantly to the chemical weathering reactions that produced degradation products in the martian regolith. By analogy with terrestrial processes, a model is proposed whereby supergene alteration of these primary Fe-Ni sulfides on Mars has generated secondary sulfides (e.g. pyrite) below the water table and produced acidic groundwater containing high concentrations of dissolved Fe, Ni and sulfate ions. The low pH solutions also initiated weathering reactions of igneous feldspars and ferromagnesian silicates to form clay silicate and ferric oxyhydroxide phases. Near-surface oxidation and hydrolysis of ferric sulfato- and hydroxo-complex ions and sols formed gossans above the water table consisting of poorly crystalline hydrated ferric sulfates (e.g jarosite), oxides (ferrihydrite, goethite) and silica (opal). Underlying groundwater, now permafrost, contains hydroxo sulfato complexes of Fe, Al, Mg, Ni, etc., which may be stabilized in frozen acidic solutions beneath the surface of Mars. Sublimation of permafrost may replenish colloidal ferric oxides, sulfates and phyllosilicates during dust storms on Mars.

Background. The presence of massive volcanoes in the Tharsis and Elysium regions, the distinctive petrology of SNC meteorites, and a compendium of results from the Viking Lander experiments all point to extrusive and plutonic mafic and ultramafic igneous rocks on Mars having analogies to terrestrial komatiites [1]. On Earth, the latter are associated with massive and disseminated sulfides containing pyrrhotite, pentlandite, and accessory pyrite and chalcopyrite [2]. Near-surface oxidation of these sulfides have produced conspicuous rust-colored gossans, which often betray the occurrence of unexposed ore deposits (Figure 1). Studies of gossans and sub-surface minerals [3-5] suggest pathways of oxidative weathering reactions that may be applicable to Mars.

Pyrite is pivotal to chemical weathering reactions of sulfides. It may occur as a minor constituent of primary igneous sulfides, or be formed by supergene reactions involving deep weathering of pyrrhotite (see equation {1} in Table 1.). At or near the water table, oxidation of pyrite by aerated groundwater occurs {6},{7}. Ferric iron liberated in this reaction, not only promotes the initial alteration of pyrrhotite {1} and of pentlandite {2} to secondary sulfides in the absence of dissolved oxygen, but also aids the dissolution of pyrite {5} below the water table. Supergene enrichment reactions also occur there {3},{4}, leading to high concentrations of Ni, etc. in secondary sulfides. Strongly acidic and sulfate-rich groundwater is produced which stabilizes dissolved ferrous iron and a variety of complex ferric ions [6] including those listed in {8} and {9}. At elevated temperatures, these complexes produce of a variety of hydroxo-ferric sulfate sols [7] (e.g carphosiderite {8},{9}), which may be the precursors to a number of ferric sulfate minerals [8] often found in gossans in arid regions. In less acidic environments above the water table, dissolved ferric ions and monodispersed sols are hydrolysed to poorly crystalline FeOOH phases (e.g. ferrihydrite, goethite {10},{11},{12}), which coexist with silica (opal, jasper) and the hydrated ferric sulfate minerals in gossans. The fields of relative stabilities of gossaniferous phases are depicted in the oxidation-acidity diagram shown in Figure 2.

Reactions {4} to {11} formulated in Table 1 demonstrate that groundwater in the vicinity of oxidizing sulfides is highly acidic. Such low pH solutions promote the chemical weathering of feldpars, pyroxenes and olivine in host igneous rocks [9], liberating dissolved silica, Al, Ca, Mg, Na and additional Fe ions, and producing secondary clay silicates (e.g. smectite) and iron oxyhydroxides. On Earth, seafloor basalts and gabbros erupting along submarine spreading centers have undergone extensive hydrothermal alteration by seawater circulating through underlying tectonically-fractured oceanic crust. As a result, the acidity of aqueous solutions is buffered by seawater-basalt interactions, leading to the slight alkalinity (pH 8.2) of present-day terrestrial oceans.

The oxidative power of atmospheric oxygen is the driving force in the weathering of sulfides (in the absence of bacterial activity). The dissolution of oxygen in groundwater and its migration to sulfide reaction centers involve diffusion processes and are probably rate-controlling. When the concentration of dissolved oxygen is very low and the supply of water is limited, oxidative reactions become sluggish and involve hydrogen peroxide. Furthermore, ferric-bearing solutions may liberate elemental sulfur {13},{14},{15}. Thus, metastable sulfur is observed in pyrite-jarosite-sulfur assemblages associated with some ultramafic pyrrhotite-pentlandite deposits [10].

Martian Weathering. On Mars, where plate tectonic activity appears to have been insignificant, vast volumes of iron-rich basaltic magma has reached the surface of the planet via immense shield volcanoes. Fracturing associated with this volcanism, as well as impact cratering, facilitated deep-weathering reactions by permeating groundwater early in the history of Mars. However, the apparent absence of spreading centers and subduction zones, which cause recycling of the Earth's crust, has minimized acid-buffering of aqueous solutions by wall-rock alteration on Mars. Therefore, the acidity of groundwater, now permafrost, may have been maintained during the chemical evolution of the martian surface, thereby aiding the solubility and transport of Fe, Al, Mg, Ni, silica, etc. Geomorphological evidence attesting to the flow of water on Mars suggests that gossan-forming reactions may have occurred in the past. However, the present-day cold surface of Mars has impeded deep-weathering of sulfides in host basaltic rocks due to slow reaction rates and restricted access of dissolved oxygen or ferric iron to reaction centers. Nevertheless, some oxidative weathering may still be occuring in the frozen environment on Mars, as indicated by the oxidation of Fe and FeS phases observed in Antarctic meteorites [11]. When sublimation of martian permafrost occurs, species held in solution could be hydrolysed, precipitated as colloidal materialland transported in dust storms..

Discussion. Evidence for gossan formation on Mars stems from several sources. First, remote-sensed reflectance spectral profiles are matched closely by ferrihydrite-silica gels and jarosite-bearing clay assemblages [12]. Second, jarosite which is so characteristically an oxidative weathering product of iron sulfides, may be present in SNC meteorites [13,14] believed to have originated from Mars. Third, the magnetic phase detected in the Viking magnetic experiment [15] may be remnant pyrrhotite which has been incompletely oxidized, particularly if the level of the water table has dropped on Mars. Finally, a limited supply of water and a low concentration of dissolved water, which favor the formation of hydrogen peroxide and promote the production of peroxide and superoxide phases, may account for results obtained in the Viking biology experiments [16].

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Table 1. CHEMICAL WEATHERING REACTIONS INVOLVING SULFIDES

{1} Fe_7S_8 (pyrrhotite) + $6Fe^{3+} = 4FeS_2$ (pyrite) + $9Fe^{2+}$

{2} $(Fe,Ni)_9S_8$ (pentlandite) + $2Fe^{3+} \Rightarrow 3Fe^{2+}$ + $(Fe,Ni)Ni_2S_4$ (violarite)

{3} $(Fe,Ni)Ni_2S_4$ (violarite) + $Ni^{2+} \Rightarrow Fe^{2+}$ + $(Ni,Fe)Ni_2S_4$ (polydymite)

{4} Ni_3S_4 (polydymite) + $H_2O + 15/2\, O_2 = 3Ni^{2+} + 4SO_4{}^{2-} + 2H^+$

{5} $FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+$

{6} $2FeS_2 + 2H_2O + 7\,O_2 = 2Fe^{2+} + 4SO_4{}^{2-} + 4H^+$

{7} $4FeS_2 + 2H_2O + 15\,O_2 = 4Fe^{3+} + 8SO_4{}^{2-} + 4H^+$

{8} $2FeSO_4{}^+ + FeOH^{2+} + 6H_2O = Fe_3(SO_4)_2(OH)_5.2H_2O$ (carphosiderite) + $4H^+$

{9} $Fe(SO_4)_2{}^- + 2FeOH^+ + 4H_2O = Fe_3(SO_4)_2(OH)_5.2H_2O + H^+$

{10} $Fe^{3+} + 2H_2O = FeOOH$ (ferrihydrite, goethite) + $3H^+$

{11} $FeSO_4{}^+ + 2H_2O = FeOOH + SO_4{}^{2-} + 3H^+$

{12} $Fe_3(SO_4)_2(OH)_5.2H_2O = 3FeOOH + 2SO_4{}^{2-} + 4H^+ + H_2O$

{13} $FeS_2 + 2Fe^{3+} = 3Fe^{2+} + 2S$

{14} $Fe_7S_8 + 14Fe^{3+} = 21Fe^{2+} + 8S$

{15} $(Fe,Ni)_9S_8 + xFe^{3+} \Rightarrow yFe^{2+} + zNi^{2+} + 8S$

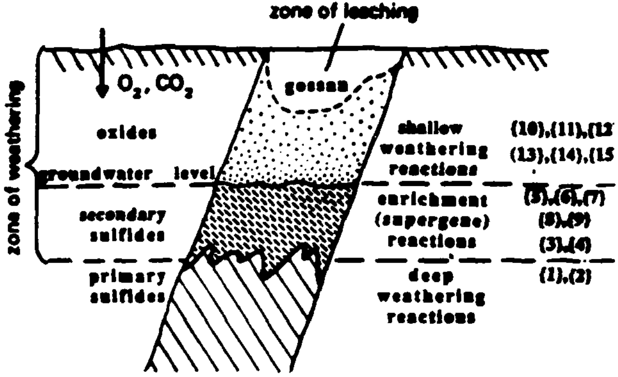

Figure 1 (above). Zones of weathering associated with gossan formation above sulfide mineralization. The scale of the sulfide vein may be a few microns to several meters in diameter. Reactions {1} to {15} correspond to those in Table 1.

Figure 2 (right). Equilibrium diagram for pyrite and its oxidative products, including jarosite and FeOOH, occurring in gossans at 25°C (modified from [5]). Ranges of pE and pH measured in oxidized pyrrhotite-pentlandite assemblages are shown [3-4], as well as values for dissolved oxygen in groundwater on Earth and Mars. (At 298.16°K, Eh = 0.05916 x pE.)