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SAMPLING THE OXIDATIVE WEATHERING PRODUCTS AND THE POTENTIALLY ACIDIC PERMAFROST ON MARS

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Summary. Large areas of Mars' surface are covered by oxidative weathering products containing ferric and sulfate ions having analogies to terrestrial gossans derived from sulfide mineralization associated with iron-rich basalts. Chemical weathering of such massive and disseminated pyrrhotite-pentlandite assemblages and host basaltic rocks in the martian environment could have produced metastable gossaniferous phases ("limonite" containing poorly crystalline hydrated ferric sulfates and oxyhydroxides, clay silicates and opal). Underlying groundwater, now permafrost on Mars, may still be acidic due to incomplete buffering reactions by wall-rock alteration of unfractured host rock. Such acidic solutions stabilize temperature-sensitive complex ions and sols which flocculate to colloidal precipitates at elevated temperatures. Sampling procedures of martian regolith will need to be designed bearing in mind that the frozen permafrost may be corrosive and be stabilizing unique complex ions and sols of Fe, Al, Mg, Ni and other minor elements.

Background. The high concentrations of Fe and S analysed by the Viking XRF spectrometers, together with optical properties, remote-sensed spectra, magnetic measurements, biological experiments, and thermodynamic calculations, indicate that oxidized Fe^{3+}- and SO_4^{2-}-bearing phases exist on the surface of Mars [1,2]. Because constituent minerals on Mars have not yet been identified directly, considerable speculation exists about the nature and origin of parent igneous rocks, their mantle sources, and weathering processes that have generated materials in the martian regolith. Many ambiguities could be alleviated if pristine samples now stable on Mars could be retrieved without being degraded under ambient conditions on Earth.

The mantle of Mars is believed to be more iron-rich than the Earth's mantle and to contain sulfur concentrations approximating chondritic compositions. Partial melting of this martian mantle would produce iron-rich basaltic magma which could be olivine-rich and/or pyroxene-rich and resemble terrestrial Precambrian komatiites. The normative mineralogy of such mafic or ultramafic rocks indicates the presence of Fe-rich olivines and pyroxenes plus accessory Fe-Ni sulfides, correlating with mineralogical and analytical data for SNC meteorites believed to have originated from Mars. Such iron-rich silicate and sulfide phases on Earth are highly vulnerable to oxidative chemical weathering reactions, during which metastable phases and transcient chemical species in aqueous solution are formed.. They may still exist near the surface of Mars. Research on oxidized cappings or gossans [3,4] overlying sulfur-bearing mafic and ultramafic igneous rocks provide guidelines for sampling and storing pristine materials from the weathered surface of Mars.

Chemical Weathering Reactions. Near-surface oxidation reactions [4,5] of pyrrhotite-pentlandite (+/- pyrite, chalcopyrite) assemblages associated with terrestrial komatiites are catalysed by pyrite which may be present either as a primary phase or be formed during deep-weathering reactions (e.g. $Fe_7S_8 + 6Fe^{3+} = 4FeS_2 + 9Fe^{2+}$). Pyrite in contact with aerated groundwater generates strongly acidic (pH 2 to 5) and sulfate-rich ($\sim 10^{-2}m$) solutions (e.g. $2FeS_2 + 2H_2O + 7O_2 = 2Fe^{2+} + 4SO_4^{2-} + 4H^+$) which stabilize and mobilize simple and complex ions of Fe, Al, Mg, Ni, etc. Above the water table further oxidation occurs to insoluble Fe(III) oxides (e.g. ferrihydrite: $4Fe^{2+} + 6H_2O + O_2 = 4FeOOH + 8H^+$) and sulfates (e.g. jarosite: $6Fe^{2+} + 4SO_4^{2-} + 9H_2O + 3/2\ O_2 + 2(K,Na)^+ = 2(K,Na)Fe_3(SO_4)_2(OH)_6 + 6H^+$). Acidic groundwater produced by the oxidation of sulfides promotes chemical weathering reactions of feldspars and ferromagnesian silicates to clay silicates and Fe(III) oxides in host igneous rocks. On Earth, the pH of such aqueous solutions, now predominantly oceans, is raised when seawater permeates through highly fractured basalts erupting along spreading centers. Similar acid-buffering reactions by wall-rock alteration may be incomplete on Mars because plate tectonic activity appears to have been minimal there. The fields of relative stabilities of simple Fe^{2+} and Fe^{3+} ions and some of the more common Fe(III) minerals found in gossans are depicted on Figure 1. This pE-pH diagram shows that dissolved Fe^{2+} ions could be stabilized in less oxygenated groundwater if it were acidic on Mars. However, ferrous ions would be readily oxidized to Fe^{3+}-bearing phases when returned to Earth unless adequate precautions were taken to avoid conversion to ferric iron.

More rigorous analyses of ion speciation in aqueous sulfuric acid solutions [6-9] indicate that at low pH dissolved complex ions of Fe, Al, Mg, etc., exist, including $FeSO_4^0$, $FeSO_4^+$ and $Fe(SO_4)_2^-$, and that at elevated temperatures significant concentrations of $FeOH^+$, $FeOH^{2+}$ and $Fe(OH)_2^+$ appear. These complex ions faciliate the formation of sols containing $Fe_3(SO_4)_2(OH)_5.2H_2O$ (carphosiderite) and $Fe_4SO_4(OH)_{10}$ (glockterite) which are precursors to colloidal jarosite and other insoluble hyroxo ferric sulfate minerals [2,6]. Therefore, temperature must be controlled (in addition to pH and dissolved oxygen) during sample retrieval from Mars in order to stabilize prisine complex ions and sols that may be present in frozen permafrost there.

Measurements on Returned Martian Samples. After refrigerated drill-cores taken through a gossan - frozen permafrost horizon on Mars are returned to Earth, they would be amenable to a variety of techniques including: (1) x-ray diffraction using cold-finger stages, to identify mineral phases present; (2) spectrophotometric determinations of dissolved complex ions of Fe and Ni in frozen solutions; (3) transmission electron microscopy, to examine sols and colloids; (4) low temperature Mossbauer spectroscopy, to characterize Fe-bearing phases; (5) near infrared spectroscopy, to identify H_2O, OH^- and H_3O^+ species in solid phases and frozen solution; and (6) measurements of E_h and pH.

References

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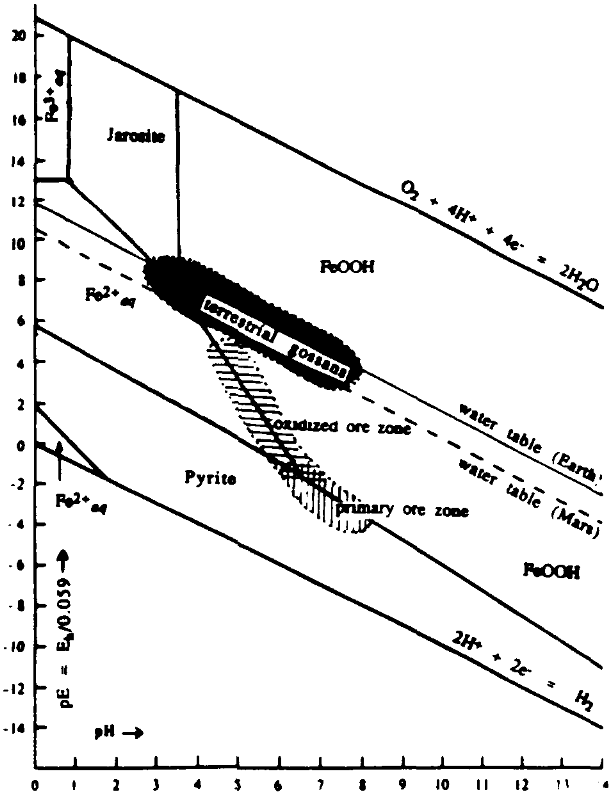

Figure 1. Eh-pH diagram for pyrite in equilibrium at 25^o with dissolved Fe (10^{-4}m), S (10^{-2}m) and K (10^{-4}m) ions and the oxidative products jarosite {$KFe_3(SO_4)_2(OH)_6$} and FeOOH [based on reference 10]. Ranges of pE and pH values associated with oxidized pyrrhotite-pentlandite ore assemblages are shown [see references 3-5]. Note that at 298.15^oK, $E_h = 0.05916 \times pE$.