CHEMICAL EVOLUTION AND OXIDATIVE WEATHERING OF MAGMATIC IRON SULFIDES ON MARS

Roger G. Burns and Duncan S. Fisher, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139

INTRODUCTION. Ferric-bearing phases in the martian regolith testify to oxidative weathering reactions near the surface of Mars. A paragenetic link between primary magmatic sulfide minerals on Mars and their weathering products (gossans) has been proposed by us [1-3]. This model is based on petrogenetic associations between komatiitic rock-types, Viking geochemical data, SNC meteorites, and terrestrial magmatic sulfide ore deposits [4]. It appears that unique conditions during the evolution of the martian crust have conspired to generate an acidic groundwater (permafrost) environment that has facilitated chemical weathering of basaltic rocks on Mars.

Some of the steps that have been proposed during oxidative weathering of iron sulfides [1-4] are summarized by reactions formulated in Table 1. Initially, deep-weathering reactions involving dissolved ferric iron in acidic groundwater percolating from the surface converts pyrrhotite to pyrite (reaction {1}). Pyrite is then oxidized either by ferric ions {2} or by groundwater equilibrated with oxygen in the atmosphere {3}, even under an oxygen partial pressure of 10^{-5} bar existing in the present-day martian atmosphere. Strongly acidic (pH 1 to 5) and sulfate-rich solutions are generated which stabilize and mobilize a variety of simple and complex ions of Fe, including Fe^{2+}, Fe^{3+}, $FeSO_4^+$, $FeOH^{2+}$, etc. Above the water table, these dissolved ions become unstable and produce hydronium jarosite {4} or eventually goethite by further oxidation {5}, hydrolysis {6}, and decomposition {7} reactions, each of which liberates H^+ ions thereby promoting chemical weathering of basaltic silicate minerals {8}.

To test this weathering model, komatiitic pyrrhotites and olivines have been exposed to sulfuric acid solutions, with and without the addition of ferric iron to simulate deep-weathering processes. We report here measurements made on the reaction products, and summarize tectonic and geochemical processes that might have modified the surface of Mars.

EXPERIMENTAL PROCEDURES. Powdered samples of pyrrhotite (Fe_7S_8) and olivine (Fa_{49}) were reacted in stoppered flasks with sulfuric acid (pH 2) at 60°C, with and without the addition of dissolved 1M ferric sulfate, for time periods ranging from 1 to 5 weeks. Reaction products were filtered, washed with cold distilled water, air-dried and measured by Mossbauer spectroscopy at ambient (295K) and liquid helium (4.2K) temperatures to characterize the X-ray amorphous Fe^{3+}-bearing phases formed in the reactions. Correlative Mossbauer spectra were also obtained for pyrite, marcasite, hematite, goethite, and jarosite. The spectra were calibrated against a metallic iron foil standard.

RESULTS. Examples of 4.2K Mossbauer spectra of pyrrhotite before and after reaction with pH 2 sulfuric acid are shown in Figure 1. The unreacted pyrrhotite spectrum (Fig. 1a) is complex and consists of 3 or 4 superimposed magnetic hyperfine sextets. After reaction with H_2SO_4, additional peaks appear at approx. 0.1 and 0.7 mm s^{-1} (Figs 1b & 1c) attributable to FeS_2 (pyrite or marcasite), which are intensified (Fig. 1c) when $Fe_2(SO_4)_3$ is present as a lixiviant. New peaks also occur near -7.75 and +8.5 mm s^{-1} and represent another component sextet, the magnetic hyperfine splitting parameter of which (H = 50.6T) resembles the value of goethite [5]. The breadth (Fig. 1b) or asymmetry (Fig. 1c) of the two goethite peaks suggest that some hydronium jarosite (H = 49.3T) may also be present in the reaction products. The Mossbauer spectra of reacted pyrrhotites, therefore, indicate that sulfuric acid has induced the pyrrhotite → FeS_2 (pyrite or marcasite) → goethite (+ jarosite) oxidative reactions formulated in Table 1. Nanophase goethite is also formed during reactions of olivine with H_2SO_4 [4], particularly in the presence of dissolved Fe^{3+} ions, hydrolysis of which is unlikely in acidic (pH 2) solutions.

DISCUSSION. The experimental results for H_2SO_4-degraded pyrrhotites support our proposed model for the oxidative weathering of Fe-S sulfide minerals, in which supergene alteration of pyrrhotite in groundwater and the formation of secondary FeS_2 phases precedes the deposition of goethite and jarosite in gossans above the water table [1-4]. Dissolved Fe^{3+} ions clearly promote the formation of supergene pyrite or marcasite, and the acidic groundwater causes chemical weathering of ferromagnesian silicates such as olivine to nanophase goethite. Similar oxidative weathering reactions involving pyrrhotite and olivine in komatiitic basalts are suggested to have occurred on Mars, contributing to the ferric-bearing materials present in the regolith there.

EVOLUTION OF THE MARTIAN SURFACE. Oxidative weathering of sulfides on Mars has been largely confined to pyrrhotite, perhaps associated with pentlandite and minor chalcopyrite, which predominate as accessory minerals in mafic igneous rocks and in associated ore deposits. Partial melting of the martian mantle estimated to contain about 4.5 wt. % S [4] produced iron-rich basaltic magma which

© Lunar and Planetary Institute • Provided by the NASA Astrophysics Data System

IRON SULFIDES ON MARS: Burns, R.G. and Fisher, D.S,

reached the surface of the planet via massive shield volcanoes and as fissure eruptions, transporting high concentrations of dissolved S^{2-} and HS^- to the surface. Extrusion of turbulent low viscosity lava, segregation of immiscible FeS liquids during cooling, gravitational settling and fractional crystallization of sulfide minerals in the lava flows, produced thinly disseminated iron sulfide mineralization over large areas of Mars. Massive ore deposits were also deposited locally at the base of structural depressions or in channels eroded by advancing lava flows [6]. Fracturing associated with this volcanism facilitated deep-weathering reactions by permeating groundwater early in the history of Mars. However, because plate tectonic activity appears to have been insignificant on Mars, the apparent absence of spreading centers and subduction zones has minimized acid-buffering of aqueous solutions by wall-rock alteration. Therefore, the acidity of groundwater, now permafrost, has been maintained during the chemical evolution of the martian surface, aiding the chemical weathering of silicates in the basaltic crust when water is present. Furthermore, since tectonic-induced interactions of martian mantle with crust, hydrosphere and atmosphere have been minimal, sulfide mineralization has not evolved on Mars beyond pyrrhotite-pentlandite assemblages associated with mafic igneous rocks. Therefore, common terrestrial ore deposits such as porphyry copper and molydenum, granite-hosted mineralization, and sediment-hosted galena-sphalerite assemblages [7] have not formed on Mars.

REFERENCES. [1] R.G.Burns, *Proc. 17th LPSC, JGR*, 92, E570 (1987); [2] R.G.Burns, *Proc. 18th LPSC*, 713 (1988); [3] R.G.Burns & D.S.Fisher, *LPI Tech. Rept., 88-05* 34 (1988); [4] R.G.Burns & D.S.Fisher, *LPI Tech Rept., 89-04*; 20(1989); [5] E.Murad & J.H.Johnston, in *Mossbauer Spectroscopy Applied to Inorganic Chemistry* (G.J.Long, ed.; Plenum) 2, 507 (1987); [6] A.K.Baird & B.C.Clark, *Nature*, 311, 18 (1984); [7] C.Meyer, *Ann. Rev. Earth Planet. Sci.*, 16, 147 (1988); [8] Research supported by NASA grants NSG-7604 and NAGW-1078.

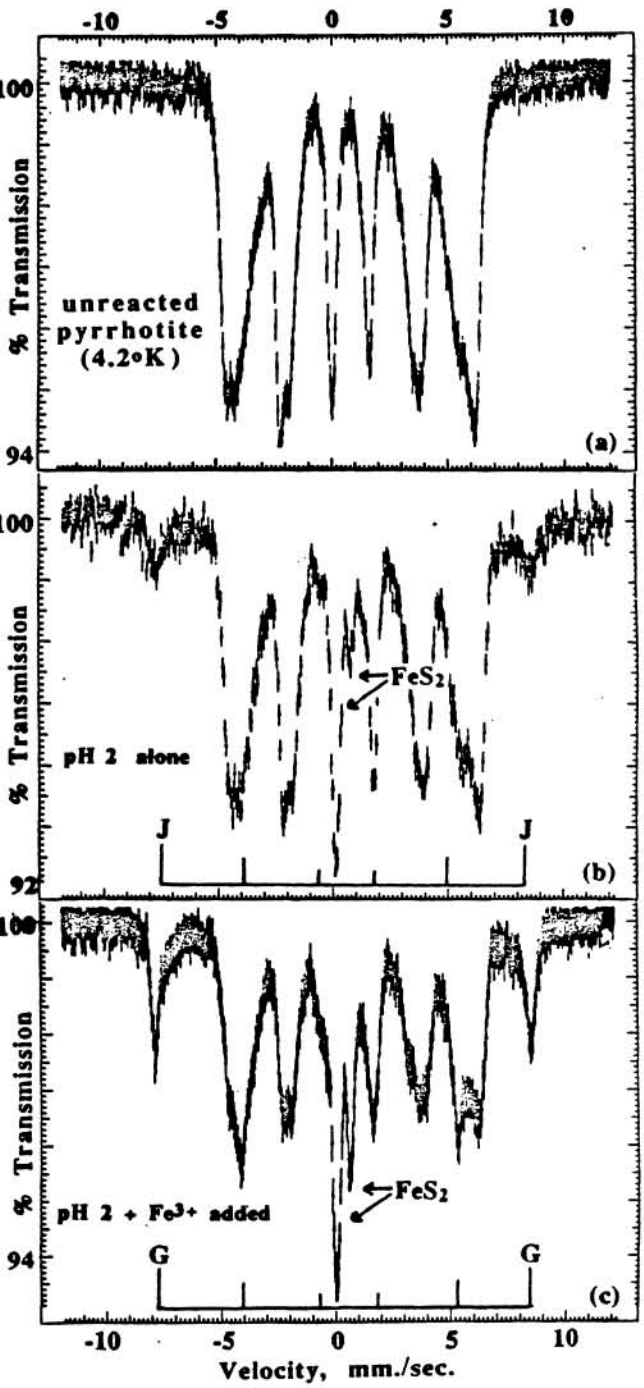

FIGURE 1. Mossbauer spectra measured at 4.2K of pyrrhotite (a) before, and (b,c) after, reaction with pH 2 sulfuric acid for 5 weeks at 60°C, in the absence (b) and presence (c) of dissolved 1M ferric sulfate. Peaks attributed to FeS_2 are identified, as are the positions of the goethite (G) and jarosite (J) sextet spectra

TABLE 1. Chemical weathering reactions of iron sulfides and silicates

{1} $Fe_7S_8 + 6\,Fe^{3+} \Rightarrow 4\,FeS_2 + 9\,Fe^{2+}$

{2} $FeS_2 + 14\,Fe^{3+} + 8\,H_2O \Rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+$

{3} $2\,FeS_2 + 2\,H_2O + 7\,O_{2\,(aq)} \Rightarrow 2\,Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+$

{4} $2\,FeSO_4^+ + FeOH^{2+} + 6\,H_2O \Rightarrow (H_3O)Fe_3(SO_4)_2(OH)_6 \Downarrow + 4\,H^+$

{5} $4\,Fe^{2+} + 6\,H_2O + O_{2\,(aq)} \Rightarrow 4\,FeOOH + 8\,H^+$

{6} $Fe^{3+} + 2\,H_2O \Rightarrow FeOOH \Downarrow + 3\,H^+$

{7} $(H_3O)Fe_3(SO_4)_2(OH)_6 \Rightarrow 3\,FeOOH + 2\,SO_4^{2-} + 4\,H^+ + H_2O$

{8} $(Mg,Fe)_2SiO_4 + 4\,H^+ \Rightarrow 2\,(Mg^{2+} + Fe^{2+}) + SiO_{2\,(aq)} + 2\,H_2O$

© Lunar and Planetary Institute • Provided by the NASA Astrophysics Data System