

FERROLYSIS OF IRON-BEARING MARTIAN BRINES: ORIGIN OF DUST-STORM PARTICULATES ON MARS

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INTRODUCTION. Brines have been proposed on Mars [1] to explain salt weathering erosional features [2], regions of high radar reflectivity [3,4], and the high concentrations of S and Cl in Viking Lander XRF measurements of the regolith [5]. These elements were interpreted to be present as chlorides and sulfates in evaporites [6] and gossans [7]. The formation of such evaporite and gossaniferous deposits implies that oxidative weathering reactions in an aqueous environment must have occurred sometime during the evolution of the martian surface. However, such water environments are not conspicuous on the surface of Mars now, except perhaps in the Solis Lacus region (14°-22°S; 84°-120°W) and other areas of comparable latitudes [8] having high radar reflectivities [3] from which local and global dust storms appear to originate [9,10]. Attention on possible martian brine compositions has focussed on eutectic temperatures of salt mixtures containing chlorides and sulfates of Na, K, Mg and Ca [1,4]. However, other dissolved cations must also be present in such brines, particularly ferric and ferrous iron, which are stabilized in aqueous solutions at relatively low values of pH (acidity) and Eh (redox potential) [7].

Ferrolysis, the process of oxidation of ferrous iron accompanied by the hydrolysis of ferric iron, is the ultimate fate of dissolved iron and is likely to occur during sublimation and melting of the permafrost on Mars [11], leading to the precipitation of iron phases which could be transported around the planet in dust storms. This has led to a study of residues formed during the oxidation and precipitation of iron phases from evaporated salt solutions. We report here preliminary results on the nature of ferrolysis products that might have been deposited from martian brines and be constituents of dust storms on Mars.

EXPERIMENTAL PROCEDURES. A number of mixed-salt solutions were prepared from sulfates and chlorides of Mg, K, and Na, to which were added ferrous sulfate. During the experiment, air was bubbled through the solutions to increase the rate of oxidation. In some cases, solutions were acidified to stabilize ferric iron, or the pH was adjusted to produce a precipitate. Other solutions were allowed to evaporate at ambient temperatures. Precipitates from the solutions and products of evaporation were examined by Mossbauer spectroscopy to determine the formation of ferric iron and to identify the ferric hydrolysates. Measurements made at liquid helium temperature (4.2K) proved to be particularly useful for characterizing the nanophase precipitates.

RESULTS. Many of the experiments are still in progress. However, some trends so far established are as follows. Acidified $MgCl_2$ and $MgSO_4$ solutions containing $FeSO_4$ yielded akaganeite (β - $FeOOH$) and goethite (α - $FeOOH$) plus ferrihydrite, respectively. However, lepidocrocite (γ - $FeOOH$) formed from $MgCl_2$ and $MgSO_4$ solutions at near-neutral pH. In the presence of KCl or NaCl, jarosite was the observed ferrolysis product.

Acidified solutions, where the Fe^{3+} ion is stabilized, produced complex ferrolysis products as evaporation neared completion. Mossbauer spectra at 4.2K of several samples exhibited two magnetic sextets. The first sextet is attributed to either akaganeite, goethite, or lepidocrocite, while the second sextet is believed to be produced by any number of mixed valence Fe^{2+} - Fe^{3+} minerals (e.g. roemerite, voltaite). In one experiment, the ferrolysis product left after evaporation produced a solid in which the Fe was predominantly non-magnetically ordered, suggesting sub-nanophase particles or an anion-disordered phase.

The ferrolysis reactions in the high ionic strength salt solutions, before an extensive amount of evaporation has occurred, generally adhere to trends observed during the oxidation of dissolved ferrous iron and the subsequent hydrolysis of ferric iron in less saline solutions [12]. When extensive evaporation has occurred, new ferrolysis products are produced having compositions and hues resembling surface fines in martian regolith.

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ORIGIN OF DUST STORM PARTICULATES. Experimental measurements described in an accompanying abstract [13] and geochemical models published elsewhere [7,11,14] suggest that acid weathering has been a significant surface process on Mars and that groundwater, now permafrost, may be acidic. Such low pH solutions dissolve significant concentrations of silica, Al, Mg, Fe, and other ionic species. They also hold in suspension considerable amounts of monodispersed sols of hydrous oxides and sulfates of Fe and Al [11]. These ions and sols are precursors to clay silicate, oxyhydroxide and hydroxo-sulfate minerals which form as precipitates in response to changes of temperature, pH and salinity.

On the surface of Mars, volatilization of H₂O during sublimation of permafrost or evaporation of the brine eutectic will induce the precipitation of dissolved salts of Na, Ca, Mg, Fe²⁺, etc. and cause the flocculation of colloidal ferric-bearing aluminosilicate, oxide, oxyhydroxide and hydroxo sulfate phases. These nanophase materials may constitute the particulates of local and global dust storms when they are generated in the Solis Lacus and similar regions of low radar reflectivities on Mars. During aeolian transport, any unoxidised ferrous salts liberated from volatilized permafrost will be completely oxidized, while dessication of ferric hydrolysis products to Fe₂O₃ phases [15] will be facilitated. Such ferric oxides include the formation of maghemite from lepidocrocite [16] considered to be the magnetic phase on Mars [17], as well as the occurrence of nanophase hematite believed to be present in bright regions of Mars [18].

REFERENCES. [1] G.W.Brass, *Icarus*, 42, 20 (1980); [2] M.C.Malin, *JGR*, 79, 3888 (1974); [3] S.H.Zisk & P.J.Mouginis-Mark, *Nature*, 44, 735 (1980); [4] A.P.Zent & F.P.Fanale, *JGR*, 91, D439 (1986); [5] P. Toulmin *et al.*, *JGR*, 82, 4625 (1977); [6] B.C.Clark & D.C.Van Hart, *Icarus*, 45, 370 (1981); [7] R.G.Burns, *Proc. 18th LPSC*, 713 (1988); [8] L.E.Roth *et al.*, *Lunar Planet.Sci.*, XVI, 712 (1987); [9] G. De Mottoni, *Icarus*, 25, 296 (1975); [10] S.W.Lee, *Lunar Planet.Sci.*, XVI, 483 (1987); [11] R.G.Burns, *Proc. 17th LPSC, JGR*, 92, E570 (1987); [12] J.W.Murray, *Rev. Mineral.*, 6, 47 (1979); [13] R.G.Burns & D.S.Fisher, *Lunar Planet. Sci.*, XXI, this vol. (1990); [14] R.G.Burns & D.S.Fisher, *LPI Tech. Rept.*, 88-05, 34 (1988); *JGR*, in press; [15] J.L.Gooding, *Icarus*, 33, 483 (1978); [16] J.Posey-Dowty *et al.*, *Icarus*, 66, 105 (1986); [17] R.B.Hargraves *et al.*, *JGR*, 82, 4547 (1977); [18] R.V.Morris *et al.*, *JGR*, 94, 2760 (1989); [19] Research supported by NASA grants NSG-7604 and NAGW-1078.