**FE(II) OXIDATION AND SOURCES OF ACIDITY ON MARS.** P. B. Niles[1], T.S. Peretyazkho[2], and B. Sutter[2]

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Introduction: There is an apparent paradox between the evidence that aqueous environments on Mars were predominantly acidic [1-3] and the fact that Mars is predominantly a basaltic (and olivine - rich) planet [4, 5]. The problem being that basalt and olivine will act to neutralize acidic solutions they come into contact with [5, 6] and that there is a lot more basaltic crust on Mars than water or acid. This is especially true if there is an appreciable amount of water available to bring the acid in contact with the basaltic crust. Several hypotheses for ancient martian environments call on long lived groundwater and aqueous systems [7-9].

Fe Oxidation: Previous work proposed a possible solution to this paradox suggesting that acidity was produced by rapid oxidation of Fe(II) and subsequent hydrolysis of Fe(III) in the presence of potent atmospheric oxidants [10]. This model has been applied to several locations on Mars by subsequent studies [e.g. 11-13]. Using Merdiani Planum as an example, 2.63-3.36 mol H^+/kg outcrop were calculated to be produced during Fe(II) oxidation and Fe(III) hydrolysis as upwelling groundwater encountered powerful oxidants at the surface [10]. The acid producing reactions occur during hydrolysis and precipitation of Fe(III):

$$Fe^{3+} + 3H_2O --> Fe(OH)_3 + 3H^+ \qquad (1)$$
$$Fe(OH)_3 --> FeO(OH) + H_2O \qquad (2)$$
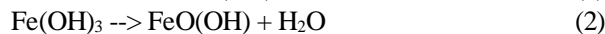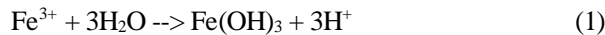
This model is based on a critical assumption of a starting "neutral" Fe(II)-rich starting solution. By making this assumption, the model avoids having to account for the dissolution reactions which are an essential part of understanding this system. The dissolved Fe(II) is proposed to have originated from anoxic weathering of primary Fe-rich basaltic minerals (olivine,pyroxene) [10] which weather according to the following reactions:

$$Fe_2Si_2O_6 + 2H_2O --> 2Fe^{2+} + 2SiO_2 + 4 OH^- \qquad (3)$$
$$Fe_2SiO_4 + 2H_2O --> 2Fe^{2+} + SiO_2 + 4OH^- \qquad (4)$$
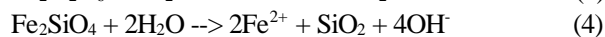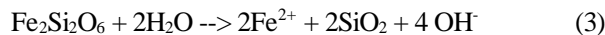
The model does not indicate what anion provides the charge balance for the dissolved iron. The important thing to note in reactions (3) and (4) is that the Fe(II) is charge balanced by OH^-. This is inescapable in this simple system because there are no other anions by which to balance the positive charge of the Fe(II). Likewise, simple oxidation of the Fe(II) consumes H^+ and in fact makes the aqueous solution more alkaline rather than more acidic (after eq 2 [10]):

$$2Fe^{2+} + 0.5O_2 + 2H^+ --> 2Fe^{3+} + H_2O \qquad (5)$$
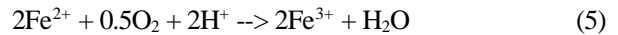
Viewing all of these equations together, it becomes clear that in the hydrolysis/precipitation step the iron has simply paired up with the OH^- that was its original charge balance in the solution. The complete chemical reaction including weathering, oxidation, and hydrolysis can be written as the following:

$$2FeO(pyx, ol) + H_2O + 0.5O_2 --> 2FeO(OH) \qquad (6)$$
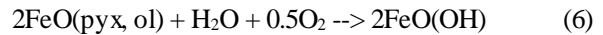
This reaction shows that weathering of Fe(II)-rich minerals in basalt leads to zero acidity production and in fact is neutral. This is born out in the terrestrial environment where oxic weathering of basalt, which includes Fe(II)-oxidation and Fe(III) hydrolysis, yields neutral to basic solutions.

Acidity Calculations: The H^+ production model was recalculated to include the full reaction sequence from dissolution to precipitation (i.e., reactions 3-6) following the detailed description of acidity calculations [10]. Fe abundance (in mol/kg) in schwermannite, jarosite and hematite was first calculated using total Fe content determined by alpha-particle X-ray spectrometer (APXS) and Mössbauer subspectral areas reported for jarosite, hematite and nanophase Fe(III) (hydr)oxides. Then, the cumulative H^+ reaction coefficient was calculated for formation of 1 mole jarosite, hematite or schwermannite (Table 1). We calculate that the sequence of Fe dissolution, oxidation, and hydrolysis would result in consumption, rather than production, of H^+ (i.e., negative total H^+ concentration, Table 1). These calculations only account for Fe and do not consider the release of Mg, Ca, and Na from the basalts which will also be accompanied by release of OH^- which will contribute to generation of additional alkalinity that is not accounted for in Table 1.

Table 1. Calculated H+ Production (after [10])

Sample name, sol#[1]	H+, mol/kg			Total H+ mol/kg
	Sch[2]	Jar[3]	Hem[4]	
McKittrick_RAT, 31	-0.13	-0.60	0	-0.73
Guadalupe_RAT, 36	-0.08	-0.78	0	-0.86
Mojo2_RAT, 45	-0.13	-0.47	0	-0.60
Golf_Post_RAT_FRAM, 87	-0.11	-0.72	0	-0.83
Lion-Stone_Numa_RAT, 108	-0.11	-0.60	0	-0.71
Kentucky_Cobble_Hill2_RAT, 145	-0.10	-0.57	0	-0.67
Virginia_RAT, 147	-0.10	-0.60	0	-0.70
Ontario_London_RAT, 149	-0.10	-0.55	0	-0.65
Grindstone_RAT, 153	-0.10	-0.58	0	-0.68
Kettle-stone_RAT, 155	-0.11	-0.61	0	-0.72
Mill-stone_Dramensfjord_RAT, 162	-0.10	-0.59	0	-0.69
Diamond_Jenness_Holman3_RAT	-0.10	-0.62	0	-0.72
MacKenzie_Campell_RAT, 184	-0.10	-0.67	0	-0.77
Inuvik_Toruyuktuk_RAT, 187	-0.11	-0.62	0	-0.73
Bylot_RAT, 195	-0.09	-0.74	0	-0.83
Escher_Kirchner_RAT, 220	-0.11	-0.66	0	-0.77
Wharenhui_RAT, 312	-0.10	-0.59	0	-0.69
Gagarin_RAT, 403	-0.13	-0.71	0	-0.84
IceCream_RAT, 548	-0.10	-0.70	0	-0.81

[1]Sample name and sol number for the Mars Exploration Rover *Opportunity*; [2]Sch- schwertmannite; [3]Jar- jarosite; [4]Hem-hematite

Sources of Acidity on Mars: Simple weathering of Fe-bearing silicate minerals does not result in the production of acidity. However, there are several ways in which acidity can be produced in Mars-like environments. However, maintaining such acidity in long lived aqueous environments remains problematic. Fe(II)-sulfide minerals have long been proposed as a potential source of acidity in aqueous solutions on Mars [14]. However, they are present only as minor phases (0.16 wt% in Shergottites) [15] and any acidity would be overwhelmed by OH^- production during silicate dissolution. Volcanic release of SO_2 or H_2S has also been hypothesized to be a source of acidity on early Mars [1]. We calculate that during the Noachian and early Hesperian Mars outgassed $\sim 5 \times 10^{21}$ g of SO_2 which would be capable of producing 1.6×10^{20} moles of H^+ during photo-oxidation of SO_2 in the atmosphere. This amount of acidity would be 100% neutralized by a gobal layer of basalt 40 m thick, which provides sufficient material to form the observed Hesperian sulfate deposits [16]. Evidence for large-scale acidic aqueous environments like Meridian Planum almost certainly requires that aqueous activity remained short-lived and that the acidic solutions were prevented from long duration exposure to basaltic crustal materials. This can be accomplished through closed system weathering of dust grains by small amounts of immobile fluids or in surface sediments where substantial acidity has been collected due to concentration mechanisms like evaporation or sublimation [4].

Conclusions: Dissolution, oxidation of Fe(II), and hydrolysis of Fe(III) derived from silicate minerals are not a net source of martian acidity. However estimated volcanic SO_2 and H_2S emissions during the Noachian and early Hesperian are sufficient to explain the observed mineralogy and acidic environments could be preserved through short lived aqueous environments.

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