CHEMICAL WEATHERING ON MARS: RATE OF OXIDATION OF IRON DISSOLVED IN BRINES
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Overview. Salts believed to occur in Martian regolith imply that brines occur on Mars, which may have facilitated the oxidation of dissolved Fe$^{2+}$ ions after they were released during chemical weathering of basaltic ferromagnesian silicate and iron sulfide minerals. Calculations show that the rate of oxidation of Fe$^{2+}$ ions at -35 °C in a 6M chloride-sulfate brine that might exist on Mars is about $10^6$ times slower than the oxidation rate of iron in ice-cold terrestrial seawater.

Introduction. The existence of ferric-bearing materials on Mars bears testimony to the fact that, at some time during the evolution of the martian regolith, oxidative weathering has occurred of the ferromagnesian silicate and iron sulfide minerals which were originally present in the basalts that flowed onto the surface of the planet. Less certain are the chemical environments, reaction rates and timing of the oxidation events. Intuitively, chemical weathering is expected to have progressed most rapidly when warmer, wetter conditions prevailed on Mars, since the processes of dissolution and oxidation of Fe$^{2+}$-bearing olivines, pyroxenes and sulfides are facilitated in aqueous environments [1]. Such reactions would be inhibited in the present-day frozen surface of Mars. However, periodic melt-waters suspected to occur in equatorial regions of Mars and the possible existence of brine eutectics in the regolith could provide chemical environments in which aqueous oxidation of dissolved Fe$^{2+}$ is still occurring near the Martian surface. Factors affecting the rate of oxidation of iron at low temperatures in brine solutions are addressed here.

Rate Equations. The most commonly verified rate law for the oxidation of dissolved ferrous iron at near-neutral pH (≥ 4.5) is given by

$$-d[Fe^{2+}] / dt = k_1 [Fe^{2+}] P_{O_2} \cdot (OH^-)^2$$

(1)

where [Fe$^{2+}$] is the molar concentration of dissolved iron, $P_{O_2}$ is the partial pressure of oxygen saturating the aqueous solution, $(OH^-)$ is the activity of hydroxyl ions, and $k_1$ is the rate constant [2-5]. On Earth, in water saturated with atmospheric oxygen, the rate constant near 25 °C has a value $k_1 = (8.0 \pm 2.5) \times 10^{13}$ M$^{-2}$ atm$^{-1}$ min$^{-1}$, or log$_{10}$ $k_1 = 13.9$ [2,3]. Note that the activity of OH$^-$ ions in eq. (1) is linked to the pH (where pH = - log$_{10}$($H^+$)) by the ionic product of water, $K_w = [H^+] \cdot (OH^-)$, which is the equilibrium constant for the dissociation of water ($H_2O = H^+ + OH^-$). At 25 °C, $K_w = 1 \times 10^{-14}$ M$^2$ or $pK_w = 14$, so that acidic solutions prevail when pH < 7. At 0 °C, $pK_w = 14.93$, so that solutions are acidic when pH < 7.46.

Equation (1) indicates that the rate of oxidation of dissolved Fe$^{2+}$ ions is strongly dependent on pH, decreasing one hundred-fold for each unit decrease of pH. Thus, reaction rates are lowered in acidic solutions, such as those resulting from oxidative weathering of iron sulfides [6,7] and the precipitation of acid rainwater that contains dissolved volcanic gases. Temperature also has a strong effect on the rate of oxidation of Fe$^{2+}$ expressed by eq. (1), which is reported to decrease by a factor of 10 for a temperature decrease of 15 °C [2]. Such a rate decrease may be accounted for by the temperature variation of $K_w$ and the resultant decrease of $(OH^-)$ at constant pH [3]. Since solubilities of dissolved gases increase at low temperatures, the higher solubility of oxygen in cold water partially offsets the effect of lower temperature on rates of oxidation of Fe$^{2+}$ ions. For example, the concentration of dissolved oxygen in pure water at 25 °C ($[O_2] = 2.58 \times 10^{-4}$ M) increases to $[O_2] = 4.57 \times 10^{-4}$ M at 0 °C [8]. To account for the solubility of oxygen, the rate equation for the oxidation of dissolved Fe$^{2+}$ is expressed as

$$-d[Fe^{2+}] / dt = k_0 [Fe^{2+}] \cdot [O_2] \cdot (OH^-)^2,$$

(2)

where $[O_2]$ is the molar concentration of dissolved oxygen [9]. The rate constant in air-saturated pure water at 25 °C is $k_0 = 2.37 \times 10^{16}$ M$^{-3}$ min$^{-1}$, or log $k_0 = 16.375$. The temperature variation of $k_0$ may be estimated from log $k_0 = 21.56 - 1.545/T$ (where T is in degrees Kelvin) [9], yielding log $k_0 = 15.90$ in air-saturated pure water at 0 °C. At -25 °C, log $k_0 = 15.33$.
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Salinity Dependence. To determine the effect of salinity on the oxidation of Fe$^{2+}$ in aqueous solutions, it is necessary to make corrections for variations of the pH and the concentration of dissolved oxygen with rising ionic strength. For example, in reference seawater with salinity, S = 35% (i.e. 3.5 wt. % dissolved salts), corresponding to the ionic strength I = 0.7 M, the concentration of dissolved oxygen at 0°C decreases to [O$_2$] = 3.58 x 10$^{-4}$ M [8] due to a salting-out effect. At 25°C, pK$_w$ = 13.62, so that seawater is acidic at pH < 6.81. At 0°C, seawater is acidic at pH < 6.82. The effect of salinity on the rate of oxidation of Fe$^{2+}$ dissolved in air-saturated seawater is expressed by [9]

$$\log k_1 = 21.56 - 1545/T + 3.29\sqrt{I} + 1.52 I.$$  
(3)

Thus, in reference seawater at 25°C, log $k_1$ is lowered to 14.69. At 0°C, log $k_1$ = 14.21. Extrapolation to -25°C, yields log $k_1$ = 13.64. The decreased rate constant in seawater results from the slower rate of oxidation of Fe$^{2+}$ ions relative to Fe$^{2+}$ ions in pure water.

Oxidation of Fe$^{2+}$ in Brines. Studies of the effects of ionic strength and ion interactions on the oxidation of Fe$^{2+}$ in brine solutions with ionic strengths as high as I = 6M [10] have yielded the following expression for the rate constant

$$\log k_2 = 21.56 - 1545/T + 0.470\sqrt{I} - 646\sqrt{I}/T + 0.723 I.$$  
(4)

Rates of oxidation of Fe$^{2+}$ ions initially decrease with increasing ionic strength [10]. However, above I = 2M, reaction rates increase; in 6 M NaCl solutions, for example, rate constants are comparable to values in pure water. In 6 M NaCl brines at 25°C and 0°C, the values of log $k_2$ are 16.55 and 15.59, respectively, leading to an estimated value of log $k_2$ = 14.63 at -25°C. The rate constants are also anion dependent; they decrease in the order HCO$_3^-$ > Br$^-$ > Cl$^-$ > NO$_3^-$ > SO$_4^{2-}$. Rates of oxidation of Fe$^{2+}$ are considerably lower in sulfate solutions than in chloride solutions, reflecting the greater stability of the FeSO$_4^{2-}$ ion-pair relative to the FeCl$^+$ ion-pair [10]. Thus, rate constants for the oxidation of Fe$^{2+}$ ions in mixed-anion Cl$^-$/SO$_4^{2-}$ brines with I = 6M are roughly half the rate constants in pure ice-water at 0°C, corresponding to log $k_B$ = 15.6. At -25°C, the estimated log $k_B$ = 15.0 for the oxidation of Fe$^{2+}$ ions in a chloride-sulfate brine with I = 6M. In this brine, the estimated concentration of dissolved oxygen is [O$_2$] = 3.5 x 10$^{-4}$ M.

Oxidation of Fe$^{2+}$ in Brines on Mars. The high concentrations of S, Cl and, perhaps, Br analysed in the martian soil by the Viking Lander XRF experiment [11] suggest that salts containing SO$_4^{2-}$, Cl$^-$ and, perhaps, Br$^-$, NO$_3^-$ and CO$_3^{2-}$ anions may exist near the surface of Mars [12]. Aqueous solutions permeating these salts may have ionic strengths exceeding 5M, based on ion concentrations estimated from the XRF analyses [12,13]. A variety of brine eutectics proposed for Mars [14,15], including the mixture of ice + MgCl$_2$.12H$_2$O + MgSO$_4$.7H$_2$O, could maintain a fluid phase at temperatures as low as -35°C [14], thereby creating an environment for the oxidation of dissolved Fe$^{2+}$ ions.

The concentration of oxygen in a brine equilibrated with the Martian atmosphere (PO$_2$ = 10$^{-5}$ bar) would be about 2 x 10$^{-4}$ smaller than that at the same temperature in an aerated brine on Earth. The rate of oxidation of dissolved Fe$^{2+}$ in an aerated brine on Mars is about 0.3 ppm Fe$^{2+}$ per year, based on trends summarized above. Assumptions made in this calculation are: (1) the existence on Mars of a 6M brine containing Cl$^+$ + SO$_4^{2-}$ anions; (2) a rate constant of log $k_B$ = 15.0 at -25°C; (3) pH = 6 and pK$_w$ = 13.5 in this brine; (4) dissolved [O$_2$] = 7 x 10$^{-8}$ M; and (5) the concentration of dissolved iron is maintained at [Fe$^{2+}$] = 10$^{-4}$ M by the solubility of siderite. Therefore, oxidation of Fe$^{2+}$ dissolved in a brine on Mars is about 10$^6$ times slower than the rate of oxidation of Fe$^{2+}$ ions dissolved in pH 8, ice-cold terrestrial seawater.