

representative samples of the crust and crystallized recently; if they are from a single impact in young lavas, they force the large crater ages downward, because they were ejected recently. In either case the cratering rate must move upward to produce the required downward shift in ages of the surface areas of interest. Finally, the very fact that recent impacts on Mars have transported comparable or even larger masses of martian material to Earth than has been transported from the Moon (the ratio of SNC to lunar meteorite recovered masses is quite large) reinforces the suggestion that the martian cratering rate must be many times lunar, though it is difficult to quantify this latter argument at this time. In any case, the simplest SNC scenario, that the SNCs were ejected by multiple events, appears only reconcilable with the NHII model or even higher cratering rate models.

Summary: Therefore, following two independent lines of evidence—estimates of the age and formation time of a portion of the martian geologic column exposed in the layered deposits and the crystallization and ejection ages of the of the SNC meteorites—it appears that the martian cratering rate must be double the lunar rate or even higher. This means models such as NHII or NHIII, which estimate the martian cratering rate as being several times lunar, are probably far closer to reality on Mars than lunar rates. The effect of such a shift is profound: Mars is transformed from a rather Moon-like place into a planet with vigorous dynamics, multiple large impacts, erosion, floods, and volcanism throughout its history.

A strong shift upward in cratering rates on Mars apparently solves some glaring problems; however, it creates others. The period of time during which Earth-like atmospheric conditions existed, the liquid water era on Mars, persists in NHIII up to only 0.5 b.y. ago. Scenarios of extended Earth-like conditions on Mars have been discounted in the past because they would have removed many of the craters from the early bombardment era found in the south. It does appear that some process of crater removal was quite vigorous in the north during Mars' past. Evidence exists that the northern plains may have been the home of long-lived seas [11] or perhaps even a paleo-ocean [12], so models exist for highly localized destruction of craters in the north. However, the question of how the ancient crater population could be preserved in the south under a long liquid-water era found in any high-cratering-rate models is a serious question that must be addressed. It does appear to be a higher-order problem because it involves low-energy dynamics acting in localized areas, i.e., erosion of craters in the south of Mars, whereas the two problems with the low-cratering-rate models involve high-energy events acting over large areas: the formation of the Vallis Marineris, the SNC ejecting impacts, and the global atmospheric pressure and temperature conditions that allow liquid water to exist as a robust entity anywhere on the martian surface.

In any case, it appears Mars is a more complex and dynamic planet than previously supposed. It has canyons dating from the middle to late period of its history that contain apparent lake sediments bedded deeper than most sediments on Earth. Recent multiple, violent impacts on Mars have apparently provided us with multiple random samples of its surface that all crystallized less than 1.5 b.y. ago. These things cannot be accommodated in our present cratering chronologies of Mars, based on 1× lunar cratering rates, without great difficulties. These difficulties suggest that a new chronology, probably based on NHII or even NHIII, should be adopted; this new chronology will provide us with a new view of Mars as a dynamic planet of rich history.

References: [1] Nédell S. S. and Squyres S W. (1986) *LPI*

Tech. Rpt. 87-01, 20–23. [2] McGetchin T. R et al. (1981) *BVSP*, 1246–1254, Pergamon. [3] Masursky H. et al. (1977) *JGR*, 82, 4016–4038. [4] Neukum G. and Greeley R. (1988) *LPS XIX*, 852–853. [5] Lucchitta B. K. (1987) *Science*, 235, 565–567. [6] Blatt H. et al. (1980) *Origin of Sedimentary Rocks*, 645, Prentice Hall. [7] *Origin of Sedimentary Rocks*, 32. [8] Bannin A. et al. (1992) in *Mars* (H. Hugh et al., eds.), 610–611, Tucson. [9] Vickery A. M. and Melosh H. J. (1987) *Science*, 237, 738–743. [10] Klause K. et al. (1992) *JGR*, 97, 10213–10225. [11] Parker T. J. et al. (1986) *LPI Tech. Rpt. 87-01*, 96–97. [12] Brandenburg J. E. (1986) *LPI Tech. Rpt. 87-01*, 20–23.

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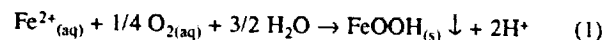
DEPOSITION RATES OF OXIDIZED IRON ON MARS.

R. G. Burns, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge MA 02139, USA.

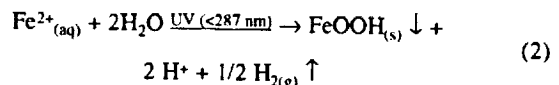
Introduction: The reddened oxidized surface of Mars is indicative of temporal interactions between the martian atmosphere and its surface. During the evolution of the martian regolith, primary ferromagnesian silicate and sulfide minerals in basaltic rocks apparently have been oxidized to secondary ferric-bearing assemblages. To evaluate how and when such oxidized deposits were formed on Mars, information about the mechanisms and rates of chemical weathering of Fe²⁺-bearing minerals has been determined [1,2]. In this paper, mechanisms and rates of deposition of ferric oxide phases on the martian surface are discussed.

Mechanisms of Oxidation of Ferrous Iron: Oxidation of Fe²⁺ ions derived from basaltic olivine, pyroxene, and sulfide minerals may have proceeded via several mechanisms. They include:

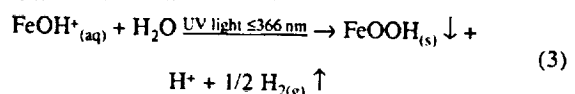
1. *Solid-state processes involving atmosphere-surface interactions that occur without the intervention of water.* However, the kinetics of such processes involving dry mineral surfaces are extremely slow, as testified by the negligible oxidation products observable in the Magellan radar images of the surface of Venus. Nevertheless, photochemical processes may have produced coatings of oxidants on outermost arid surfaces of Mars [3], which subsequently could influence redox reactions of Fe.
2. *Reactions that occur in an aqueous medium.* Such processes involving dissolved Fe include (a) oxidation of aqueous Fe²⁺ in groundwater by dissolved atmospheric O



the O being derived from photolysis of CO₂ or water vapor in the atmosphere [4]; and (b) photochemical oxidation in UV light of either Fe²⁺ ions in acidic solutions [5,6]



or FeOH⁺ complex ions in near-neutral pH or slightly alkaline solutions [4–7]



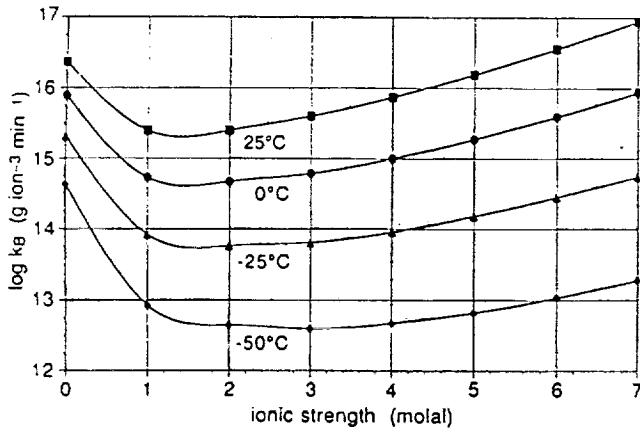


Fig. 1. Rate constants for the oxidation of dissolved Fe^{2+} ions as a function of ionic strength at different temperatures.

Note that gaseous H_2 is liberated in these photo-oxidation reactions (equations (2) and (3)), some of which could escape from the gravitational field of Mars, while O is retained by the martian regolith [8].

Before aqueous oxidation of Fe by reactions (1), (2), or (3) occurred on Mars, soluble ferrous iron had to exist in solution. These Fe^{2+} ions were produced by dissolution of silicates and sulfides that were initially present in basaltic rocks when they were exposed to permeating groundwater near the surface of Mars. Experimental data [2] show that in groundwater derived from the precipitation of acid rain ($\text{pH} \leq 4.5$), basaltic minerals and glass dissolve rapidly, yielding a steady supply of aqueous Fe^{2+} ions. In less acidic and near-neutral pH groundwater, mineral dissolution would be much slower. For example, rates of dissolution of Fe from olivine and pyroxenes range from about $1400 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$ ($\text{pH} 2$ at 25°C) to $2 \times 10^{-2} \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$ ($\text{pH} 6$ at 0°C). In acidic ice-cold saline solutions ($\text{pH} 4.5$ at 0°C), dissolution rates are about $1 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$.

Rates of Oxidation of Iron in Aerated Groundwaters:

Rates of oxidation of aqueous Fe^{2+} ions by dissolved O are strongly influenced by acidity or pH, as well as salinity or ionic strength, temperature, and the concentration of dissolved O in aerated groundwater [2]. Rates of Fe^{2+} oxidation are slowest in acidic solutions, in contrast to dissolution rates of ferromagnesian silicates, but are much higher in near-neutral pH saline groundwater and brines. The rate-constant data illustrated in Fig. 1 show that the oxidation of dissolved Fe^{2+} initially decreases with rising ionic strength, but increases significantly in brine solutions. Figure 2 shows rates of oxidation of aqueous Fe^{2+} in saline groundwaters saturated by atmospheric O corresponding to the present-day martian atmosphere ($P_{\text{O}_2} = 10^{-5}$ bar) for a variety of temperatures and ionic strengths [2]. Rates of oxidation of dissolved Fe^{2+} in pH 6 groundwater range from about 500 to $1000 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$ in ice-cold saline solutions to about $100 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$ in low-temperature brine solutions. Such relatively low rates of oxidation of dissolved Fe on Mars contrast with the very high values for terrestrial rivers ($1.8 \times 10^7 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$ at pH 6 and 25°C) and for oxygenated deep ocean bottomwaters ($5 \times 10^6 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$ at pH 8.2 and 2°C). Thus, oxidation rates in slightly acidic brines that may currently

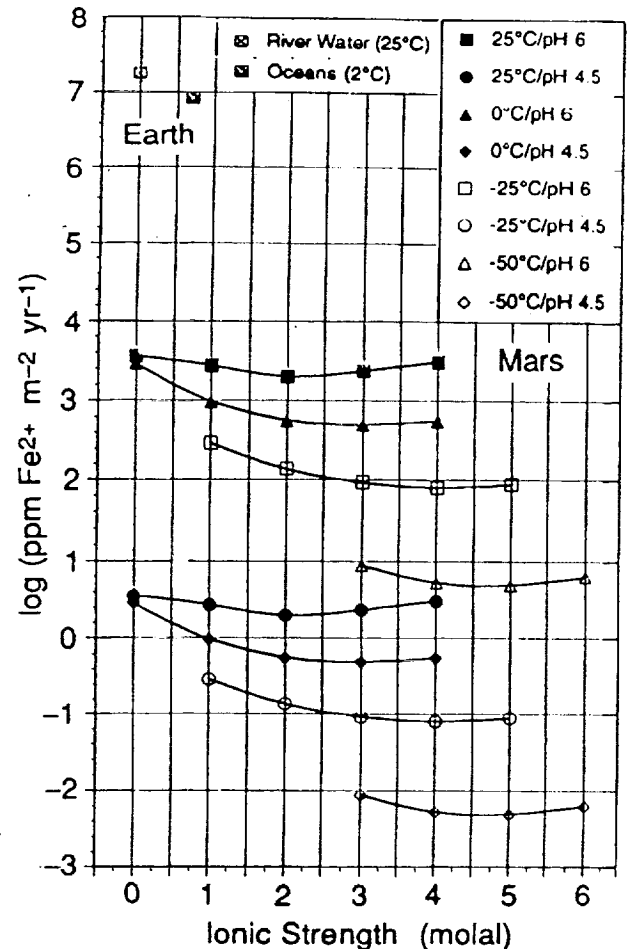


Fig. 2. Rates of oxidation of aqueous Fe^{2+} by dissolved atmospheric O as a function of ionic strength at different temperatures on Mars. Values for Fe^{2+} oxidation in terrestrial river water and oceans are also shown.

exist near the martian surface are about 10^5 times slower than those in the terrestrial hydrosphere. However, in summertime meltwaters in equatorial regions of Mars, rates of Fe^{2+} oxidation could be as high as $3000 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$.

From a global viewpoint, the depth of weathering of surface basalts on Mars during dissolution and aqueous oxidation of Fe^{2+} -bearing minerals may be estimated as follows. Shergottites contain about 19 wt% FeO, or $3 \times 10^{10} \text{ ppm Fe m}^{-3}$. Rates of oxidation of Fe^{2+} corresponding to $500\text{--}1000 \text{ ppm m}^{-2} \text{ yr}^{-1}$ indicate that weathering rates of shergottitic basalts on Mars were about 15–30 m b.y.⁻¹ when water flowed near the surface of the planet.

Deposition Rates in Aerated Water Basins on Mars: The annual deposition of hydrous ferric oxides in ocean basins on Mars may be calculated as follows. Oceanus Borealis is believed to have filled the northern plains of Mars episodically, covering an estimated area of $4 \times 10^7 \text{ km}^2$ with an average depth of 1.7 km [9]. Assuming a rate of oxidation of aqueous Fe^{2+} in a cold, slightly acidic ocean to be in the range $500\text{--}1000 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$ (Fig. 2), the annual deposition of hydrous ferric oxides would have been $\sim 2\text{--}4 \times 10^{13}$

g.Fe yr⁻¹ in Oceanus Borealis. This quantity of Fe is comparable to the estimated deposition rate (2.25×10^{13} g.Fe yr⁻¹) in a typical Precambrian Fe formation on Earth [10]. The surges of water that periodically inundated the martian northern lowland plains in the past were probably initiated by increased volcanic activity that melted frozen regolith [9]. Such volcanism would also have provided fresh sources of basaltic glass and ferromagnesian silicate minerals that underwent submarine chemical weathering, thereby replenishing the supply of dissolved Fe²⁺ ions to be oxidized near the surface of intermittent martian oceans.

In addition to the circumpolar body of water in the northern hemisphere, other semipermanent locations of deep-water stratification may have provided sites for the deposition of hydrous ferric oxides on Mars. These include numerous impact basins (e.g., Hellas and Argyre) and several closed depressions in the Valles Marineris system [11]. The bright deposits littering the Argyre and Hellas Basins may comprise wind-blown dust derived from desiccated hydrous iron oxide-silica deposits that remained there after water had evaporated from these deep depressions.

Deposition Rates in UV Irradiated Surface Water: As indicated by equations (2) and (3), oxidation of aqueous ferrous iron to hydrous ferric oxides does not require dissolved atmospheric O. Dissolved ferrous iron may also be oxidized photochemically by solar UV radiation. In dilute, near-neutral pH solutions, rates of photo-oxidation of dissolved ferrous iron are increased by the presence of the complex FeOH⁺ ion, which is sensitive to wavelengths in the 300–400-nm region [4,6]. Calculations of oxidation rates by solar UV have been made for the early Earth. In areas of vigorous upwelling in ocean basins containing 0.5–5.5 ppm total dissolved Fe, photo-oxidation could have precipitated hydrous ferric oxides at rates of $1-2 \times 10^6$ ppm Fe m⁻² yr⁻¹ [4,7,12], allowing for 50% loss of UV radiation through scattering and absorption by clouds and based on the present-day solar flux [4].

On early Mars, similar processes of photo-oxidation of dissolved Fe in surfacewaters could also have occurred, leading to the aqueous deposition of hydrous ferric oxide phases that have now been desiccated to nanophase hematite. However, since Mars is further away from the Sun than Earth, the lower solar UV flux incident on the martian surface would have induced slower deposition rates of the ferric oxides, perhaps smaller than 10^4 ppm Fe m⁻² yr⁻¹.

Ferric Oxide Deposition on Present-Day Mars: Since frozen regolith currently prevents upwelling of Fe²⁺-enriched subsurface aquifers, oxidation of aqueous Fe²⁺ by atmospheric O and solar UV radiation cannot occur, so dissolved Fe²⁺ ions may now persist beneath the martian surface. However, sublimation of permafrost and evaporation of daytime equatorial meltwaters exposed to the martian atmosphere would cause localized oxidation of dissolved ferrous iron, hydrolysis of Fe³⁺ ions, and flocculation of colloidal ferric-bearing clay silicate, oxide, and hydroxysulfate assemblages at freshly exposed surfaces on the planet. Such nanophase materials may constitute the particulate matter in local and global dust storms. During eolian transport, any unoxidized ferrous salts liberated from sublimed permafrost would be oxidized completely by exposure to atmospheric O, while desiccation of ferric hydrolysis products to Fe₂O₃ phases would be facilitated. Therefore, most of the nanophase hematite littering the martian surface is the ultimate oxidation product of dissolved Fe²⁺ ions that were derived from chemical weathering of basaltic ferromagnesian silicate minerals.

On the present-day arid martian surface, traces of O, OH, and

HO₂ radicals formed by the photolysis of H₂O vapor in the atmosphere may have yielded low concentrations of H peroxide on the martian surface [13]. Experimental studies have demonstrated that rates of oxidation of dissolved Fe²⁺ by H₂O₂ are considerably higher than reactions involving atmospheric O [14,15]. Any Fe-bearing solutions percolating to the surface of Mars or resulting from melting of frost condensates would be immediately oxidized to ferric-bearing assemblages. Thus, thin veneers of ferric oxides may be continuously forming on the outermost arid surface of Mars.

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References: [1] Burns R. G. (1993) *JGR*, 98, 3365–3372. [2] Burns R. G. (1993) *GCA*, 57, in press. [3] Zent A. P. and McKay C. P. (1992) *LPI Tech. Rpt. 92-04*, 41–42. [4] Braterman P. S. and Cairns-Smith A. G. (1987) in *Precambrian Iron-Formations* (P. W. A. Appel and G. I. LaBerge, eds.), 215–242. [5] Cairns-Smith A. G. (1978) *Nature*, 276, 807–808. [6] Braterman P. S. et al. (1983) *Nature*, 303, 163–164. [7] Francois L. M. (1987) *Paleoceanog.*, 2, 395–408. [8] McElroy M. B. and Kong T.-Y. (1976) *GRL*, 3, 569–572. [9] Baker V. R. et al. (1991) *Nature*, 352, 589–594; *Nature*, 354, 86–87. [10] Trendall A. F. (1973) *Econ. Geol.*, 68, 1023–1034. [11] Spencer J. R. and Fanale F. P. (1990) *JGR*, 95, 14301–14313. [12] Anbar A. D. and Holland H. D. (1992) *GCA*, 56, 2595–2603. [13] Barth C. A. et al. (1992) in *Mars* (H. H. Kieffer et al., eds.), 1054–1089, Univ. of Arizona, Tucson. [14] Millero F. J. and Sotolongo S. (1989) *GCA*, 53, 1867–1873. [15] Millero F. J. et al. (1991) *J. Soln. Chem.*, 20, 1079–1097

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MARSNET: A EUROPEAN NETWORK OF STATIONS ON THE SURFACE OF MARS. A. F. Chicarro, Space Science Department, ESA/ESTEC, 2200 AG Noordwijk, The Netherlands.

Introduction: Following an ESA preliminary study on the possible areas of European participation in the future international exploration of Mars [1] and an ESA call for ideas of new missions, MARSNET, a network of small surface stations, was selected for further in-depth scientific and technical assessment studies [2] as a potential European contribution to such exploration. Subsequently, the MARSNET phase A studies started in the autumn of 1991. The industrial kickoff took place in early January 1992, following the tender evaluation and the decision to select the Aérospatiale-led consortium including Dornier, Alcatel, Laben, and Etca to perform the industrial studies. The phase A studies ended in early 1993 [3]. However, critical items such as an instrument deployment device continue to be studied in the framework of ESA's Technology Research Program.

The MARSNET mission consists of a network of three semihard landers to be placed on the martian surface, several thousand kilometers apart, thus defining a regional/global seismological and meteorological network in the Tharsis region. The small stations would be targeted for landing at scientifically interesting sites in this region of Mars, which is the most likely area to still show tectonic activity; this will allow the seismometers to acquire data for the determination of the internal structure of the planet. Landing site geology and geochemistry will also be studied.

Network Concept: Following early global survey missions such as Mariner 9 and Viking, and ongoing orbital and *in situ* missions like Mars Observer and Mars '94, focusing on the atmosphere