

ULTRAVIOLET RADIATION-INDUCED ALTERATION OF MARTIAN SURFACE MATERIALS.

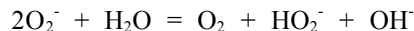
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Introduction: The nature and origin of martian surface materials cannot be fully characterized without addressing the unusual reactivity of the soil and, as pointed out in [1], the effects of exposure to the unique martian environment. Our laboratory experiments show that ultraviolet radiation at the martian surface can result in the oxidation of metal atoms and the creation of reactive oxygen species on grain surfaces. This process is important in understanding the nature and evolution of martian soils: It can explain the reactivity discovered by the Viking Landers and possibly the origin of the ferric component of the soil.

Soil reactivity: Viking results: The Viking Landers discovered that humidification of the martian soil releases oxygen [2], that ¹⁴C-labeled nutrient solutions are decomposed when exposed to soil samples [3], and that the surface is devoid of organic molecules above several parts-per-billion (and for simpler molecules, several parts-per-million) [4]. The interpretation of these results indicates that the martian soil contains one or more reactive superoxides [5]. These oxidants are incompatible with organic molecules and have likely resulted in the destruction of the primitive and meteoritic organic compounds at the martian surface. However, none of the current models describing the composition of the reactive components of the soil are completely satisfactory either because of instability in the martian environment or the need for an unlikely formation mechanism [6].

Experiments: Here, we pursue an explanation of the soil reactivity based simply upon ultraviolet irradiation in the presence of oxygen at low water vapor pressures (frostpoint less than -60° C). There is an extensive literature on the formation, characterization, stability, and reactivity of oxygen radicals on material surfaces [e.g., 7]. In our experiments, we show that these reactive oxygen species can also be formed on mineral grains under martian conditions. Natural quartz samples were crushed, dried, and sealed in 4 mm diameter tubes with 10⁻² torr of CO₂, O₂, and N₂ gas mixtures. These samples were subsequently exposed to ultraviolet photons from a mercury vapor lamp (peak flux at 254 nm) for approximately 20 hours at a temperature of -30° C. X-band electron paramagnetic resonance (EPR) spectra show the formation of oxygen radicals dominated by O₂⁻ on the irradiated samples (figure 1). These O₂⁻ superoxide ions adsorbed on grains can be stable at room temperature for several months [7] and have even longer lifetimes at lower temperatures such as those at the surface of Mars.

Chemistry: O₂⁻ is known to react with water molecules through the following pathway [8]:



HO₂⁻ and OH⁻ produced in these reactions are easily capable of oxidizing organic molecules. Thus, chemical reactions based on surface adsorbed superoxide ions may be the most straightforward explanation of the Viking Lander results regarding the reactivity of the soil and the apparent absence of organic molecules. As discussed below, the process of forming surface adsorbed O₂⁻ species may also be related to the oxidized state of the soil.

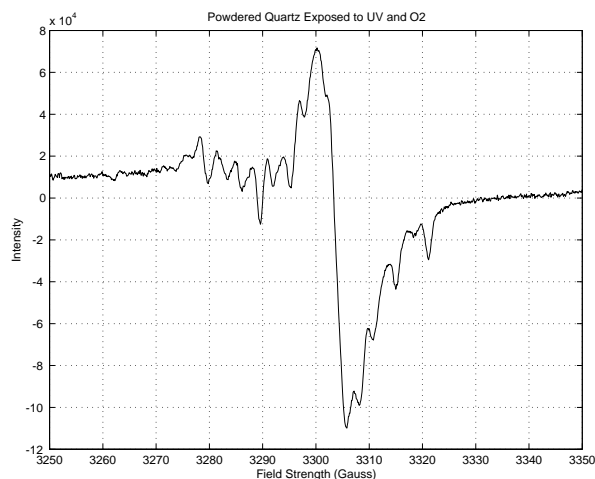


Figure 1: X-band EPR spectrum of a powdered quartz sample exposed to ultraviolet photons under a CO₂, O₂, and N₂ gas mixture. The signal is consistent with O₂⁻ superoxide ions on the sample surfaces. Spectra collected prior to UV irradiation show no measurable signal.

UV-Induced Oxidation: Ferric iron: The conventional explanation for the color of the martian soil involves the dissolution of ferrous minerals in liquid water, aqueous oxidation, and precipitation of iron oxyhydroxides [e.g., 9]. The apparent absence of extensive carbonate deposits, crystalline clay minerals [10], and a mechanism for removing bound hydrogen from minerals such as FeOOH to form oxides at the martian surface [11] suggest that an alternative explanation to aqueous oxidation is warranted for the origin of the soils. Here we show that the mobilization of elec-

trons by ultraviolet radiation in the formation of the oxygen radical species described above can also result in the formation of ferric iron minerals.

Experiments: We use electron-beam sputtering to deposit approximately 100 Å of iron between two gold contacts separated by a distance of 10 mm on fused silica substrates. Metallic thin films are good conductors when unoxidized and rapidly increase in resistance as oxide growth reduces the conductive cross section. We exposed these thin films to a mercury vapor line source under ultrahigh purity nitrogen to show that exposure to ultraviolet radiation increases the rate of oxide formation (figure 2). Additional experiments were conducted to verify that heating of the sample by the ultraviolet lamp and temperature-induced oxidation effects are negligible. Analyses by FTIR and XRD of the oxides formed by UV irradiation of metallic iron show that both hematite and maghemite are formed.

Interpretation: This demonstration of UV-stimulated oxidation of metal films indicates that metallic iron introduced to the martian surface by meteoritic infall can be oxidized under current martian conditions to produce the γ - and α - Fe_2O_3 phases that are believed to be responsible for the color of the soil [12,13]. Furthermore, the ability to mobilize electrons in non-metals and to capture them at grain surfaces as O_2^- suggests the possibility that oxidation of cations in minerals may also occur under present martian conditions.

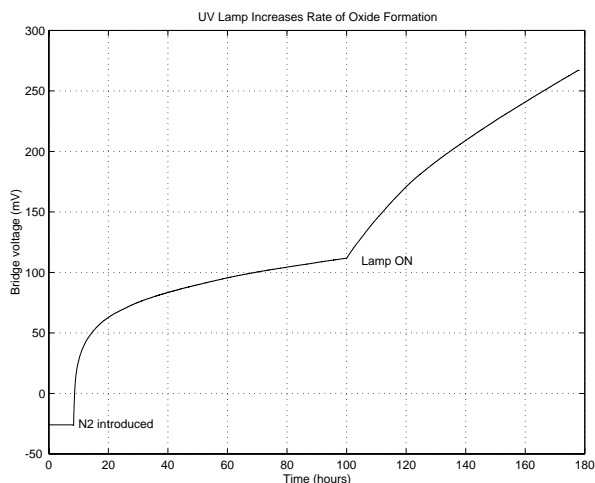


Figure 2: Bridge voltage measured across a 100 Å thick film of metallic iron: Higher voltage represents higher film resistance. The introduction of PPM-level impurities (oxygen and water vapor) associated with the nitrogen purge begins the oxidation of the film. The rate of oxidation is significantly enhanced by exposure to ultraviolet radiation.

Conclusions: The reactivity and evolution of martian surface materials is likely connected with the ultraviolet radiation reaching the soil. These wavelengths can mobilize electrons in natural mineral samples, and, in the presence of oxygen, electrons are captured at the grain surfaces forming superoxide radicals. This process can explain the reactive nature of the soil and the absence of organic compounds. The ultraviolet radiation can also oxidize metallic iron to form hematite and maghemite, likely pigmenting agents in the martian soil.

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References: [1] Bell, J. F. III (1999), *Int'l Mars Conf.*, #6017. [2] Oyama, V. I. and B. J. Berdahl (1977), *JGR*, 82, 4669-4676. [3] Levin, G. V. and P. A. Straat (1977), *JGR*, 82, 4663-4668. [4] Biemann, K. et al. (1977), *JGR*, 82, 4641-4658. [5] Klein, H. P. (1978), *Icarus*, 34, 666-674. [6] Zent, A. P. and C. P. McKay (1994), *Icarus*, 108, 146-157. [7] Che, M. and A. J. Tench (1983), *Adv. Catalysis*, 32, 1-148. [8] Cotton, F. A. and G. Wilkinson (1988), *Advanced Inorganic Chemistry*, John Wiley & Sons, Inc. [9] Burns, R. G. (1993), *Geochim. et Cosmochim. Acta*, 57, 4555-4574. [10] Banin, A. (1996), *Adv. Space Res.*, 18, 233-240. [11] Yen, A. S. et al., *JGR*, (submitted). [12] Morris, R. V. et al. (1993), *Geochim. et Cosmochim. Acta*, 57, 4597-4609. [13] Hviid, S. F. et al. (1997), *Science*, 278, 1768-1770.