

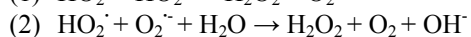
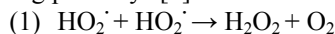
A REAPPRAISAL OF ADSORBED SUPEROXIDE ION AS THE CAUSE BEHIND THE REACTIVITY OF THE MARTIAN SOILS. J. A. Hurowitz¹, N. J. Tosca, S. M. McLennan, D. H. Lindsley, M. A. A. Schoonen.

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Introduction: It has been suggested that oxygen release from the Martian soils, detected during the Viking Gas Exchange (GEX) soil humidification and wetting experiments [1], can be attributed to reactions between water and superoxide (O_2^-) radicals adsorbed on mineral surfaces [2]. A number of chemical compounds which could be responsible for the unusual reactivity of the Martian soils have been proposed [3], however the mechanism of Yen et al. [2] is particularly appealing given its simple requirements of “ultraviolet (UV) photons, atmospheric oxygen, mineral grain surfaces, and extremely low concentrations of water vapor”, all of which are present at the Martian surface. Although experimental work relevant to the presence of adsorbed superoxides in the Martian soils has been performed [2, 4], it is unclear whether the conditions of these experiments are applicable to the Martian surface environment. We have therefore performed a number of additional experiments to test the “superoxide mechanism” under conditions relevant to Mars.

The “Superoxide Mechanism”: Using electron paramagnetic resonance spectroscopy, Yen et al. [2] demonstrated that exposure of ground natural labradorite (an important mineral constituent of basalt) to ultraviolet radiation in the presence of oxygen gas resulted in the formation of adsorbed superoxide radicals at the labradorite surface.

Upon contact with water vapor or liquid water, superoxide may desorb from the mineral surface to form aqueous superoxide/perhydroxyl radicals (O_2^-/HO_2^\cdot ; $pK_a=4.8$) which spontaneously disproportionate to form hydrogen peroxide, hydroxide and oxygen via the following pathways [5]:



The critical product in these reactions is O_2 , which may potentially explain the oxygen release from the Viking soils if, in fact, adsorbed superoxide is the causative agent of the observed reactivity. In their experiments, Yen et al. [2] formed enough superoxide to account for the highest measured oxygen release (790 nanomoles O_2) from the Viking Lander (VL) GEX experiments.

Dehydroxylated Mineral Surfaces: Labradorite is an insulating mineral phase (band gap >5 eV), and therefore does not normally exhibit photochemical reactivity. The key factor in the reactive, semiconductor-like behavior of an insulator is the presence of a dehydroxylated mineral surface [6]. Such surfaces are dominated by oxygen

atoms in a low coordination state [6, 7] which are most likely responsible for the photochemical reactivity observed by Yen et al. [2]. Hydroxylated and dehydroxylated silica surfaces are compared in Fig. 1.

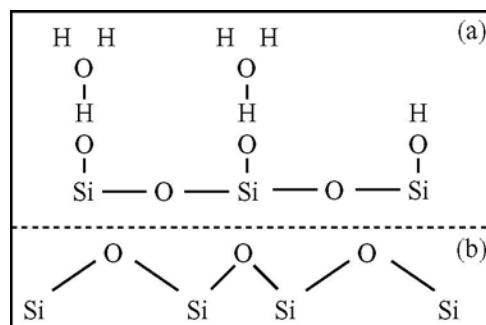


Figure 1: (a) Hydroxylated silica surface with adsorbed water on Si-OH (silanol) groups. (b) Dehydroxylated silica surface composed of Si-O (siloxane) groups. After Lasaga [8].

Under laboratory conditions, formation of dehydroxylated silicate surfaces requires heat treatment; with temperatures of 120-350°C producing a reversible, partially dehydroxylated surface, and temperatures $>350^\circ\text{C}$ producing an irreversible, fully dehydroxylated surface [9, 10]. Given these requirements, the critical question with regards to the “superoxide mechanism” becomes: Is it reasonable to expect silicate surfaces to be dehydroxylated under conditions approaching those at the Martian surface ($T \leq 25^\circ\text{C}$, $P \approx 6$ mbar)?

Experimental Protocol: Natural labradorite was ground in an agate mill to $<75\mu\text{m}$ particle size and surface area measured by BET N_2 (0.57 ± 0.02 m²/g). Four silica glass sample chambers were each loaded with ~ 425 mg of labradorite powder and placed under vacuum using a pump with a base pressure of 10 mbar. The sample chambers were then purged with 1 bar of a custom gas mixture having the composition of the Martian atmosphere. The pump/purge cycle was repeated 3x, followed by a final pumping to base pressure.

In Experiment 1 the chamber was maintained at room temperature for 30 minutes under vacuum, and then sealed. Expt.’s 2A and 2B were heated to 225°C , and Expt. 3 to 800°C , each for a period of 30 minutes under vacuum. After heating, Expt. 2A was cooled to room temperature, allowed to stand for 120 minutes under vacuum and then sealed. Expt.’s 2B and 3 were sealed immediately after heating.

The sealed sample chambers were then exposed to a 450 watt Hg-vapor UV lamp for a period of 20 hours. Following UV exposure, the sample chamber inlets were submerged in glass vials containing 5 ml of deionized water and opened, thereby immediately exposing the UV-treated labradorite to DI water. The solutions were decanted from the sample chambers, filtered, and analyzed for H₂O₂ using a method modified after that of Holm et al. [11]. A minimum detection limit of 4 nanomoles H₂O₂ liter⁻¹ (nM) was determined for the method, and a full process blank was performed on the reagents. A control (C1) was performed on untreated (no exposure to vacuum, heat, or UV radiation) labradorite powder by suspending the powder in DI water, and then analyzing for H₂O₂ using the methods described above.

Results: Oxygen release from the UV-treated samples was measured indirectly assuming that for every mol of H₂O₂ formed, 1 mol of O₂ was formed (see discussion above). The results of H₂O₂ analysis are shown in Table 1. For Expt.'s 1 and 2A, the amount of H₂O₂ released is equivalent to that of the control (C1). No H₂O₂ was detected in the blank, so contamination from the reagents cannot explain the H₂O₂ release. As a further control test (C2), untreated labradorite powder was sonicated in DI water, dried at 80°C, and then analyzed for H₂O₂ release using the methods described for C1. No H₂O₂ was detected in C2, indicating that the H₂O₂ detected in Expt.'s 1, 2A, and C1 was formed by a reaction occurring during the initial contact between DI water and ground labradorite.

Expt	Heat Treatment (°C)	H ₂ O ₂ (nM)	O ₂ /m ² (nmoles/m ²)
1	RT	42 ± 8	ND
2A	225, 120 min @ RT	40 ± 8	ND
2B	225	62 ± 12	0.5 ± 0.1
3	800	273 ± 55	4.7 ± 0.9
C1	Untreated	40 ± 8	---
C2	Untreated/DI rinsed	ND	---
VL-1 "SF" (nanomoles O ₂)		790	32
VL-2 "UNR" (nanomoles O ₂)		70	3

Table 1: Nanomoles O₂ released per m² from experiments and range in O₂/m² from VL-1 and VL-2 soils. Viking data from [1, 4]; SF is Sandy Flats humid mode data; UNR is Under Notched Rock wet mode data. RT: room temperature. ND: non-detect. Untreated: no exposure to vacuum, heat, UV.

The mechanism by which H₂O₂ was produced in Expt.'s 1, 2A, and C1 is unclear, but it does not appear to be the result of exposure to UV photons (i.e., not the result of desorption and disproportionation of UV-generated superoxide), so it is unknown whether H₂O₂ formation is accompanied by O₂ release. Expt.'s 1 and 2A are therefore treated as "non-detects" for comparison to Viking data.

For Expt.'s 2B and 3, H₂O₂ release amounted to 62 (±12) and 273 (±55) nM, respectively. Expressed as O₂ equivalent (accounting for non-UV generated H₂O₂) and normalized to surface area, the O₂ releases are 0.5 (±0.1) and 4.7 (±0.9) nmoles O₂/m², respectively. For Expt. 3, this value is greater than the amount released by one of the VL-2 soils (Table 1). The approximate amount of O₂ in each sample chamber was 2-3 nmoles, indicating that in Expt. 3 all of the O₂ gas was probably adsorbed by the labradorite during UV exposure (2O₂ (g) + hv → 2O₂⁻ (adsorbed) → H₂O₂ + O₂).

Discussion: Fully dehydroxylated labradorite (Expt. 3) produced by heat treatment to T >350°C is a highly effective O₂ scavenger in the presence of UV radiation, and is capable of producing enough O₂ upon wetting to explain the VL-2 "Under Notched Rock" O₂ release under the experimental conditions of this study. In an open system environment with an unlimited O₂ supply (e.g., the Martian surface), fully dehydroxylated labradorite might adsorb enough O₂ to explain the higher O₂ release concentrations detected by Viking.

Partially dehydroxylated labradorite (Expt. 2B) produced by heat treatment to 225°C is also capable of scavenging O₂ in the presence of UV radiation, although not enough O₂ was scavenged under our experimental conditions to explain the Viking results. Expt. 2A indicates that under Martian atmospheric conditions rehydroxylation after heating to 225°C is rapid (<120 min.), resulting in photochemical deactivation. Samples receiving no heat treatment (Expt. 1) do not scavenge O₂ in the presence of UV radiation.

We conclude that, for soils at ambient surface conditions on Mars, it is unlikely that mineral surfaces would be dehydroxylated, and are therefore incapable of reacting photochemically to produce adsorbed superoxide. Furthermore, unless the Viking soils had overlain a surface heated to >350°C (possibly in a region of volcanic or impact activity), adsorbed superoxides do not appear to provide a viable explanation for their reactivity.

References: [1] Oyama, V. & B. Berdahl (1977) *JGR*, 82, 4669-4676. [2] Yen, A., et al. (2000) *Science*, 289, 1909-1912. [3] Zent, A. & C. McKay (1994) *Icarus*, 108, 146-157. [4] Ballou, E., et al. (1978) *Nature*, 271, 644-645. [5] Bielski, B. & D. Cabelli (1991) *Int. J. Rad. Bio.*, 59, 291-319. [6] Howe, R. and W. Timmer (1986) *J. Chem. Phys.*, 85, 6129-6134. [7] Waite, T. (1990) in *Rev. Min.*, 23, 559-603, MSA. [8] Lasaga, A. (1990) in *Rev. Min.*, 23, 17-85, MSA. [9] Parks, G. (1990) in *Rev. Min.*, 23, 133-175, MSA. [10] D'Souza, A. & C. Pantano (2002) *J. Amer. Ceram. Soc.*, 85, 1499-1504. [11] Holm, T., et al. (1987) *Anal. Chem.*, 59, 582-586.