

EXPERIMENTAL CONSTRAINTS ON OXYGEN GAS RELEASE AND MOBILITY OF ADSORBED SUPEROXIDE IN MARTIAN SOILS. J. A. Hurowitz¹, A. S. Yen¹, and S. Kim¹, ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, joel.a.hurowitz@jpl.nasa.gov.

Introduction: The biology experiments onboard the 1976 Viking Landers determined that the Martian soils at Chryse and Utopia Planitia contain an unknown chemical compound of a highly oxidizing nature [1]. The GEx experiments demonstrated that the humidification of a 1cm³ Martian soil sample resulted in the production of as much as 790 nanomoles of O₂ gas [2]. The Martian soil oxidant was shown to exist in samples obtained from the surface, and in the case of the sample “Under Notched Rock” collected by Viking Lander 2, at a sampling depth of approximately 10 cm beneath a rock [2]. Explanations for the reactivity of Martian soils have called on a variety of chemical compounds and formation mechanisms [e.g., 3-6].

Yen et al. [7] have provided experimental evidence that superoxide radicals (O₂^{•-}) can be generated on plagioclase feldspar (labradorite) grain surfaces by exposure to ultraviolet (UV) light in the presence of O₂ gas. Adsorbed superoxide radicals are thought to react readily with H₂O vapor, and produce O₂ gas in quantities sufficient to explain the Viking GEx results via the following reaction:



Direct evidence for the formation of O₂ gas, however, was not provided in these experiments. In addition, since the production of superoxide radical requires exposure to UV light, this mechanism must occur at the surface, where soil materials can be exposed to the ambient Martian UV flux. Thus, superoxide ions must be mobile in order to explain the oxidizing characteristics of soils collected from the subsurface by Viking Lander 2. Experimental work indicates that superoxide ions are mobile over centimeter-scale distances on geologically short timescales [see references in 7]; however, these results have not been validated under Martian conditions.

Accordingly, the motivation of this study is to (1) demonstrate that superoxide radicals adsorbed on labradorite surfaces are capable of producing O₂ gas upon exposure to H₂O vapor, and (2) demonstrate that superoxide radicals adsorbed on labradorite surfaces are mobile under conditions relevant to the Martian near surface environment.

Experimental Design and Expected Outcome: Samples of high-purity labradorite have been obtained from Ward’s Natural Science and analyzed by X-Ray diffraction and electron microprobe to confirm their purity. The labradorite samples have been ground in an agate disk mill and the surface area of the resulting

powder measured by the BET N₂ technique using a Micromeritics ASAP 2010 surface area analyzer. The grain size produced by milling is approximately 0.5 μm to 350 μm, as determined by visual inspection of mineral powders using a Scanning Electron Microscope. This is considered a reasonable size range relative to Martian soils which exhibit a weighted mean grain size of ~1.5 μm for windblown dust [8], up to 1-2 mm for the largest soil grains examined by the Microscopic Imager onboard the Mars Exploration Rover Spirit [9].

(1) *O₂ Production:* In order to evaluate the O₂ gas producing capability of UV-treated labradorite, experiments will be performed utilizing the apparatus shown in Figure 1. Experiments will be conducted by placing an aliquot of powdered labradorite onto the stand inside the sample chamber (Fig. 1) and pumping the chamber down to a base pressure of approximately 1 mbar. After base pressure is achieved, the O₂ gas content of the sample chamber atmosphere will be continuously monitored utilizing a quadrupole mass spectrometer (QMS). Gas from the sample chamber will be admitted into the QMS via the high-precision leak valve situated between the sample chamber and the QMS.

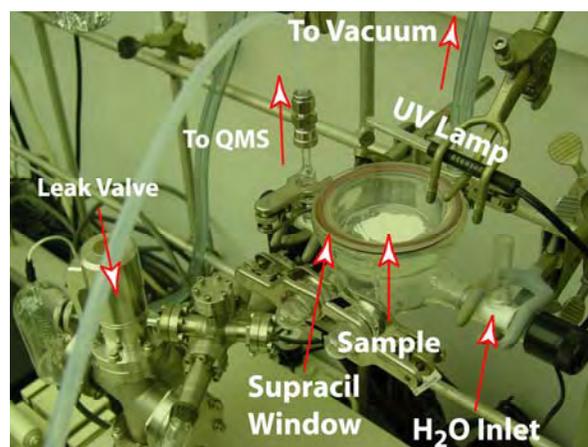


Figure 1: Labeled photograph of O₂ release experimental apparatus.

The labradorite sample will be exposed to a UV-light source (peak flux 254nm) through the Supracil window for a period of approximately 20 hours. Over this time period, it is expected that the monitored O₂ content of the sample chamber atmosphere will decrease as O₂ gas is adsorbed (as superoxide) onto the

labradorite grain surfaces. Following UV exposure, a small quantity of liquid H₂O will be admitted into the sample chamber and allowed to evaporate beneath the sample stand. It is expected that the O₂ content of the sample chamber atmosphere will then recover to pre-UV exposure levels via reaction (1) as the adsorbed superoxide is exposed the H₂O vapor in the sample chamber.

(2) *Superoxide Mobility*: The mobility of superoxide ions adsorbed on labradorite surfaces will be evaluated utilizing the apparatus shown in Figure 2. In these experiments, one aliquot of labradorite will be placed into the horizontally-mounted Supracil Electron Paramagnetic Resonance (EPR) sample tube, and a second aliquot will be placed into the vertically-mounted EPR sample tube (Fig. 2). The entire apparatus will then be pumped down to a base pressure of approximately 1 mbar. After pumping to base pressure, the sample contained in the horizontally-mounted sample tube will be exposed to UV-light for a period of approximately 20 hours. Following UV-exposure, the experimental apparatus will be sealed using the stopcock valve, and the UV-exposed labradorite will be transferred into the sample chamber containing non-UV exposed labradorite. This will be accomplished by tilting the experimental apparatus over and allowing the sample to spill into the vertical tube.

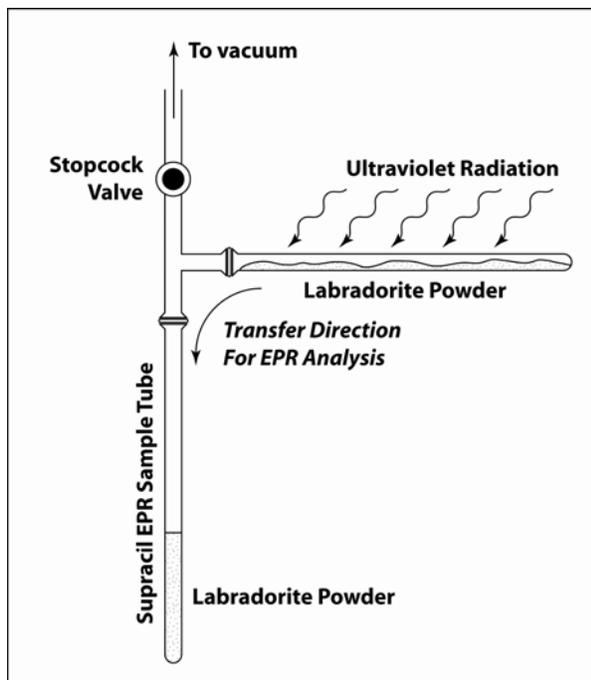


Figure 2: Labeled illustration of superoxide mobility experimental apparatus.

The EPR tube containing both samples will then be placed into the sample cavity of an EPR spectrometer, which is sensitive to unpaired electrons such as those possessed by superoxide radicals. By periodically analyzing the strength of the superoxide EPR signal at various depths in the sample tube we expect to see the migration of superoxide over time from the upper portion of the sample tube (containing UV-exposed labradorite) into the lower portion of the sample tube (containing non-UV exposed labradorite).

Initial Results: At present, we have conducted two trial O₂ release tests (experimental design #1), the results of which are shown in Figure 3. As indicated, the QMS coupled to the experimental chamber via the high precision leak valve (Fig. 1) is sensitive to small changes ($<2 \times 10^{-9}$ torr) in O₂ partial pressure caused by activation and deactivation of the UV light source. Interestingly, activation of the UV light source appears to result in an increase in O₂ partial pressure, perhaps due to an as yet unexplained reaction occurring at the surface of the labradorite particles. Ongoing work will focus on isolating the variables that may be exerting a controlling influence on the UV-induced change in O₂ partial pressure.

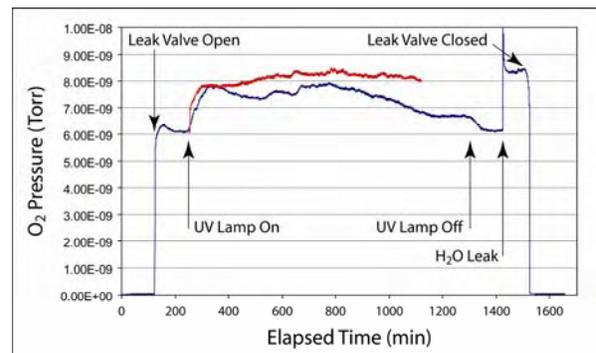


Figure 3: O₂ pressure plotted against elapsed time for two trial O₂ release tests.

References: [1] H.P. Klein, (1977) *JGR*, 82, 4677-4680. [2] V.I. Oyama and B.J. Berdahl, (1977) *JGR*, 82, 4669-4676. [3] G.T. Delory, et al., (2006) *Astro-bio.*, 6, 451-462. [4] R.C. Quinn, et al., (2005) *Planet. Space Sci.*, 53, 1376-1388. [5] A.P. Zent and C.P. McKay, (1994) *Icarus*, 108, 146-157. [6] J.A. Hurowitz, et al., (in press) *EPSL*. [7] A.S. Yen, et al., (2000) *Science*, 289, 1909-1912. [8] M.T. Lemmon, et al. (2004) *Science*, 306, 1753-1756. [9] K.E. Herkenhoff, et al. (2004) *Science*, 306, 824-826.