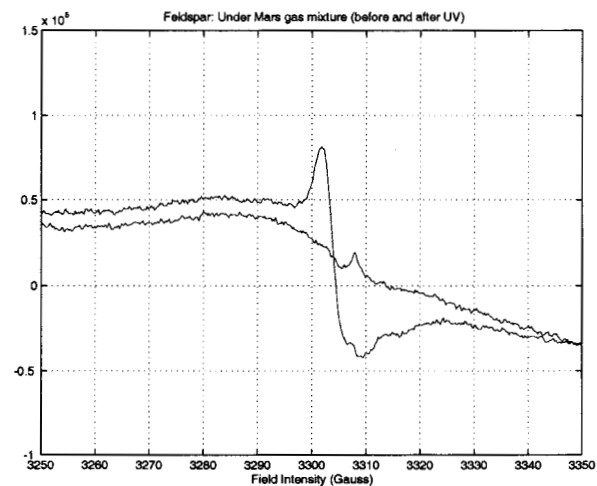


**FORMATION OF ADSORBED OXYGEN RADICALS ON MINERALS AT THE MARTIAN SURFACE AND THE DECOMPOSITION OF ORGANIC MOLECULES.** A. S. Yen<sup>1</sup>, S. S. Kim<sup>1</sup>, B. A. Freeman<sup>2</sup>, and M. H. Hecht<sup>1</sup>, <sup>1</sup>Jet Propulsion Laboratory, <sup>2</sup>University of Alabama at Birmingham.

**Introduction:** The Viking Lander missions to Mars were unable to detect organic molecules at the martian surface [1]. Here we present work which shows that superoxide radicals form on mineral grain surfaces upon exposure to a simulated martian environment and suggest that these species actively decompose organic structures. This result not only provides an explanation for the apparent absence of organic species at the martian surface, but can also account for the unusual reactivity of the soil.

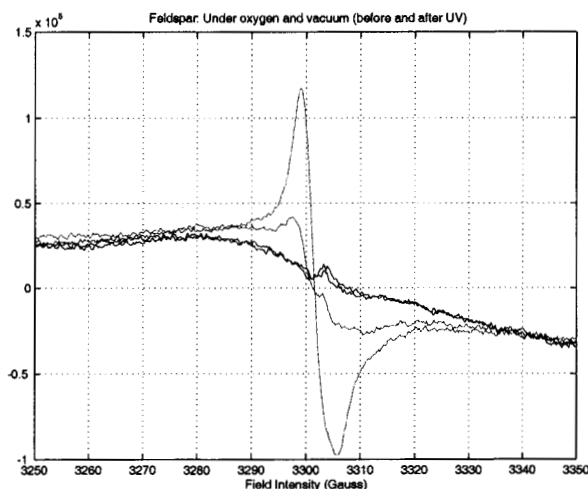
**Ultraviolet radiation effects:** Our recent laboratory experiments show that samples of plagioclase feldspar, a major component of basalt, exhibit electron paramagnetic resonance (EPR) spectra consistent with surface-adsorbed superoxide anion radicals ( $O_2^-$ ) when exposed to ultraviolet radiation under a simulated martian atmosphere. Figure 1 shows the EPR results for a sample sealed under a 5 torr gas mixture consisting of 3%  $N_2$ , 2% Ar, 0.1%  $O_2$ , and the balance  $CO_2$ . Before exposure to the ultraviolet lamp, the curve is relatively featureless. After exposure to 254 nm photons, the signature of radical species becomes apparent.



**Figure 1:** EPR spectra of crushed plagioclase feldspar (grain size < 75  $\mu m$ ) sealed under a simulated martian atmosphere before (blue) and after (green) exposure to a mercury vapor lamp.

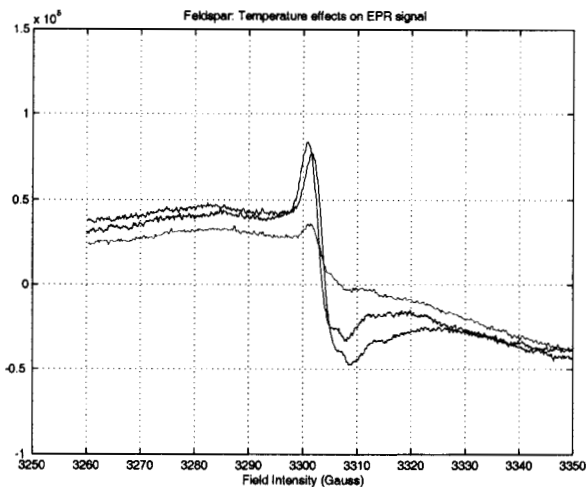
**Oxygen radical formation:** Tests with samples under vacuum ( $10^{-6}$  torr) also show a significant EPR signal after ultraviolet radiation (see figure 2). We interpret this result as either radiation damage to the mineral substrate or radicals species formed from oxygen not completely evacuated from the sample. Work

is ongoing to clarify this result. However, as shown in figure 2, it is clear that the introduction of greater concentrations of oxygen dramatically increases the intensity of the observed signal. Based upon the g-values of the spectra and results using different concentrations of oxygen, we believe that the signatures of radical species resulting from UV-irradiation under a simulated martian atmosphere are primarily a result of the 0.1% oxygen in the gas mixture.



**Figure 2:** EPR spectra of feldspar exposed to ultraviolet radiation while sealed under a  $10^{-6}$  torr vacuum (red) and under 200 torr of oxygen (light blue). The dark blue and green curve are the two samples before exposure to UV.

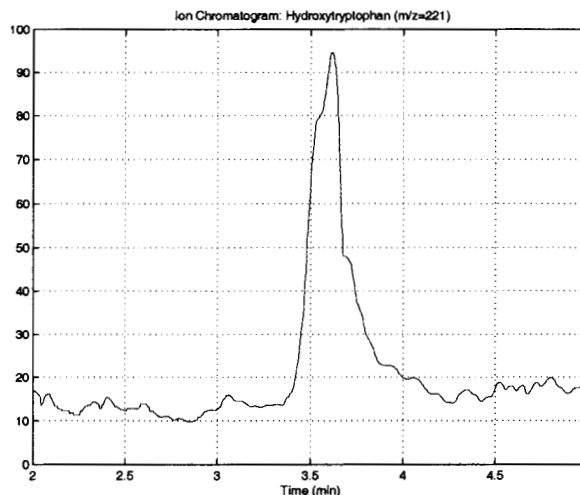
**Thermal stability:** The thermal behavior of the oxygen radicals that we produced in the lab are consistent with the results of the Viking Gas Exchange experiment (GEx). In a test for the biological origin of the gases released from the martian soil, the GEx instrument heated a sample to  $145^{\circ}C$  for 3.5 hours under a He purge. The release of excess oxygen from the heated sample eliminated biology as a source of the gas evolution [2] and also established a constraint on the chemical species that could be responsible for the reaction. Figure 3 shows that baking a sample at  $100^{\circ}C$  for 2 hours has little effect on the EPR signature. Increasing the temperature to  $200^{\circ}C$  for 1 hour, however, begins to reduce the signal to its pre-irradiated state. This temperature stability of adsorbed oxygen radicals is in agreement with the *in-situ* data and further supports the idea that ultraviolet irradiation of minerals at the martian surface is responsible for the unusual reactivity of the soil.



**Figure 3:** EPR signal from feldspar samples after exposure to UV (blue), after heating to 100°C (green), and after heating to 200°C (red).

**Reactions with organics:** Oxygen radicals such as  $O_2^-$  are known to react with water molecules producing  $OH^\cdot$ ,  $HO_2^\cdot$ , and  $O_2$ . Following this reaction, the  $OH^\cdot$  and  $HO_2^\cdot$  are available to decompose the primitive and meteoritic organic molecules at the martian surface. It is also likely that the superoxide ions directly oxidize organics in contact with the mineral grains. This straightforward explanation for the apparent absence of organic signatures at the Viking Landing sites is based only on components known to be present at the martian surface: Ultraviolet radiation, mineral grain surfaces, atmospheric oxygen, and trace quantities of water vapor. This mechanism is consistent with laboratory experiments which demonstrated the decomposition of glycine under martian surface conditions [3].

**Amino acid experiments:** Experiments to test the stability of organic molecules interacting with UV-irradiated Mars-analog minerals are ongoing. These experiments are conducted by introducing target molecules to irradiated soil analogs. Figure 4 is a sample ion-chromatogram showing that tryptophan, a readily oxidizable amino acid, will breakdown into fragments such as hydroxytryptophan when exposed to peroxy-nitrite [4]. Similar results are expected upon exposure to oxygen radicals adsorbed on mineral grain surfaces.



**Figure 4:** Ion-chromatogram illustrating one of the oxidation products of tryptophan (adapted from [4]).

**References:** [1] Biemann, K. et al. (1977) *JGR*, 82, 4641-4658. [2] Oyama, V. I. and B. J. Berdahl (1977) *JGR*, 82, 4669-4676. [3] Stoker, C. R. and M. A. Bullock (1997) *JGR*, 102, 10881-10888. [4] Alvarez, B. (1996) *Chem. Res. Toxicol.*, 9, 390-396.