

**MARS OXIDANT AND RADICAL DETECTOR** A. S. Yen and S. S. Kim, Jet Propulsion Laboratory, California Institute of Technology (Albert.Yen@jpl.nasa.gov, JPL 183-501, 4800 Oak Grove Dr., Pasadena, CA 91109).

**Introduction:** The Mars Oxidant and Radical Detector is an instrument designed to characterize the reactive nature of the martian surface environment. Using Electron Paramagnetic Resonance (EPR) techniques, this instrument can detect, identify, and quantify radical species in soil samples, including those inferred to be present by the Viking experiments. This instrument is currently funded by the Mars Instrument Development Program and is compatible with the Mars Science Laboratory mission.

**Viking Results:** The Viking Landers showed that the addition of water to a martian soil sample produced an unexpected release of excess oxygen [1], that radioactively labeled nutrient solutions were decomposed upon contact with the soil [2], that chemical rather than biological reactions were modifying the liquid reagents of the life detection experiments [3], and that the martian soil was free of detectable organic material [4]. The most widely accepted explanation of these results is the presence of one or more reactive compounds in the soil at the parts-per-million level which actively destroy both primitive and meteoritic organic molecules [5]. The specific nature of this reactive phase, including composition, mechanisms of formation, and interaction with biomolecules, has not yet been identified.

**Testable hypotheses:** A number of explanations for the unusual reactivity of the martian soil have been proposed [6], many of which involve the presence of active oxygen species [1, 4]. Experiments under simulated martian conditions, for example, have shown that superoxide radical ions,  $O_2^-$ , form readily on mineral grain surfaces [7]. The stability, mobility, and reactivity of  $O_2^-$  is consistent with the results of the Viking Lander investigations.  $O_2^-$  as well other likely candidates for the martian oxidant are paramagnetic in nature and can be readily detected in native form by Electron Paramagnetic Resonance (EPR) spectroscopy techniques.

**EPR:** Electron Paramagnetic Resonance spectroscopy is likely the most sensitive technique for characterization of atoms and molecules with unpaired electrons. Detection limits achievable in the laboratory are better than  $10^{11}$  unpaired electron spins per cubic centimeter of sample. Thus, active oxygen species present at tens of part-per-trillion are routinely analyzed with laboratory hardware. For the Mars Oxidant and Radical Detector, we expect a sensitivity at the parts-per-billion level, which would easily detect the reactive compounds and other paramagnetic species present at the Viking sites.

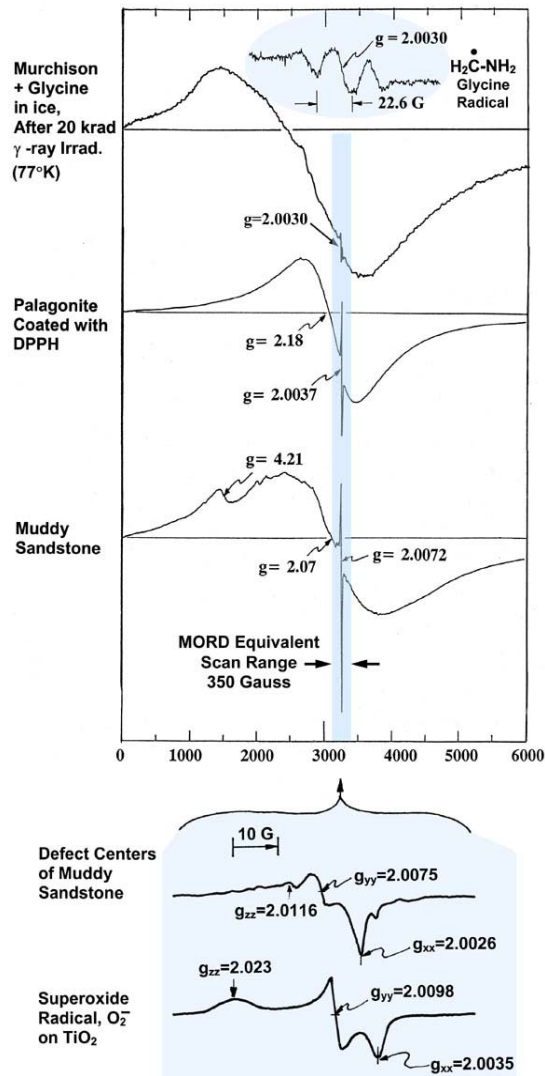
**Spin state transitions:** The spins from unpaired electrons ( $S=1/2$ ) behave as tiny magnets, and when placed in a magnetic field these electrons will align either parallel or antiparallel to the field. The unpaired electron can be made to transition between the two states (Zeeman energy levels) by absorption of microwave energy. When the microwave energy matches the energy difference between the Zeeman levels (resonance), energy absorption takes place and this is detected by EPR. By recording the frequency ( $\nu$ ) and applied magnetic field ( $H_0$ ) where the resonance occurred, one can determine the g-values of the spectra ( $g=h\nu/\beta H_0$ ,  $h$ , Planck's constant;  $\beta$ , Bohr magneton). These g-values are diagnostic characteristics of the paramagnetic species and are used to determine which radicals or defect centers are responsible for the signal.

**Samples:** With microcrystalline, powdered, or glassy samples, the resulting EPR spectrum is a superposition of resonances from paramagnetic centers in all possible orientations with respect to the applied magnetic field,  $H_0$ . The principal values of the magnetic interaction tensor ( $g_{xx}$ ,  $g_{yy}$  and  $g_{zz}$ ) are obtained from the peaks and inflection points of the EPR spectrum [8, 9]. These parameters are used for identification of paramagnetic species. Thus, with powdered samples, such as ones we would obtain from a landed platform on Mars, one can obtain resonance from centers of all the orientations in a single scan. Figure 1 illustrates the superposition of radical signatures on iron-containing samples, showing that even in the presence of a strong  $Fe^{3+}$  background the spectra of the reactive species can be extracted.

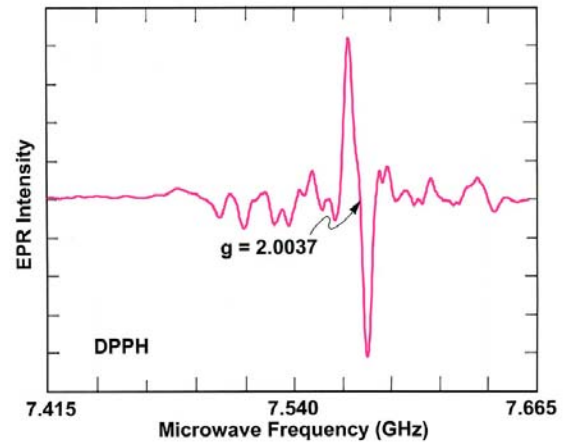
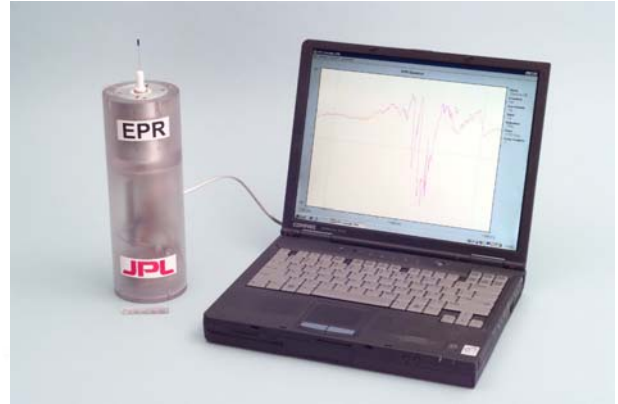
**Breadboard development:** Figure 2 shows the recently developed breadboard of the Mars Oxidant and Radical Detector during data collection. A sample spectrum of a stable radical standard (DPPH: Di-Phenyl Picryl Hydrazil) is also shown.

**Conclusion:** We expect EPR measurements for a landed Mars mission to be instrumental in developing an understanding of the chemical processes that actively destroy organic molecules. Such an understanding is necessary in order to pursue a biological assessment of the planet.

**References:** [1] Oyama V. I. and Berdahl B. J. (1977) *JGR*, 82, 4669-4676. [2] Levin G. V. and Straat P. A. (1977) *JGR*, 82, 4663-4667. [3] Horowitz N. H. et al. (1977) *JGR*, 82, 4659-4662. [4] Biemann K. et al. (1977) *JGR*, 82, 4641-4658. [5] Klein H. P. (1978) *Origins of Life*, 9, 157-160. [6] Zent A. P. and McKay C. P. (1994) *Icarus*, 108, 146-157. [7] Yen A. S. et al. (2000) *Science*, 287, 1909-1912. [8] Sands R. H. (1955) *Phys. Rev.*, 99, 1222-1226. [9] Taylor P. C. and Bray P. J. (1970) *J. Mag. Res.*, 2, 305-331



**Fig. 1:** EPR spectra of iron containing minerals with glycine radicals, DPPH (Di-Phenyl Picryl Hydrazil, a radical standard),  $\gamma$ -ray induced defect centers, and  $O_2^-$ . Each of the radical signatures are present as sharp peaks over the broad iron background.



**Fig. 2:** (Top) Our breadboard EPR during data collection. (Bottom) Spectrum of DPPH obtained by the breadboard instrument.