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ELECTRON SPIN RESONANCE (ESR) DETECTION
OF ACTIVE OXYGEN SPECIES AND ORGANIC PHASES
IN MARTIAN SOILS

Fun-Dow Tsay, Soon Sam Kim and Ranty H. Liang
Jet Propulsion Laboratory J574450
California Institute of Technology
Pasadena, CA 91109

INTRODUCTION. The presence of active oxygen species (O^- , O_2^- and O_3^-) and other strong oxidants (Fe_2O_3 and Fe_3O_4) has been invoked in interpretations of the Viking biological experiments and a model has also been suggested for Martian surface chemistry^{1,2}. The non-biological interpretations of the biological results gain further support as no organic compounds have been detected in the Viking pyrolysis-GCMS experiments at concentrations as low as 10 ppb.³ This apparent non-detection of organic compounds has been suggested as caused by photocatalytic oxidation processes involving active oxygen species.¹⁻⁴ At present, one knows very little about the destructive oxidation mechanisms operating on Mars. Since no organic material has been found in Martian surface soils, it is imperative for exobiology and future Mars missions to search for organic compounds preserved in Martian subsurface samples. The highly active, oxidized and weathered Martian soils as indicated in the Viking results emphasized the need to develop sample selection and *in situ* analysis techniques for the Mars Sample Return Mission.

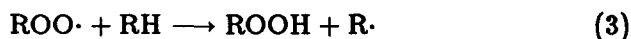
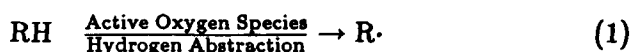
WHY ESR? Electron Spin Resonance (ESR) measures the absorption of microwaves by a paramagnetic and/or ferromagnetic center in the presence of an external magnetic field. A full interpretation of the observed ESR signals provides a description of the magnetic species on an atomic scale. In many instances, ESR has the advantage of detailed submicroscopic identification of the transient species and/or unstable reaction intermediates in their environments. Since the highly active oxygen species (O^- , O_2^- , O_2^- , O_3^- and $R-O-O^-$) are all paramagnetic in nature, they can be readily detected in native form by the ESR method. In addition, ESR can easily detect organic compounds in the form of free radicals generated in UV and/or γ -ray radiation as reaction intermediates and/or end-products. A lightweight magnet assembly (2.5 kg in weight, and $2.0 \times 3.5 \times 4.5$ inches in dimensions) has been built at JPL which in its present form is quite adequate for the detection of paramagnetic Fe^{3+} , active oxygen species and organic free radicals at X-band frequency (9.2 GHz)⁵. A miniature ESR within the given rover science payload constraints (5-10 kg) and power requirements (5-20 watt) can be developed as an effective, non-destructive sample selection and characterization instrument for the Mars Rover/Sample Return Mission. It is shown in the Viking results that average Martian surface samples contain about 3.7×10^{17} molecules/gram of highly active species (1). Thus, a miniaturized ESR spectrometer should have the sensitivity to examine gram to milligram size samples, and minimum or no sample preparation is required.

ESR DETECTION OF ACTIVE OXYGEN SPECIES. Active oxygen species likely to occur in the Martian surface samples have been detected by ESR in UV-irradiated samples containing MgO. A considerable number of ESR studies have been carried out on active oxygen species formed in thermally activated and/or in γ -ray or UV-irradiated oxides (MgO , CaO , ZnO , Al_2O_3 , NaO_2 and TiO_2), zeolites and apatites. The ESR studies have indicated that thermal activation, UV and/or γ -ray irradiation of metal oxides produce paramagnetic defect centers (electron trapping sites), which upon exposure to oxygen results in the formation of active oxygen species such as O^- ,

O_2^- , and O_3^- . The active oxygen species thus formed in most metal oxides are found to be highly reactive and thermally stable even up to 200°C (MgO). Numerous examples have been reported on the oxidation and/or decomposition of organic compounds involving active oxygen species in an environment comparable to that observed on Mars.^{6,7}

DEGRADATION MECHANISMS. A significant portion of the solar UV flux with photons in the 200 to 300 nm wavelength region readily reaches the Martian surface. The active oxygen species thus formed via UV-irradiation in the presence of metal oxides as catalysts could degrade complex organic into simple organic compounds, and finally into CO_2 and H_2O . The reaction mechanisms of oxidation and decomposition processes of organic materials which could occur in the Martian environments may be simplified as follows:

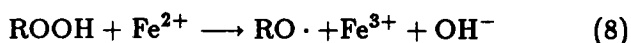
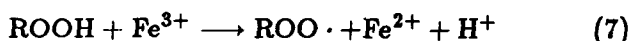
A. Photocatalytic Oxidation:



B. Direct Photooxidation:



C. Oxidation/Reduction by Transition Metals:



where RH is an organic compound containing hydrogen. The organic free radicals ($ROO\cdot$, $RO\cdot$, and $\cdot OH$) formed as reaction intermediates are the reactive oxidants themselves, whereas the polymeric radicals $R\cdot$ are the precursors to further degradation. These organic free radicals are all paramagnetic, and thus can be detected and identified by ESR. In fact, ESR has been successfully applied to the characterization of photooxidation processes occurring in polymeric systems.^{8,9}

ESR DETECTION OF ORGANIC PHASES. We have carried out ESR studies of organic phases in C-1, C-2, and C-3 carbonaceous meteorites. These meteorites are known to contain large amounts of high molecular weight organic compounds and the C-2 chondrites show evidence of

extra-terrestrial aqueous alteration as indicated by the presence of carbonates in this group. ESR signals attributable to organic free radicals along with the characteristic ESR signals of calcite are detected in the C-2 group (Mighei, Murchison, Murray, Nogoya and Cold Bokkeveld). Carbonaceous chondrites which contain organic compounds have been shown to give rise to detectable ESR signals of organic free radicals arising from kerogen-like materials present.^{10,11}

Recent studies¹²⁻¹⁴ have suggested that major objectives of a Mars sample Return Mission should include: (1) Searching for evidence of fossil life forms, because a wetter climate once prevailed and life may have evolved and flourished on Mars in the past; (2) Study of the chemical environment in the subsoil and within rocks, because endolithic life forms can survive on Mars, protected from the harsh ionizing radiation and highly oxidizing chemical environment. Thus, ESR can aid in the search of organic compounds in the form of free radicals preserved in Martian subsoils or in organic fossils such as kerogen-like materials which are difficult to detect by the Viking type pyrolysis-GCMS experiments.

CONCLUSIONS. A miniaturized ESR spectrometer system can be developed for the Mars Rover Sample Return Mission. The instrument can perform the following *in situ* Martian sample analyses:

1. Detection of active oxygen species.
2. Characterization of Martian surface chemistry and photooxidation processes.
3. Searching for organic compounds in the form of free radicals preserved in subsoils, and detection of microfossils associated with Martian carbonate sediments.

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