DETECTION OF ORGANIC RADICALS IN POLAR ICES BY ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY. A. S. Yen and S. S. Kim, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109 (Albert.Yen@jpl.nasa.gov)

Introduction: The ice caps of Mars and associated layered deposits contain a record of the martian environmental history. Organic material, including higher hydrocarbons of exobiological interest, are more likely to survive in polar ices than in equatorial soils due to lower temperatures, lower UV flux, and likely a less oxidizing environment. Detection of organic molecules in these ices would provide insight into the nature and stability of carbon compounds over geological timescales.

Search for Organic Compounds: Instruments onboard the 1976 Viking Landers were unable to detect martian or meteoritic organic matter [1], likely due to the presence of active oxygen species [2] which decompose carbon compounds. Future opportunities in the search for organic molecules on Mars include the 2007 Phoenix lander and the 2009 Mars Science Laboratory. Like the Viking Landers, each of these future missions will utilize a mass spectrometer in attempts to detect, identify, and quantify organic species. An alternative to mass spectroscopic techniques for characterizing organics is Electron Paramagnetic Resonance (EPR) spectroscopy.

Electron Paramagnetic Resonance (EPR) Spectroscopy: EPR spectroscopy is likely the most sensitive technique for characterization of atoms and molecules with unpaired electrons. 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 energy levels by absorption of microwave energy. When the microwave energy matches the energy difference between the Zeeman energy levels (resonance), energy absorption takes place and this is detected by EPR. By recording the frequency (ν) and applied magnetic field (H₀) where the resonance occurred, one can determine the "g-values" of the spectra (g=νβH₀, h, Plank’s constant; β, Bohr magneton). These g-values are diagnostic characteristics of the species with unpaired electrons and are used to determine which radicals or defect centers are responsible for the signal.

Detection limits achievable in the laboratory are better than 10⁻¹¹ unpaired electron spins per cubic centimeter of sample. Thus, organic radical species present at tens of part-per-trillion are routinely analyzed with laboratory hardware.

Miniature EPR Spectrometer: As part of an ongoing Mars Instrument Development Program activity, we have built a miniature flight prototype EPR. In order to minimize the size of the instrument, we implement a scan of microwave frequency with a fixed magnetic field strength provided by a permanent magnet [3]. The sensitivity to organic radical species with this prototype is at the parts-per-billion level.

Ice as a radiation sensitizer: Most organic molecules do not have unpaired electrons and thus are not directly detectable by EPR spectroscopy. In the presence of high energy radiation (e.g. galactic cosmic rays), however, metastable organic radicals will be produced in polar deposits. Upon irradiation of the water ice matrix, OH radicals are generated and are diffusively mobile at temperatures as low as 100 K. Reactions between OH radicals and organic compounds produce organic radicals and water (figure 2). The majority of these radicals will decay by recombination processes, but over geologic timescales OH-produced radicals (figure 3) will likely accumulate to levels detectable by EPR.

Summary: The habitability of the ancient martian environment can be assessed through detections of organic compounds in polar ices. Electron Paramagnetic Resonance spectroscopy provides an alternative to mass spectroscopy for sensitive detection of organic molecules.
**Figure 2:** Reactions likely occurring in polar ices which produce metastable organic radicals.

**Figure 3:** Examples of EPR spectra of radical species produced by radiation chemistry.