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SAMPLE SELECTION AND PRESERVATION TECHNIQUES FOR THE MARS SAMPLE RETURN MISSION;

Fun-Dow Tsay, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

It is proposed that a miniaturized electron spin resonance (ESR) spectrometer can be developed as an effective, non-destructive sample selection and characterization instrument for the Mars-Rover-Sample Return mission. The ESR instrument can meet rover science payload requirements (5-10 Kg), and yet has the capability and versatility to perform the following <u>in situ</u> Martian sample analyses:

1. Detection of active oxygen species (superoxide O_2^-, peroxide $-O-O^-$, ozonide O_3^-, and hydroxy radical), and characterization of Martian surface chemistry and photocatalytic oxidation processes.

2. Determination of paramagnetic Fe^{3+} in clay/silicate minerals, Mn^{2+} in carbonates, and ferromagnetic centers of magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3).

3. Search for organic compounds in the form of free radicals in subsoil, and detection of Martian fossil organic matter likely to be associated with carbonate and other sedimentary deposits.

These analyses can be carried out on gram- to milligram-size Martian surface and subsurface samples; minimum or no sample preparation is required.

The presence of active oxygen species has been invoked in interpretations of the Viking biological experiments and a model has also been suggested for Martian surface chemistry[1,2]. In addition, photocatalytic oxidation processes involving these oxygen species has been suggested as the cause of the apparent non-detection of organic compounds in the Viking GCMS (gas chromatography-mass spectrometry) experiments[3,4]. At present, one knows very little about the destructive oxidation mechanisms operating on Mars. Since these oxygen species are all paramagnetic in nature, they can be readily detected in native form by ESR. Thus, a Rover ESR instrument should uniquely provide information on the oxidation/reduction conditions of Martian surface and subsurface samples, and on the detailed mechanisms of photo-oxidation processes if occurring on Mars. Such information may not be obtainable simply from returned sample analyses, in view of the reactivity and transient nature of these active species. Furthermore, these paramagnetic and ferromagnetic centers can be used as probes to define the physical and chemical properties of Martian samples in terms of their surface oxidant content. We can also perform ESR studies on the distribution of paramagnetic and ferromagnetic centers as a function of the depth from the Martian surface. This will help to define the nature of Martian surface layers and the regolith depth, formation conditions and processes; and thus to define criteria in the selection of samples for the return mission. The ESR data such as concentration, reactivity and thermal stability for the active oxygen species generated under simulated Martian conditions can be used to develop sample preservation techniques. The ESR experiments are needed in the screening of sample container materials as well as in the design of procedures required for sample handling, storage and preservation during the trip to Earth in the return mission.

The proposed ESR experiments are based on the unique ESR signals characteristic of organic free radicals, Mn^{2+} in calcite (Fig. 1), superparamagnetism of ferromagnetic centers[5], O_2^- and $-O-O^-$ (Fig. 2). A lightweight magnet for the proposed miniaturized ESR instrument has been developed at JPL[6]. Magnetic susceptibility measurements as well as simple magnetic separation can be performed using this already developed miniature magnet assembly.

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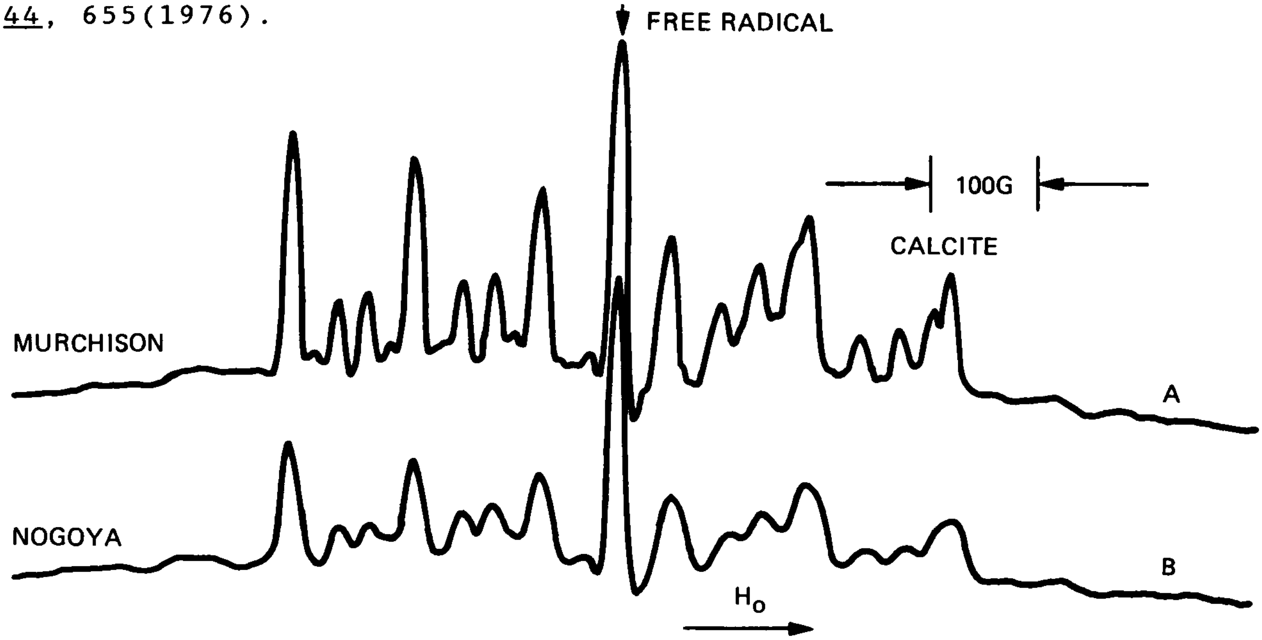

Figure 1. Second-derivative ESR signals attributable to organic free radicals and Mn^{2+} in calcite observed in CM2 chondrites.

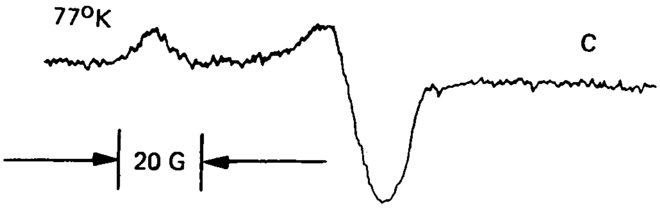

Figure 2. First-derivative ESR signals of peroxy radicals ($-O-O^-$) observed in a polymer at 77°K.