

CHARACTERIZATION OF MARTIAN SURFACE CHEMISTRY BY A MINIATURE MAGNETIC RESONANCE SPECTROMETER

SOON SAM KIM and JAMES C. BRADLEY

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CA 91109

1. INTRODUCTION

The Mars lander missions will involve in-situ sample analysis techniques and we are proposing the Magnetic Resonance Spectroscopy to obtain much needed martian surface chemical information. From the Viking missions in 1976, the first phase of information was obtained through analytical instruments such as X-Ray Fluorescence Spectrometer (XRFS) and Gas Chromatography/Mass Spectrometry (GC/MS). They obtained elemental analysis, as well as the presence of active oxygen species inferred through biology labelled release and gas exchange experiments. Other instruments already developed or in the development stages are: Neutron Activation γ -ray Spectrometer for the measurement of elemental composition of the Martian surface and the atmosphere, Differential Scanning Calorimeter - Gas Chromatography for the characterization of physical states of water in the soil, and Mars Oxidant Experiment (MOx) planned for Russian 94 Landers Missions. The MOX will measure the level of oxidation activity of the Martian soil as it comes in contact with thin metallic and organic coatings of the sensor probes. The logical step for the next Mars exploration should involve efforts to understand the chemical aspects of the Martian soil in molecular detail, such as the structure of active oxygen species, the presence of water in the soil, carbonates, clay mineralogy, to name a few.

The proposed magnetic resonance method has inherent advantages over most other analytical techniques because it allows investigation of samples under near-ambient conditions with little disruption of surface structures or chemical equilibria and requires little sample preparation. Studies of minerals or clays can be performed under environmentally realistic conditions. For example, there is no need for surface preparation, and it is not confounded by the sample matrix regardless of its chemical complexity, as long as it is diamagnetic. Therefore all diamagnetic materials with paramagnetic centers are accessible to study. The analyses can be carried out with gram- to milligram- size Martian surface or subsurface samples with minimum or no extra sample preparation. Similar to the case of Viking Lander, preparation by a mechanical arm which can scoop the soil samples and pour them into fused silica sample tubes (0.3- 1 cm dia, 3~5 cm long) through a funnel (with a mesh screen for size selection, if necessary) will be adequate.

The Magnetic Resonance Spectrometer (MRS) with combined capabilities of Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR) will be one of the most powerful techniques for understanding the chemical aspects of Martian soil. At JPL, we are in the preliminary phase of development of such miniature MRS instrument (light weight -2 kg, low power - 15 W). So far as we know, this is the first attempt to produce a combined EPR/NMR capability in one miniature instrument.

2. SCIENCE RATIONALE

NATURE OF OXIDANT IN MARTIAN SOIL: Through the Viking Biology Experiments, it is speculated that there is about >1 ppm of a thermally labile oxidant such as H_2O_2 , and about 10 ppm of a thermally stable oxidant in the Martian soil¹. Many of the thermally stable yet highly reactive oxygen species are paramagnetic in nature and they can be readily detected in native form by the EPR method. Compared with the planned Mars 94 Oxidant Experiment (MOx), the EPR will be able to characterize the electronic state and molecular structure of the oxidant with specificity and higher sensitivity.

DETECTION OF WATER IN THE SOIL, MINERALS AND ROCKS: According to the models based on volatile inventory of Mars, it is possible and even likely that orders of magnitude more of H_2O and CO_2 are adsorbed on Martian regolith than are present in the atmosphere-plus-caps system^{2,3}. There can be many forms of water in the Martian soil, for example, surface adsorbed H_2O on soil or crushed rocks, interlayer

water in smectite or chemically bound water as oxyhydroxides. Such different forms of water including capillary or bulk H₂O can be characterized and quantified by the proton NMR spectroscopy. As an example, NMR was used to characterize protons of nontronite (37 wt% Fe₂O₃) in the form of H₂O and hydroxyl ions⁴. The presence of adsorbed CO₂ on the regolith in the form of carbonates can be studied from the frozen soil particles by the detection of carbonate radical, CO₃^{•-}, formed by ionizing radiations (cosmic ray, γ-ray and solar wind proton) by the use of EPR spectroscopy.

OXIDATION STATES OF PARAMAGNETIC IONS: As of secondary importance, the oxidation states of paramagnetic ions (e.g., Fe, Mn, Ti), including those produced photochemically in the soil can be characterized. Under favorable conditions, such paramagnetic ions, Fe⁺³, Mn⁺², or VO⁺², can be utilized as probes for obtaining structure of minerals⁵, such as crystalline, glassy or the extreme case of completely disordered gel like structures. One can also perform EPR studies on the distribution of paramagnetic and ferromagnetic centers as a function of the depth from the Martian surface. This will help define the nature of Martian surface layers and the regolith depth, formation conditions and various geologic processes.

COLOR CENTERS IN ICY SAMPLES: At the Martian surface, the ice caps receive a continuous flux of solar wind particles and galactic cosmic rays (GCR) which will create radicals and color centers in the ice matrix. Such radicals or color centers (RCC) can be characterized with high sensitivity by EPR spectroscopy and used as probes to obtain chemical information of the ice caps. The variation in RCC concentration as a function of depth can be related to past climatic variation of the planet, the temperature variation as one of the chief factors. Polar ice caps contain an archive of solid precipitation over geologic times. The concentrations of trace substances in the precipitation are related to the concentrations of corresponding substances in the atmosphere at the time of precipitation. Inorganic and organic molecules including higher hydrocarbons of exobiological interest may have better chance of survival in the ice matrices shielded from solar UV and also from highly oxidative soil environments. Through detection of radicals derived from such molecules by EPR spectroscopy, one can deduce the original molecular structures and their concentrations.

DETECTION OF POSSIBLE ORGANICS FROM SUBSOIL: The general consensus formed on the basis of the Viking results is that there is now no life on Mars. However, this conclusion has to be reconsidered in view of the later suggestions% (1) That a wetter climate once prevailed and life may have evolved and flourished on Mars in the past; (2) Endolithic life forms can theoretically survive on Mars, protected from the harsh ionizing radiation and highly oxidizing chemical environment. Therefore, it has been suggested⁶ that major objectives of a Mars lander missions should include: (1) Search for evidence of fossil life forms; and (2) Study of the chemical environment in the subsoil and within rocks. Since EPR is a specific, non-destructive analytical tool for the characterization of paramagnetic species having unpaired electrons, it can also detect 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-GC/MS experiments. Carbonaceous chondrites which contain a substantial amount of organic free radicals have been shown to give rise to detectable EPR signals characteristic of kerogen-like materials present^{9,10}.

3. REFERENCES

1. A.P. Zent and C.P. McKay, "The Chemical Reactivity of the Martian Soil and Implications for Future Missions," Submitted to Icarus.
2. F. P. Fanale and W.A. Cannon, J. Geophys. Res., 79, 3397-3402 (1974).
3. F.P. Fanale, Icarus, 28, 179-202 (1976).
4. a) D. Bonnin, Ph.D. Thesis, University of Paris, 1981, b) D. Bonnin, et al, Phys. Chem. Minerals, 12, 55-64 (1985).
5. P.L. Hall, Clay Minerals, 15, 321-349 (1980).
6. M. H. Carr, "Mars: A Water-Rich Planet?," Icarus, 68 1S7-216 (1986).
7. S.S. Nedell, S.W. Squyres and D.W. Anderscn, "Origin and Evolution of the Layered Deposits in the Valles Marineris, Mars," Icarus, 70, 409-441 (1987).
8. C.P. McKay, " Early Martian Environments: The Antarctic and Other Terrestrial Analogs," Adv. Space Research, 9, (6) 147-153 (1989).
9. K. Schulz and R. Eloffson, Geochim. Cosmochim. Acta, 29, 157 (1965).
10. R. Lewis, M. Ebihara and I. Anders, Meteoritics, 17, 244 (1982).