DETECTION OF PARAMAGNETIC Fe^{3+} AND RADIATION DAMAGE CENTERS IN LUNAR SOILS*, F. D. Tsay and D. H. Live, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103.

Electron spin resonance (ESR) spectra of lunar soils are distinguished by intense ferromagnetic features which originate in the ubiquitous metallic Fe particles present (1). These particles are in the superparamagnetic (sp) and single domain (sd) states and have resonance fields centered at about 3300 G at X-band frequency (9.2 GHz), and linewidths which range from 500 to 1000 G. It is within this resonance field that ESR signals due to paramagnetic species such as Ti^{3+}, Mn^{2+}, Fe^{3+} and radiation damage centered (trapped electrons and holes) are detected in lunar rocks (2-5) in the absence of sp and sd metallic Fe particles. Although such paramagnetic species might be expected to be present in lunar soils they have generally eluded detection due to interference by the very strong ferromagnetic resonance present. We report here ESR signals arising from paramagnetic Fe^{3+} and radiation damage centers in very fine grains of lunar surface material, and present ESR evidence which indicates the presence of minute amounts of paramagnetic Fe^{3+} in orange soil 74220,120 and rusty rock 66095,131.

The detection of these paramagnetic centers is made possible by means of the second derivative ESR detection method. Since ESR linewidths of paramagnetic species are expected to be two or more orders of magnitude narrower than those characteristic of lunar metallic Fe phases, this great difference in linewidth allows ready detection of weak, narrow paramagnetic resonances concealed in the broad, intense ferromagnetic resonance on recording a second derivative spectrum. As seen in Fig. 1, the first derivative of the broad ferromagnetic resonance has a steep relatively constant slope which manifests itself as a relatively constant low-amplitude portion of the second derivative plot. However, the sharp paramagnetic resonance components remain as narrow and easily discernible features in the latter presentation.

When a lunar soil (75081) was examined at room temperature there was an indication of a weak, sharp indigenous peak in the second derivative, and when the sample was examined at 77°K a noticeable sharp peak was observed (see Fig. 1). In an attempt to ascertain the origin of this resonance a 4 mg. sample of 75081 was irradiated for 19 hrs. in a ^{60}Co source at 3.1×10^5 rad/hr. and the intensity of the sharp peak in question thereby increased (see Fig. 1). We were unable to directly observe this paramagnetic resonance in the first derivative plot before or after irradiation. The ESR signals due to radiation damage were found to have a g-value of 2.001 and a linewidth of 14 G similar to those observed in lunar rock 12021 (3). Annealing experiments showed that the radiation damage ESR signals persist even after heating in vacuo for 1 hr. at 500°C, indicating that they could survive lunar diurnal heating for longer than 3×10^5 yrs. The naturally occurring and artificially induced radiation damage ESR signals were also detected in lunar soil 63341.

We have also succeeded in detecting paramagnetic Fe^{3+} signals in lunar

*Supported by NASA under Contract No. NAS 7-100 to the Jet Propulsion Lab.

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soils, particularly in orange soil 74220, by means of the second derivative method, in the presence of strong interference from the ferromagnetic resonance of metallic Fe. This is shown in Figs. 1 and 2 where the Fe^{3+} signals which have a resonance field at about 1530 G (g = 4.3) are clearly seen in the second derivative plot at low temperature, but not in the first derivative. Because of its low concentration, the paramagnetic Fe^{3+} is not detected in orange soil at temperatures above 77°K. ESR signals attributable to radiation damage centers are not detected in orange soil, in agreement with its low surface exposure age. Although ESR signals with g-values ranging from 1.93 to 1.97 which are indicative of the presence of Ti^{3+} are observed in orange soil at 77°K (see spectrum (c) and expanded scale portion in Fig. 2), further work is needed to confirm this attribution.

Paramagnetic Fe^{3+} is also detected in rusty rock 66095 at 77°K (see Fig. 3), and in rock samples 15499, 15418, 67915 and 68416. For the latter the paramagnetic Fe^{3+} signals are sufficiently intense to permit their detection easily by the conventional first derivative ESR method, even at 300°K. Both rusty rock 66095 and orange soil 74220 were protected from further terrestrial contamination prior to our receiving them, and are found to have a relatively low paramagnetic Fe^{3+} content as compared to other soils (75081, 63341) and rocks (15499, 15418, 67915, 68416) which were previously exposed to air prior to their arrival in our laboratory. Thus, the paramagnetic Fe^{3+} ions are very likely formed by terrestrial oxidation. However, the relatively high Fe^{3+} concentration observed in rock samples suggests that some of these Fe^{3+} ions are indigenous and associated with certain minerals such as plagioclass (5); this possibility can not be ruled out entirely.

In addition to providing a better characterization of lunar metallic Fe phases the second derivative ESR method demonstrated here has proved to be the most powerful tool and perhaps the only spectroscopic method available at this writing capable of detecting paramagnetic Fe^{3+} in concentrations of a few ppm or less in very fine grains of lunar surface material.

References

1. Tsay, F.D., Chan, S.I., and Manatt, S.L., 1971, Geochim. Cosmochim. Acta, 35, pp. 865-875.
2. Kolopus, J.L., Kline, D., Chatelain, A., and Weeks, R.A., 1971, Proc. Second Lunar Sci. Conf., pp. 2501-2514.
3. Tsay, F.D., Chan, S.I., Manatt, S.L., 1972, Nature (Physical Science), 237, pp. 121-122; Proc. Second Lunar Sci. Conf., pp. 2515-2528.
4. Weeks, R.A., 1972, Proc. Fourth Lunar Sci. Conf., pp. 2503-2517; 1974, Lunar Science V, pp. 836-838.
5. Niebuhr, H.H., Zeira, S., and Hafner, S.S., 1973, Proc. Fourth Lunar Sci. Conf., pp. 971-982.

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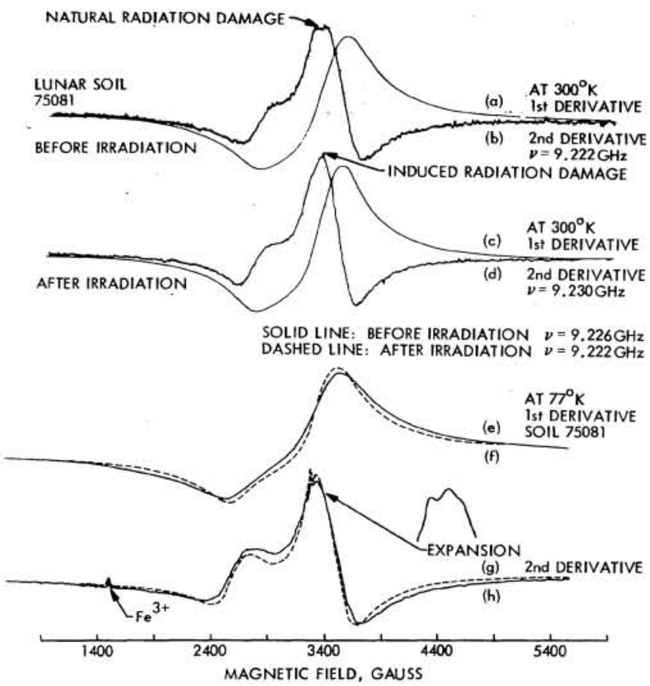

Fig. 1. First and second derivative ESR spectra of soil 75081 before and after ^{60}Co gamma ray irradiation. Spectral features due to radiation damage and paramagnetic Fe^{3+} are seen in the second derivative only. Note lineshape change and increase in radiation damage signal due to radiation effects.

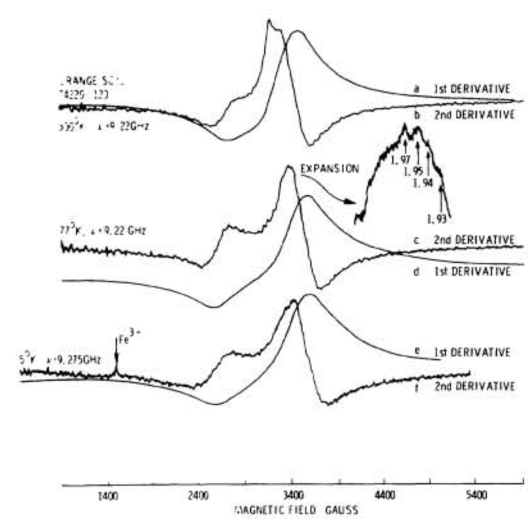

Fig. 2. First and second derivative ESR spectra at 300°K, 77°K and 5°K for orange soil 74220,120. Note paramagnetic Fe^{3+} signal detected in the second derivative at 5°K.

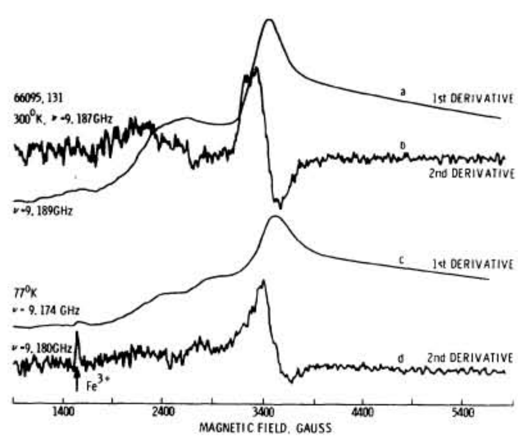

Fig. 3. First and second derivative ESR spectra for rusty rock 66095,131. Paramagnetic Fe^{3+} signals are seen in both first and second derivative at 77°K.