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OPTICAL EXCITATION SPECTROSCOPY OF THE LUNA 24 SAMPLE 24125

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CONTENTS

Luminescence optical excitation spectroscopy carried out at room temperature on sample L24125 with light made monochromatic from a 450 W xenon source has shown that Fe^{3+} ions are present in the plagioclase component at concentrations such that the ligand field bands of this species are observed. The spectrum closely resembles that of Fe^{3+} in plagioclase-rich Apollo samples and in terrestrial calcic plagioclases, including synthetic material activated with this ion.

Although the amount of sample was small (5 mg) compared with those for which comparison spectra were obtained (30 mg) and the albedo was lower, resolution of spectral bands was achieved with the aid of a digital signal averager, giving an eight-fold enhancement of signal:noise ratio. It would be very instructive and of great value to compare these results with those obtained for samples from the same core but at several different depths and also with an 'interior' rock (as opposed to breccia) sample suite, for which the Fe^{3+} luminescence centres would be relatively well shielded from environmental influences, particularly those implicated in the formation of Fe^0 (metal) and Fe^{2+} in the lunar regolith.

Introduction

In previous studies of d^5 ions in lunar samples probably the most important technique has been e.s.r. (Weeks 1972; Geake *et al.* 1970; Niebuhr *et al.* 1973).

Niebuhr *et al.* (1973) were thus able to draw reasoned conclusions about the site occupancy of Fe^{3+} in a single crystal of the calcic plagioclase, anorthite ($CaAl_2Si_2O_8$) from the Apollo 15 rock 15415. They estimated that the Fe^{3+}/Fe^{2+} ratio in their sample was about 1 % of the total iron (Ca 0.1 % by mass as FeO) in the parent sample.

Following the earlier investigations of luminescence emission excited by protons (Nash & Greer 1970) and electrons (Sippel & Spencer 1970; Geake *et al.* 1972) and the more recent optical excitation spectroscopy of plagioclase, (Geake *et al.* 1977; Telfer & Walker 1978) the

Mn^{2+} ion, substituting for Ca^{2+}, has been confirmed as the centre responsible for green emission (560 nm), whereas Fe^{3+}, substituting for Al^{3+}, gives rise to the near infrared emission at 700 nm (Telfer & Walker 1975, 1978).

Optical excitation of luminescence

Optical excitation spectra give profiles corresponding to the absorption spectra of the particular luminescence centre under investigation. The sample is irradiated with monochromatic light which is scanned in wavelength while the total luminescence emission, selected with a suitable filter, is detected and recorded. The technique is non-destructive and, in addition to allowing transition metal ion centres to be used as probes to investigate site occupancy, co-ordinate geometry and bonding, it affords a useful means of detecting low levels of these ions in the presence of other species.

The technique and equipment used here are described more fully elsewhere (Telfer & Walker 1978).

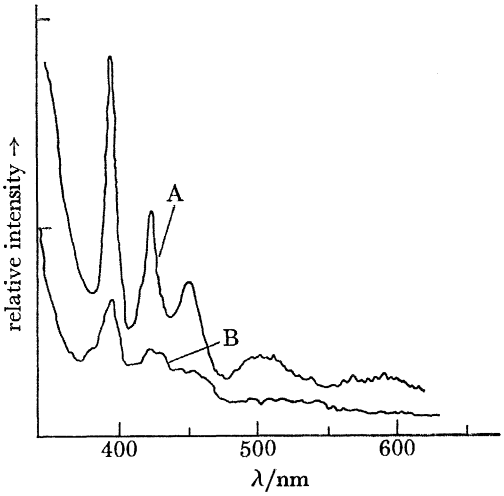

FIGURE 1. Optical excitation spectra for Fe^{3+} luminescence centres in an Apollo 16 breccia, 67455.3.1 (A), and for the Luna 24 sample (B). Relative intensity in arbitrary units is plotted against wavelength of incident radiation. Curve B is the resultant of 64 scans. The outputs are normalized with respect to sample mass; A was 30 mg and B was 5 mg. Both measurements were made with the use of a Wrattan 29 IR isolating filter, and are corrected for instrument response.

Optical excitation spectrum of Fe^{3+}

Incident light was obtained from a 450 W xenon lamp used in conjunction with a Hilger Monospek 1000 monochromator, and luminescence emission was measured with a photomultiplier tube.

In the sample provided (5 mg), green emission was too weak to provide a satisfactory Mn^{2+} excitation spectrum, but Fe^{3+} bands were readily resolved. This behaviour contrasts with that of previous Apollo samples, in which the green emission band tends to predominate.

Figure 1 shows the spectrum obtained after electronically averaging 64 scans (eightfold improvement in signal:noise ratio). For comparison, the spectrum of an Apollo plagioclase-rich breccia is also shown. Prominent features of the spectrum are identified as the $^4E(^4D)$,

$^4T_2(^4D)$ and ^4E, $^4A_1(^4G)$ bands of Fe^{3+} in plagioclase occurring at 25800×10^3 cm^{-1}, 23600×10^3 cm^{-1} and 22200×10^3 cm^{-1} respectively (Telfer & Walker 1978).

The conclusion reached is that there is sufficient Fe^{3+} in the plagioclase component to give rise to the observed optical excitation spectrum. A prerequisite for such observations is that the luminescence centres are well dispersed in the host structure. Experiments with synthetic plagioclase activated with Fe^{3+} (Telfer & Walker 1978), for which a similar excitation spectrum profile was obtained, revealed that concentrations above 1 mol.% Fe^{3+} produced a falling off in emission intensity (self-quenching). In the Luna 24 sample it is unlikely that the concentration of Fe^{3+} dispersed in the plagioclase structure amounts to more than several hundred atoms/10^6, particularly in view of the relatively reducing environment at the lunar surface. However, it is important to know how the relative concentration of Fe^{3+} in plagioclase changes with the degree of protection from influences conducive to chemical reduction and the formation of Fe^0 (metal) and Fe^{2+} (ferrous ions) at the lunar regolith.

Plagioclase-rich grains are individually of relatively high albedo, but the albedo of this sample was low and, in part, responsible for the small signal.

Attempts were made to normalize the curves with respect to sample mass. The very small amount of Luna 24 material, and the unavailability of the Apollo and Luna samples within the same 24 h period, will have given rise to considerable inaccuracy in relative intensity for the two samples. However, they are expected to be correct to within an order of magnitude. Better results would be expected if samples were approximately equal in amount and in the region of 30 mg. It is hoped to pursue further studies of this kind on more samples from the same core at different depths and on other 'interior' samples taken from crystalline rocks, as this may throw further light on the nature of reduction processes at the surface of the Moon and other atmosphereless bodies in the Solar System.

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