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Developments in Quantitative Luminescence Techniques

In conjunction with the use of luminescence for the identification of lunar materials, a basic laboratory study has demonstrated the feasibility of obtaining useful correlations of mineral luminescent phenomena. Two monochromator-photomultiplier attachments to an electron microprobe have been developed which permit the study of cathodoluminescence phenomena on a micron scale. The attachments extend the analytical capabilities of the instrument and facilitate: (1) recording of luminescence spectra, (2) obtaining the distribution of luminescent phases in microspecimens and bulk specimens, (3) evaluating and recording the relationships between fluorescence patterns and conventional X-ray representation of an area scan, (4) studying radiation influence on fluorescence decay, and (5) relating luminescence intensity to composition within a phase. This information provides a basis more reasonable than that formerly used for interpreting recent observations of lunar luminescence.

INTRODUCTION

The use of luminescence to characterize lunar-surface materials was prompted by observations of lunar luminescence reported by Kopal (ref. 1), Rackham (ref. 2), and Cameron and Gilheany (ref. 3). An investigation of terrestrial minerals likely to occur on the Moon has demonstrated the feasibility of obtaining quantitative measurements of mineral luminescence. It has also indicated striking variations of spectral energy distributions and excitation efficiencies within the individual specimen grains and thus emphasized the importance of a precise localized investigation of a multiphase assemblage to provide an understanding of the bulk luminescent response of the material.

In order to achieve the level of precision and discrimination necessary for evaluating the interrelations of wavelength and intensity with various elements, compositions, structures, and degree of recrystallization, two equipment modifications were developed for use with an electron-microprobe X-ray analyzer. The work reported here describes the development and application of two basic cathodoluminescence detector units: (1) an electron-microprobe, interference filter attachment; and (2) an electron-microprobe, light-wire grating monochromator assembly. Although other equipment units are available for observing luminescence phenomena (refs. 4 to 9), the microprobe and cathodoluminescence detector units offer a comprehensive analytical system for detailed investigations.

Some of the electron-excited luminescence information obtained in this study may be used to predict the physical, and to some extent the chemical, properties of minerals which may be present on the lunar surface and which have been exposed to various forms of radiation. This may then lead to the determination of the spatial distribution or availability of specific indigenous lunar or planetary surface resources.

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EXPERIMENTAL

Luminescence Display System

The two cathodoluminescence units are used

for the identification and distinction of phase assemblages, for the determination of the distribution of reaction products, and for the quantitative evaluation of the luminescent properties for specimens of microscopic size. The two units facilitate the study of cathodoluminescence phenomena on a micron scale of the specimen without disturbing the normal function of the microprobe. Either detector unit replaces the ocular tube on the microscope of an Applied Research Laboratories model EMX microprobe. Most nonmetallic materials luminesce in the visible region when bombarded by relatively high energy electrons (5 to 50 keV). Since the intensity and spectral distribution of the luminescence can vary even with small changes in impurity content, the luminescence characteristics give important information concerning the trace composition and growth characteristics of a given phase. With these detection units, quantitative measurements of the luminescence spectra are obtained without impeding the inherent use of the microprobe as an analytical tool.

The monochromator (interference filter) attachment consists of a housing, a monochromator, an ocular tube, a selection of interchangeable slits, and interchangeable photomultiplier detectors. A diagram of this attachment is shown in figure 1. The attachment replaces the ocular tube of the optical microscope on the microprobe. The interchangeable components are easily permuted so that the operator can perform a variety of experiments or use the microscope in the normal manner without having to remove the attachment. For visual microscopic examination, the ocular is inserted in the attachment. Then the specimen can be viewed through the monochromator, in which case the specimen is seen in a given colored light, or, alternatively, the monochromator can be bypassed for normal microscopic observation. Defining slits for the monochromator are inserted in place of the ocular, and then photomultiplier tubes in light-tight housings are slipped onto the attachment for electronic detection of light intensities.

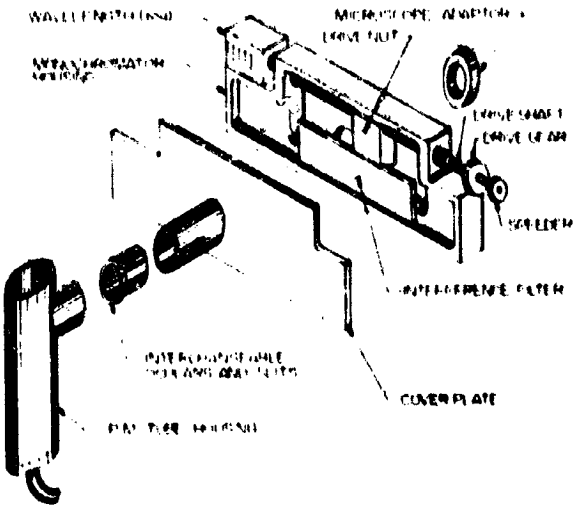

FIGURE 1.—Cathodoluminescence interference filter attachment.

The monochromator within the attachment is a Bausch & Lomb wedge interference filter of narrow bandwidth (20 nanometers (nm)) and 35 percent transmission. The linear dispersion is 5.5 nm/mm with a useful wavelength range of 400 to 700 nanometers. An odometer is used to read wavelength directly to the nearest 1.0. The visible spectrum is scanned by use of a synchronous motor drive on the monochromator with strip-chart recording of the signal. In this manner the complete visible emission spectrum of a luminescent area on the surface of the sample can be obtained. The amplified photomultiplier signal can also be displayed on the oscilloscope in a way analogous to the conventional electron-backscatter image or X-ray images as described earlier by Heinrich (refs. 10 and 11). Recently, infrared microprobe display capabilities have been developed (refs. 12 to 15); however, with this attachment, light intensity displays at a particular wavelength in the visible spectrum can be photographically recorded.

A second cathodoluminescence detection unit is a light-wire grating monochromator assembly. The light generated by the action of the electron beam (typically, 30 keV and 0.03 microampere) on the specimen is collected by replacing the ocular of the electron-microprobe optical microscope with a flexible, ¼-inch Bausch & Lomb noncoherent light wire. Typical incident light-gathering efficiency of the fiber optic rod is 60 percent at the receiving

end, with a light-transmitting efficiency of 5 percent absorbance loss per foot and a transmittance capability in the visible and near-infrared zones. A variety of signal readouts, such as Teletype printout, strip-chart recording, and oscillographic display, are available.

A Bausch & Lomb 500-millimeter-focal-length monochromator with two interchangeable diffraction gratings, one blazed at 7500 Å with 600 grooves/mm and one blazed at 3000 Å with 1200 grooves/mm, permits narrowband spectra to be obtained when necessary.

Experimental Procedure

As one part of a systematic study of luminescence of natural materials likely to occur on lunar and planetary surfaces, a variety of meteorite specimens were examined under electron bombardment. Detailed examination of what at first appeared to be homogeneous material, free from obvious inclusions of extraneous phases (i.e., metals, sulfides, and silicates other than enstatite), revealed striking variation in fluorescence and chemical composition between meteorites. In order to characterize the extent of such variation, an electron microprobe was utilized to examine enstatite ($MgSiO_3$) grains derived from the following meteorite specimens: (1) enstatite chondrites: Abee, Adhi Kot, Atlanta, Blithfield, Khairpur, Jajh deh Kot Lalu, and Hvittis; and (2) enstatite achondrites: Bishopville, Cumberland Falls, Khor Temiki, Pesyanoe, and Shallowater. Individual grains, 10 to 200 microns in diameter, were selected for analysis, and these samples were embedded in ½-inch-diameter plastic rods. Polishing was done by the sequential use of 6-, 3-, and 1-micron diamond paste and ¼-micron Gamol polishing suspension. The samples were carbon coated to a thickness of about 200 to 400 Å to provide a conducting path for absorbed electrons and were placed in a brass holder in the microprobe chamber for analysis.

Intensity of luminescence was recorded on a dual-pen strip recorder. The wavelength range from 400 to 700 nanometers was investigated in two ways: At monochromator settings to monitor and compare the blue and the red portion of the spectrum (for enstatite, the host crystal luminescence emission is in the blue, and the activator-induced luminescence emission is in the red, portion of the spectrum), and at a variety of settings to obtain oscillographic displays of the luminescence for comparison with conventional electron-backscatter and X-ray images.

All the X-ray measurements were made on an Applied Research Laboratories model EMX microprobe equipped with three dispersive channels. X-ray intensities were read from Hamner 6-decade scalers or printed by a Teletype machine. The probe was operated with a 1-micron spot size. The majority of the intensities were measured on a 4-inch LiF spectrometer using a sealed 0.001-inch beryllium-window argon detector (argon Exatron); silicon intensities were measured using a 4-inch ADP (ammonium dihydrogen phosphate) spectrometer with a 0.004-mm-thick, carbon-coated, nonsupported, Mylar window and a flow proportional counter with P–10 gas at atmospheric pressure.

The procedure for making X-ray intensity measurements was to select a grain using reflected light optics and simultaneously record the luminescence signal from the instant the electron beam impinged on the specimen and the X-ray signals. For individual grains derived from the larger samples, iron (Fe), manganese (Mn), chromium (Cr), calcium (Ca), and silicon (Si) were determined. The intensity of the SiK_α X-ray emission line signal was utilized to monitor the phase (in this case, enstatite, $MgSiO_3$). The Fe, Ca, and Cr were monitored so as to determine their influence on the optical fluorescence response of the enstatite host crystal. The Mn was monitored to determine its contribution to the activator-induced red luminescence band for an enstatite host. Although group IVB oxides can increase the host luminescence (in the blue), they were not monitored since their presence in these meteorite grains is well below the 1 weight-percent necessary to enhance the enstatite blue emission band. The LiF spectrometer was used to scan for the K_α X-ray emission lines of the elements Ca, Fe, Mn, and Cr; the ADP spectrometer

was used to identify the K_α X-ray emission lines for Si.

Operational technique was as follows: (1) obtain the luminescence intensity measurements; (2) record five replications at each element odometer setting and at the background odometer setting for that element for a series of points within a grain or grains (ref. 16); and (3) photograph luminescence oscillographic displays and the conventional cathode-ray-tube electron-backscatter image and X-ray images.

Procedure for Analysis of Experimental Data

Multivariate statistical analytical techniques (refs. 17 and 18) were utilized to process the data. From this information it was possible to determine to what extent fluorescence spectra of the meteorites vary from sample to sample and to correlate the intensity and wavelength of fluorescence with chemical composition. Since some zero values for the elements were present (corresponding to the probe analysis detection limit for the element), the data transformation $\log (X+1)$ was appropriate for the statistical analysis.

RESULTS AND DISCUSSION

When the samples were observed microscopically during electron bombardment, large differences in both intensity and wavelength of the resulting luminescence were evident. Different portions of a single mineral sample emitted at wavelengths ranging to both limits of the visible spectrum. Within an individual specimen the variation in intensity and/or wavelength of fluorescence appears to be accounted for by corresponding variation in chemical composition. Higher concentrations of Fe, Ca, and Cr tend to suppress fluorescence. In many cases, exsolution phenomena (refs. 19 and 20) representing areas of high Ca and low Ca pyroxene are sharply contrasted by monitoring the optical fluorescent emission intensity with the monochromator set in the red portion of the visible spectrum. Both the high and low Ca pyroxene luminesce in the blue; however, the high Ca quenches strong luminescence in the red, and consequently the oscillographic displays clearly show the location of each.

Fluorescence is most intense in the red portion of the spectrum. Almost all of the strong luminescent samples contain very little Fe or Ca, and the achondrite enstatite specimens luminesce stronger than do the chondrites throughout the visible spectrum.

The clinoenstatite specimens luminesce with relatively low efficiency and primarily in the blue, and the orthorhombic enstatite specimens luminesce with relatively higher efficiency both in the blue and in the red part of the visible spectrum. Fe readily substitutes for Mg in enstatite and diopside and is in larger concentrations in the clinoenstatite specimens. The presence of Fe quenches luminescence and also can effectively reduce the Mn luminescent emission contribution to red emission. (Manganese in $MgSiO_3$ produces new emission bands at the expense of the original bands of the host crystal; the Mn activator would normally be responsible for the long-wavelength emission band in this case.) In numerous measurements the Mn and Fe indicated a significant positive correlation, and this association usually decreased the red contribution to the luminescent response for the specimens. In addition, the observed decrease in luminescent efficiency in going from an orthorhombic enstatite to a monoclinic enstatite specimen is consistent with the crystal-field-theory explanation concerning the environment of the atoms when the lattice spacing is altered and also when there is a reduction in site symmetry.

An examination of selected mineral grains by the electron microprobe revealed that the dispersion of concentrations of Fe, Mn, Cr, and Ca in these samples is also large. This variability indicates why a variety of intensity and wavelength responses may be possible within a specimen. These chemical peculiarities effectively define the two groups (enstatite chondrites and enstatite achondrites) (refs. 21 to 27), as well as tend to delineate the enstatite polymorph present. The enstatite chondrites are characterized by a high degree of reduction. The principal mineral is pure or nearly pure $MgSiO_3$ as rhombic enstatite, or clinoenstatite in part. Some chondrites show well-developed

chondritic structure; others are primarily granular aggregates of enstatite. The luminescence efficiency tends to follow the textural relationships in terms of the sample purity represented by coarse grains and, consequently, the slow crystallization of the granular aggregates (poor chondrules) compared with the lower intensity registered for the good chondrule types. Also, the degree of recrystallization results in minor chemical and mineralogical changes which can influence unique luminescent response. For example, the Blithfield specimen lacks chondritic structure, and the recrystallization is clearly indicated by red luminescent rings corresponding to areas depleted in impurities by the recrystallization process. The enstatite achondrites represent an even higher degree of reduction than the chondrites, and the achondrite pyroxene is essentially Fe free. This purity is mirrored by the greater luminescence intensity shown by the enstatite achondrites for both the range of 400 to 500 and 600 to 700 nanometers.

Constant exposure of the enstatite specimen point to the electron beam causes a fatigue of the phorphor which is described by power-law decay relating intensity and time:

$$I = t^{-n}$$

where I is the intensity at a time, n is a constant evaluated for the particular curve, and t is the time in seconds. Young (ref. 28), Massey and Burhop (ref. 29), Leverenz (refs. 30 and 31), and others (refs. 32 to 34) provide appropriate discussions of electronic and ionic impact, penetration, and reaction phenomena.

CONCLUDING REMARKS

Quantitative optical fluorescence spectra and color pattern displays have application in the characterization of inorganic solids as demonstrated by newly developed, nondestructive, analytical techniques. By conveniently utilizing the analytical capabilities of an electron-microprobe X-ray analyzer and specialized monochromator-photomultiplier cathodoluminescence detection units, spectral data of micron-size particles and of preselected micron-size areas of larger mineral grains can be collected, and the variations in the optical fluorescence response of the specimens can be correlated with chemical composition and structure. The scheme of successive operations permits the investigation of natural phosphors singly or in mixtures, with the luminescence emphasized as a complementary diagnostic tool.

By demonstrating the influence and interrelations of such system parameters as crystal host, activator, purity, and chemical composition, luminescence may eventually be used as a satisfactory remote sensing technique similar to the statistical air-survey evaluations of various sand deposits accomplished by Romanova (ref. 35) and the variety of natural resources by Colwell (ref. 36).

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