spectra of which show, at −196°C, the plateau near 5000 Å characteristic of all our lunar specimens. The enstatite achondrites do not show such bright blue thermoluminescence as do the lunar rocks. They have been studied by ourselves [Khor Temiki (*1*)], and by Sun and Gonzales [Cumberland Falls (*4*)], and we both find a red glow peak near 0°C. Sun and Gonzales saw a blue glow peak near −120°C, but we found this peak to be much less intense than the red one, which does not appear at all in the lunar rocks.

Presumably the red luminescence shown by all our specimens is due either to a mineral phase common to all fractions or to the ubiquitous presence of an activator that is increasingly quenched by the larger concentrations of iron in the more magnetic fractions. In view of the modal analysis above, showing a moderately clean separation, we incline to the second suggestion.

The blue thermoluminescence might be ascribed to the same activator were it not for its complete absence from the ilmenite fraction. As regards its nonrepeatability, such an effect is observed in some crystalline phosphors, particularly alkali halides, in which thermoluminescent recombination occurs at *F* centers that are thermally stable up to the annealing temperature. However, we had not previously seen this effect in any of our terrestrial or meteoritic specimens. The phenomenon is obviously highly relevant to the problem of transient lunar phenomena, many of which have recurred in the same areas of the moon's surface.

Two lines of thought have been suggested. Either the surface is irradiated at night and glows on heating during the day, or subsurface layers at temperatures near − 50°C (*5*) are sporadically exposed and heated and give off as light the energy accumulated during many years of irradiation (by high-energy particles). We can now state, at least for the Sea of Tranquillity, that the energy efficiency of thermoluminescence is too low for the first effect to be seen and that the glow appears at a temperature too low for the second hypothesis to hold. Moreover, repeated thermoluminescence of the same material is unlikely as local temperatures never exceed 200°C.

J. A. EDGINGTON

Queen Mary College,
University of London, England

I. M. BLAIR

Atomic Energy Research
Establishment, Harwell, England

References and Notes

1. I. M. Blair and J. A. Edgington, *Nature* 217, 157 (1968).
2. D. B. Nash, *J. Geophys. Res.* 71, 2517 (1966).
3. C. J. Derham, J. E. Geake, G. Walker, *Nature* 203, 134 (1964).
4. K. H. Sun and J. L. Gonzales, *ibid.* 212, 23 (1966).
5. We thank Dr. W. J. French and Dr. A. B. Poole of the Geology Department, Queen Mary College, University of London, for assistance in separating and identifying the various mineral phases. We also thank Dr. J. A. Bastin for discussions particularly on lunar temperatures.

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Luminescence, Electron Paramagnetic Resonance, and Optical Properties of Lunar Material

Abstract. *Dust samples have been found to luminesce weakly under proton excitation, but not under ultraviolet. Damage, recovery, and heating effects have been investigated. Chips of breccia show luminescence, from white inclusions only, under ultraviolet and protons. Some rock chips show general luminescence, mainly from plagioclase. No natural or excited thermoluminescence has been found for dust or chips. The electron paramagnetic resonance spectrum shows the same broad* Fe^{3+} *dipole resonance for dust and for some chips; other chips show no response. The polarization characteristics of dust are found to be identical to those of the Sea of Tranquillity, independently of proton damage. Chips show characteristics unlike any part of the lunar surface.*

Dust sample 10084.6 showed no visible luminescence under ultraviolet excitation at room temperature, or when cooled in liquid nitrogen; two lamps emitting radiation at mainly 3650 and 2537 Å, respectively, were used. No infrared emission (beyond 7300 Å) was detected by a Ag-AgO-Cs photomultiplier or by a PbS cell when dust at either temperature was irradiated by intense visible light (cutoff at 6000 Å) from a quartz/iodine lamp.

Under excitation by 60-kev protons, weak luminescence with no afterglow was observed; the spectrum of this luminescence was scanned by a grating spectrophotometer with successive trialkali and Ag-AgO-Cs photomultipliers (Fig. 1). The emission is nearly white, with a low green peak at about 5600 Å and a lower blue one at about 4500 Å. The efficiency is very low; for fresh dust it is about an order of magnitude less than for Gnadenfrei meteorite (*1*) or standard basalt BCR-1 (*2*) and is estimated at about 10^{-5}. Basalt gave a peak of emission at about 7300 Å, and this was not found for the lunar dust.

The albedo, with a fresh MgO screen taken as unity, was about 7 percent when a tungsten lamp at 2850°K and a trialkali photomultiplier were used; for basalt it was about 40 percent. Heating the dust to about 760°C in argon (as described later) doubled both the luminescence efficiency under proton excitation and the albedo. The emission spectrum changed (Fig. 1) and so did the diffuse-reflection spectrum (Fig. 2), the dust now appearing brown in color. There is some x-ray evidence that heating produces some structural annealing, and this may be the cause of the increased efficiency. Dust heated to 960°C in argon appeared slightly darker than the 760°C sample, and its luminescence emission spectrum (Fig. 1) was slightly more like that for the fresh dust.

Damage by proton irradiation caused

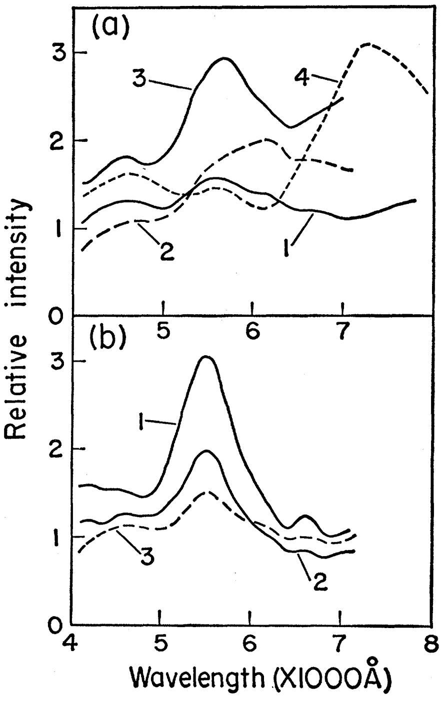

Fig. 1. Luminescence emission spectra with 60-kev proton excitation. (a) 1. Lunar dust 10084.6, fresh; 2. after heating to 760°C in argon; 3. after heating to 960°C in argon; 4. basalt BCR-1. (b) 1. Light fraction from rock 10044.43—mainly plagioclase. 2. Rock chip 10058.37. 3. Rock chip 10057.54. The intensity scales of the separate spectra are unrelated.

a rapid initial falloff in luminescence efficiency (typically, by a factor of 2½ in the first 5 minutes at 1 μa/cm^2 followed by a decreasing rate of falloff). However, the decrease was less rapid than for basalt, possibly suggesting that the lunar dust is already significantly damaged throughout (as discussed later); furthermore, there was no detectable change in visual appearance or in albedo, even after 8 hours of such damage. Heating the damaged dust to 600°C, for example, caused a recovery to double the "undamaged" efficiency and turned the dust brown. There was some indication of recovery without any color change after heating to only 150°C, but this may have been due to accidental disturbance of the dust surface. The dust which had been turned brown by heating was found to darken slowly with proton damage; perhaps after prolonged damage it would revert to the color of the fresh lunar dust.

All our rock chips were inspected with a microscope, under ultraviolet radiation of mainly 3650 or 2537 Å, separately. Most of the chips are breccias and showed no general luminescence; under 3650 Å excitation, several of them showed some faint blue-white luminescence from white inclusions. Under 2537 Å excitation, the effect was the same, plus some fainter white luminescence from clear inclusions. Only 10058.37,38, a coarse-grained rock, showed general luminescence except from its black ilmenite regions.

Under excitation with 60-kev protons, the effect was similar but more striking; there was negligible overall luminescence from the breccias, but bright blue-white or white luminescence from many white or glassy-looking inclusions, including those observed under ultraviolet. Fragments of some of the white inclusions were removed in an attempt to identify them by inspection with a polarizing microscope and by refractive index measurements (*3*). They were very soft (probably because they were highly fractured) and complex in structure. One large, white (blue-white luminescent) inclusion was found to be (probably) mainly cristobalite; other inclusions were probably complex mixtures of clinopyroxene and plagioclase, sometimes in the form of very small crystals embedded in glass. The coarse-grained rock 10058 luminesced brightly from all except its ilmenite regions, the luminescent parts apparently consisting of plagioclase with some pyroxene; its spectrum was scanned (Fig. 1). No difference was detected between the external chip 10058.37 and the internal one 10058.38. For comparison, a separated light fraction (probably 95 percent plagioclase) from another rock, 10044.43 (*4*), was scanned (Fig. 1). The efficiency was high (about 10^{-3}) and the spectrum very similar to that for 10058.37,38 except for a somewhat higher green peak—probably because in the rock the plagioclase peak is diluted by whiter pyroxene emission. Microprobe analysis of the separated plagioclase showed a high Sr content (800 ppm) and a trace of Yt.

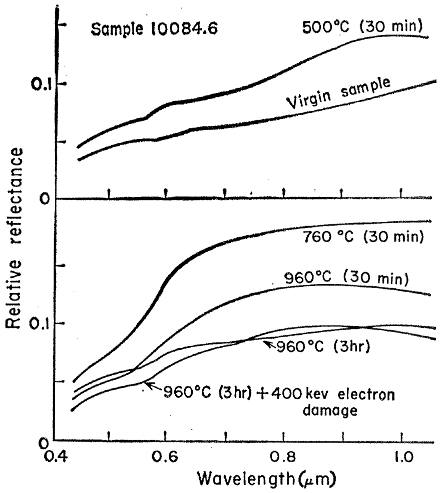

Fig. 2. Diffuse-reflection spectra of lunar dust 10084.6, measured at 18°C before and after various thermal treatments.

To look for thermoluminescence, samples were heated in a vacuum at a uniform rate (1°C per second) from 20°C to above 500°C and viewed through a chopper disk by cooled photomultipliers covering the range 0.35 to 1.1 μm. No detectable emission was obtained from either virgin samples or those subjected previously to ultraviolet irradiation, x-rays, 30-kev ions, or 400-kev electrons. Experiments with excitation by ultraviolet radiation at 77°K likewise gave no detectable thermoluminescence. This correlates with the absence of photoluminescence in most samples. Samples with small luminescent inclusions are still being studied.

Diffuse-reflection spectra were measured at room temperature before and after each thermoluminescence experiment and after excitation by ionizing radiation. Significant changes in body color of all dust samples are observed after they are heated in a vacuum or in an inert atmosphere to temperatures just above 200°C. The changes are even more marked after heating to higher temperatures; at 760°C, the dust assumes a medium brown color that is much nearer that of virgin samples when treatment at 900° to 960°C is carried out. No change in weight was found after such treatments and the microscopic appearance, apart from color, was unchanged. There was a slight tendency to sinter. The overall albedo, increased by heating to 760°C, then decreased with further rise in temperature. The change in body color is associated with a loss of broad absorption bands in the red and near-infrared regions; these absorptions return if treatment is carried out at 900° to 960°C. Electron bombardment of the latter samples does not produce significant changes, even for large doses (Fig. 2). However, proton irradiation does have an effect, as described above. Studies of x-ray diffraction patterns of powders from virgin and treated samples (960°C) indicate structure development after heating, due perhaps to the annealing out of crystalline defects. More investigations of these changes are in progress, including the detailed study of separated components.

The X-band (3 cm) equipment was used for measurement of the electron paramagnetic resonance spectra of samples at room temperature. Samples of dust showed a very broad but strong resonance of the dipole interaction broadened type with maximum at about the free spin value (g value slightly greater than that for free spin); this spectrum was relatively unaffected by thermal treatment involved in successive thermoluminescence experiments. However, heating at 900° to 960°C produced a strong, relatively unresolved, spectrum across the 6-kgauss field width of the usual spectrum. The above resonance spectrum for dust samples (10084.6) was also found for all rocks chips (10057.54,55; 10057.53,54,55; 10023.7,8; 10059.35,36; 10020.42; and for core samples 10004.31,32). However, in the case of clear fragments, 10058.37,38, no detectable signal was obtained. Observed signals are most likely due to Fe^{3+} ions in the components. The electron paramagnetic resonance results correlate with data on paramagnetic susceptibility given in the Lunar Receiving Laboratory preliminary report.

Since large changes in albedo and in reflection spectra can be obtained at temperatures not much greater than 200° to 250°C it seems unlikely that the lunar surface, or layers near to the surface, have been at such temperatures since their original formation or deposit. Formation at high temperatures must have been followed by relatively rapid cooling since only minutes at a few

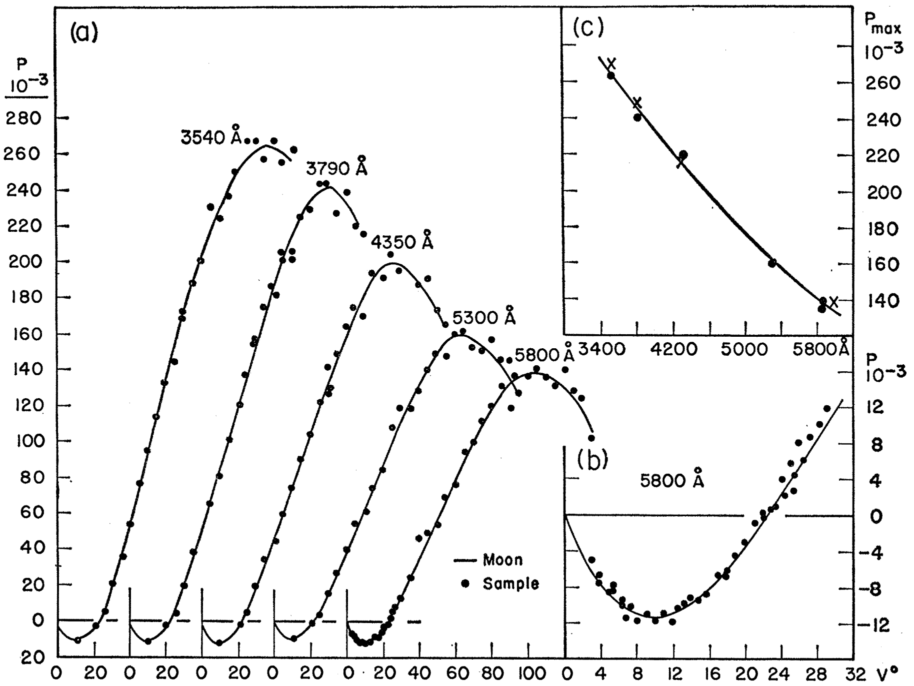

Fig. 3. Polarization curves for lunar dust 10084.6 and for Sea of Tranquillity. (a) Complete curves. (b) The negative branch, on a larger scale. (c) The change of P_{max} with wavelength. Crosses, Sea of Tranquillity; circles, lunar sample.

hundred degrees centigrade are needed to produce changes in the reflection spectra and hence in the body color. In view of the marked effects of heating to 900°C or so on the electron paramagnetic resonance spectrum, which suggests magnetic ordering, it would seem that the known magnetic properties of the lunar samples are also related to a rapid cooling process.

The polarization of light scattered by a surface gives a powerful indication of its texture and optical properties (*5*). We have investigated both dust and rock chips, and these gave different results.

The variation of degree of plane polarization *P* with angle between incident and emergent light *V* has been investigated for part of lunar dust sample 10084.6 and found to be identical with that obtained by telescopic measurements (*6*) of the Sea of Tranquillity. The results are shown in Fig. 3, where polarization is given as negative when in the plane of the incident and emergent rays, and as positive when at right angles to this (the only two cases found). The agreement between the lunar and sample results is within the experimental error of both of them; for example, the shape of the characteristic negative branch plotted in Fig. 3b agrees with the lunar curve to within 10^{-3} in *P*, providing the surface of the sample is roughened. Smooth dust gives a slightly shallower negative branch. The agreement is also good for the maximum of positive polarization, as regards the angle at which it occurs and particularly as regards the way its height, P_{max}, changes with wavelength as shown in Fig. 3c. Five filters were used with peaks from 3520 to 5850 Å.

It had already been shown, by comparison with terrestrial samples (*5*), that the characteristics of the lunar curve, as represented by the shape of the negative branch and by the wavelength variation of P_{max}, could only be produced by a fine, dark, roughened powder. The main significance of the agreement between the telescopic measurements and our lunar sample ones is that it suggests that the optical properties of the exposed surface layer may be taken as also representing the subsurface material which constitutes the bulk sample. This could not previously be confirmed. That the surface layer was not changed by its exposure to solar radiation was confirmed by attempts to damage a lunar dust sample by irradiation; prolonged bombardment with 60 kev protons produced no change in either the visual appearance of the dust, or in its polarization characteristics or albedo (measurements were made after 2 hours at about 1 μa/cm^2; the appearance was still unchanged after 7 hours). This may be because the dust is already damaged to saturation throughout the depth sampled, each individual grain having at some time spent a prolonged period on the exposed surface.

One of the heated dust samples referred to earlier was investigated. After proton bombardment it darkened perceptibly, but no change in its polarization curve was observed.

Surface chips were investigated from two rocks as different in appearance as possible.

1) Chip 10057.54 from the top (and presumably exposed) surface of a very dark grey rock. This showed a negative branch nearly as deep as for the dust sample and extending to $V = 19°$; P_{max} was about 350×10^{-3} and occurred at $V = 130°$. Its height was very sensitive to the position of the sample, and the value of P_{max} could be moved up and down over a range of at least 50×10^{-3}. The wavelength variation of P_{max} also changed with position. Photographs taken with a scanning electron microscope of part of the same region of this chip revealed a complex surface grain structure down to a scale comparable to the wavelength of light; this, combined with the darkness and opacity of the grains, probably accounts for the strong negative branch.

2) Chip 10058.37 from the surface of a rock containing much light-colored material. This showed no negative branch; P_{max} was about the same as for the previous rock. These results are consistent with the much larger amount of light material present.

The characteristics of these two extreme types of rock chip are both sufficiently different from those observed for any part of the lunar surface to suggest that exposed rocks have little influence on the optical properties of the moon, as observed from the earth. However, information about the characteristics of these exposed rocks is important in explaining measurements made for asteroids, which may be composed of the same materials but are too small to have sufficient gravitational attraction to retain a dust layer (*7*).

J. E. Geake
University of Manchester Institute of Science and Technology, Manchester, England
A. Dollfus
Paris Observatory, France
G. F. J. Garlick, W. Lamb
University of Hull, England
C. Walker
University of Manchester Institute of Science and Technology
G. A. Steigmann
University of Hull, England
C. Titulaer
Paris Observatory, France

References and Notes

1. J. E. Geake and G. Walker, *Geochim. Cosmochim. Acta* **30**, 929 (1966). Meteorite samples on loan from the British Museum (Natural History), to whom we are grateful.
2. F. J. Flanagan, *ibid.* **31**, 289 (1967).
3. We thank Professor W. S. MacKenzie for help with these identifications.
4. We thank Prof. J. Zussman for the loan of this sample, and for the data.
5. A. Dollfus, *Physics and Astronomy of the Moon,* Z. Kopal, Ed. (Academic Press, New York, 1962), chap. 5.
6. ——— and E. Bowell, final report U.S. Air Force contract 61(052)-914, June 1969.
7. We thank I. Robinson, A. Manwaring, and R. J. Fryer for assistance with the experimental work, and to the Science Research Council for grants (Manchester and Hull). We thank the Textile Technology Department, U.M.I.S.T., for the use of their Stereoscan miscroscope, and J. Sparrow for operating it.

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Luminescence of Apollo 11 Lunar Samples

Abstract. *Luminescence measurements were made of four lunar rocks, two terrestrial rocks (granite and gabbro), and one terrestrial mineral (willemite) by comparing the spectral curves with the curve of a barium sulfate standard. Efficiencies with 3000 angstrom excitation were* $\leqslant 6 \times 10^{-5}$ *for the lunar samples,* $\leqslant 8 \times 10^{-5}$ *for gabbro of very similar composition to the lunar samples, approximately* 10^{-4} *for granite, and approximately* 2×10^{-2} *for willemite. If these are typical values for other ultraviolet excitation wavelengths, the Apollo 11 site appears to contribute little to the observed lunar luminescence.*

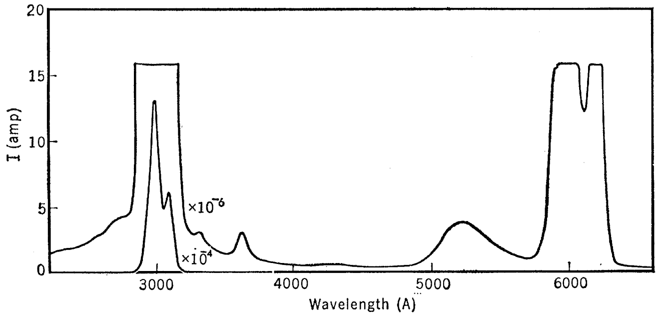
On the basis of lunar eclipse observations, Link *(1)* proposed that the light of the moon contained a luminescence component in addition to the reflected solar component. Later observations, especially by means of the Fraunhofer line-depth technique, seemed to confirm this idea *(2–5)*. Our objective is to evaluate these observations and understand the luminescence behavior of lunar lithologic materials by measuring the luminescence spectra and efficiencies of the lunar samples with the chief excitation sources in the space environment and by comparing the results with those of similar measurements of terrestrial rocks and minerals. The excitation sources of interest are ultraviolet, x-rays, protons, and electrons.

We give here some results of our measurements of the Apollo 11 samples with ultraviolet excitation. A Hanovia 2500-watt high pressure xenon-mercury lamp was the source of ultraviolet. The light, before striking the samples, passed through a Gaertner quartz prism monochromator with a Corning 7-54 filter at the exit slit to cut out wavelengths longer than 4000 Å. The light from the sample passed through a Jarrell-Ash 0.25-m grating spectrometer, either with or without a Corning 3-74 filter at the entrance slit to cut out wavelengths shorter than 4000 Å, and finally to an EMI 9558Q photomultiplier tube. The photomultiplier output was recorded by a Moseley 2D-2 X-Y recorder.

Initially, some runs were made on terrestrial comparison samples with a Hunter hydrogen capillary glow discharge lamp as a source. This lamp, which concentrates the glow discharge within a small capillary, is used as our source of hydrogen Lyman-alpha (1216 Å). The light in this case irradiated the sample directly with only a magnesium fluoride window intervening. Preliminary results appeared to show no significant luminescence. The luminescence excited by Lyman-alpha appears to be less than that excited by the middle and near ultraviolet and will require a different experimental set-up to be detected and measured. For this reason, subsequent runs on the lunar and terrestrial samples were made with maximized irradiation intensity with the Hanovia lamp. A wavelength band of about 200 Å width at half maximum, centered at about 3000 Å, was used.

The samples were mounted on a 12-position turntable inside a vacuum chamber. Six samples from four lunar rocks were included: 10044,38 (exterior) and 10044,53 (interior) from a coarse-grained igneous rock, 10048,36 (interior) and 10048,37 (bottom) from a breccia, and 10057,45 (interior) and 10022,55 (surface) from two fine-grained igneous rocks. The exposed surface area ranged from a little less than 1 to a little less than 2 cm^2. Terrestrial comparison samples consisted of granite (El Capitan formation, Mariposa County, California), gabbro (near San Marcos, San Diego County, California), and willemite (Franklin Furnace, New Jersey), the latter a highly luminescent mineral. The remaining three turntable positions were occupied by a barium sulfate surface to serve as a reflectance standard, a thermopile for absolute energy calibration of the excitation beam and the system, and an aluminized mirror for alignment of the system.

The luminescence efficiencies at 3000 Å excitation for all samples except the willemite proved to be too low to give a distinct, unambiguous luminescence spectrum. The curve for willemite (Fig. 1) shows the spectrum obtainable from a material of high efficiency, in this case about 2×10^{-2}. The other eight samples gave curves of the type shown in Fig. 2 recorded for lunar sample 10057,45. In these cases, at the maximized intensity of irradiation and the high sensitivities required to sense any luminescence, the effects of scattered light and of the small, nonzero transmission of the filter made



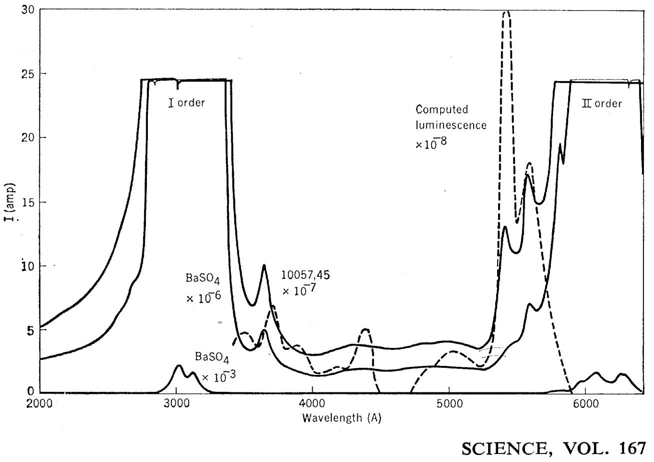


Fig. 1 (above). Luminescence of willemite with 3000-Å excitation. Fig. 2 (right). Luminescence of lunar sample 10057,45 compared with barium sulfate standard (3000-Å excitation).