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The cause and significance of luminescence in lunar plagioclase

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[Plate 1]

Most lunar samples luminesce under proton or electron excitation, and most of the emission comes from the plagioclase present. The cause of this luminescence has been found by investigating the emission and excitation spectra of lunar, terrestrial and synthesized plagioclases. Emission spectra show three broad peaks: a weak one around 450 nm which is common to most silicates; a dominant one around 560 nm for which the activator is found to be Mn^{2+} in Ca sites; and a very weak one between 700 and 780 nm for which we conclude the activator to be Fe^{3+} in Al sites. However, this near-infrared peak is usually the dominant one for terrestrial plagioclases; its weakness in lunar samples is attributed to reducing conditions when the lunar surface materials were formed causing more of the iron to be present as Fe^{2+}.

Luminescence photography of lunar rock chips is found to be a simple method of surveying plagioclase crystal forms in rough samples.

Introduction

We have now investigated the luminescence properties of a wide range of lunar samples, and most of them show some luminescence emission under proton or electron excitation. The component mainly responsible is found to be plagioclase $[(Na,Ca)(Al,Si)AlSi_2O_8]$, which nearly all lunar samples contain in the form of almost pure calcic plagioclase, or anorthite $[CaAl_2Si_2O_8]$; all their emission spectra are therefore very similar, and the dominant feature is found to be a green peak. However, comparison with terrestrial plagioclases shows one major difference, namely the strength of another emission peak which is in the near infrared, and which is usually dominant for terrestrial plagioclases but very weak for lunar samples.

Our aim has therefore been to identify the activators responsible for these two peaks, and particularly to interpret the difference in the near infrared emission for lunar and terrestrial materials in terms of the different conditions prevailing during their formation. The method used to identify the activators was based on theoretical prediction and comparison with known phosphors, followed by tests using pure synthesized plagioclase doped with the predicted activators. Final confirmation came from excitation spectra.

The luminescence efficiencies of lunar samples are low, ranging from about 10^{-5} for the darker fines to 10^{-3} for separated lunar plagioclase. The efficiency depends mainly on the plagioclase content, with some reduction by radiation-damage and grain-coating effects for fines samples; as these effects also darken the material, and as plagioclase is the main white component, the efficiency is roughly proportional to the albedo. Several workers (e.g. Nash & Greer 1970) have shown that any such luminescence of the lunar surface would be far too

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weak for it to be seen from the Earth, assuming credible excitation fluxes, so luminescence is no help in explaining any of the observed transient phenomena. It is nevertheless of interest as a means of exploring the solid-state physics of the lunar samples, and of giving some information about the conditions under which they were formed.

One application of luminescence is that, because the plagioclase present emits most of the light, this emission can be used to inspect and photograph the form and distribution of plagioclase crystals embedded in other materials, and a quick survey of rough samples can be carried out without the need to make thin sections.

Luminescence emission spectra

Figure 1 shows some typical emission spectra for lunar samples, showing fines, rocks and breccia from different missions. Figure 2 shows spectra for separated lunar plagioclase, for terrestrial plagioclases and for a plagioclase-rich meteorite – the eucrite Juvinas. In all these spectra emission is confined to the same three main peaks, but with considerable differences in their relative intensities.

All the spectra show some emission in the blue at about 450 nm; this peak is common to most silicates, and is probably due to lattice defects rather than to any particular activator. Sippel & Spencer (1970) have shown it to be shock-enhanced, so its relative strength in different samples may be an indication of their shock history.

Activation by Mn^{2+}

For most lunar samples the dominant emission peak is at about 560 nm, and this has been shown, by ourselves and others, to be caused by Mn^{2+} ions in Ca sites. This identification was predicted theoretically, and then tested by doping pure synthesized anorthite with Mn, which indeed resulted in a strong emission peak at 560 nm as shown in figure 3. More conclusive evidence has now been obtained from excitation spectra (Telfer & Walker 1975); these were obtained by recording the total luminescence emission with a photomultiplier and filter combination responding only to a narrow wavelength range centred on the 560 nm emission band, as the excitation wavelength was scanned through the range shown. The excitation spectra shown in figure 4a for lunar and terrestrial plagioclases are very similar to the one for synthesized anorthite deliberately doped with Mn^{2+}: they all contain the same two sharp peaks and a broader one at a longer wavelength, and are characteristic of a d^5 electron configuration, as expected for Mn^{2+}. The positions of the sharp peaks indicate that the bonding is mainly ionic, and the position of the longer wavelength band in relation to the larger sharp peak at 400 nm indicates a low crystal field strength. These factors suggest that Mn^{2+} is substituting mainly for Ca^{2+}.

Mn^{2+} is therefore shown to be the activator responsible for the most efficient luminescence of lunar materials. It is interesting that we earlier concluded (Geake & Walker 1966) that Mn^{2+}, in magnesium metasilicate, was also the activator responsible for the most efficient luminescence to be found for meteorites – the red peak for the enstatite achondrites. Mn^{2+} thus emerges as the most efficient luminescence activator for all the extra-terrestrial material as yet available to us. This is presumably because it is ubiquitous, and because of the ease with which it substitutes for Ca and Mg in silicates.
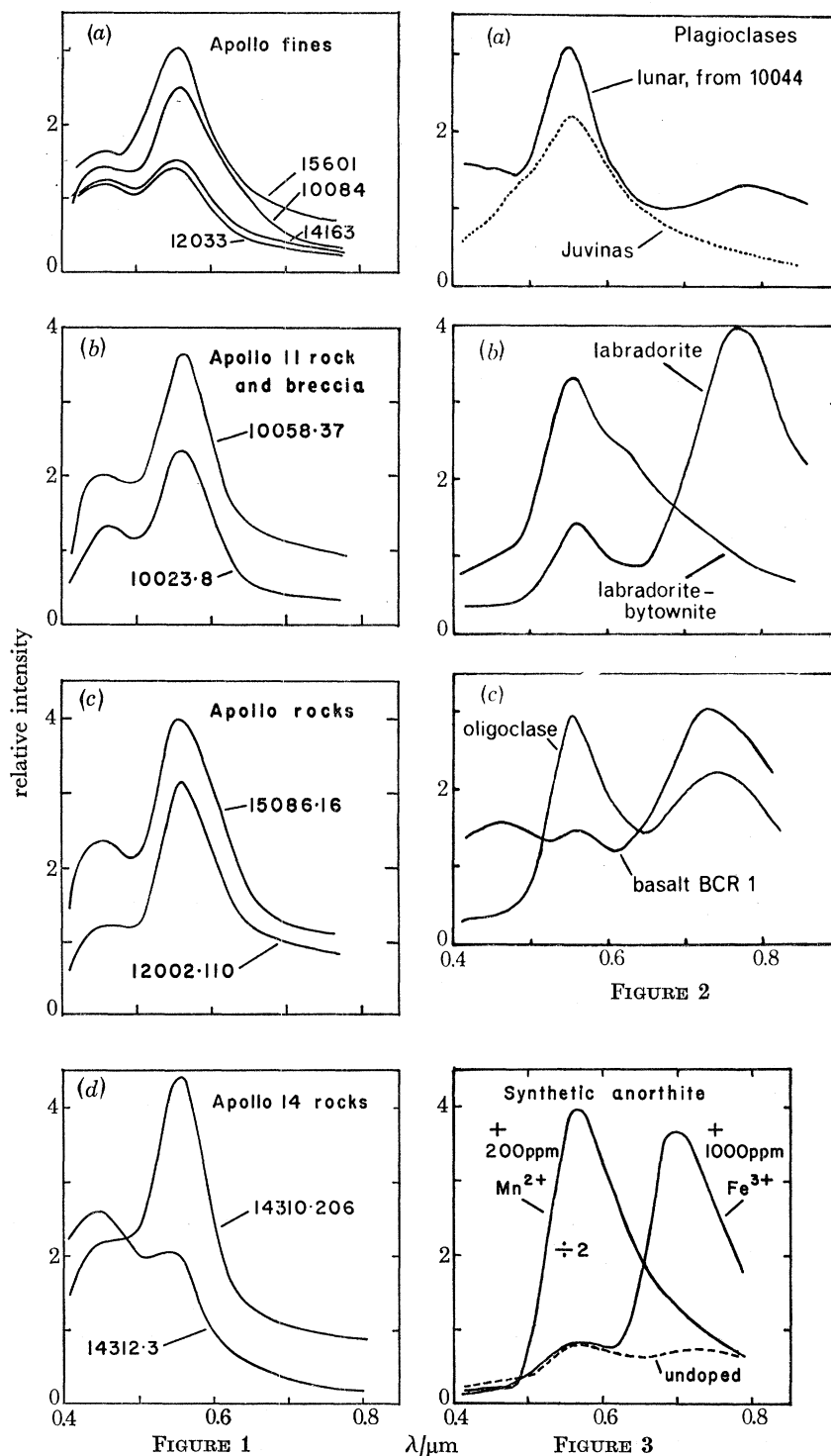
FIGURE 1. Luminescence emission spectra for lunar samples, under 10 keV electron excitation. The relative intensity scales for the different samples are unrelated. (From Geake *et al.* 1973.)

FIGURE 2. Luminescence emission spectra under 10 keV electron excitation for (*a*) a plagioclase-rich meteorite (the eucrite Juvinas) and for separated plagioclase from lunar rock 10044; (*b*) and (*c*) terrestrial materials. (From Geake *et al.* 1973.)

FIGURE 3. Luminescence emission spectra for synthetic anorthite, before doping, and after adding either Mn^{2+} or Fe^{3+}. (From Geake *et al.* 1973.)

Activation by Fe^{3+}

For most terrestrial plagioclases the dominant emission peak is in the near infrared between 700 and 780 nm, as shown in figure 2 *b*, *c*, although it is occasionally weak as for the labradorite-bytownite shown. However, for lunar samples this peak is always very weak; some of them do show a small peak, as shown in figure 2 *a*, but none of those in figure 1 do so, although most of them show a flattening out of the spectrum which indicates some very weak emission in this region.
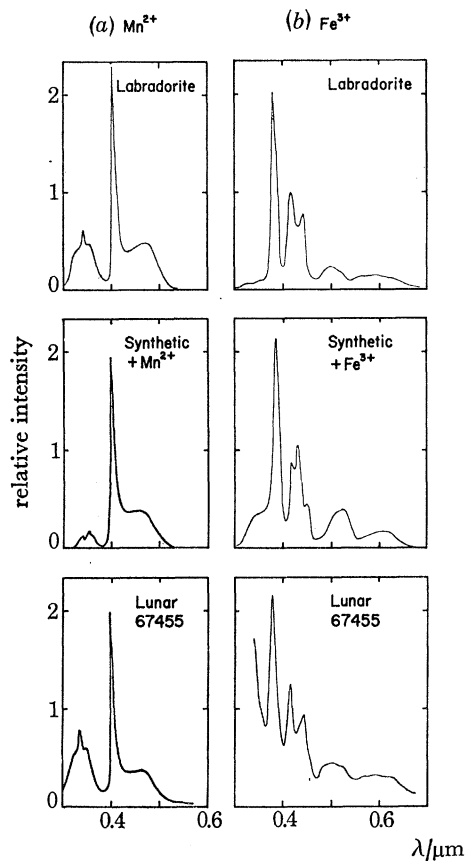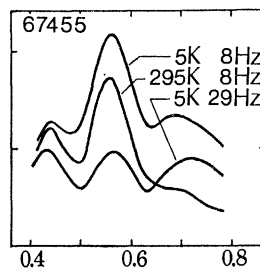

FIGURE 4. Luminescence excitation spectra for terrestrial labradorite, synthetic anorthite doped with Mn^{2+} or Fe^{3+}, and lunar rock 67455 (*a*) for the 560 nm emission peak, at room temperature, and (*b*) for 700–800 nm emission, with the samples cooled to 5 K.

FIGURE 5. Luminescence emission spectra for lunar rock 67455, showing the effect of cooling from room temperature (295 K) to 5 K, and of increasing the beam modulation frequency from 8 to 29 Hz.

We concluded on theoretical grounds that Fe^{3+} might be the activator responsible for this emission in the near infrared. This was tested by doping pure synthesized anorthite with iron under oxidizing conditions, so that it would be expected to go in as Fe^{3+}; this indeed resulted in a strong emission peak at about 700 nm, as shown in figure 3. Other evidence of the properties of this near infrared emission for a lunar sample is shown in figure 5. This sample shows a very slight peak at room temperature, but cooling to 5 K considerably enhances it; also, increasing the beam modulation frequency from 8 to 29 Hz reduces the Mn^{2+} peak in relation

to the infrared one, until the two are about equal. This is consistent with the expectation that Fe^{3+} should have a shorter decay time than Mn^{2+}, making it less affected by an increase in the modulation frequency.

More conclusive evidence was once again provided by excitation spectra (Telfer & Walker 1975); those in figure 4*b* were obtained by recording the total luminescence emission between 700 and 800 nm as the excitation wavelength was scanned through the range shown. In this case it was found necessary to cool the samples to 5 K: figure 5 indeed shows that cooling enhances the infrared emission peak – but not the green one. Once again a characteristic d^5 emission spectrum is obtained in each case, as is also to be expected if Fe^{3+} is the activator responsible, and the spectra for the terrestrial and lunar samples are very similar to that for synthesized anorthite to which Fe^{3+} has been deliberately added. The spectra are also very similar to that found by Pott & McNicol (1972) for Fe^{3+} in lithium aluminate. The single strong sharp peak at 380 nm with a weaker double or triple one around 420 nm is characteristic of Fe^{3+} in oxygen coordination, and the positions of these peaks suggest a high covalency. The wider spread of the whole group of d^5 bands, as compared with the Mn^{2+} group, is caused by the higher charge; its range indicates a relatively high crystal field strength, but it is not high enough for the iron to be in other than a tetrahedral site. From all the evidence available, it seems most likely that the activator responsible is Fe^{3+} in Al^{3+} sites.

The main interest in this emission band in the near infrared arises because its strength represents the main difference between the luminescence emission spectra for lunar plagioclase, for which it is very weak, and terrestrial plagioclases for which it is usually dominant. We suggest that this is because a higher proportion of the iron in lunar materials is present as Fe^{2+}, which quenches luminescence rather than causing it; this would imply that reducing conditions were prevailing when the lunar surface materials were formed, a conclusion which is supported by geological evidence. We also find that the strength of the luminescence emission tends to decrease with time under our excitation beam, which is probably due at least in part to the reducing effect of the beam converting Fe^{3+} to Fe^{2+}.

The other extra-terrestrial plagioclase represented in figure 2*a* – the plagioclase-rich meteorite Juvinas – also has an emission spectrum that is very weak in the near infrared, suggesting that it too was formed under reducing conditions.

Only two of all the lunar samples we have investigated showed a discernible luminescence emission peak in the near infrared at room temperature – but of these, the weaker one nevertheless showed a strong low-temperature excitation spectrum characteristic of Fe^{3+}, showing this is to be a much more sensitive method of detecting it. We therefore suggest that the low-temperature excitation spectrum method should now be used to survey the Fe^{3+} content of a wide range of lunar samples, in the hope of correlating the information thus obtained about the state of reduction during their formation with other evidence as to their history and location.

LUMINESCENCE PHOTOGRAPHY

As plagioclase is the most luminescent component of lunar samples, and as most of the samples do contain plagioclase, it is possible to use visual inspection or photographic recording of luminescence emission as a quick way of inspecting the size and form of the plagioclase crystals present. This can be carried out with rough chips, without the need to make polished thin sections, and it therefore provides a quick survey method for use in deciding which samples

to examine in more detail by conventional methods. We have shown several examples of such photographs elsewhere (Geake *et al.* 1972*a, b*), and one of them is shown in figure 6, plate 1. It is a luminescence photograph of a rough-sawn slab of lunar rock, and it shows fan-shaped arrays of plagioclase crystals; these seem to resemble sections of arrays of rod-shaped crystals radiating from points in three dimensions, as found in lunar rocks by Gancarz *et al.* (1972) and in terrestrial harrisite on a much larger scale by Donaldson *et al.* (1973).

If luminescence colour photographs of thin sections are used, variations of colour can show variations in activator content across a crystal. Also, Sippel & Spencer (1970) have shown, by taking colour photographs with a luminescence microscope, that the blue emission of plagioclase is enhanced by strain and can indicate the shock history of the crystal.

Electron microprobe analysis, used in conjunction with luminescence photography of the same region of a thin section, has been used to identify luminescent components (Geake *et al.* 1973). So far, regions luminescing blue, green or white have been identified as plagioclase; regions luminescing orange have been found also to be plagioclase, but in a partially vitrified state. Other components present as very small regions and luminescing in the red have yet to be identified.

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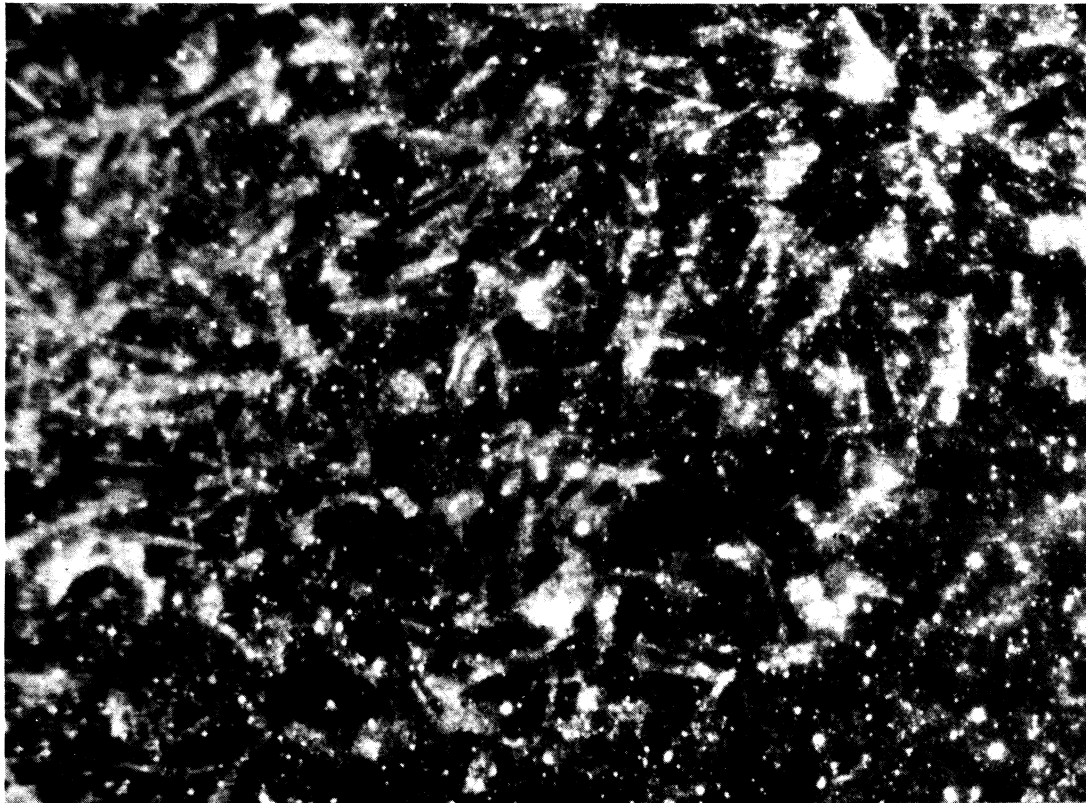Telfer, D. J. & Walker, G. 1975 *Nature, Lond.* **258**, 694–695.

FIGURE 6. Luminescence emission photograph of lunar rock sample 12051.16; the height of the print represents about 1 cm. (Enhanced-contrast black-and-white print by N. W. Scott from colour transparency by Mills & Geake.)
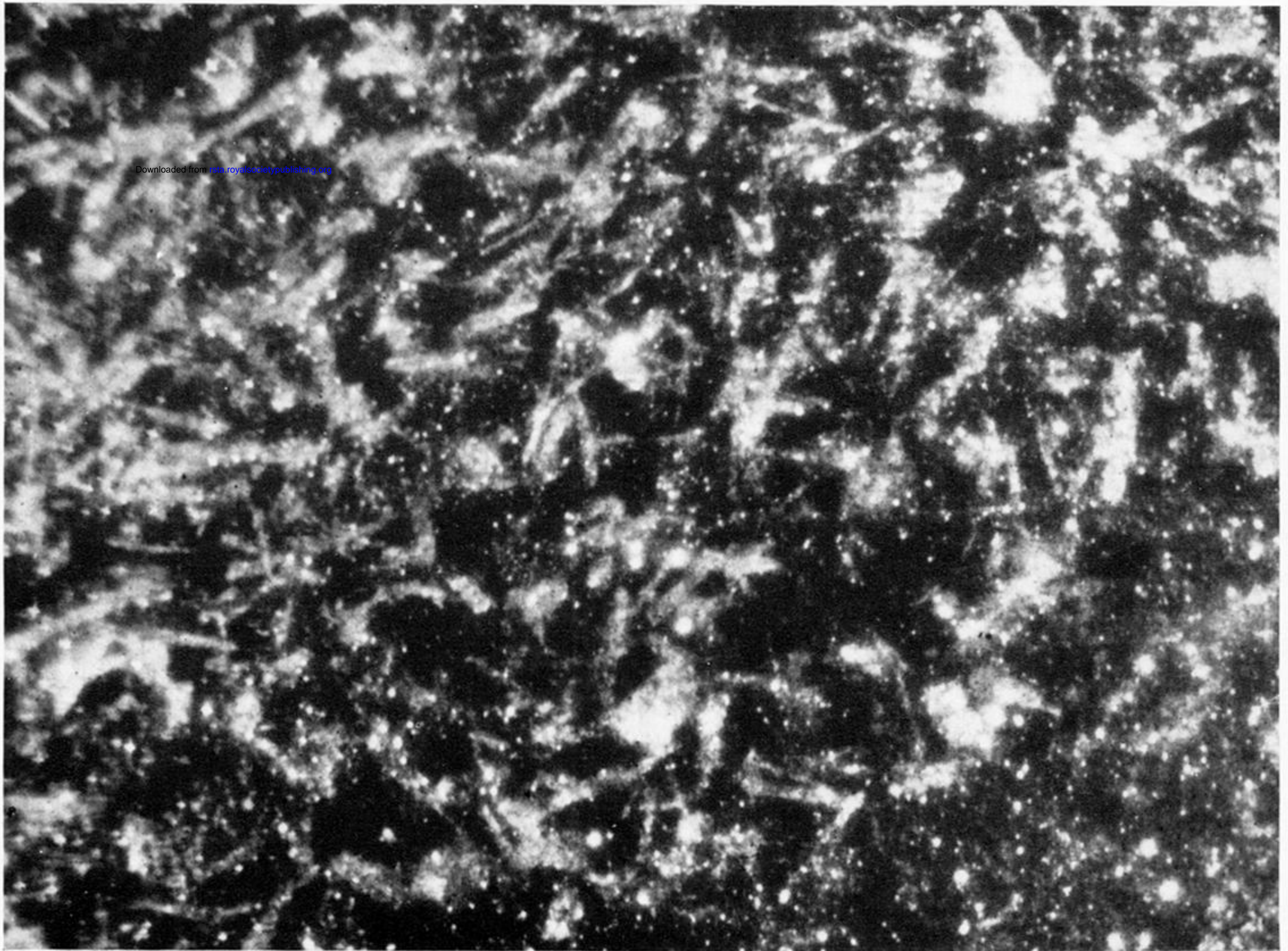
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