The cathodo-luminescence of minerals in thin section

With Plates X and XI

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Summary. The cathodo-luminescence of minerals in thin sections of rocks has been examined with the aid of an electron-probe microanalyser and also with a simple electron source producing an unfocused beam. Experimental details of the technique are briefly described and colour photographs, taken at a primary magnification of 30 times, are included. The observed variations in colour and intensity of luminescence are interpreted in the light of electron-probe and spectrochemical determinations of trace elements. Applications of the technique are discussed.

SINCE it was first reported by Crookes in 1879, the phenomenon of cathodo-luminescence in minerals has been extensively investigated, both on account of its fundamental interest and of its technical importance. Ultraviolet-excited fluorescence has also been widely studied and used for mineral identification, mainly on a hand-specimen scale, but little attention appears to have been given to the possibilities afforded by the microscopical examination of minerals and rocks in thin section while under electron bombardment.

The intensity of the luminescence produced by electrons is normally considerably greater than that induced by ultraviolet light; Crookes, who in collaboration with Maskelyne examined the effect in diamond, sapphire, ruby, emerald, various sulphides, quartz, and zircon, observed that 'substances known to be phosphorescent under ordinary circumstances shine with a great splendour when subjected to the negative discharge in high vacuum'. Cathodo-luminescence is also observed in minerals in which ultraviolet or visible light produces no effect. It may be noted that the cathodo-luminescence will be generated only in a very thin layer at the surface of the target material. In silicates for example, the extreme range of 10 keV electrons is only of the order of 1 μm.

Luminescent minerals are of three main types. Those in which luminescence is an intrinsic property of the pure substance are comparatively rare; scheelite and some uranium minerals fall into this group. The second group contains minerals which are non-luminescent in the pure state but which are 'activated' by the presence of small concentrations of impurities: for example, many specimens of calcite exhibit an orange-red luminescence due to traces of manganese and lead. In the third group are minerals which have been exposed to ionizing radiation and which become luminescent when subsequently illuminated with visible or ultraviolet light, or in some cases, when heated. In this case, impurities may also play a part in determining the wavelength of the emitted light. The examples discussed here are from the second group and one of the applications of the technique to be described is to give information about the distribution of certain trace elements in and among the mineral grains within a rock.

Experimental method

Cathodo-luminescence in thin sections is conveniently observed in the electron-probe analyser. Figs. 1*a* and *b* illustrate alternative arrangements of the light-optical objective in relation to the magnetic lens of the instrument. The point of impact of the focused electron probe may be seen as a bright spot of light in luminescent minerals; by increasing the current through the magnetic lens, the focal length is reduced and the diameter of the electron-beam at the specimen may be made equal to that of the optical field.

The illustrations in this paper have been obtained with a simple hot-cathode electron gun with no auxiliary electron lenses. The equipment was mounted on a normal microscope from which the condenser sub-stage had been removed. In order to prevent light from the filament from reaching the specimen, the electron beam was directed through two misaligned apertures by means of a small magnet. Many variations in design are possible and the equipment could almost certainly be further simplified by using a cold-cathode discharge tube.

Colour photographs have been taken at an electron-beam accelerating voltage of 9 kV. The current density of the beam was not accurately controlled but was of the order of 0·1 μA/mm^2. Under these conditions, with an 0·25 N.A. objective, the luminescence was clearly visible in the microscope in a normally lighted room. Exposure times on 'Ferrania' colour film (daylight type) were approximately 20 minutes.

The specimens used were normal uncovered thin sections, polished only when also examined in the electron probe. They were coated with a conducting film of evaporated aluminium, to prevent charging of the surface by the electron beam. With lower accelerating voltages—of the order of 2–3 kV—the rise in the secondary emission coefficient for electrons would probably eliminate the need for the conducting layer.

The sharp definition of the pictures, which is much better than that of corresponding transmitted light photomicrographs of the uncovered sections, is due to the very small penetration of the electrons into the surface, which although rough, lies entirely within the depth of focus of the objective.

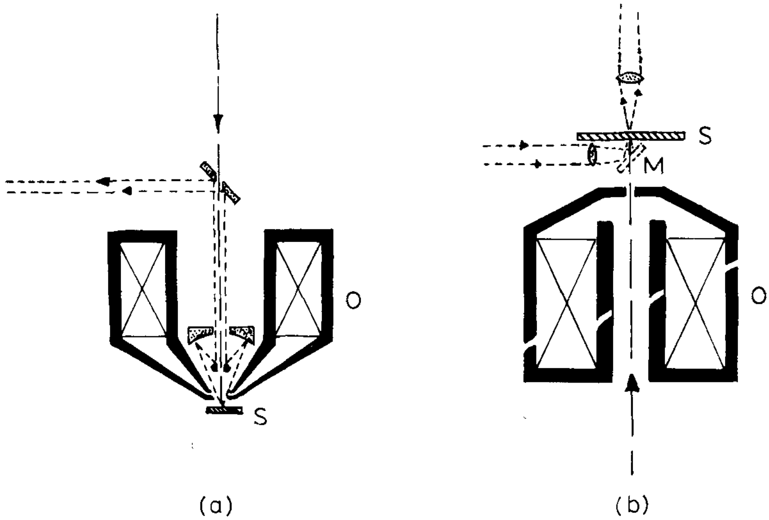

FIG. 1. Arrangement of the light-optical microscope objective in relation to the specimen (*s*) and the final electron lens (*o*) in (*a*) an instrument using a reflecting objective (Cameca) and (*b*) the instrument used in this work. (Electron beam axis — —; light path- - - -.) The mirror *M* is inserted for normal transmitted light examination of the section in arrangement (*b*).

Calcite-dolomite

The calcite in this section of a carbonatite from Palabora, S. Africa (No. 65919), shows the typical orange-red fluorescence produced by the presence of Mn^{2+}. The exsolved dolomite, however, shows only a very weak bluish fluorescence which appears black in the colour plate X*a*. Analysis for Mn with the electron probe showed that this element is chiefly concentrated in the calcite (0·13 ±0·02 %) but that its concentration in the dolomite is still significant (0·07±0·02 %). The very great difference in luminescence properties, although possibly associated with the different composition of the host minerals, probably results from the difference in iron contents of the two phases. The dolomite was found to contain 0·8 ±0·1 % Fe and the bulk of the calcite approximately 0·2 ± 0·02 % Fe. In almost all phosphors the effect of iron is to depress the fluorescence intensity.

The dependence of intensity on iron content is also indicated by the behaviour of the calcite in the immediate neighbourhood of dolomite where the intensity of the red colour is noticeably greater. A traverse with the electron probe across this zone reveals (fig. 2) an iron-depleted region, presumably resulting from the diffusion-limited uptake of iron by the dolomite in the late stages of exsolution.

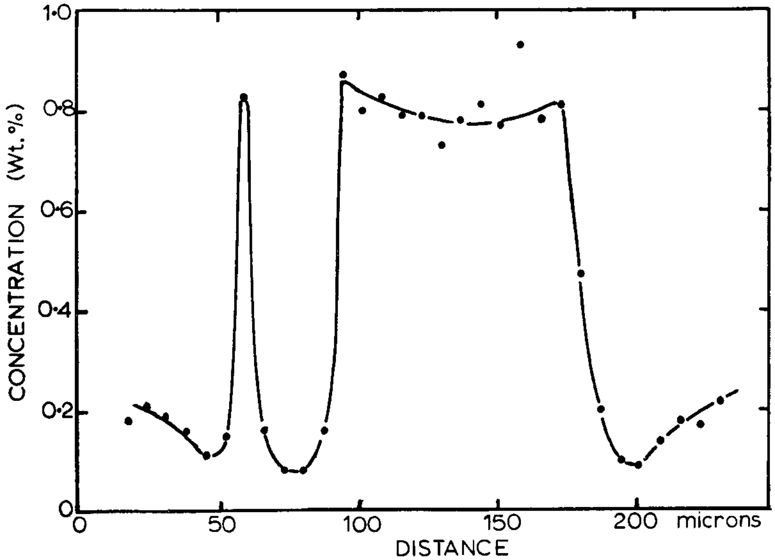

Fig. 2. Variation of iron concentration in calcite near boundaries with dolomite (Palabora carbonatite).

Zoned calcite

The sensitivity of the fluorescence intensity to the Mn/Fe ratio in Mn excited phosphors is illustrated by plate X*b*. This shows a luminescent thin section of a single crystal of calcite from Strontian, Scotland (Carne Collection, No. 347). The alternation between brightly fluorescent and non-fluorescent zones within this crystal is not correlated with any obvious change in optical properties and in transmitted light is only marked by occasional opaque inclusions aligned parallel to the crystal faces. Electron-probe measurements showed a marked variation in Mn and Fe contents between light and dark regions, with approximately

1·0 % Mn and 0·1 % Fe in the former, and 0·1 % Mn and 1·0 % Fe in the latter, the zones of medium brightness showing intermediate values. The alternation of Fe and Mn is shown in the scanning pictures (fig. 3) of part of a similar crystal. The calcite in a hand specimen of this rock fluoresced brightly under UV, implying trace concentrations of lead in addition to manganese (Schulman *et al.*, 1947). Spectrographic analysis of the whole rock gave 10 ppm Pb.

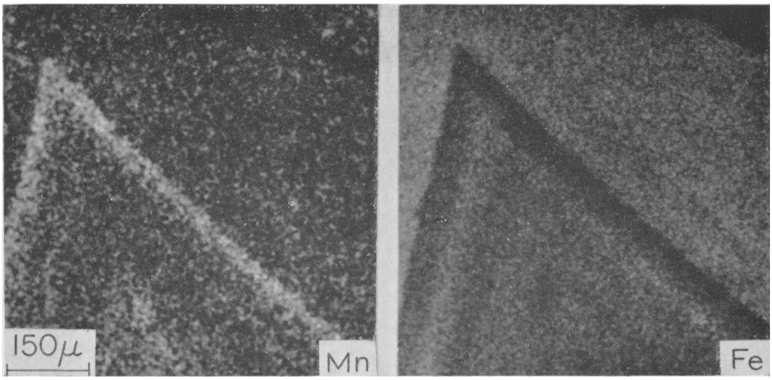

FIG. 3. X-ray scanning pictures showing the distribution of Mn and Fe in part of a zoned calcite crystal from Strontian.

The observations on this material and on the Palabora carbonatite suggest that concentrations of iron in excess of about 0·3–0·5 % are effective in extinguishing the Mn-induced cathodo-luminescence of calcite.

Calcium silicates and silicate-carbonates

Plate XI*a* shows the luminescence of a tilleyite–spurrite–calcite marble from an area ¾ mile north of the hotel at Kilchoan, Ardnamurchan, Scotland (No. 79682). The activator has not been positively identified; electron-probe analysis showed that the concentration of both manganese and iron in each of the three principal phases is less than 0·05 %. Optical spectrographic analysis of the whole rock, however, gave an Mn content of approximately 0·05 %, the greater part of which is possibly contained within grossularite, also present in the rock.

In a further specimen (No. 84786) from the same general locality, wollastonite and kilchoanite (Agrell, 1964) occur together as shown in plate XI*b*. Manganese has been found in equal amounts in both phases (approximately 0·05 %), whereas iron is concentrated in the wollastonite which contains 0·1 % as compared with less than 0·03 % in the kilchoanite.

A third section (No. 79677) containing a reaction zone of tilleyite between wollastonite and calcite gave colours consistent with those in the previous two sections, i.e. wollastonite, bright green; tilleyite, red; and calcite, blue-black. Here again manganese was found in the tilleyite (0·15 %) and in the wollastonite (0·11 %), iron also being present to about 0·07 % in both minerals. The calcite, on the other hand, contained less than 0·03 % of both manganese and iron.

The luminescence spectrum of single grains of the kilchoanite and wollastonite in the section shown in plate XI*b* were obtained with the aid of the electron-probe and a low-dispersion spectroscope. Both showed a band extending from the green to the red, the red emission being very weak in the case of wollastonite. A qualitative estimate of the lifetime of the phosphorescence was obtained by traversing the electron beam across individual grains and noting the colour and length of the trail remaining in its path. Both minerals showed a red phosphoresence with a duration estimated to be between 1/10 and 1/100 sec similar to that observed in manganese-activated calcite. It is therefore almost certain that manganese is responsible for the luminescence in the last two sections, and since no other activator could be identified in the calcite–tilleyite–spurrite intergrowth, it seems reasonable to suggest that the colours in this case are due to the same element but at considerably lower concentration and below the limit of detection of the electron-probe.

The range of colours observed here is the same as that recorded for other solid phosphors containing divalent manganese. Early work by Linwood and Wehl (1942) suggested that the wavelength of the emitted light was a function of the co-ordination number of the manganese in the host lattice and further that short Mn–O interatomic distances should favour short wavelengths. The work of Klasens *et al.* (1953) on a series of compounds of the type ABF_3–Mn which have the perovskite structure shows conclusively, however, that the wavelength of emission decreases as the distance Mn–F increases. Similar correlations for other structures were obtained by Fonda (1957). These results are consistent with the view that the emission of the free Mn^{2+} ion is shifted from the ultraviolet to the visible by an amount which depends on the magnitude of the perturbing effect of the field of surrounding atoms in the structure.

Although it now appears possible to correlate the wavelengths of emission with cation–anion distance or ionic radius in certain groups of isostructural compounds, no useful predictions can be made on a theoretical basis about the luminescence from a given combination of host and activator. This is particularly true of the complex calcium silicates where a variety of possible sites for Mn-substitution exist, and where structural information is often incomplete.

Quartz

Under electron bombardment most sections of quartz show only a faint blue luminescence, although Claffy and Ginther (1959) have described a red-luminescent material synthesized from amorphous silicic acid and containing minor amounts of Al^{3+} and Mn^{2+}. Only rarely during the course of electron-probe analysis of thin sections have we observed a colour other than pale blue; in one such exception the quartz of a kyanite–staurolite–biotite–muscovite schist (No. 83235, locality 41, Chinner, this volume, p. 134) showed a pinkish colour. Although manganese is present in other minerals in the rock, extended measurements with the electron-probe failed to detect manganese above 0·01 %, and the luminescence did not exhibit the phosphorescent red tail referred to above.

Perthite

The two feldspars in the coarse perthite of the Madoc granite (Tuttle, 1952) gave distinctly different intensities of a bluish-purple fluorescence, suggesting the unequal partition of an activator between the two phases. No identification of the activator has been made.

Discussion

The main practical application of the cathodo-luminescence of thin sections is clearly its use in association with the electron-probe analyser. Here it aids identification of small grains in those sections in which a colour may be associated with a particular mineral. It also serves to draw attention to variations in trace concentrations of elements which behave as activators, and also those such as iron which quench fluorescence. Since the concentrations involved are often small, their variation would normally pass unnoticed except as a result of detailed electron-probe measurements involving long counting times.

Recently Stenstrom and Smith (1963) have shown that primary and secondary calcite in crinoids and primary and secondary quartz in sandstones and quartzites can be distinguished by differences in cathodo-luminescence in the electron probe. They suggest further that in some cases intensity may be correlated approximately with temperature of formation. It would appear that the most probable reason for such a correlation, apart from the existence of polymorphic forms of the host mineral, would be the effect of temperature on the distribution of an activator between different minerals in a rock. The experiments of Dobischek (1934) on synthetic willemite activated with manganese suggest also the possibility of correlating luminescence colour with temperature of formation when substitution of the activator may take place at more than one type of site in the host lattice.

It is clear that only very limited information on the nature of the activator or the host may be obtained from an examination of the luminescence alone. In the carefully controlled conditions used in synthetic work, it may however be possible to use known cathodo-luminescence colours of, for example, manganese, to identify mineral grains and to assess the homogeneity of products of reaction. With a broad electron beam a slide containing many hundred small grains could be examined rapidly and the proportion of minor constituents determined by grain counting.

Acknowledgements. We should like to thank Mr. A. Tredale for his valued assistance in taking the colour photographs and also Mr. B. K. Harvey of the Cavendish Laboratory for his kindness in preparing enlarged copies of the original transparencies for publication.

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EXPLANATIONS TO PLATES

PLATE X

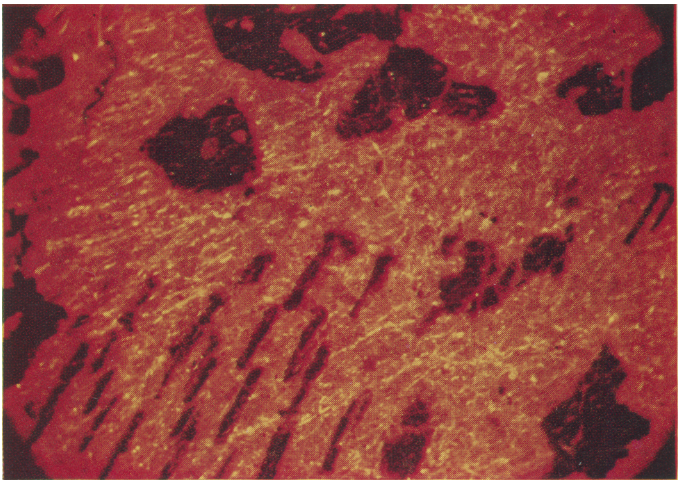
(*a*) Cathodo-luminescence of a section of calcite (red)–dolomite (black) intergrowth from Palabora (× 80).

(*b*) Cathodo-luminescence of a single crystal of calcite showing rhythmic variations due to fluctuating Mn/Fe ratio (× 80).

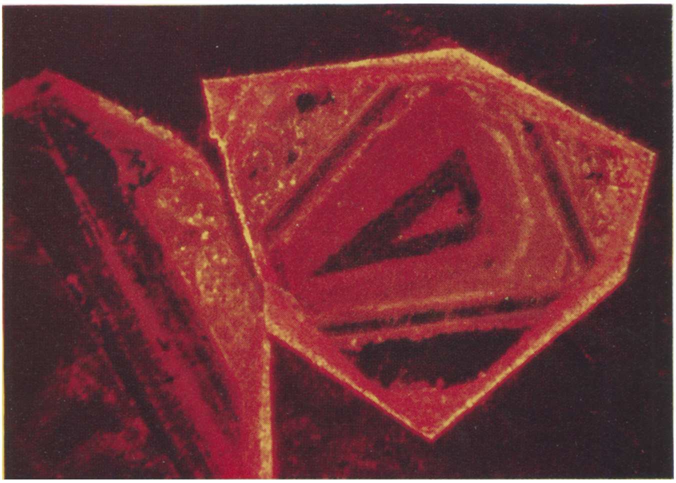
PLATE XI

(*a*) Cathodo-luminescence of a tilleyite (red)–spurrite (green)–calcite (blue-black)–marble from Kilchoan (× 80).

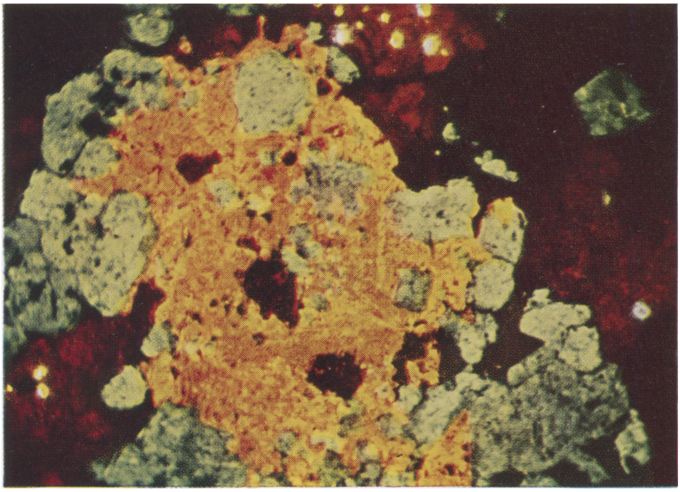
(*b*) Cathodo-luminescence of kilchoanite (orange-yellow) and wollastonite (green) (× 80).



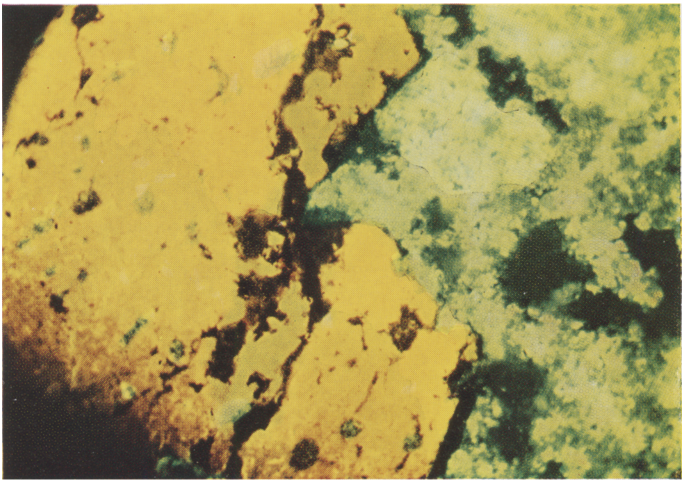
a. Cathodoluminescence of a thin section of a calcite (red)-dolomite (black) intergrowth from Palabora. (×80)



b. Cathodoluminescence of a single crystal of calcite showing rhythmic variations in colour due to fluctuating Mn/Fe ratio. (×80)



a. Cathodoluminescence of a tilleyite (red)-spurrite (green)-calcite (blue-black) marble from Kilchoan. (×80)



b. Cathodoluminescence of kilchoanite (orange-yellow) and wollastonite (green). (×80)