



J. GONI AND G. RÉMOND ON CATHODOLUMINESCENCE IN  
BLENDE

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## Localization and distribution of impurities in blende by cathodoluminescence

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**SUMMARY.** Cathodoluminescence, produced by electronic bombardment in the microprobe, can serve to indicate the nature and distribution of elements present in amounts below the normal detection limit of the probe. This is illustrated by a study of specimens of blende from various localities.

AMONG the tasks of the geochemist is the determination of the nature, amount, and distribution of trace elements in rocks. Electron microprobe studies have shown that these elements are localized in primary or secondary discontinuities in the minerals or in the rocks, where the local concentration may attain high values. When, however, the impurities are in very small amount, the electron microprobe may be unable to reveal and localize them, yet their local concentration may be sufficient to make certain minerals luminescent under the electron beam. The light emission sometimes observed during a microprobe analysis is termed cathodoluminescence and is produced by diffusion of electrons in the mineral and transfer of energy to 'impurity centres' (*centres luminogènes*) due to the presence of impurities.

We have chosen blendes from several localities for study. Several examples of zoning apparent only under the electron beam are shown in Plate I; they illustrate the zoned distribution of impurities, though no heterogeneity is disclosed by classical microscopy. These photographs were obtained with the electron microprobe when the electron beam was defocused so as to irradiate an area about 300  $\mu$  in diameter.

We have been able to divide the specimens studied into four groups: those that neither luminesce under excitation by ultra-violet light nor under cathodic excitation (in these specimens iron can be shown to be present in appreciable amounts, and it is well known that this element tends to quench luminescence, as do nickel and cobalt); those that are not photoluminescent but are characterized by a more or less intense cathodoluminescence; those that are both photoluminescent and cathodoluminescent, the emissions being similar in colour under the two forms of excitation, though the intensities may be different; and those that show a cathodoluminescence decreasing with time of exposure, but a steady luminescence under ultra-violet irradiation.

A qualitative analysis of each specimen for trace elements was made by emission

spectrography before undertaking their localization by examination, in the electron microprobe, of areas showing different luminescence. An impurity present to an amount below the limit of detection of the microprobe may suffice to modify the colour or the intensity of the luminescence, and one can utilize the cathodoluminescence to demonstrate heterogeneities without seeking to identify the impurities precisely.

However, we note that the colour of the luminescence is the same under electronic bombardment and under ultra-violet irradiation; hence one may form some idea of the impurity or group of impurities associated with a luminescent zone by considering the known photoluminescence of spectrographically analysed blends. Thus in certain blends one may reasonably assume the presence of traces of copper in zones emitting a green luminescence, of cadmium in yellow areas, and of manganese in orange-yellow ones. And this hypothesis is confirmed, so far as copper is concerned, by a comparison of the luminescence of natural specimens with that of a synthetic blende containing a trace of copper.

We have been able to identify the same group of elements, copper, gallium, and germanium, in several specimens of different origins, and to associate gallium and copper with red luminescence, germanium and copper with green.

It is difficult to identify the nature of structural defects, but comparison of the luminescent spectra of natural and synthetic specimens of a mineral will permit a more precise identification of the nature of impurities. As many minerals are cathodoluminescent, one may use this phenomenon to disclose growth figures and the distribution of defects in crystals. The role of physical and chemical defects in the emission of luminescence by crystals, together with the results of a study of a large number of specimens of blende, of various origins, are discussed in full in a paper to be published by the Centre National de la Recherche Scientifique under the title 'Dosage des éléments à l'état de traces dans les roches et les autres substances minérales naturelles'.

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## EXPLANATION OF PLATE I

FIGS. 1-4. Cathodoluminescence of blende from Orpierre, Hautes-Alpes, France. Spectrographic analysis reveals the presence of copper, cadmium, and manganese, which may be associated with green and blue, with yellow, and with orange-yellow luminescence respectively.

FIGS. 5 and 6. Cathodoluminescence of blende from Djebel Gustar, Algeria. Spectrography reveals the presence of copper, gallium, and germanium. The electron microprobe shows these three elements to be present in areas luminescing red and blue-green; an enrichment in gallium and impoverishment in germanium is noted in the red areas as compared with the blue-green ones.

FIG. 7. Photoluminescence of blende from Tarvisio, Tirol, Austria. The same luminescence is observed under cathodic bombardment, but its intensity falls off very rapidly and could not be recorded.

FIG. 8. Cathodoluminescence of blende from Mežica, Slovenia, Yugoslavia.

FIG. 9. Photoluminescence of blende from Lafatsch, Tirol, Austria. Its cathodoluminescence is identical.

FIGS. 10 and 11. Cathodoluminescence of blende from Kipushi, Katanga. The behaviour in respect of copper, gallium, and germanium is the same as that shown by the blende from Djebel Gustar.

FIGS. 12 and 13. Cathodoluminescence of blende from Santander, Spain.

FIG. 14. Cathodoluminescence of blende from Kirki, Alexandropolis, Greece.