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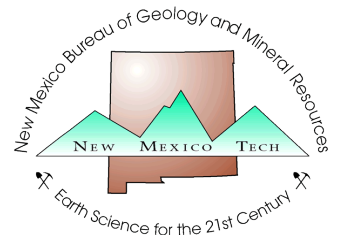
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# Some geological applications of cathodoluminescence

## examples from the Lemitar Mountains and Riley travertine, Socorro County, New Mexico

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### Introduction

Cathodoluminescence (CL), the characteristic visible radiation (color) produced in a mineral subjected to bombardment by electrons, was first observed in the 1870's by Crookes (1879). It has significant applications in petrology, although many petrologists do not utilize it. Luminescence in CL is typically more intense than that produced by ultraviolet light (see pp. 25–30, this issue); CL is also observed in minerals that do not luminesce under ultraviolet light.

Cathodoluminescence is produced by excitation of electrons in specific chemical impurities (activators) within a crystal structure. When excited electrons return to their ground state, visible light may be emitted. CL may be produced at sites altered by radiation damage, chemical heterogeneity, electron charge displacements, and structural defects (Mariano, 1976; Nickel, 1978), or by unidentified processes (Barker and Wood, 1986a). CL may be inhibited in a mineral by other impurities (quenchers), which counteract the activators to prevent or diminish luminescence. Other impurities (sensitizers) can enhance CL by aiding transfer of energy to activator electrons (Barker and Wood, 1986a). The observed color of a mineral under CL depends upon complex interactions among activators, quenchers, and enhancers along with instrument conditions (manufacturer, accelerating voltage, beam intensity, vacuum, ambient gas, and others), specific microscopes and objective lens/condenser combinations, and an individual's perception of color. Heating of the sample by the electron beam can decrease luminescence and/or change the color. Therefore, most descriptions of CL color in the literature are subjective. Detailed CL studies that minimize this subjectivity require an emission spectrograph to record the wavelength and relative intensity of the luminescence (Mariano, 1976); this equipment was not available to us.

### Instrumental conditions

Cathodoluminescence was observed using a Technosyn Cathodoluminescence Stage, Model 8200 MK II, attached to a Nikon Optiphot nonpolarizing microscope. An electron microprobe can be used to observe CL; however, the electron beam ellipse is much larger ( $4 \times 7$  mm) with the Technosyn. The electron microprobe has an electron beam diameter as small as 1 micron. The samples used were uncoated, uncovered, polished thin sections. General operating conditions were a beam energy (accelerating voltage) of 18–21 kv, beam current of 460–600 milliamps, and operating vacuum of 0.03–0.05 torr. Air was the ambient gas used in the CL chamber. Additional specifications of the Technosyn are discussed by Barker and Wood (1986a, b).

Color slides were taken with a Nikon camera using Ektachrome ASA 400 Daylight, Ektachrome P800/1600, and Ektachrome ASA 200 Daylight. Slides were also taken using Ektachrome ASA 100 Daylight, but these generally were unsuitable. Exposure times varied from less than a second for nonpolarized light to more than 300 seconds depending on CL intensity. Normal commercial processing of the film sometimes yields slides that do not show the observed colors because of variations in the development process. This probably can be mitigated by supplying examples of colored slides with the correct color balance to the processor. All slides (Figs. 1–6) were processed at the same commercial laboratory.

### Geological applications

Cathodoluminescence can be an important petrologic tool for many types of rocks, although most work has been done on sedimentary rocks. CL has been used in sedimentary petrology to determine texture, sediment source, degree of compaction, diagenetic history,

ratio of authigenic and detrital minerals (Sippel, 1968), stratigraphy, siliclastic components, cementation history, and provenance (Owen and Carrozi, 1986). CL has been used in paleontology to study structure and chemistry of fossils (Nickel, 1978; Barker and Wood, 1986a).

The CL of a sample reveals geochemical, rather than optical, variations in a sample, which provides important compositional, textural, and structural information not readily obtained by other methods. However, CL is most useful when used in conjunction with other studies such as optical microscopy, x-ray diffraction, electron microprobe, scanning electron microscopy, and geochemistry. Unlike ultraviolet light, where an entire specimen can be exposed, CL requires a thin section or relatively thin slab, preferably with doubly polished surfaces. The doubly polished thin sections also can be used in the electron microprobe or fluid inclusion stage. Depending on the CL unit involved, samples can be several square inches in area, which is an advantage with some rocks.

Certain textural studies are only possible using CL. Textures such as intergrowths, overgrowths, growth rings, healed fractures (Sprunt and Nur, 1979), and radiation damage are readily observed by CL. Interpretation of these textures aids in relative dating of mineralization (Harwood, 1983) and in determining microstratigraphy (Ebers and Kopp, 1979).

CL can be used in mineral identification and mineral distribution because many minerals have diagnostic luminescence properties within a suite of rocks. Small mineral grains (such as apatite and zircon) may be readily identified by CL when they cannot be identified by optical microscopy due to their small size or when obscured by alteration effects in transmitted light. However, minerals typically cannot be identified only by their CL appearance; a detailed electron microprobe and/or optical microscopy study is needed. Mineral CL colors are not unique (Nickel, 1978) and can change due to slight compositional changes or to different origins (Mariano, 1976; Machel, 1986).

Some aspects of geochemistry can be determined on the basis of CL color (Long and Agrell, 1965; Mariano, 1976; Mariano and Ring, 1975). Quartz, which has a high titanium content relative to iron content, luminesces blue, whereas low-titanium quartz (relative to iron content) luminesces red (Barker and Wood, 1986a). Apatites luminesce yellow, yellow-green, blue, or gray depending on the concentrations of rare-earth elements and manganese (Mariano, 1976). Apatite without impurities does not luminesce. Calcite typically luminesces bright yellow or orange compared to the red or reddish-purple of dolomite (Kopp, 1981). Extreme caution must be used in correlating color with chemistry. Sprunt et al. (1978) have demonstrated that quartz displays CL colors that vary according to differences in its metamorphic grade.

### Examples

CL was observed on samples from carbonatites in the Precambrian terrane of the Lemitar Mountains and from the Riley travertine of the western Ladron Mountains as part of our ongoing research in these areas. It is beyond the scope of this report to describe the geology of these regions, which is discussed by McLemore (1982, 1983, 1987) for the Lemitar Mountains and summarized by Barker (1983) for the western Ladron Mountains.

### Lemitar Mountains

CL is especially useful when studying carbonatite complexes (Mariano and Ring, 1975; Mariano, 1976). Numerous polished thin sections of carbonatites from the Lemitar Mountains were examined with the CL microscope. ☐

Figure 1a is a typical example of a carbonatite showing CL. The red luminescence is due to the carbonate matrix and is brighter than most samples under CL. The large magnetite crystal exhibits CL zoning, which is not observed in nonpolarized transmitted light (Fig. 1b). Examination of this crystal with the electron microprobe reveals a complex intergrowth of magnetite, ilmenite, quartz, rutile and/or leucoxene, and calcite. Alteration of the xenolith is readily observed by a carbonate with bright red CL rim. Apatite crystals luminesce blue to blue-gray to green-gray. Due to variations in processing of the film, the apatites in Fig. 1a are darker than the blue-gray to green-gray observed. Extremely small apatite crystals in carbonatites, especially rodbergs, are readily identified by their CL when transmitted light microscopy fails.

Zoning within an apatite crystal (Fig. 2a) may be due to trace-element compositional changes. This zoning is not observed in polarized or nonpolarized light. Epoxy (brown in nonpolarized light) forms the edge of Figs. 2a and 2b and does not luminesce under CL. The patches of nonluminescing (brown) material, not observed in nonpolarized light (Fig. 2b), have not been identified.

Pale red growth zones of calcite crystals are observed in a carbonate vein cutting Polvadera granite (Fig. 3a). These zones are not easily distinguished by transmitted-light microscopy (Fig. 3b). The Polvadera granite consists of plagioclase, K-feldspar, and quartz, all of which luminesce red under CL.

When CL is used, fluorite from a vein associated with a carbonatite exhibits zoning possibly due to compositional changes (Fig. 4a); bright orange CL in calcite and yellowish-brown CL in quartz are observed. The black nonluminescing material is probably hematite.

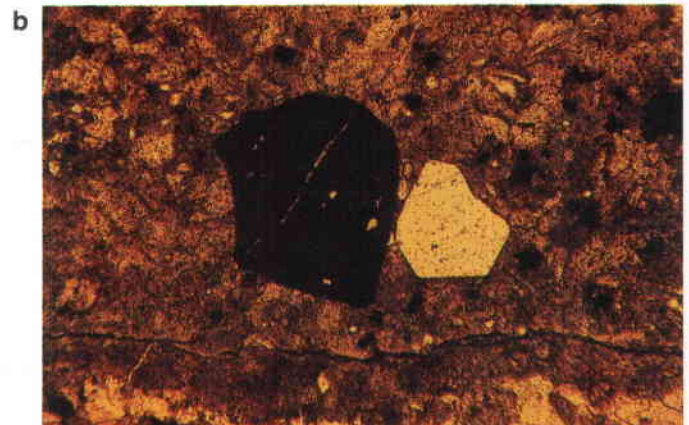
#### Riley travertine

The Riley travertine is a near-surface or surface accumulation of carbonate. Various hypotheses about its depositional environment have been proposed; they range from lake (Kottowski, 1962; Masingill, 1977) to soil (Denny, 1941) to spring (Bachman and Machette, 1977) environments. CL data used in testing these hypotheses were gathered from numerous polished thin sections. The views in Figs. 5a, 5b, 6a, and 6b are of thin sections cut from drill core taken from the north mesa portion of the Riley travertine (Barker, 1983). The hole was drilled in the SW corner of sec. 16, T2N, R3W, and the sections were cut from a core depth of 19 ft 10 inches. The textures revealed by CL are consistent with a spring origin for the Riley travertine at North Mesa.

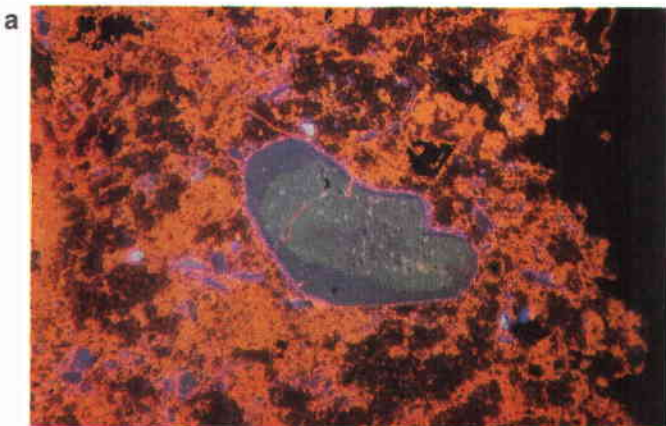
Two powerful uses of CL in carbonates are to delineate trace-element chemistry and to highlight obscure clastic content. Variations in carbonate chemistry can be produced during deposition or during diagenetic dissolution and redeposition. Figure 5 shows sparry calcite that has several distinctive layers whose CL is probably due



FIGURES 1a & b—1a is a zoned magnetite crystal (red and black) next to smaller apatite (black) in carbonatite (sample LEM CC) under CL. Matrix is carbonate (red). Field of view is approximately



2 mm. Exposure time was 138 sec using Ektachrome ASA 400 Daylight film. Fig. 1b is the same view in unfiltered nonpolarized transmitted light. Exposure time was 0.5 sec.



FIGURES 2a & b—2a is a zoned apatite (blue) in carbonatite (sample LEM CA) under CL. Matrix is carbonate (orange). Field of view is approximately 2 mm. Exposure time was 43.7 sec using Ektachrome



ASA 400 Daylight film. Fig. 2b is the same view in unfiltered nonpolarized transmitted light. Exposure time was 0.04 sec.



to trace-element variations. These layers are not prominent in the same view in nonpolarized transmitted light (Fig. 5b).

Figure 6a shows the ability of CL to highlight textural and compositional details. The siliclastic layer in the Riley travertine is bounded by calcite, which exhibits different textures. The carbonate in the upper left corner of the photograph is more uniform than the complexly banded, and probably younger, recrystallized calcite in the lower right corner. Between these carbonates is a siliclastic layer. Using CL, the yellow luminescence of reworked travertine is easily distinguished from the blue to purple luminescence of the feldspar and quartz grains. These relationships are not obvious in nonpolarized transmitted light (Fig. 6b).

#### Disadvantages of CL microscopy

Some problems inherent with CL have been mentioned previously. Most samples, either thin sections or thin slabs, must have at least one polished surface, which adds to preparation time and expense. Perception of CL colors is subjective and difficult to compare with colors reported in other studies. CL work should be done in conjunction with other methods if complex hypotheses are to be tested. Some minerals will not luminesce under CL.

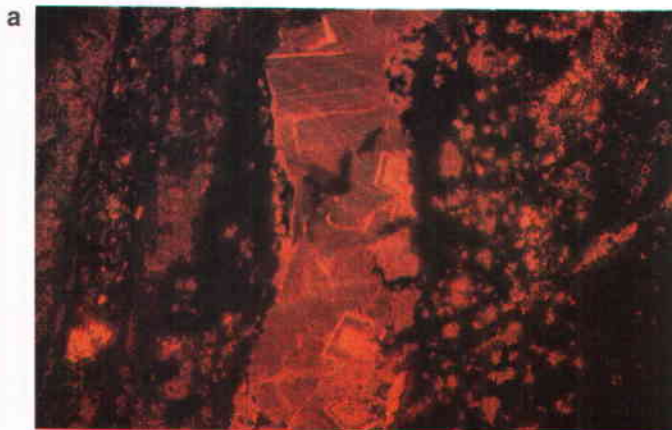
Heating of the sample with the electron beam can cause problems. Some organic-rich samples, such as coal, can volatilize and cause instability in, or even damage to, the CL instrument (Barker and

Wood, 1986a). Easily volatilized bonding agents must be avoided. Heating can also cause leakage or stretching of low-temperature fluid inclusions; fluid inclusion work must be completed before CL analyses are done. Relatively unstable minerals, such as some uranium minerals, can be altered by heating.

Some additional problems encountered with CL include: 1) the quality of the image transmitted through the stage, particularly at high magnification, 2) the need for long-working-distance objective lenses and condensers, and 3) the low-intensity CL image produced in some minerals at the beam energies now available. Specific data on mineral identification and chemistry are often not available. Standards for reporting CL data, such as those proposed by Marshall (1978), should be incorporated into reports.

Despite these problems, CL is an important petrologic tool, especially when used in conjunction with other studies. Many of the problems listed will be overcome with future research.

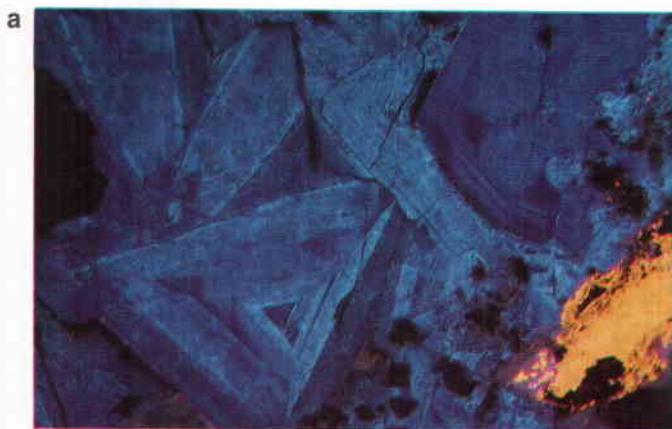
**ACKNOWLEDGMENTS**—We are indebted to Charles Barker of the Branch of Petroleum Geology, U.S. Geological Survey (Denver, Colorado), for assistance in this study and for the use of CL equipment. Peter Modreski of the U.S. Geological Survey (Denver) assisted with the electron microprobe studies. We gratefully acknowledge reviews of this manuscript by Charles Barker, Peter Modreski, and Jacques Renault. Technical assistance by Linda Frank and Robert Bolton is appreciated.



FIGURES 3a & b—3a is a vein cutting Polvadera granite (LEM 531a) under CL. Nonluminescing material (black) is hematite. Field of view is approximately 3.4 mm. Exposure time was 19.5 sec using



Ektachrome ASA 200 Daylight film. Fig. 3b is the same view in nonpolarized transmitted light. Exposure time was 0.3 sec.



FIGURES 4a & b—4a is a fluorite vein (sample LEM 813) associated with a carbonatite under CL. Field of view is approximately 2 mm. Exposure time was 209 sec using Ektachrome ASA 400 Daylight



film. Fig. 4b is the same view in nonpolarized transmitted light. Exposure time was 0.12 sec.



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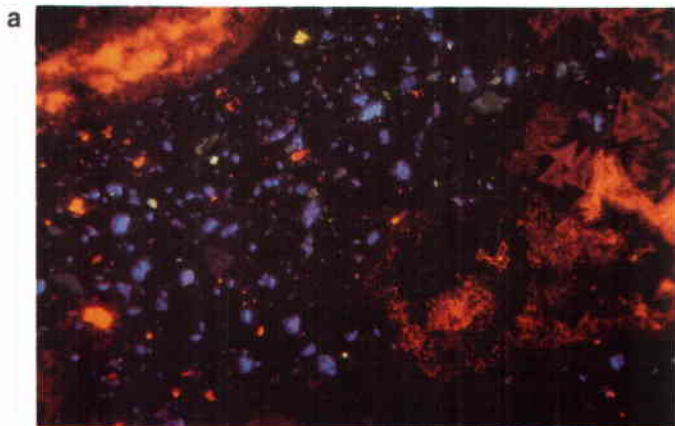
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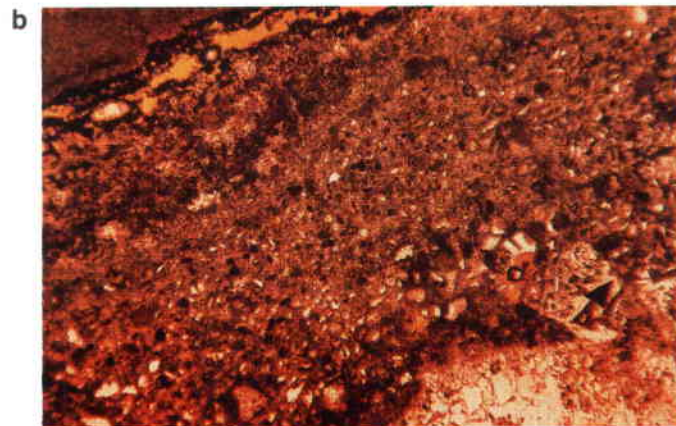
FIGURES 5a & b—5a is a radial sparry calcite showing one prominent and several lesser luminescent bands (yellow to reddish range) under CL. Field of view is approximately 3.4 mm. Exposure time



was about 90 sec using Ektachrome Daylight 400 film. Fig. 5b is the same view in nonpolarized transmitted light. Exposure time was less than 1 sec.



FIGURES 6a & b—6a is a siliclastic layer (blue luminescent clasts) bounded by luminescent calcite (reddish orange) under CL. Field of view is 0.86 mm. Exposure time was 331 sec using Ektachrome



ASA 400 Daylight film. Fig. 6b is the same view in nonpolarized transmitted light. Exposure time was less than 1 sec.