

Luminescent Lithology

You've seen what it does for television, now see what it can do for geology

BY SUSAN WEST

The flicker of green chasing a heartbeat across an oscilloscope face and the clash of red, white and brown when football teams collide on a television screen are produced by a phenomenon that has been known to geologists for at least a century. Yet only in the past five years has it become recognized as a unique, often indispensable tool in the earth sciences.

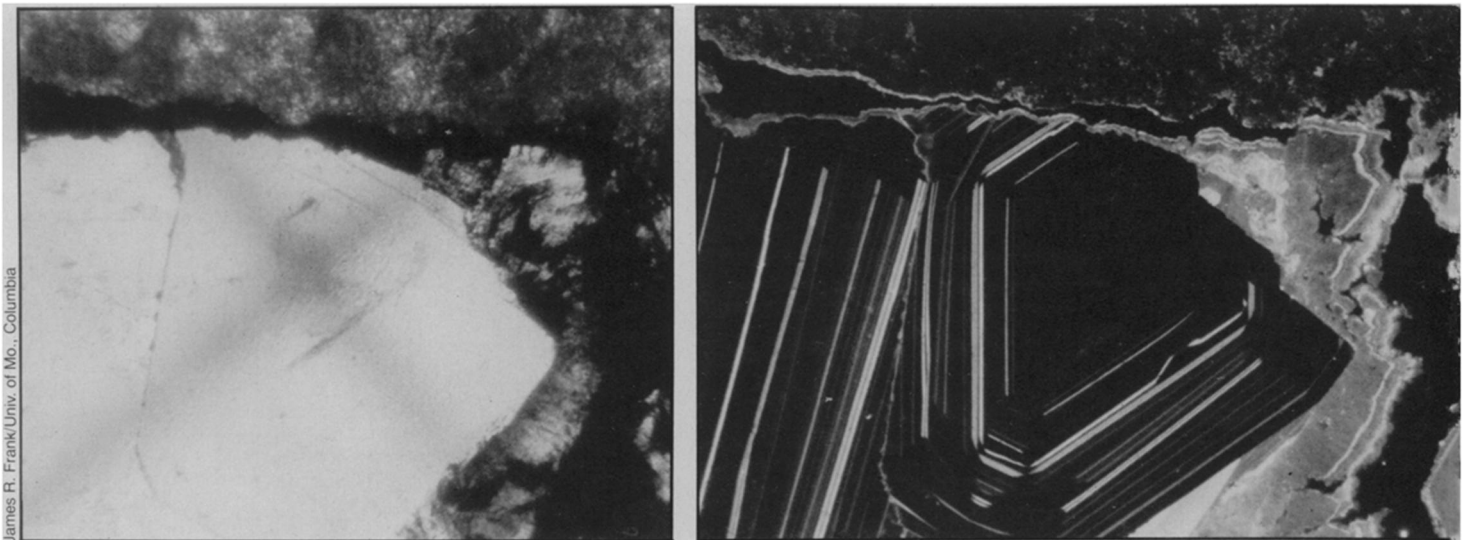
The phenomenon is called cathodoluminescence. It is a sparkling sibling of fluorescence, differing only in that it results from bombardment of certain materials with electrons (cathode rays). The color emitted by a particular rock or crystal (or by your TV screen) depends on the type of crystal, the defects in its structure and the concentration and location of certain trace elements. Called activators, the elements responsible for CL most often are manganese and iron, sometimes europi-

technique in the 1960s: "In some fields, it's practically a necessity — you can't live without it. It shows things that simply cannot be seen any other way."

In sedimentary rocks, CL spotlights the difference between original and secondary crystals, indistinguishable in ordinary light. It can show how the composition of a crystal changed as it grew, how the pores between loose sand grains filled to create hard rock and, marked only by a ghostly light, where salt crystals, since disappeared, once evaporated out of solution.

ence as a method to study thin sections of rocks using an electron microprobe as the source of electrons. The electron probe was used with some success (it has long been used for quantitative analysis of rocks), but it was too much instrument.

That same year, Robert Sippel, then and now at Field Research Laboratory of Mobil Oil Co. in Dallas, Tex., designed a simpler electron emitter and mounted it on the commonly used petrographic microscope. Combining the luminoscope, as it was called, with the microscope has definite advantages. It allows easy, immediate comparison of samples by polarized light and luminescence and makes the use of ordinary, unpolished and even uncovered slides possible. In addition, the system uses lower voltages (usually 8 to 20 kV), can view more area (up to 2 cm) and is less time-consuming than the electron probe.



The drama of CL: Left, a calcite crystal under transmitted light. Right, same crystal under CL, its growth marked by glowing bands. Varying intensities of "growth rings" result from the amounts and possibly the ratio of Mn and Fe.

um and titanium and less often lead, tungsten and yttrium.

Thin sections of rock, 30 to 100 microns thick, are placed in a vacuum chamber under a petrographic microscope (a microscope equipped with two prisms that is routinely used in geologic studies) and bombarded with electrons. What appears a dull, drab rock in visible light suddenly blushes with fantastic hues. Feldspars glow blue, red, mustard brown and yellow-green. Quartz shines shades of blue and red. Calcium carbonate rocks gleam orange and red. Igneous rocks flash violet, yellow and tan.

But CL is not just glitter. It does what no other petrographic method can. Says Robert Sippel, who pioneered use of the

In igneous rocks, minerals from different sources can be picked out by their characteristic colors. Imaginative researchers are adapting it as a probe for uranium exploration and in paleobotany.

Despite a spectrum of uses as broad as its range of colors, CL has been a dark horse in geology, at least until recently. In 1879, a researcher named W. Cooke published an article on "molecular physics in high vacua" which included his observations on the cathodoluminescence of whole rocks. But not until 1965 were researchers able to apply the phenomenon to sedimentological problems. Then a University of Chicago researcher, J.V. Smith, and R.C. Stenstrom now of Beloit College in Beloit, Wis., suggested lumines-

cence as a method to study thin sections of rocks using an electron microprobe as the source of electrons. The electron probe was used with some success (it has long been used for quantitative analysis of rocks), but it was too much instrument. That same year, Robert Sippel, then and now at Field Research Laboratory of Mobil Oil Co. in Dallas, Tex., designed a simpler electron emitter and mounted it on the commonly used petrographic microscope. Combining the luminoscope, as it was called, with the microscope has definite advantages. It allows easy, immediate comparison of samples by polarized light and luminescence and makes the use of ordinary, unpolished and even uncovered slides possible. In addition, the system uses lower voltages (usually 8 to 20 kV), can view more area (up to 2 cm) and is less time-consuming than the electron probe.

When the two workers described the "weird and wondrous things" they saw, as Glover says, "It was like the first movies — everyone got excited." But the shine wore off quickly. Researchers found that not all samples luminesce (though this tells

something of the history as well) and “it sort of took the bloom off the rose,” says one investigator. In addition, the technique wasn’t as easy as it looked; it required patience and care.

Perhaps the major obstacles to CL’s popularization were the high costs of printing in color and the lack of a commercially available instrument. When pictures were printed in black and white, they required tedious captions, such as “The darkest area corresponds to red-orange, the next darkest to deep orange; the bright vein to bright orange; the faint areas to yellow . . .” Depending on the type of film, the intensity of the electron beam and whether a worker described a color by observation (barring color-blindness) or wavelength, comparing the results of the sprinkling of papers was difficult to impossible.

In the late 1960s, the Nuclide Corp. of Acton, Mass., developed a commercially available instrument. This standardized experimental conditions somewhat, with the result that interest and the number of papers on the technique increased.

Even so, CL was little known outside Sippel and Glover’s chosen field — sandstone petrography. Only in the last five years, since William J. Meyers, now of the State University of New York at Stony Brook, pioneered its use in plotting the history of calcium carbonate rocks, has CL developed more than just a cult following. Including the major oil companies, which routinely use CL to better their odds in drilling, about 150 research facilities have luminoscopes.

But CL still is not used as much as other more expensive and tedious methods. Little is published — “We’re all waiting for someone else to start,” says Zuhair Al-Shaieb of Oklahoma State University. Workshops, such as ones recently held in Tulsa, Okla., and at the Geological Society of America meeting in Toronto last week,

Numbers mark time-correlative zones, invisible under normal light, of single calcite crystal filling limestone pore between grains (top and bottom).



William J. Meyers/SUNY

are often the first chance many researchers have to learn of its myriad and growing uses. “We don’t yet know the whole potential. There are many ideas and many possibilities,” says Al-Shaieb.

So far, CL has been most often used to trace the history of sedimentary rocks, particularly sandstones. It is here that Sippel says “you can’t live without it.” Sandstone consists of fine grains of rock and mineral fragments that eventually become cemented together. Because the primary and secondary materials often have the same chemical composition, a typical problem in sandstone analysis has been distinguishing the original, rounded grains that were deposited with the sediment from the material that grows over them. Sippel showed that the primary core luminesces brightly while the overgrowth does not. Using the light of CL, he found it is possible to determine the degree of roundness of the original grains, their size and shape. Expanding on this, M.R. Buyce and Gerald Friedman in 1975 combined staining and CL to estimate the ratio of original to new feldspar crystals in rocks 450 million years old.

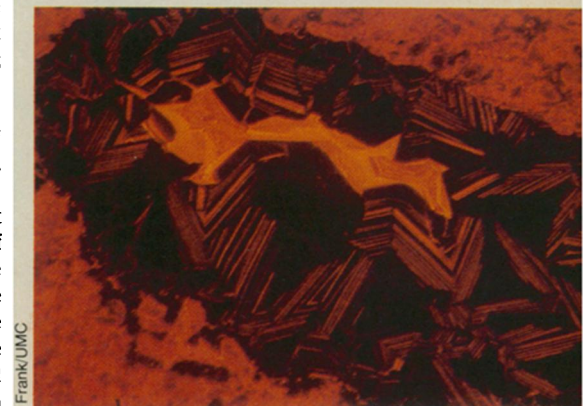
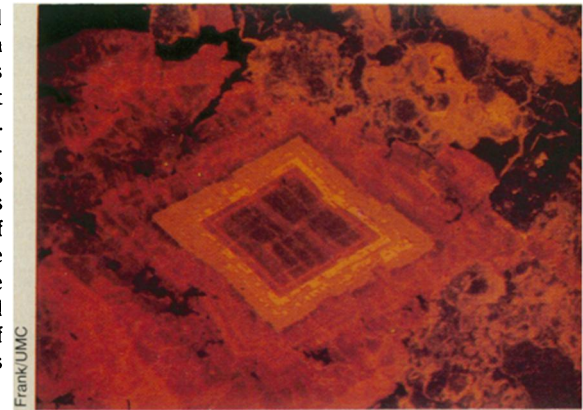
The guiding light of CL can also illuminate the diverse sources of rock fragments making up a sediment. Due to characteristic chemical composition, minerals luminesce differently depending on their origins. Tedious chemical analysis can reveal the source, but CL can do the same thing in the blink of an eye. Jack Thomas of Amoco Products Co. in Denver, Colo., was able to classify the sources of a mixed group of minerals of a sandstone formation in Oklahoma.

Sippel also found that CL highlights changes wrought by pressure and solution at the surfaces of grains and that he could differentiate those changes from ones due to overgrowth. He saw bright veins of light that marked internal fracturing of crystals; where the fractures extended into adjacent crystals, it was clearly due to *in situ* events. CL thus provides a means of measuring how much a sediment has compacted.

Since then, Eve Sprunt and colleagues at Stanford University have honed the use of luminescence in determining the degree of alteration of quartzite sandstone. In the May 1978 *GEOLOGY*, she reported the analysis of samples showing a wide range of metamorphism. She found that original grains in undeformed rock luminesce a mixture of colors, ranging from dull red to blue. As sediments are more deformed, secondary overgrowth and veins associated with fracturing glow a rusty red. Recrystallized samples, indicating more intense deforming, luminesce blue-violet. Based on her observations, Sprunt tentatively concludes that metamorphism causes a homogenization of color: Rocks changed under low temperatures tend to glow uniformly red while those altered under high temperatures become uniformly blue.

CL’s other major use is in tracing the history of carbonate rocks (rocks composed of calcium and magnesium with carbonate and formed by precipitation). Sippel and Glover noted variably glowing “growth bands” — which resemble tree rings — around crystals of calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). They suggested that, like tree rings, they might be read for variations in their trace element content. Subsequent studies showed this

Continued on page 319.



Top: A rhombohedral dolomite ($\text{CaMg}(\text{CO}_3)_2$) crystal glows deep red with a bright orange center in an orange-luminescing calcite matrix. Colored bands mark how the crystal incorporated impurities as it grew. Middle: Blue speck surrounded by red halo indicates uranium impurity in quartzite from Australia. Bottom: Calcite crystals filling pores in limestone from southeast Missouri. Intensities correlate to changing water chemistry and can be used as stratigraphic markers.

... Lithology

was possible and that the growth of individual crystals could be traced.

In 1974, William Meyers took the analysis of growth bands one step further. Crystals grow into and eventually completely cement the pores of limestone, incorporating the trace elements present in the water. In an exhaustive study of the CL of 180 thin sections from New Mexico, Meyers found five distinct zones in pore-filling calcite crystals correlating to varying amounts of manganese and iron. He was able to correlate the zones between adjacent samples within the same section and between sections covering a distance of about 16 kilometers. Such work showed CL could tell something about water temperature and chemistry and could mark the difference between cements precipitated from marine and fresh waters. "Each zone is believed to represent a time-correlative discrete episode of cementation," he noted, thus designating CL as a stratigraphic marker.

More recently, Meyers developed a model for cementation of New Mexico limestones during sea level changes 10 million years ago. In tracing the specific times when each zone formed, he found that, contrary to other studies that did not use CL, cementation occurred *during* sea level changes, not only when the water level was at a standstill.

Meyers hopes eventually to develop several models for the cementation of limestones. Such models would be of particular interest in oil exploration, because the pores in limestone can hold oil as well as water. Currently, most major companies use CL to evaluate the timing and severity of cementation before drilling.

Sedimentary rocks may also contain evaporites, salts deposited by water. They are easily removed by re-solution or biological activity and leave no clues detectable by transmitted light microscopy. However, their "ghosts" are visible under CL. According to David E. Eby of the University of Texas in Dallas, the outline of an evaporite crystal, because it is made of different minerals, can be marked, gleaming through a newer structure. The most crucial clue CL can provide about long-vanished evaporites, Eby says, is whether they were leached or removed bit by bit, as by bacterial action. Eby believes his most recent studies show luminescent differences between the two processes.

Similar studies are yielding results for paleobotanists. In a paper presented at the Tulsa workshop, K. F. Ferrigno of the University of Tennessee described the use of CL in classification of bryozoans (fossil invertebrates with calcareous skeletons). CL accentuates the bryozoan wall structure, and it is this feature, Ferrigno says, that is important in their taxonomy.

The application of CL to the study of igneous rocks is still in its early stages. Most investigations concentrate on detecting fine grains of heavy mineral groups

and, following the lead of sedimentologists, on finding the origins of rocks. In igneous rocks under CL, specks of deep blue pinpoint grains of apatite and yellow characterizes zircon. H.Görz and his colleagues at Pennsylvania State University showed that CL of zircon is polarized, though the significance of the phenomenon is unknown. CL-brightened veins clue researchers to tectonic activity and to crystals filling fracture lines. In research presented at the Toronto GSA meeting, R. P. Tolo and A. N. Mariano separated apatite characteristic of magmatic rock from apatite of the local "mother rock" into which it had intruded. The igneous apatite glowed blue, activated by europium. The apatite distinctive of local rock glowed with a manganese-activated yellow.

Such studies in igneous rocks have led to speculation about the use of CL in mineral exploration. Smith and Stenstrom noted that radiation damage in quartz was marked by a CL halo with the wavelength of zirconium. Researchers in Canada are attempting to use CL in exploration for niobium, but, according to Glover, workers would have to already be in a deposit by the time they saw CL halos.

The technique may yet have application in ore exploration and other exotic areas, says Sippel, but more basic research on the causes and controls of luminescence is needed. For example, CL of a particular mineral in moon rocks brought back by the Apollo missions showed one less band than CL of its terrestrial counterpart. Sippel's interpretations of the missing band range from shock damage to lack of oxygen needed to reduce iron, but he isn't sure of the real reason.

"Like many phenomena, it is poorly understood," he says. "It may be telling us something we don't understand, particularly in the spectral distribution and polarizing properties."

Some researchers, such as Sprunt, have already altered thinking about the causes of quartz CL. In an unpublished paper she presents findings that titanium, rather than manganese, may be responsible for blue CL in quartz and iron may cause red luminescence. Sprunt agrees with Sippel: "People could get a lot more out of this technique if they understood the mechanism."

Though no other method reveals the same features CL shows, it is not a panacea, say researchers such as Jack Babcock of City Service Oil Co. in Tulsa. The best possible use for CL, according to its advocates, is as a qualitative tool in combination with quantitative techniques. In tandem with methods such as analysis by electron microprobe, wet chemical analysis or X-ray diffraction, CL can yield the most complete information available on a rock or sediment, Babcock and others say.

With more work, cathodoluminescence may become as common a tool for the geologist as it is for the TV viewer. □

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