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APPLICATIONS OF CATHODOLUMINESCENCE OF QUARTZ AND FELDSPAR TO SEDIMENTARY PETROLOGY

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Abstract

Cathodoluminescence (CL), the emission of visible light during electron bombardment, was first used in sandstone petrology in the mid-1960's. CL techniques are especially useful for determining the origin and source of quartz and feldspar, two of the most common constituents in clastic rocks. CL properties of both minerals are dependent on their temperature of crystallization, duration of cooling, and/or history of deformation. Detrital quartz and feldspar are typically derived from igneous and metamorphic sources and luminesce in the visible range whereas authigenic quartz and feldspar form at low temperatures and do not luminesce. Quantification of luminescent and non-luminescent quartz and feldspar with the scanning electron microscope, electron microprobe, or a commercial CL device can allow for the determination of origin, diagenesis, and source of clastic rocks when used in conjunction with field and other petrographic analyses. Future expansion and documentation of the classifications and causes of CL in these minerals may increase the usefulness of CL techniques in sandstone petrology.

KEY WORDS: Cathodoluminescence, quartz, feldspar, scanning electron microscope, electron microprobe, detrital, authigenic, core, overgrowth.

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Introduction

Cathodoluminescence (CL), the emission of visible light during electron bombardment, is a diagnostic luminescence technique that is used in sedimentary petrology. CL is typically used to distinguish between authigenic and detrital silicates, particularly quartz and feldspar, and to characterize the genesis of carbonate minerals. The phenomenon of CL in natural crystals was originally reported in 1879 by Anthony Crookes (1879) but CL was not applied to mineralogic and sandstone studies until the mid-1960's.

Smith and Stenstrom (1965) and Long and Agrell (1965) presented some of the first data on the luminescence properties of quartz, feldspar, and various carbonates. Smith and Stenstrom (1965) were able to distinguish between authigenic (formed in place) quartz overgrowths which exhibited a dull red luminescence and detrital (wind- or water-borne) quartz grains which luminesced blue; Long and Agrell (1965) reported faint blue to pinkish luminescent quartz in a kyanite-staurolite-biotite-muscovite schist.

The direct application of CL to sandstone petrology was first detailed by Sipple in 1968. He delineated detrital quartz grains (cores) from surrounding authigenic quartz overgrowths based on color contrasts in mature and immature sandstones and reported the presence of both red and blue luminescent grains. Unlike Long and Agrell (1965) and Smith and Stenstrom (1965), Sipple's work was performed with an instrument (Sipple, 1965) that could be easily mounted on a standard petrographic microscope and was much less expensive than the instruments that had been used previously for CL studies--the scanning electron microscope (SEM) and the electron microprobe.

Since Sipple's 1968 work, CL studies of the constituents of sedimentary rocks have become a valuable tool in sedimentary petrology. CL is now routinely used to distinguish between detrital quartz and cement, to identify original grain shape and size including the degree of alteration that has occurred during diagenesis, to infer provenance or source of detrital grains, and to understand the genesis of sedimentary rocks and systems. This review will concentrate on the use of CL to study quartz and feldspar which are the dominant silicates in most sandstones. Gorz et al. (1970) published a study of the CL characteristics of some common silicates including most of the heavy minerals which are minor or accessory components in sandstones. Carbonates may also be present in sandstones as detrital components or cement, but their CL properties will only be briefly discussed in this review. Sommer (1972a, 1972b), Nickel (1978), and Amieux (1982) contain excellent reviews and examples of the CL characteristics of carbonates.

Quartz is the most abundant constituent in most sedimentary terrestrial rocks followed typically by feldspar, clays, and minor amounts of "heavy" minerals which are composed of both silicates and oxides. All of these minerals with the exception of some authigenic clays are primarily derived from the chemical and mechanical breakdown of pre-existing igneous, metamorphic, and sedimentary rocks. Sedimentary units can be derived from either a single source or multiple sources; therefore, the mineralogy of the unit should directly reflect its source. Unfortunately, the identification of source is often obscured by the dissolution of unstable minerals during weathering and/or transport, the alteration of less stable components, sorting during transport by shape and size, and diagenetic or burial changes that can both add and subtract constituents.

Sedimentary techniques typically used to determine origin include detailed field investigations of primary structures, paleocurrent direction indicators, and grain shape or size data, coupled with petrographic and analytical examinations of the minerals that compose the rock. Petrographic analyses include identification and quantification of rock fragments, feldspar, quartz (polycrystalline and monocrystalline grains), other non-silicate minerals, cement or matrix, and accessory heavy minerals that make up the rock. However, field investigations and laboratory analyses commonly indicate more than one possible source for a particular sandstone. CL analyses often provide data to clarify a specific origin and source area.

Causes of Cathodoluminescence

Theoretical explanations of CL are reviewed by Marfunin (1979) and Holt and Datta (1980) and will not be the focus of this paper. In general, the phenomenon of CL results from molecular distortions within the crystal lattice of naturally occurring crystals. Specific distortions have been identified for some minerals but not for others. It has been suggested that (1) the presence of extraneous ions ("activators" or "quenchers"), (2) lattice disorder due to rapid crystallization at high temperatures or later deformational episodes (metamorphism), and (3) lattice oscillations are responsible for the presence of CL in naturally occurring crystals. These distortions may be related to the spectral emission and intensity of luminescence in quartz and feldspar.

The CL characteristics of carbonates have been extensively studied (Sommer, 1972a, 1972b; Nickel, 1978; Machel, 1985) and explanations for the phenomenon is well developed. For example, orthorhombic and trigonal carbonates show different CL emission spectra because each crystal class is capable of accepting only cations of a specific radius (Nickel, 1978). The presence of the "activator" ion Mn^{2+}, the most commonly reported cation, produces yellow to red-orange luminescence in calcite and dolomite (Sommer, 1972a). Other activators include Sr^{2+} and Pb^{2+} (Amieux, 1982) and some of the rare earth elements (Gies, 1976). Fe^{2+} or Fe^{3+} quench carbonate luminescence (Amieux, 1982) as do trace concentrations of Ni^{2+} and Co^{2+} (Gies, 1976). Because specific ions that induce or quench carbonate luminescence and their lattice positions have been identified, luminescence studies of these minerals can offer detailed chemical information on their genesis when all of the ions affecting CL have been identified by multielemental analysis (Machel, 1985). Because many sandstones contain carbonate components or cement, carbonate CL studies can be very important to the clastic sedimentary petrologist.

Unfortunately, the specific causes of CL in quartz and feldspar, two of the most common constituents in sandstones, are not as well understood as they are in carbonates. There is no general consensus concerning the specific causes of CL in framework silicates. Reported causes of CL in quartz include:

(1) **Fe in the absence of Ti (orange CL),**
  Ti in the absence of Fe (blue CL);
    (Sprunt, 1981)
(2) **oscillations within the SiO_4**
  tetrahedron;
    (Hanusiak and White, 1975)
(3) **the presence of interstitial Al;**
    (Cohen, 1959; Grant and White, 1978)
(4) **lattice defects or distortions.**
    (Zinkernagel, 1978; Krinsley and Tovey, 1978; A. Matter, 1985, University of Bern, personal communication; Dietrich and Grant, 1985)

Disagreements on the causes of CL in quartz appear to result primarily because the amount of data is limited and quantification of impurity ions is difficult in concentrations below the detection level of the electron microprobe. Future studies that concentrate on the identification and quantification of lattice defects and/or impurity ions that produce CL in quartz and feldspar could be used to document the genesis of authigenic silicate minerals and cements.

Very little data has been published on the causes of CL in feldspar (Smith and Stenstrom, 1965; Sipple and Spencer, 1970; Kastner, 1971; Mariano et al., 1973; Hagni, 1985; Matter and Ramseyer, 1985). Smith and Stenstrom (1965) examined microcline and perthite and correlated CL intensity and polarity to the orientation of the crystal lattice; CL color was correlated with either potassium-sodic exchange reactions between phases or the temperature of formation. Sipple and Spencer (1970) reported that CL in calcium and potassium plagioclase feldspar from lunar breccias was controlled by both lattice deformation or strain and the presence of activator ions. They based their conclusions on (1) a spectral shift from green to higher wavelengths in anorthite (calcium-rich plagioclase) that had been shock metamorphosed, and (2) a direct correlation between luminescent zones and composition zones.

In contrast to lunar feldspar, there are no data on shock induced CL in terrestrial feldspar. Although the absence of data does not rule out the possibility that metamorphically induced lattice deformation could produce CL, it is generally thought that the CL characteristics of terrestrial feldspar are controlled solely by the inclusion of trace elements in the crystal lattice. Trace concentrations of Ti, Mn, Cu, and Fe have been identified in luminescent feldspars from diverse geologic environments (Mariano et al., 1973). (See table 1.)

Table 1 - Reported causes of CL in feldspar.

TYPE	ACTIVATOR ION	CL COLOR
plagioclase	**Fe^{3+}**	**dark blue** (1)
	Fe^{2+}	**green** (2)
	Mn^{2+}	**yellowish-green** (2)
	Ti^{4+}	**blue** (2)
	Cu^{2+}	**blue** (2)
orthoclase	--	**light blue** (2)

(1) Thomas, 1974.
(2) Mariano et al., 1973.

Despite the paucity of quantitative data on the causes of CL in silicates, it is generally agreed that authigenic and detrital quartz and feldspar can be distinguished based on their CL properties. Detrital quartz and feldspar are typically derived from metamorphic and igneous sources and silicates from these sources luminesce in the visible range. In contrast, authigenic quartz does not luminesce in the visible range, nor does authigenic feldspar. These authigenic minerals apparently do not usually exhibit CL because extraneous ions or distortions are not generally present in the crystal lattice at low temperatures (Sipple, 1968; Pettijohn et al., 1973; Zinkernagel, 1978; Hearn and Sutter, 1985).

Methods of Study

The most frequently used instrument for CL studies is the commercially available CL device which is an adaptation of a design originally developed by Sipple (1965) that utilizes a cold cathode gun. This device is advantageous because (1) it is relatively inexpensive, (2) it is compatible with most simple optical microscopes, (3) it is possible to examine samples in both polarized and transmitted light and CL, and (4) relatively large areas of view can be examined.

Unfortunately, few commercially available CL devices are equipped with photometers and monochromators to obtain spectral data. Without such quantitative measurements, all CL color reports are highly subjective and equipment specific. Because the ability to visually distinguish among red, orange, and brown hues differs between operators, color photographs should be taken of the samples under electron bombardment. Care must be taken to keep instrument conditions as stable and as similar as possible to compare hue and intensity of grains in an individual CL study. In addition, because of differences in film type, sensitivity, and exposure time, it is difficult to directly compare CL results from one study to another. This problem can be avoided by actually recording spectral emission.

Recent advances in CL instrument design include the CL devices designed by Zinkernagel (1978) and Ramseyer (1982a). The main advantages of the newer designs include (1) the dull luminescence of quartz is easily observed and (2) both designs are equipped with monochromators to obtain quantitative spectral emission data.

In addition to the instruments based on Sipple's design (Sipple, 1965) both the SEM (see Yoffe and Howlett, 1973, and Holt and Saba, 1985) and the electron microprobe are used in CL studies of silicates. Quantitative chemical analyses can be obtained from the electron microprobe and most SEMs are equipped with energy dispersive X-ray units which allow for qualitative chemical analysis.

Attached CL devices that measure spectral emission greatly increase the usefulness of the SEM and the electron microprobe. Although several spectroscopic CL systems, which allow for both high resolution imaging and spectral measurements, have been designed for use with an SEM (Trigg, 1985), most SEM CL studies report only the presence or absence of luminescence. In some cases CL devices have been attached to SEMs, but the linearity and range of their photometers have not been established and the monochromators have not covered the entire visible spectrum (see Krinsley and Tovey, 1978).

Polished blocks or uncovered polished thin sections are typically used in CL studies. Relatively thick (approximately 60 µm) thin sections are used to help compensate for heating effects which occur with electron bombardment. Polished surfaces are critical for CL studies because topographic relief can affect CL interpretations; however, abrasional defects that are a few microns thick can result from polishing (Hanusiak and White, 1975). Therefore, samples are often coated with either carbon or gold to minimize heating effects and to prevent charging.

Cathodoluminescent Studies of Feldspars

Feldspars are one of the major components of igneous and metamorphic rocks, and are therefore found throughout the sedimentary environment. Their abundance is controlled by various factors but the most important ones include the composition of the source rock, the degree of weathering at the source, the distance and type of transport, and the type and severity of diagenesis (Pettijohn et al., 1973). Feldspars are major constituents in sandstones and siltstones but they are much less durable than quartz and are generally concentrated in less mature sandstones.

Very few CL studies of feldspars have been reported (Smith and Stenstrom, 1965; Sipple and Spencer, 1970; Kastner, 1971; Mariano et al., 1973; Mariano and Ring, 1975; Hagni, 1985; Matter and Ramseyer, 1985; Hearn and Sutter, 1985; Hearn et al., 1985; Hearn et al., 1986), and of the few published papers most report only the absence or presence of luminescence. Quantitative measurements of the wavelength of emitted light have been published by Sipple and Spencer (1970), Mariano et al. (1973), Mariano and Ring (1975), and Matter and Ramseyer (1985).

Examples- Feldspar Studies

Kastner (1971) used an electron microprobe (20 kV, 0.3 µA sample current, and 1-3 µm beam diameter) to examine authigenic feldspar in carbonates of late Precambrian to Eocene age collected from the U.S., Canada, Greece, Crete, and France. The authigenic albite ($NaAlSi_3O_8$) rarely nucleated around detrital cores, but when cores were present their composition included calcite, dolomite, quartz, and potassium and plagioclase feldspar; authigenic microcline was found to nucleate only on detrital cores of potassium feldspar (Kastner, 1971). All of the non-luminescing feldspars she examined were euhedral with pinacoid faces, contained carbonate inclusions, and were chemically homogeneous and very close to end-member composition (99 mole percent $NaAlSi_3O_8$ and 99 mole percent $KAlSi_3O_8$). Unit cell parameters for these end-member feldspars indicated a high degree of order (Kastner, 1971) which, together with their high chemical purity, agrees with the premise that insertion of impurity ions does not occur at low temperatures.

Hearn and Sutter (1985) examined both authigenic and detrital potassium feldspars (K-feldspar) in Cambrian-Ordovician shelf carbonates in the central Appalachians. Authigenic feldspar, which occurred as overgrowths on detrital K-feldspar and as a fine grained matrix, was distinguished from detrital cores based on the presence or absence of luminescence. The amount of authigenic feldspar was considerable, ratios of authigenic to detrital feldspar varied from approximately 1:1 in limestone interbeds to 3:1 in muddy dolostone interbeds. The majority of authigenic feldspar was in the form of clay-sized grains (<4µm) and not metasomatized overgrowths (P.P. Hearn, 1985, personal communication). Whole rock chemical analyses of insoluble residues of the K-feldspar showed a depletion of rubidium and barium (Hearn and Sutter, 1985). In contrast to Kastner's (1971) study, optical measurements of axial angles on the overgrowths indicated that Al-Si ordering was very low (Hearn and Sutter, 1985).

The authigenic K-feldpar overgrowths and detrital cores were analyzed by electron microprobe in a separate study (Hearn et al., 1986). Analyses indicated that the overgrowths were chemically purer than the detrital cores, although not as pure as Kastner's (1971); chemical purity was interpreted to be a function of the lower temperature of formation of the overgrowths. $^{40}Ar/^{39}Ar$ dating of the feldspar indicated that the overgrowths were formed during the Late Paleozoic Allegheny orogeny from the mobilization of brines (Hearn and Sutter, 1985). Fluid inclusion analyses (Hearn et al., 1987) indicated that the brines were hot (150 - 200°C) and hypersaline (18 - 20 weight percent NaCl equivalent). Hearn et al. (1985) have recently reported the presence of large amounts of authigenic K-feldspar throughout the entire central and southern Appalachians which indicates brine migration and mobilization was very extensive.

Cathodoluminescence Studies of Quartz

CL properties of quartz grains have been used in numerous studies to distinguish between authigenic and detrital quartz. Dust rims or vacuoles between the non-luminescing overgrowths and the luminescing cores are commonly absent, but the authigenic and detrital phases can be easily discriminated with CL (Figs. 1 and 2). CL has been used to document and quantify the degree of pressure solution that had taken place within a specific sandstone unit, the origin of specific quartz grains, and the source area of the quartz grains that make up sandstone units.

It is generally assumed that detrital quartz luminesces in the visible range and that authigenic quartz which has not been subjected to metamorphism or deformation does not luminesce in the visible range (Zinkernagel, 1978). However, some authigenic quartz does appear to luminesce very faintly (Matter and Ramseyer, 1985; Ruppert et al., 1985). The faint CL exhibited by some authigenic quartz may have been overlooked when it was close to more brightly luminescing detrital grains.

Early CL studies with relatively high beam currents (20kV and 0.4µA) (Long and Agrell, 1965) reported dull red CL of overgrowths in an orthoquartzite. Ramseyer (1982b) reported faint luminescent zoning in overgrowths; zones were occasionally separated by thin clay-rich rims or dust rings which may imply discontinuous precipitation or precipitation from a series of pore fluids. Ruppert et al. (1985), in an attempt to determine the origin of silt-sized quartz in coal, found that three out of four quartz samples which were analyzed for possible reference samples showed very faint luminesce which was originally considered to be due to

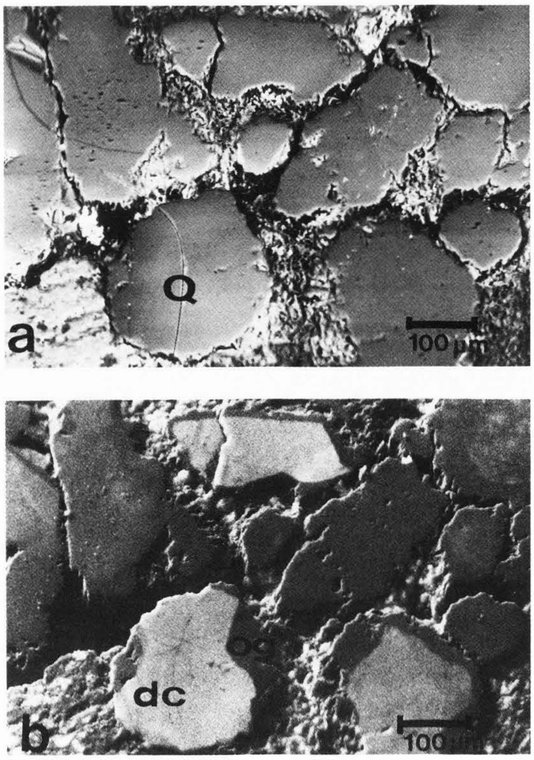

Fig. 1 - (a) SEM photomicrograph of a quartz (Q) arenite; (b) SEM CL photomicrograph of fig. 1a. Note the luminescent detrital core (dc) and the non-luminescent authigenic overgrowth (og).

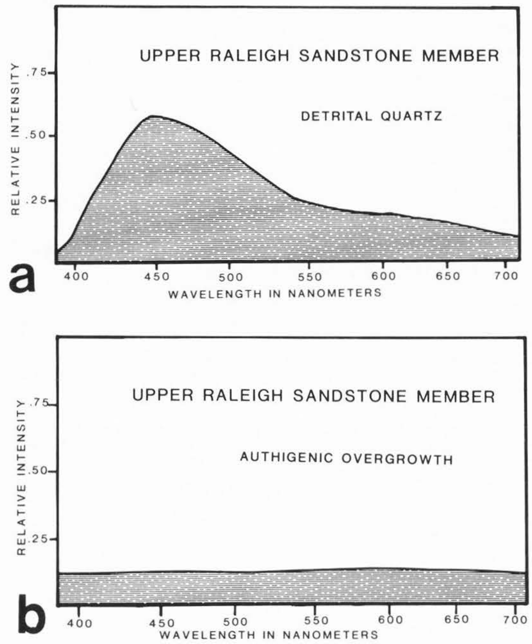

Fig. 2 - (a) Spectrum of a blue luminescent core, and (b) spectrum of a non-luminescent authigenic overgrowth.

thermal effects. None of these samples were known to be heat tempered or subjected to structural deformation. Despite these examples of faint orange CL in authigenic quartz, it is still possible to distinguish authigenic and detrital quartz based on CL contrast.

Pressure solution, the dissolution of crystals at contact surfaces, is relatively common in sandstones and results in a decrease in pore space among grains. Pressure solution is common in quartz, and the dissolved silica may precipitate locally in pressure solution shadows or may be carried outside of the bed and precipitated in another rock unit. Pressure solution can result in as much as a 50 percent decrease in volume in the bed (Sprunt and Nur, 1977).

Pressure solution is recognized optically by the presence of sutured contacts between grains or the presence of stylolites. However, CL is especially useful because authigenic cement (reprecipitated silica that may have been originally derived from pressure solution, groundwater, or the breakdown of silicate minerals) is clearly distinguishable from the detrital cores which are typically monocrystalline. The distinction allows for clear separation between original grain boundaries and pore space. Primary and secondary porosity and permeability changes in sandstone can be quantified with CL and this can be very important in oil exploration studies.

Examples- Pore reduction in sandstones

Sibley and Blatt (1976) used CL to quantify the amount of pressure solution that occurred in the Tuscarora Sandstone, a quartz arenite of Silurian age which is very tightly cemented. Their data indicate that up to one third of the quartz cement in the Tuscarora was derived from pressure solution but that the majority of the quartz had been derived from monomeric silicic acid in groundwater.

Sprunt and Nur (1977) used CL to show that considerable porosity reduction in sandstones was possible with pressure solution without grain crushing from stress on either individual grain contacts or shear stress acting on the rock unit itself. They reported that grain size affected the amount of porosity reduction that occurred with pressure solution; fine grained sandstones showed higher degrees of porosity reduction than coarse grained sandstones. Their CL data was in agreement with earlier experimental data by Cecil (1969) and Renton et al. (1969).

Cathodoluminescence Classifications of Quartz

The usefulness of CL for investigating sedimentary systems has been substantially improved by the development of classification systems based on the color of luminescence in quartz and the temperature of crystallization. Zinkernagel (1978) published one of the first CL classifications for use in sandstones. He examined the CL characteristics of igneous, metamorphic, and authigenic quartz in rocks that ranged in age from Precambrian to Tertiary and recognized three distinct types of luminescence.

These included (1) "violet" or blue luminescent quartz derived from igneous or fast-cooled, high-grade metamorphic sources (>573° C), with spectral peaks at 430-460 nm and 610-630 nm; (2) "brown" or orange luminescent quartz derived from slow-cooled, high-grade metamorphic or low-grade metamorphic sources (<573° C) with a spectral peak at 610-630 nm; and (3) nonluminescent quartz formed at temperatures less than 300° C and which had not been subjected to heating events.

Fuchtbauer et al. (1982) refined Zinkernagel's (1978) classification of quartz types and proposed six classes of luminescing monocrystalline quartz. They divided the luminescent properties of quartz into (1) blue migmatic quartz formed above 573° C and rapidly cooled, (2) violet plutonic quartz, (3) brown-violet quartz which was strongly metamorphosed, (4) brown quartz which was either slow-cooled high-temperature quartz or quartz formed between 300° and 573° C, (5) red fast-cooled quartz formed below 573° C, and (6) green hydrothermal quartz. Matter and Ramseyer (1985) also divided the luminescent characteristics of quartz grains into six classes which include (1) bluish-black luminescent quartz characteristic of plastically deformed plutonic quartz; (2) light blue to blue, (3) blue-violet, and (4) violet which are all characteristic of plutonic and volcanic rocks; (5) orange luminescent quartz which is noted in regionally metamorphosed rocks; and (6) red luminescent quartz derived from the silica matrix in volcanic rocks. Both classifications are essentially the same and are based on the temperature of crystallization and the length of cooling. In all three classifications authigenic quartz which formed below 300° C and was not subjected to heat tempering does not luminesce in the visible range.

Hydrothermal quartz does not luminesce according to the scheme outlined above. All hydrothermal quartz samples that Zinkernagel (1978) examined luminesced a "bottle-green" color that was interpreted to be due to the presence of H^+ or Li^+ inserted in structural channels parallel to the C-axis (Ramseyer and Mullis, in prep., cited in Matter and Ramseyer, 1985).

Metamorphism or heat tempering does affect the CL properties of quartz grains. Both Zinkernagel (1978) and Sprunt et al. (1978) reported the presence of induced orange CL in heat tempered and metamorphosed authigenic quartz. In addition, Sprunt et al. (1978) were able to correlate heating effects with an overall homogeneity of CL; low-grade metamorphism causes orange CL while high-grade metamorphism causes blue CL. Owen (1984) reported that blue luminescent quartz characterized rocks that he defined as garnet grade metamorphism and orange luminescent quartz characterized rocks of lower than garnet grade metamorphism.

However, experimental recycling of quartz grains through the alpha-beta transition (573° C) failed to duplicate field observations and was contradictory. Sprunt (1981) reported that the color of CL was not affected by either experimental shock metamorphism (up to 22 kb) or recycling through the transition. In contrast, Tovey and Krinsley (1980) reported that reduced contrast and temporary CL reversals result from heating quartz grains above 573° C. Failure to duplicate naturally observed CL phenomenon in the laboratory could result from the inability to extend experiments over geologic time.

Deformation episodes also affect the CL properties of quartz. For example, Dietrich and Grant (1985) reported the presence of blue and orange luminescing quartz fibers that had originally formed in pressure solution shadows in low-grade metamorphic rocks from the Helvetic Alps, Switzerland and Parys Mountain, Anglesey, U.K. The CL characteristics of the fibers were correlated to the degree of deformation and not to temperature effects on the fibers (Dietrich and Grant, 1985). Previous studies had reported the effects of deformation on CL properties of quartz but had failed to separate heating and deformation effects.

Lastly, mechanical abrasion appears to affect quartz CL. Krinsley and Tovey (1978) examined individual unpolished quartz grains in the CL mode of an SEM. Although they found non-luminescent bands in the quartz grains which they attributed to the alteration of the crystal lattice by mechanical abrasion during transport their photomultiplier response efficiency was very low in the orange and red range so the bands they examined could have actually been luminescent. In contrast, Hanusiak and White (1975) noted an increase in CL intensity in quartz grains that had been damaged with SiC abrasives, and SiC abrasives are commonly used for polishing thin sections.

Examples- Origin and Provenance Studies

Ruppert et al. (1985) examined silt-sized quartz grains in the Upper Freeport coal bed and the overlying shale from west-central Pennsylvania using an SEM and an electron microprobe and attached CL device in order to ascertain the origin of quartz in the coal. Previous workers had interpreted the quartz to be detrital in origin based on grain-shape and grain-size data (Finkelman, 1981a, 1981b; Davis et al., 1981, 1984). However, the majority of quartz grains from interior portions of the Upper Freeport paleoswamp did not exhibit CL and were therefore inferred to be authigenic in origin (Ruppert et al., 1985). Sources for the silica include the breakdown of silicate minerals and crystallization of silica derived from plant phytoliths. In contrast, the majority of the silt-sized quartz examined in the shale directly overlying the coal did luminesce implying a predominantly detrital origin for that quartz.

In an expanded study, quartz grains from an outer edge of the Upper Freeport paleoswamp were analyzed for CL characteristics. A continuous core of coal, parting material, and roof shale were collected immediately adjacent to a penecontemporaneous sandstone channel that bordered the paleopeat swamp. The majority of the quartz grains analyzed were luminescent (probably because of sediment influx from the channel) and are inferred to be detrital in origin (L.F. Ruppert, unpublished data).

Fuchtbauer et al. (1982) examined sand and sandstones of Tertiary age from borehole cores of western Germany in order to ascertain sediment source. Various petrographic parameters were measured which included (1) standard petrographic identification of light and heavy minerals and lithic fragments, (2) undulosity of quartz grains, (3) types of inclusions, (4) size-shape parameters, and (5) CL properties. Examination of the Bunter Sandstone led them to conclude that it had been originally derived from a granitic source. Analyses of other Tertiary sandstones to ascertain the provenance or source were successful, especially when CL was used in conjunction with other petrographic techniques.

With CL techniques Owen and Carozzi (1986) were able to interpret the source of the upper Jackfork Sandstone, Arkansas, a deep marine arenaceous turbidite complex of Pennsylvanian age. Previous workers had favored two different sources for the upper Jackfork: a northern cratonic source and a southerly source based on stratigraphic and structural data and petrographic techniques. Owen and Carozzi (1986) quantified the ratio of orange- to blue-luminescing quartz in the upper Jackfork and equivalent sandstones in adjacent basins. They analyzed 200 to 250 grains on each of 112 thin sections and concluded that the upper Jackfork had been derived from sediments that were transported from the south.

Other examples of provenance or source studies include the work of Thomas (1974) who used CL and other petrographic properties to trace the Pennsylvanian-Permian Vanoss Formation in Oklahoma to its Precambrian plutonic and pre-Vanoss sandstone and carbonate sources. Benner et al. (1980) used CL petrography to quantify detrital and authigenic quartz in Pennsylvanian age sandstones in Kansas and Wyoming for chemical mass balance calculations. Dorobek (1984) estimated the amounts of carbonate and quartz cement in the Silurian-Devonian Helderburg Group of the central Appalachian basin with CL techniques as part of an effort to model the diagenetic history of the group. He concluded that silica had been derived from the breakdown of siliceous sponge spicules, pressure solution, and the alteration of clay minerals.

Conclusions

CL is a powerful tool in sandstone and sedimentary petrology. CL properties of feldspar are still being documented; however, it is generally accepted that detrital feldspar luminesces in the visible range and authigenic feldspar does not. Based on reported data it appears that the CL characteristics of feldspar are controlled by the presence or absence of impurity ions in the crystal lattice. The development of a feldspar classification system that correlates the color of CL to the concentration and type of impurity ion would be very useful in sandstone petrology.

CL can be used very effectively in determining the origin of quartz. Authigenic quartz that has not been subjected to metamorphism or deformation luminesces very faintly or not at all, whereas detrital or high temperature quartz does. The wavelength or color of emitted light from detrital quartz is indicative of its temperature of crystallization and the duration of cooling, and therefore can be used to assess its origin. In general, sandstones that contain predominantly blue-luminescent quartz have been derived from an igneous or fast cooled regionally metamorphic source; predominantly orange-luminescent quartz implies a metamorphic source.

Although CL is a valuable tool it must be used in conjunction with field and other petrographic and chemical techniques. When these techniques are used in combination they can provide definitive explanations of origin and source of sedimentary units.

Future studies might usefully concentrate on the causes of CL of quartz and feldspar. The presence of low temperature authigenic quartz that exhibits faint CL may have important implications for our understanding of diagenetic processes and deformational episodes in the rock record. A more detailed understanding of the specific causes of CL could allow for further development of CL classifications (Zinkernagel, 1978; Fuchtbauer et al., 1982; Matter and Ramseyer, 1985) and aid in the reconstruction of sedimentary and diagenetic environments.

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Discussion with Reviewers:

G. Remond: Have you observed a decrease of the cathodoluminescence as a function of irradiation time and if so can this effect be correlated with the thermoluminescence emission property of quartz?
Author: It took approximately two minutes to obtain spectra of quartz grains using the

equipment I had available to me and thermoluminescent effects were evident. The CL intensity very rarely decreased during the time it took to collect spectra, more commonly intensity increased. Because the luminescence of quartz does not remain stable through time, care was taken to obtain spectra with a defocused beam on the electron microprobe to minimize induced thermal effects that could be confused with CL. Spectra were obtained from even weakly luminescing grains because the CL device was more sensitive than the human eye and all grains that exhibited an emission were classified as detrital.

G. Remond: Different defects can lead to identical CL properties, therefore can you conclude that the color of luminescence can be associated with a unique geological parameter?
Author: Although different defects lead to identical CL properties, classifications of quartz based on the color of CL do work. The temperature and cooling history of the quartz grains used to develop CL classification studies were well known from field and petrographic studies. Thousands of quartz samples from igneous, metamorphic and sedimentary environments which ranged in age from the Precambrian to the recent were collected from world wide localities. Only after the geologic history of the rocks that contained quartz was known, were CL spectra obtained and the CL characteristics were then correlated with unique geologic parameters.

G. Remond: What were the experimental conditions used to record the images and spectra shown in the text?
Author: The instrument conditions used for the CL work are as follows:

	SEM	Electron Microprobe
Acceleration potential-	30kV	15kV
Condenser current-	<2.0A	--
Sample current-	--	10 na on brass
Spot size-	--	13 μm
Photomultiplier tube (CL)- Spectral response-	350-650 nm	185-930nm
Time required to obtain spectra-	instantaneous	approximately 2 min.

J. Castaing: Is surface preparation critical for observing intrinsic CL?
Author: Polishing can introduce defects into the crystal subsurface which correspond to the depth of electron penetration. Polished surfaces are necessary for CL analysis therefore care must be taken to prepare and polish all reference and unknown samples under identical conditions. Because wet grinding appears to produce less lattice disruption than does dry grinding (Lidstrom, 1968), I have used automatic polishing equipment for all of my CL work with good results. Polishing was done using a series of steps which included the use of (1) 400 SiC grit, (2) 600 SiC grit, (3) 1 μm AlO_2, and (4) .05 μm AlO_2.

F. Laabs: If one coats with Au or carbon, does not one alter the spectral distribution and diminish the observed intensity to unacceptable levels?
Author: The spectral distribution does not appear to change with either gold or carbon coatings, however spectral intensity does diminish. Au tends to diminish CL emission more than carbon does. I have used an automatic carbon sputterer to coat all of my samples to prevent static charges. Although the carbon coating does diminish the CL intensity somewhat, I have always been able to obtain a spectrum from even the most faintly luminescing grains.

N. Scofield: Are there applications of CL for the exploration for mineral deposits and unravelling the genesis of mineral deposits?
Author: Yes, CL, especially of carbonates associated with Mississippi Valley-type Pb-Zn deposits, has been used in numerous studies to help determine the genesis of mineral deposits (Ebers and Kopp, 1979; Rowan, 1987). Because CL zoning corresponds to changes in trace element concentrations phases of mineralization can be distinguished and used to determine diagenetic sequences. Growth zones in carbonates have been used to interpret the redox potential and pH of cements, but care must be taken in this type of research because other factors besides trace element concentration can affect CL properties (Machel, 1985). CL examinations of quartz cements can lead to information on sequences of mineralization and allow for the modeling of fluid pathways in unmetamorphosed sandstones. Because many minerals that exhibit CL are associated with ore forming minerals, CL should prove very important in exploration.

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