

# Cathodoluminescence in Calcite and Dolomite and Its Chemical Interpretation

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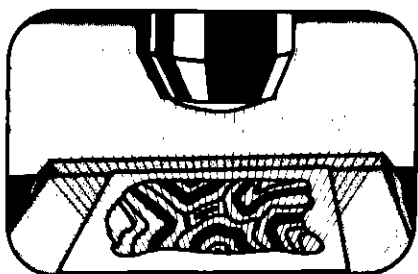
Article abstract

Most carbonate petrologists consider Mn<sup>2+</sup> and Fe<sup>2+</sup> to be the only trace elements responsible for cathodoluminescence in carbonates. However, luminescence in carbonates is caused or inhibited by a number of trace elements. The main activators in calcite and dolomite are Mn<sup>2+</sup>, Pb<sup>2+</sup> and several rare earth elements. For Mn-activated luminescence in these minerals, the main sensitizers are Pb<sup>2+</sup> and Ce<sup>2+</sup>, and the main quenchers are Fe<sup>2+</sup>, Ni<sup>3+</sup>, and Co<sup>2+</sup>. Non-sensitized Mn-activated luminescence in calcite and dolomite occurs at a minimum concentration of 20–40 ppm, perhaps as little as 5 ppm. Pb<sup>2+</sup> and Ce<sup>2+</sup> can sensitize Mn-activated luminescence at levels as low as 10 and 20 ppm, respectively. Fe<sup>2+</sup>, the most abundant quencher, begins to quench Mn-activated luminescence at about 35 ppm. Ni<sup>3+</sup>, Fe<sup>3+</sup> quench at even lower concentrations. The quencher concentrations necessary for extinction of Mn-activated luminescence have not been determined with sufficient accuracy, and probably depend on the quencher/activator ratios.

It may be misleading to assign a specific activator or quencher element to a carbonate crystal on the basis of the luminescence colour without spectroscopic measurement. Several elements can interact to produce a certain luminescence colour that is a mixture of different emission peaks. These peaks are distinctive for certain activators and/or sensitizers and may be used to identify these elements.

The variable cathodoluminescence of diagenetic carbonates is commonly used to infer the pH and redox potential of diagenetic environments by means of pHE diagrams that contain only Mn and Fe as cations. This is permissible only if elements other than Mn and Fe are insufficiently abundant to be effective. Other important processes that lead to significant luminescence variations in diagenetic carbonates are closed- and open-system partitioning, clay mineral and organic matter diagenesis and variations in trace element supply. Considering the multitude of parameters that determine and influence the luminescence of carbonates, environmental and stratigraphic interpretations of diagenetic carbonates on the basis of their cathodoluminescence should be undertaken with extreme caution.

# Articles



## Cathodoluminescence in Calcite and Dolomite and Its Chemical Interpretation

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### Abstract

Most carbonate petrologists consider  $Mn^{2+}$  and  $Fe^{2+}$  to be the only trace elements responsible for cathodoluminescence in carbonates. However, luminescence in carbonates is caused or inhibited by a number of trace elements. The main activators in calcite and dolomite are  $Mn^{2+}$ ,  $Pb^{2+}$  and several rare earth elements. For Mn-activated luminescence in these minerals, the main sensitizers are  $Pb^{2+}$  and  $Ce^{2+}$ , and the main quenchers are  $Fe^{2+}$ ,  $Ni^{2+}$ , and  $Co^{2+}$ . Non-sensitized Mn-activated luminescence in calcite and dolomite occurs at a minimum concentration of 20-40 ppm, perhaps as little as 5 ppm.  $Pb^{2+}$  and  $Ce^{2+}$  can sensitize Mn-activated luminescence at levels as low as 10 and 20 ppm, respectively.  $Fe^{2+}$ , the most abundant quencher, begins to quench Mn-activated luminescence at about 35 ppm.  $Ni^{2+}$ ,  $Co^{2+}$  and  $Fe^{3+}$  quench at even lower concentrations. The quencher concentrations

necessary for extinction of Mn-activated luminescence have not been determined with sufficient accuracy, and probably depend on the quencher/activator ratios.

It may be misleading to assign a specific activator or quencher element to a carbonate crystal on the basis of the luminescence colour without spectroscopic measurement. Several elements can interact to produce a certain luminescence colour that is a mixture of different emission peaks. These peaks are distinctive for certain activators and/or sensitizers and may be used to identify these elements.

The variable cathodoluminescence of diagenetic carbonates is commonly used to infer the pH and redox potential of diagenetic environments by means of pH/E<sub>h</sub> diagrams that contain only Mn and Fe as cations. This is permissible only if elements other than Mn and Fe are insufficiently abundant to be effective. Other important processes that lead to significant luminescence variations in diagenetic carbonates are closed- and open-system partitioning, clay mineral and organic matter diagenesis, and variations in trace element supply. Considering the multitude of parameters that determine and influence the luminescence of carbonates, environmental and stratigraphic interpretations of diagenetic carbonates on the basis of their cathodoluminescence should be undertaken with extreme caution.

### Introduction

Cathodoluminescence (CL) microscopy has become a popular tool in carbonate petrography. Three areas of application are common: (1) making fabrics visible that are not visible by standard petrographic microscopy, such as recrystallization nuclei and fronts in skeletal carbonates (e.g. Richter and Zinkernagel, 1981; Sippel and Glover, 1965); (2) "cement stratigraphy", that is, correlation in cemented carbonate rocks by interpreting equally luminescing zones as diagenetically coeval, and by inferring cement sequences (e.g. Meyers, 1974, 1978; Koepnick, 1976); and (3) geochemical interpretation of the trace element content and the redox potential of the formation fluids ambient at the time of cement precipitation (e.g. Meyers, 1974). The third point is the main subject of this paper.

Most published literature on CL treats  $Mn^{2+}$  and  $Fe^{2+}$  in solid solution as the only activator and quencher, respectively, in luminescing carbonates. However, Gies (1973, 1975, 1976), and to a lesser degree earlier papers (e.g. Schulmann *et al.*, 1947; Mukherjee, 1948; Medlin, 1959, 1963; Larach, 1968; Sommer, 1972), showed convincingly that a large number of trace elements participate in carbonate luminescence. Furthermore, the reported concentrations of  $Mn^{2+}$  and  $Fe^{2+}$  responsible for the CL of carbonates vary considerably (e.g. Fairchild, 1983). This is due mainly to the presence of other trace elements, and more precise quantitative data are presented below. Also, recent studies relate the visual CL colours unequivocally to particular trace element contents and/or concentrations (e.g. Meyers, 1974, 1978; Grover and Read, 1983), which is not always possible without spectroscopic measurements. This paper attempts to clarify the following three points: (1) the trace elements responsible for the luminescence behaviour of calcite and dolomite; (2) the concentrations of the elements responsible for CL; and (3) the relationships between these trace elements and visual CL. An attempt is then made to relate the CL of diagenetic carbonates to possible physicochemical environments of formation.

### Causes of luminescence in carbonates

Luminescence in carbonates is caused mainly by the presence of trace elements in solid solution. Less important causes of luminescence are distorted crystal surfaces and cracks, distorted internal structures between mosaic and intergrown crystals, inhomogeneities of composition between different parts of a crystal, impurities in surface sites and interstitial lattice sites, and charge displacements due to abnormally ionized or sized atoms and/or separated cation-anion pairs (e.g. Gies, 1976; Nickel, 1978; Marfunin, 1979). These factors interact to a certain degree, and the above sites are the potential centres of activation, temporary storage of energy, and emission of radiation in the form of luminescence.

Phosphors (or crystallophosphors: substances, usually crystallized solids, capable of luminescing), such as calcite or dolomite,

can be excited in a number of ways, which led to the differentiation of several luminescence types, such as photo-, cathodo-, electro-, radio-, chemo-, thermoluminescence and others. Absorption and emission spectra generally consist of broad bands which cover a wide range of wavelengths and consist of one or more peaks. Importantly, even a small part of any absorption band can stimulate the full emission spectrum (Schleede, 1960), which has been recognized as a general characteristic of phosphors (Elenbaas, 1962). Consequently, the broader the absorption bands, the more possibilities exist for excitation, and vice versa (Gies, 1976). These findings allow the luminescence behaviour of carbonates to be discussed largely independently of the kind of excitation. If an element produces an emission band, it will do so generally with any of the above excitation methods. However, the luminescence intensity decreases with decreasing excitation energy, and the peaks specific for certain trace elements may shift toward longer wavelengths.

#### Recording of luminescence

The emitted luminescence can be observed visually and/or recorded with a spectrometer. In standard CL work only visual investigation is undertaken. Thus calcite or dolomite are described simplistically as "bright", "dull" or "non-luminescent", or the visually predominant colour is noted, such as "red-orange luminescent". However, the visual impression is a composite of several emission peaks (see below), and a particular visual colour can have several different spectra. Furthermore, any colour description is dependent on the visual perception of the investigator. This problem could be eliminated by using a colour chart (e.g. Munsell, 1975), but only a measurement of the emission spectra reveals an unambiguous picture of the trace element composition of a phosphor. The specific wavelength of 590 nm, for example, is characteristic of  $Mn^{2+}$ -activated CL in calcite (with respect to the typical  $4G(T_{2g}) \rightarrow {}^6S$  energy transition; Sommer, 1972; Nickel, 1978). As mentioned above, excitation methods other than cathode beams may result in a slight shift of this peak and/or different intensity of the luminescence. Activators other than  $Mn^{2+}$  would lead to a very different radiation. Moreover, the wavelengths also depend on the chemical composition and structure of the host crystal. Therefore, equal amounts of a particular activator, such as  $Mn^{2+}$ , will give rise to a different luminescence colour and intensity in other minerals and/or polymorphs.

The CL intensity and colour of several minerals evolves through time, which has been attributed to radiation damage (Remond *et al.*, 1979) and a combination of CL and thermoluminescence (Coy-yll, 1969). The CL of carbonates remains stable with continuing excitation (Amieux, 1982), hence for CL it is irrelevant how long after the onset of excitation the spectra and intensities are recorded.

#### Activators, sensitizers, quenchers

The most energetic luminescence is caused and/or inhibited by trace elements in solid solution. These elements are conveniently subdivided into activators, sensitizers, and quenchers (e.g. Gies, 1975; Marfunin, 1979).

Activators are elements that promote active luminescence. The outer electrons of these ions are the ones that undergo the energy transitions upon excitation. The luminescence intensity decreases above a certain activator concentration (concentration quenching, and then concentration extinction).

Sensitizers are able to absorb some of the excitation energy and transmit part or all of it to the activators. Thus they promote (sensitize) the luminescence of the activators. Moreover, they may themselves produce a typical emission band different from that of the activators. Sensitizing was demonstrated in experiments where synthetic calcite crystals were laced with controlled amounts of an activator ( $Mn^{2+}$ ) and a sensitizer ( $Pb^{2+}$ ); with the activator concentration held constant, increasing amounts of the sensitizer caused its emission peak to appear and the activator's peak to increase (Gies, 1973).

Quenchers suppress activator and sensitizer luminescence, leading to a lower intensity of luminescence and finally to extinction of the phosphor, if sufficiently abundant. They may also cause a slight shift of the activator peak toward longer wavelengths. Quenchers absorb most of the excitation energy undergoing energy transitions without emitting radiation.

#### Trace elements in luminescing calcite

The most systematic and comprehensive study of the role of trace elements in the luminescence of carbonates was conducted by Gies (1973, 1975, 1976), who measured hydrothermal and synthetic crystals in photoluminescence. A small UV-band at 250-260 nm proved to be the most efficient kind of excitation in the range tested. The luminescence spectra were related to 38 trace elements. The concentrations were determined by atomic absorption and neutron activation analyses (accuracies and precision are discussed in Gies, 1973) on sufficiently large samples which were tested for homogeneity (up to six samples were taken from each specimen with homogeneous luminescence). The results of this study are applicable qualitatively to luminescence in carbonates in general. Therefore, the following discussion is based mainly on the work of Gies, supplemented by information reported in a large number of other papers on the luminescence of carbonates.

Gies subdivided luminescing calcite into seven types on the basis of the emitted spectra. Three of these types are shown in Figures 1 to 3 (the figures are taken from Gies (1975) without any attempt to improve his ambiguous trace element plots, in order

to avoid misinterpretations of his data). Each spectrum is generalized from a number of slightly different curves. These spectral types and related visible colours correspond to certain associations of trace elements and/or lattice defects, as opposed to *only one* activator or quencher.

The characteristic spectrum of Gies' Calcite Type I (Fig. 1) shows a broad, bell-shaped emission curve with a maximum between 380 and 440 nm. This main peak may be accompanied by a weak emission in the UV (330-335 nm, not shown) and a further peak in the red to red-orange around 620 nm. The visible colour varies, but a pale pink-white colour predominates. Less common are blue-violet or green with yellow tints. These colours result from variable trace element contents (Fig. 1), from variable participation of lattice defects (Gies, 1976), from Mn in variable valence states ( $Mn^{2+}$  and  $Mn^{4+}$ ; Kroger, 1948; Fonda, 1957; Osiko and Maksimova, 1960), or from a combination of these effects (this may also be pertinent to the other types discussed below). Relatively high Mn-, Zn- and Sr-contents, and low Ni- and Cu-contents, are typical for this type. The peak at around 620 nm is characteristic for Mn-activation in photoluminescence.

Calcite Type IV (Fig. 2) includes most sedimentary and diagenetic calcites. Their spectra are characterized by two pronounced peaks at approximately 327 nm and 620 nm. The shorter wavelength usually has a greater intensity but is invisible (UV). The visible colour is bright red to red-orange. The trace element association shows relatively high Mn-, Zn- and Pb-contents, or lower Pb-contents paired with higher Mn-contents, or vice versa, and mostly low Fe- and Ni-contents (the two samples in Fig. 2 with high Fe-contents have quenched spectra; Gies, 1973, 1976). This type can be described as the Mn-Pb-type. The peak at 620 nm is characteristic for Mn-activation, and the peak at 327 nm for Pb-activation in photoluminescence. As discussed earlier, Pb acts also as sensitizer for the Mn-activated luminescence, which was previously reported for CL by Schulmann *et al.* (1947).

Calcite Type VI (Fig. 3) represents a group of samples with luminescence spectra produced mainly by rare earth elements (REE). The strongest emission occurs in the UV (345-365 nm), and a broad band covers the visible spectrum. Superimposed on this broad band are narrow, sharp peaks. One of these peaks is the Mn-peak at 620 nm, but any other peak is due to a REE (mostly the "medium-heavy" lanthanides, particularly  $Eu^{3+}$  and  $Tb^{3+}$ ; Gies depicted several separate plots for the lanthanides). For CL, Larach (1968) reported 533 nm and 538 nm as the main peaks for  $Eu^{3+}$ , and 543 nm for  $Tb^{3+}$ . The various REE-peaks may be present or not, depending on the concentration of the activating REE. The visible colours vary from bright red to pink, and can be similar to Calcite Type IV if Mn-

### Luminescence spectrum and element distribution in calcite-type I (activated mainly by lattice defects)

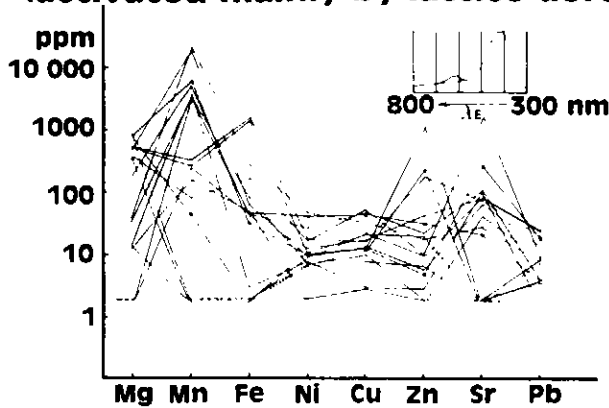


Figure 1 Luminescence spectrum and element distribution of Calcite Type I, activated by  $Mn^{2+}$  and lattice defects; every line represents one sample (after Gies, 1975).

### Luminescence spectrum and element distribution in calcite-type IV (Mn-Pb-activated)

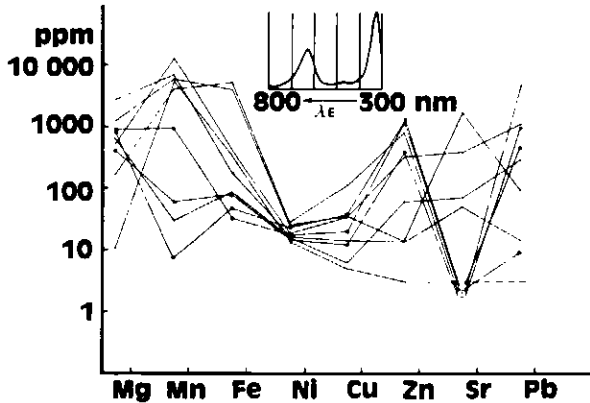


Figure 2 Luminescence spectrum and element distribution of Calcite Type IV,  $Mn^{2+}$ - and  $Pb^{2+}$ -activated; every line represents one sample (after Gies, 1975).

### Luminescence spectrum and element distribution in calcite-type VI (REE-activated, with complete emission-spectrum)

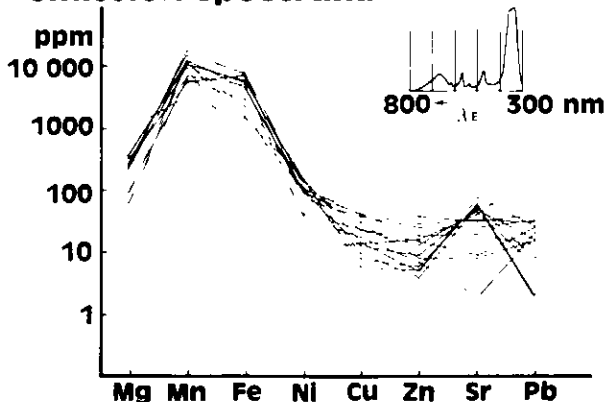


Figure 3 Luminescence spectrum and element distribution of Calcite Type VI, REE-activated, with complete emission spectrum; every line represents one sample (after Gies, 1975).

activation or Mn-sensitization are strong, or if certain REE-peaks interfere. It is not clear how abundant Calcite Type VI is in sedimentary/diagenetic rocks, but it is important to recognize that there are a number of activators other than Mn that may produce a visually similar CL.

Some of the present author's samples (diagenetic calcite) were run both in CL and photoluminescence. Most samples belong to Type IV. The CL of these samples is orange, red-orange, and yellow-orange; thus the main Mn-peak is shifted toward shorter wavelengths compared to that under UV-excitation. Since Sommer (1972) reported 590 nm as the typical wavelength of Mn-activated CL in calcite, the other peaks discussed can also be expected to experience slight shifts upon different excitation. However, the key results obtained with one method can be transferred to the other, which is also true for the qualitative results on activators and quenchers determined for calcite in thermoluminescence by Medlin (1959, 1963). Thus more than 15 trace elements have been identified that cause or inhibit luminescence (Table I). According to Marfunin (1979), all trivalent and most divalent REE have been identified in the luminescence spectra of minerals, which suggests that many REE are activators and/or sensitizers in carbonates. Furthermore, the sensitizers and quenchers listed in Table I refer only to Mn-activation. A Mn-quencher may act as a sensitizer for a different activator (e.g.  $Ni^{2+}$  may sensitize  $Pb^{2+}$ -activated luminescence; Medlin, 1959).

Amieux (1981) discriminated five types of CL intensities in calcite, and described various CL colours of calcite and dolomite. Without spectroscopic measurements and/or chemical analyses of elements other than Mn and Fe, Amieux (1981, 1982) discussed various hypotheses to explain his observations. However, the CL-types and -colours of Amieux are better explained by the same activators, sensitizers, and quenchers as in the types described by Gies.

**Trace elements in luminescing dolomite**  
Gies (1973, 1976) also examined dolomite, but he did not establish luminescence types for them as he did for calcite. However, he recognized the same elements as the principal activators, sensitizers and quenchers for both minerals.

Pierson (1981) reported the CL emission of dolomite to be concentrated in a broad spectral band ranging from 620 nm to 690 nm, with a peak at approximately 650 nm. Sommer (1972), however, reported 590 nm as the main peak, just as in the case of calcite, and a strong secondary peak at about 676 nm. He attributed the main peak to Mn substituting in the Ca-sites and the secondary peak to Mn substituting in the Mg-sites in the lattice. Variable Mn valences may complicate this pattern as in the case of calcite. Thus the

variable luminescence behaviour of dolomite with the same activator concentrations (e.g. Mn) might be due to a combination of different substitution sites in the crystals and the presence of Mn of different valence states. With increasing Fe-content and Fe/Mn-ratios, Sommer (1972), Machel (1979) and Pierson (1979) observed orange to deep-red as the predominant CL colours, and Richter and Zinkernagel (1981) described a weak dark-brown CL at very high iron concentrations (several weight percent). Apparently, the orange to deep-red colours occur if the Mn-activated CL is quenched moderately by  $Fe^{2+}$ , and the colour shifts further to brown at higher  $Fe^{2+}$ -concentrations. These colour shifts, and the accompanying decreases in intensity, are much more common in dolomite than in calcite, because dolomite often contains much more  $Fe^{2+}$ . Amieux (1982) attributed similar CL changes in calcite to quenching by  $Fe^{1+}$ . However,  $Fe^{3+}$  is extremely rare in carbonates, and high amounts of Fe are almost exclusively  $Fe^{2+}$  (note: Glover (1977) concluded, on the basis of experiments with natural and synthetic calcite, that  $Fe^{3+}$ -levels in carbonates are too low to greatly change luminescence intensities).

#### Effective concentrations

Activators, sensitizers and quenchers usually are effective only above a certain minimum concentration. The luminescence intensity increases with increasing amount of the activator or sensitizer, but decreases after passing through a maximum, ultimately leading to concentration extinction (Northrup, 1972; Gies, 1976; Marfunin, 1979). Quenchers begin to suppress luminescence at certain minimum effective concentrations and completely inhibit the activator sensitizer luminescence at higher levels. Various minimum effective concentrations of  $Mn^{2+}$  and  $Fe^{2+}$  have been reported for calcite and dolomite in CL, but almost none for the other elements involved. On the other hand, it is important to recall that the luminescence intensity depends on the excitation energy, and therefore on (a) beam voltage, (b) beam current, (c) current density, (d) type of vacuum gas, etc. (Marshall, 1978; Marfunin, 1979). Therefore, the effective trace element concentrations depend on the technical set-up of the CL-microscope and *cannot* be taken as absolute but rather as relative concentrations. Strictly speaking, *generally applicable concentration values for trace elements in luminescence do not exist*. However, most CL-microscopes are operated under similar conditions, so the values given below indicate reasonably well the orders of magnitude for practical work in CL carbonate petrography.

In the absence of better data, all concentrations given below are valid for both calcite and dolomite, as suggested for Mn-activation by Pierson (1981) and Richter and Zinkernagel (1981) (note: Fairchild (1983) suggested that the effective quencher

**Table 1** Trace elements involved in luminescence of calcite and dolomite, summarized from Gies (1973, 1975, 1976), Glover (1977), Marfunin (1979), Medlin (1959, 1963), Schrank and Fredman (1975), Schulmann et al. (1947), and Sippel and Glover (1965). The various ions are listed in approximate order of importance. It is not clear how many REE act as activators and sensitizers in carbonates (see Gies (1973, 1975, 1976) and Marfunin (1979) for details).  $Fe^{2+}$  is probably the most important quencher in carbonates because it is the most abundant one.  $Ni^{2+}$  and  $Co^{2+}$  may be important in carbonates because they are more effective than  $Fe^{2+}$  and may be present in sufficient quantities, but  $Fe^{3+}$  is probably not important (Glover, 1977).

ACTIVATORS	SENSITIZERS	QUENCHERS
$Mn^{2+}$	$Pb^{2+}$	$Fe^{2+}$
$Pb^{2+}$	$Ce^{2+}$ , $Ce^{4+}$	$Ni^{2+}$
several REE (particularly $Eu^{3+}$ , $Tb^{3+}$ )	several REE	$Co^{2+}$
$Cu^{2+}$		
$Zn^{2+}$		
$Ag^{+}$		
$Bi^{+}$		
$Mg^{2+}$ (?)		

concentrations differ for these two minerals). No reliable quantitative data have been published for activators other than  $Mn^{2+}$ . The following discussion of sensitizing and quenching considers *only Mn-activated* luminescence, because no quantitative data are available for sensitizing and quenching of other activators.

The lowest effective minimum concentration for Mn-activated luminescence of calcite published to date is 20-40 ppm Mn (Richter and Zinkernagel, 1981), which is close to the 50 ppm determined for photoluminescence by Gies (1976) (note: T. ten Have (unpub. data) found luminescing calcite with only 5 ppm Mn). These concentrations are much lower than most other published values (e.g. Fairchild, 1983). Northrup (1972) reported the concentration extinction to occur at 17 mole% (93300 ppm)  $Mn^{2+}$ , with the emission intensity maximum at 3.7 mole% (20300 ppm).

Sensitizing of Mn-activated photoluminescence in calcite begins at concentrations as low as 10 ppm  $Pb^{2+}$  and 20 ppm  $Ce^{2+}$  (Gies, 1976). As in the case of  $Mn^{2+}$ , these figures can probably be transferred to cathodoluminescence with some degree of confidence.

According to Gies (1976), the quenching effect of  $Fe^{2+}$  in Mn-activated photoluminescence begins at about 30 ppm, whereas  $Ni^{2+}$  is reported to be much more effective because it leads to appreciable quenching or even extinction at 30-35 ppm. For cathodoluminescence, the lowest effective Fe-concentration was tentatively determined at about 200 ppm (Machel, 1979). Fairchild (1983) concluded that the onset of  $Fe^{2+}$ -quenching is variable for calcite (but not for dolomite), a contention that remains to be tested. No quantitative data are available for  $Co^{2+}$ ,  $Ni^{2+}$  and  $Fe^{1+}$ , but these quenchers

are probably more effective than  $Fe^{2+}$  (Medlin, 1959; Marfunin, 1979).

The quencher concentrations necessary for extinction are often debated. Pierson (1981) reported, for dolomite, and implied for calcite, that the crystals are extinct above about 1 weight% (wt.%) (10000 ppm)  $Fe^{2+}$ , regardless of the Mn-concentration. Meyers (written communication, 1983) argues that there is no total quenching at 1 wt.% (10000 ppm)  $Fe^{2+}$  because he has found luminescing calcite with more than 3 wt.% FeO (23300 ppm Fe) and 0.05-0.2 wt.% MnO (400-15000 ppm Mn) (the sensitizer concentrations were not determined). Richter and Zinkernagel (1981) reported a weak brown luminescence in dolomite with up to 15 wt.%  $FeCO_3$  (72300 ppm Fe). Several authors suggested that extinction depends on the Fe/Mn ratio (e.g. Machel, 1979; Pierson, 1981; Frank et al., 1982). Frank et al. (1982) suggested that calcites with Fe/Mn ratio greater than 1.0 display generally a weak luminescence. Machel (1979) documented calcite with bright yellow luminescence at a Fe/Mn ratio of 10.9 (1357:126 ppm), another sample was extinct at a ratio of 11.4 (1620:142 ppm). There are various possibilities for these discrepancies, i.e. the presence of other activators, sensitizers, or quenchers, or different valence states of the trace elements involved. If quenching does indeed depend on the quencher:activator ratio, the  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ , and  $Fe^{3+}$ ,  $Mn^{2+}$  ratios must also be taken into account.

#### Physicochemical constraints on cathodoluminescence in carbonates

Following Meyers (1974), various authors have interpreted "bright", "dull" or "non-luminescent" calcite and dolomite cement crystals and zones in terms of  $Mn^{2+}$ - and  $Fe^{2+}$ -supply

and/or the redox potential of the diagenetic environment (Koeppnick, 1976; Amieux, 1982; Grover and Read, 1983; and several others). Nearly all papers neglect trace elements other than Mn and Fe. As demonstrated above, however, it is not always possible to take a given luminescence colour or intensity of a particular crystal and equate its luminescence to high  $Mn^{2+}$  and/or  $Fe^{2+}$ -contents without making sure that ions other than these two may be involved. Furthermore, the  $Mn^{2+}$  and  $Fe^{2+}$ -concentrations in natural waters also vary due to processes other than changes in the redox potential, such as trace element partitioning or clay mineral and organic matter diagenesis. These factors are neglected frequently in the chemical interpretation of CL.

**Changes in the redox potential.** The CL of calcite and dolomite can be interpreted in terms of pH and  $E_h$  using standard pH/ $E_h$  diagrams of carbonate species of these elements, if it can be assured that ions other than  $Mn^{2+}$  and  $Fe^{2+}$  are insufficiently abundant to be effective, or that they occur in such small quantities that their effects can be neglected. This can be assured only for crystals that are large enough to be analyzed by AAS or ICP, because the detection limits of these instruments are low enough. Unfortunately, the crystals or growth zones of interest are often so small that the microprobe is the only

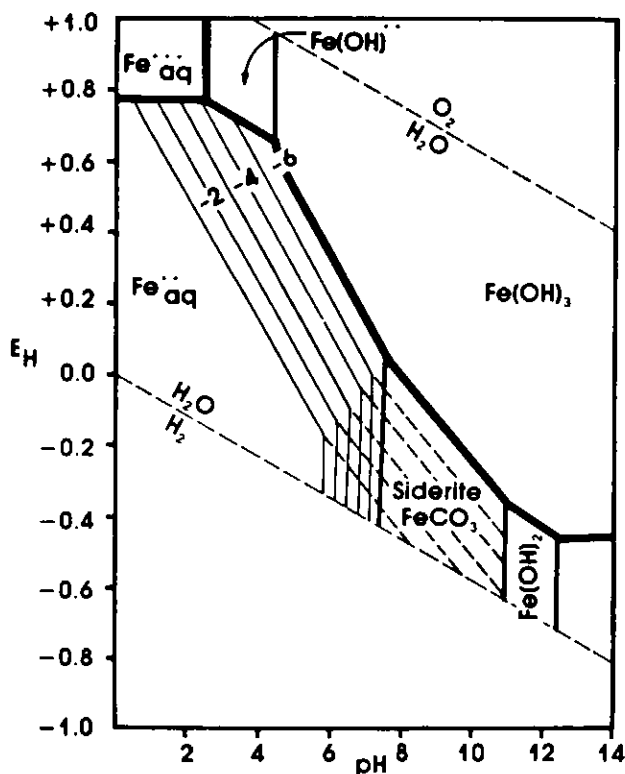
tool which can be used to determine the trace element contents. Since the detection limits of most microprobes are below the effective minimum concentrations of the activators, sensitizers, and quenchers discussed above, pH  $E_h$  interpretations of these crystals and growth zones must be undertaken with extreme caution.

Figure 4 is a pH/ $E_h$  diagram for Fe-species in aqueous solution in contact with solid siderite. The lines in the left field indicate increasing activity of  $Fe^{2+}_{aq}$  towards lower pH and  $E_h$ . This diagram can be interpreted as follows. If the ion activity product of the solution is lower than the solubility constant of siderite, the siderite field can be considered to represent ferroan calcite or dolomite, if the solution is in equilibrium with these minerals. In these cases, the activity lines of  $Fe^{2+}$  can be projected from the left part of the diagram into the siderite field (dashed lines of Fig. 4), intersecting the  $Fe^{2+}_{aq}/FeCO_3$  boundary. If the composition of a diagenetic solution plots in this "ferroan field", precipitating calcite and dolomite would incorporate more  $Fe^{2+}$  the higher the  $Fe^{2+}$ -activity of the solution, that is, the lower the  $E_h$ . Figure 5 is the analogous diagram for Mn-species in a solution in contact with solid rhodochrosite. This diagram can be interpreted analogously to Figure 4.

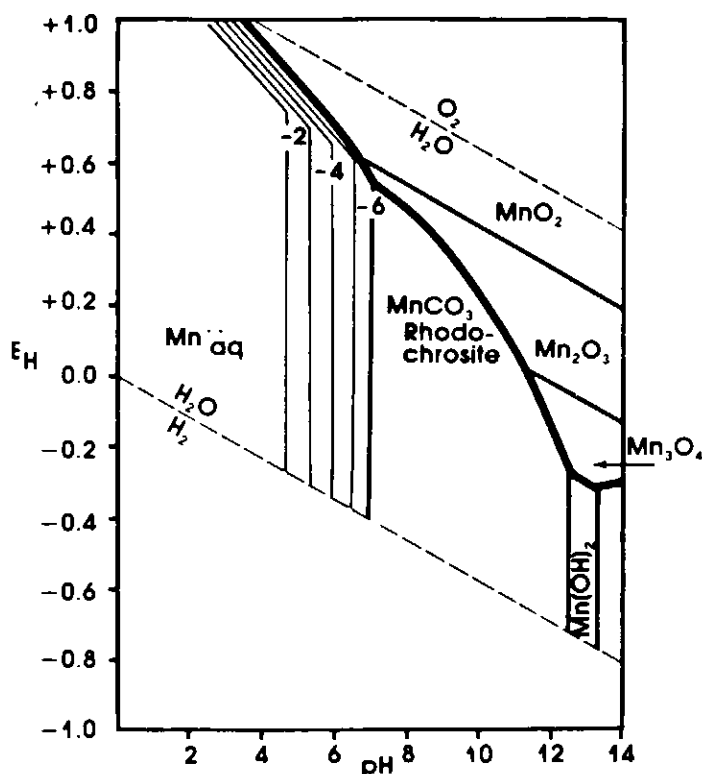
If Figures 4 and 5 are superimposed (Fig. 6), the two thick lines subdivide three fields, one above, one between (stippled), and one below

these lines. Diagenetic environments most commonly have pH-values between about 5 and 10 (Garrels and Christ, 1965), so that only this range is considered. Suppose a formation water precipitating calcite cements starts at X and evolves toward B. Above A, the calcite would be very  $Mn^{2+}$ -poor and non-luminescent. Below A (in the stippled area), calcite would contain  $Mn^{2+}$  above the minimum effective concentration. This calcite would be luminescent, and the luminescence intensity increases if the pH and  $E_h$  drop during precipitation as  $Mn^{2+}$  is increasingly incorporated. Below B, calcite would incorporate  $Fe^{2+}$  above the effective minimum concentration, thus undergoing more quenching of the Mn-activated luminescence the more pH and  $E_h$  drop. Therefore, down to about C (arbitrarily set to represent the level of complete quenching), the crystal would display decreasing intensity and red-shift of the Mn-peak. Below C the calcite would be non-luminescent. This is exactly the kind of luminescence zonation shown in the sample in Figures 7 and 8. A path along A'-B'-C', involving no change in pH, would be interpreted in an analogous way (Fig. 6).

This approach is, of course, rather simplified. First, the partition coefficients for  $Mn^{2+}$  and  $Fe^{2+}$  with respect to water and calcite and dolomite are not known with sufficient accuracy (Veizer, 1983), especially over the temperature range of diagenetic reactions.



**Figure 4** Metastable iron hydroxides and siderite at 25°C and 1 atm total pressure; boundaries between solids and ions at total activity of dissolved species  $10^{-6}$ , and boundaries of  $Fe^{3+}:Fe(OH)^{2+}:Fe^{2+}$  at activity ratios = 1; total dissolved carbonate  $10^{-2}$  molal (modified after Garrels and Christ, 1965).



**Figure 5** Stability relations among manganese compounds in water at 25°C and 1 atm total pressure; total dissolved carbonate  $\cdot 10^{-2}$  (modified after Garrels and Christ, 1965).

Second, no clear-cut definition exists regarding how much  $Mn^{2+}$  and  $Fe^{2+}$  these carbonate minerals have to contain in order to be called manganon or ferroan. Third, the lines in Figures 4 and 5 vary somewhat with P, T,  $pCO_2$  and/or total dissolved carbonate ( $H_2CO_3 + HCO_3^- + CO_3^{2-}$ ) and the occurrence of species not considered (for example  $H_2S$ ). However, considering that all these parameters are either poorly defined or partly counteracting, the choices of P, T, and  $pCO_2$  in Figures 4 and 5 (see captions) are reasonable in the context of this merely qualitative discussion.

Frank *et al.* (1982) have proposed a similar model for CL zones in calcite. Their fields of "dead", "bright", and "dull" luminescence are comparable to the ones presented in this paper. Frank *et al.* (1982) proposed one more "bright" field, which would plot between B B' and C/C' in Figure 6, for systems containing  $H_2S$ . Waters in this field might precipitate  $FeS_2$ . Coeval calcite would be  $Fe^{2+}$ -poor, and therefore show "bright" luminescence. Such calcite would form in environments where sulfate reduction produces reduced sulfur species. Hence the above luminescence fields depend not only on the pH and  $E_h$  of the environment, but also on the amount of reduced sulfur species (as well as on the amount of the other activators, sensitizers, and quenchers). Similar pH/ $E_h$  diagrams should also be constructed for other elements that occur in different valence states. Clearly, pH/ $E_h$  interpretations of CL are much more complicated than commonly thought.

**Trace element partitioning.** Trace element variations in diagenetic carbonates are also governed by partition laws (see Veizer (1983) for a comprehensive review). Trace element variations due to partitioning are ubiquitous, and they are at least as important as changes in pH and  $E_h$  in many cases.

The most important theoretical models for trace element partitioning during limestone diagenesis were developed by Pingitore (1978) and Brand and Veizer (1980) (see also discussion in Veizer, 1983). Using the parameters of distribution coefficient, water flow relative to reaction rates (open or closed system), and chemistry of the water before it enters the diagenetic site, they determined the enrichment or depletion of a number of trace elements in diagenetic calcite under various conditions. In particular, any diagenetic process will change the Mn/Fe ratios (and the other trace element ratios) of the solutions, since the partition coefficients of these elements are different. Although the exact magnitude of these changes is much debated, it is not justified to ignore these changes, as is common practice in CL work.

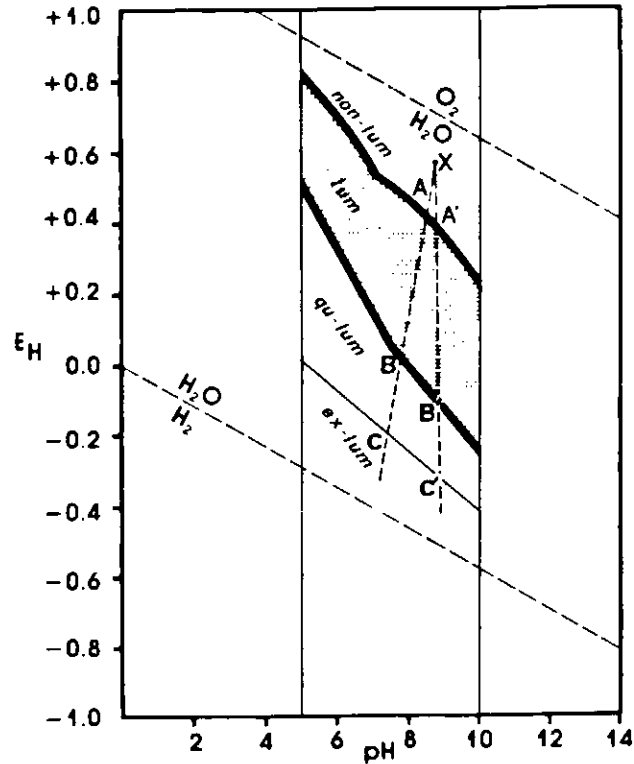
**Organic matter and clay mineral diagenesis.** Organic matter and clay minerals are known to carry various trace metals due to adsorption and complexing (chelation). Organic

matter hosts preferentially the trace metals Ag, (Co), Cr, Cu, (Eu), Ga, La, Mn, Mo, Ni, Pb, Te, U, V, Y, (Zn), whereas other elements — B, Ba, Be, Co, Cs, Hf, (Mo), (Pb), Rb, Sc, Se, Th — are associated mostly with clay minerals (Khawlie and Carozzi, 1976; Parekh *et al.*, 1977; Leventhal and Hostermann, 1982, elements in brackets are suspected, but not demonstrated, to be associated with organic matter and clay minerals, respectively). Moreover, mixed-expandable clays may host other trace elements preferentially over illite or chlorite. For example, Co occurs in illite rather than in chlorite; Mn, if associated with clay minerals, occurs preferentially in mixed-expandable clays rather than in other clay minerals (Khawlie and Carozzi, 1976). Furthermore, the associated Fe-compounds in a sediment, such as siderite, pyrite, hematite, or limonite, would also be expected to host Co and Ni.

Many of the above elements are released into pore waters upon compaction and/or diagenetic alterations of clay minerals, organic matter, or other detrital minerals. Consequently, they could be incorporated into the precipitating carbonate cements. This could take place in a sequential manner since most trace elements are released in a specific sequence during diagenesis. Furthermore, car-

bonate cements precipitated during organic matter diagenesis and hydrocarbon migration are subject to yet another fractionation process reported by Parekh *et al.* (1977), whereby the light rare earth elements become enriched in the carbonates and the heavy ones in the organic component.

**Changes in the supply.** In coastal and shelf areas, several alternative sources contribute to the trace metal composition of the surface and shallow phreatic waters (Kremling, 1983): (1) remobilization of trace metals from partly reduced sediments; (2) eolian input; (3) river discharge; and (4) anthropogenic sources, such as sewage, industrial, and other waste (only important in recent sediments). These processes will exert an influence on the composition of early diagenetic carbonate minerals where the surface and shallow phreatic waters are not thoroughly mixed with seawater. Various trace elements may also be supplied in deeper phreatic environments by formation waters of various migration paths (e.g. through sandstones, shales, evaporites). Changes in the supply of trace elements may overlap with changes in pH/ $E_h$  and trace element partitioning, particularly in meteoric aquifers of coastal areas, which is also commonly ignored in CL work.



**Figure 6** Superimposition of Figures 4 and 5; the stippled area marks the field of  $Mn^{2+}$ -activated luminescent calcite or dolomite (lum) without Fe-quenching; above this field are non-luminescent carbonates (non-lum) due to insufficient  $Mn^{2+}$ -content; below are quenched (qu-lum) and extinct (ex-lum) carbonates due to increasing  $Fe^{2+}$ -content (see text for further explanation).



### Implications for carbonate petrography

The previous sections present an almost bewildering array of factors that determine and influence the luminescence behaviour of carbonate minerals. Unfortunately, many of these factors limit the application of CL in carbonate petrography, and environmental interpretations of diagenetic carbonates should be undertaken with extreme caution.

Certainly, it is safe to apply CL in a qualitative petrographic manner. For example, Dickson (1983), Walkden and Berry (1984), and a number of authors before them, detected growth zones and discontinuities, truncations and peculiar cementation fabrics in CL which were otherwise invisible, and interpreted them in a purely petrographic manner.

Amieux (1981, 1982) subdivided a carbonate sequence into four CL zones that coincide with the sequential evolution established by stratigraphic and sedimentological data. Although his chemical interpretations are not necessarily correct, Amieux did demonstrate that supratidal versus subtidal and clay-poor versus clay-rich facies domains can be differentiated by means of carbonate CL in some cases.

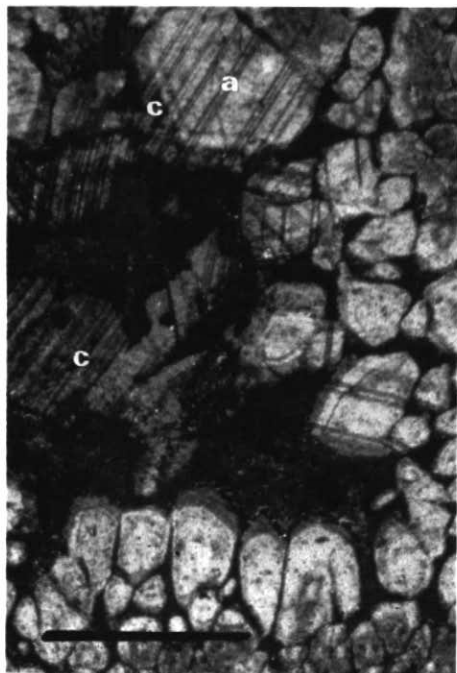
The concept of "cement stratigraphy" was introduced by Evamy (1969), and first applied in CL by Meyers (1974). Meyers correlated calcite cements with similar CL over a lateral distance of up to 16 km, and more recently over much greater areas (Meyers, 1978). He

based his interpretations of diagenetic environments (ion activities,  $\text{pH}/E_h$ ) only on  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  in luminescing carbonates. Interpretations of this kind should be reconsidered in the light of the above discussion on trace elements in luminescing carbonates. Similarly, Grover and Read (1983) found a distinctive zonation (non-bright-dull) in diagenetic carbonates of a peritidal setting interpreted to have undergone vadose/shallow phreatic diagenesis, as well as in a deeper subtidal setting that was never exposed. These authors also neglected elements other than  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ . However, should their interpretations concerning the flow direction of the diagenetic fluids be correct (and all other elements are not involved significantly in the luminescence of their samples), their equally luminescing calcites would not be synchronous (as in Meyer's work) but diachronous, which is more realistic considering the size of these aquifers.

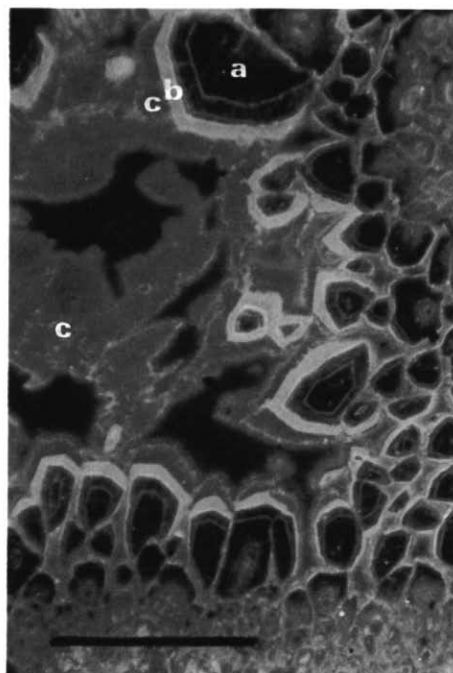
Generally marine carbonates do not luminesce. However, Glover (1977) reported luminescing Cenozoic and Cretaceous hemipelagic and pelagic carbonates that were always in contact with seawater. The significance of these findings has not yet been determined. The fairly unusual occurrence of luminescing marine calcite reported by Adams and Schofield (1983) probably has only limited importance. These authors found marine Mg-calcite cement with a bright yellow luminescence cementing a gravel deposit in

the vicinity of a decomposing shipwreck. This demonstrates the influence of anthropogenic "pollution". Potentially much more important are the findings of Scherer and Seitz (1980), who reported marine Mg-calcite cements within corals that were strongly enriched in the heavy REE relative to the corals and mollusk shells in the area. They interpreted this REE enrichment to be due to organic (bacterial) influence, which suggests that organic (bacterial/algal/fungal) fractionation might lead to REE-activated and/or -sensitized luminescence in marine carbonate cements!

Using rare earth element and isotopic distributions in calcite, Möller *et al.* (1979) demonstrated how the origin of lead/zinc veins can be deduced. They determined the following paragenetic sequence (1) assimilation of a sedimentary limestone by a hydrothermal fluid with subsequent calcite precipitation, (2) mixing of this fluid with a fluid derived mainly from carbonaceous sediments, and (3) remobilization of the first hydrothermal calcite. A number of the REE anomalies detected would lead to distinctive luminescence patterns (a part of this material was used by Gies in his study). The pioneer study of Möller *et al.* (1979) demonstrates that luminescence work has considerable application in mineral exploration. Similarly, Amieux (1982) suspected  $\text{Zn}^{2+}$  as the activator of an abnormal pale-blue CL in dolomite that occurs in the vicinity of localized Pb-Zn mineralization.



**Figure 7** Cavity in reef carbonate of the Devonian Brilon Reef Complex (West Germany); the margin of this cavity is lined by bladed calcite crystals which show a non-ferroan centre ferroan overgrowth (c); the ferroan calcite also occurs as blocky crystals in the centre of the void. Stained (alizarin-red + potassium ferricyanide) thin section, bar = 1 mm.



**Figure 8** Same sample as in Figure 7 now in CL; the bladed crystals display three-fold zonation; a and c are as in Figure 7, b, now visible, cannot be seen without CL; a is non-luminescent, b is bright-orange luminescent, c is dull-red luminescent and stained blue-violet in Figure 7. This sample may represent a continuous drop in  $E_h$  during the precipitation of calcite similar to sample X in Figure 6 (from X into the field qu-lum).



## Conclusions

The cathodoluminescence of calcite and dolomite is due to the association of many trace elements and/or lattice defects. Therefore, the chemical environment of precipitation can only be deduced by means of CL if all the important activators, sensitizers, and quenchers are determined. Hence a combination of visual CL microscopy, spectroscopic measurement of the CL, and multi-elemental chemical analysis (e.g. by ICP, AAS, etc.) is the only rigorous way to interpret CL data. This poses problems where the crystals of interest are too small to be separated mechanically for chemical analysis. In these cases, the activator, sensitizer, and quencher concentrations may be too low to be detected by the microprobe. This, however, does not justify neglecting the presence of these elements, and a rigorous interpretation of CL of such crystals is not possible until instruments with greater sensitivity become available. However, the CL of these crystals can be measured with spectrometers. At least activators and sensitizers could be detected and determined quantitatively if the peak positions and peak heights are calibrated by means of standards. Fluorite lens optics are recommended because a number of characteristic peaks are in the UV or IR part of the spectrum.

Carbonate cements may have precipitated or recrystallized in environments rich in certain elements. For example, carbonaceous or argillaceous limestones, or limestones in the vicinity of carbonaceous or argillaceous rocks, can be expected to contain different associations of CL-effective trace elements. The complexities of the sedimentary environment, like the physicochemical conditions of deposition, rates of sedimentation, degree of bioturbation (in fine-grained carbonates), mineralogical composition of detrital impurities, content of organic matter, and other factors, might all have an influence on the diagenetic environment (especially on pH, E<sub>h</sub>, and the trace element concentrations in solution). Since many trace elements are involved in the luminescence of carbonates, these complexities should be considered in any environmental interpretation of the cathodoluminescence of diagenetic calcite or dolomite.

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