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The control of cathodoluminescence in dolomite by iron and manganese

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ABSTRACT

Variations in the cathodoluminescent properties of carbonates are usually attributed to differing proportions of manganese (Mn^{2+}) as the most important activator, and iron (Fe^{2+}) as the main inhibitor of luminescence. Interactions between manganese and iron concentrations and the luminescent properties of dolomite are demonstrated by petrographic and chemical analyses of 86 samples of dolomite representing a range of depositional environments and ages (Cambrian to Cretaceous) and a wide geographical distribution (North America and Europe).

Iron and manganese are positively correlated in the dolomites, with the former showing a greater range of variation. Very small amounts of manganese are sufficient to activate the luminescence and as little as 100 ppm Mn^{2+} is present in highly luminescing samples. The intensity of luminescence is not proportional to the manganese concentration. Iron begins to quench luminescence as its concentration reaches 10,000 ppm. Above that level, luminescence is rapidly lost and total extinction occurs among samples containing more than 15,000 ppm Fe^{2+} , regardless of the manganese concentration.

INTRODUCTION

The emission of light induced by electron bombardment of a phosphor is known as cathodoluminescence. Luminescing conditions occur in impure crystalline substances, where substituted ions in the crystal structure act either as luminescent centres, activating the luminescence, or as inhibitors of luminescence. The role of manganese (Mn^{2+}) as an activator of luminescence in carbonates is recognized by most authors, while ferrous iron is considered to be the most important quencher of luminescence (Long & Agrell, 1965; Smith & Stenstrom, 1965; Martin & Zeeghers, 1969; Sommer, 1972; Meyers, 1974; Nickel, 1978).

Cathodoluminescence is rapidly gaining popularity among geologists and petrographers as a technique

allowing the observation of features often invisible with a polarizing microscope. Unfortunately, the potential use of cathodoluminescence as a tool in petrography is impaired by the lack of quantitative data relating luminescing properties of minerals to their chemical variations. Since the production of detectable luminescence depends on a sufficient amount of activator element, e.g. Mn^{2+} in carbonates, a few attempts to define that minimum amount were made by several authors who suggested that distinctly luminescing calcites contained at least 1000 ppm Mn^{2+} (Martin & Zeeghers, 1969; Meyers, 1974). No data are available concerning the amount of iron necessary to inhibit luminescence in carbonates.

This study is aimed at clarifying the role of both manganese and iron as activator and quencher of luminescence in dolomite, and at determining semi-quantitatively the correlation between luminescent properties of dolomite and iron and manganese concentrations.

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EXPERIMENTAL PROCEDURES

This study is based on the observation and analysis of 86 samples of dolomite, selected to represent a wide geographical distribution as well as a range of ages and environments of deposition and diagenesis. Included are dolomites from several locations in North America and Western Europe, ranging in age from Cambrian to Cretaceous. The samples were observed in transmitted light and in cathodoluminescence and selected specimens were analysed chemically by arc spectroscopy, atomic absorption spectrophotometry and by the electron microprobe.

Cathodoluminescence

Luminescent studies were conducted in a Nuclide Corporation Luminoscope, model ELM-2A, at 16 kV and 0.3 mA with a focused beam 2 mm in diameter, with residual gas and a chamber pressure of about 6.6 pascals. The electron gun was of the cold cathode type. Observations were made on glass-mounted, 50 μ m thick, unpolished and unstained sections, using a Zeiss photomicroscope.

The relative intensity of luminescence was estimated by reference to a standard. Sample BP 38, showing the brightest luminescence, was selected as the reference specimen and was arbitrarily assigned a value of 100% relative intensity. By visual comparison to the degree of luminescence of the standard, a relative intensity was determined for all other samples.

Colour of luminescence was determined by comparing the observed colour to a colour emission spectrum chart with indications of wavelengths (Pauling, 1970).

Arc spectroscopy

Dolomite crystals were picked from 18 samples which showed homogeneous luminescence, and analysed in duplicate for magnesium, iron, manganese, titanium and lead by arc spectroscopy in the Cabot Spectroscopic Laboratory of the University of Kentucky. Emission spectrographic techniques for the determination of trace elements used were those of Ahrens (1954) as modified by Dennen (1964). The lines used were, for magnesium 277.7 nm, for iron 262.5 nm, for manganese 279.8 nm, for titanium 332.4 nm and for lead 257.7 nm.

Atomic absorption spectrophotometry

Twenty samples were analysed for calcium, magnesium, iron, manganese, lead, strontium, copper, nickel and cobalt by atomic absorption spectrophotometry. The selected samples were weighed and dissolved in nitric acid, filtered and diluted. The analyses were conducted on a Beckman DBG spectrophotometer with atomic absorption attachment, following the method described by Robinson (1966).

Electron microprobe analyses

Nine samples showing uneven or zoned luminescence were analysed by electron microprobe at the Laboratoire de Pétrographie of the Université Catholique de Louvain, in Louvain-la-Neuve, Belgium. Analyses were conducted on an Applied Research Laboratories model 'AMX' electron microprobe, for calcium, magnesium, manganese and iron, using polished, uncovered thin sections. The resolution of the AMX microprobe analyser is of the order of 1 μ m with currents ranging from 15

Fig. 1. Examples of cathodoluminescence in dolomite. Scale bar is 300 μ m (1). Sample from a Devonian red reef at Neuville, Belgium. Euhedral crystals of dolomite are scattered through a calcitic matrix. Image in transmitted light. (2) Same sample in cathodoluminescence. The calcitic matrix luminesces brightly while the dolomite crystals remain extinct. (3) Sample from the Lower Carboniferous of Campine, Belgium, Haalen core-boring (-1163 m). Euhedral crystals of dolomite replacing the intergranular cement. Image in transmitted light. (4) Same sample in cathodoluminescence. The dolomite rhombs are luminescing brightly and relatively evenly. The calcitic cement shows a zonation in cathodoluminescence. (5) Dolomite from the Millersburg Member of the Lexington Limestone, Kentucky River Fault Zone, Kentucky. Euhedral and subhedral crystals of dolomite. Image in transmitted light. (6) Same sample in cathodoluminescence. Only a few crystals are luminescing, and show three different zones. The central zone is highly irregular and brightly luminescing, while the two outer zones are regular and have a dull luminescence. (7) Dolomitized limestone, Waulsortian, from Nenagh, County Tipperary, Ireland. Dolomite crystals show a zonation in transmitted light. (8) Same sample in cathodoluminescence. Numerous thin zones are very regular in the large euhedral crystals.

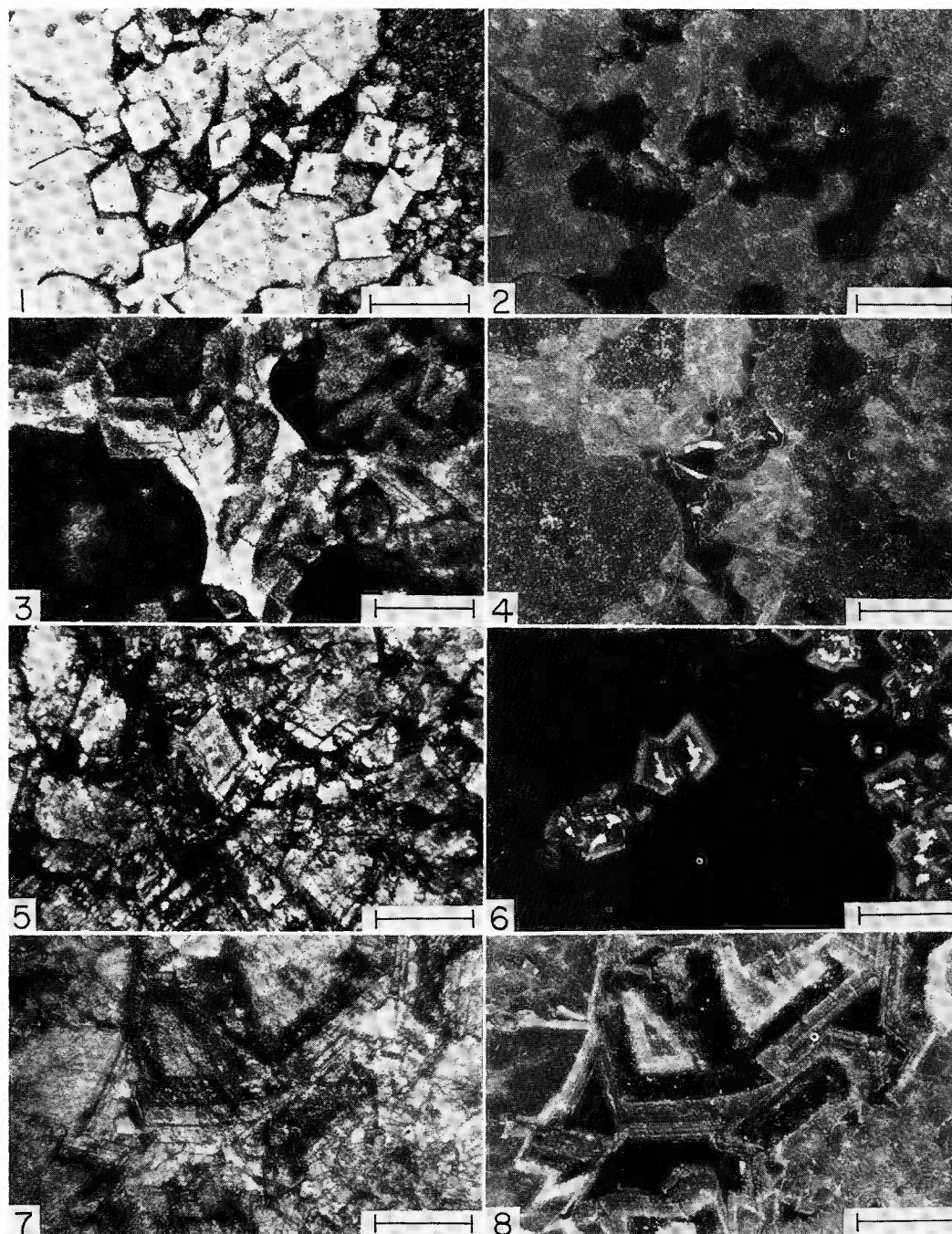


Fig. 1. For legend see opposite.

to 30 kV. Semi-quantitative analyses were made of all the samples, using as standards: wollastonite for calcium, rhodonite for manganese and olivine for magnesium and iron. The profile of a reference sample was used for peak measurements and the correction factor was calculated for each element following the method of Bence & Albee (1968).

RESULTS AND DISCUSSION

Cathodoluminescence

Several categories of crystals can be recognized according to their luminescent properties (Pierson, 1977). The two basic classes include luminescing and extinct crystals. Subclasses can be subsequently defined, based on homogeneity of luminescence and regular or irregular zonation (Fig. 1). Cathodoluminescence in dolomite and calcite is commonly visible as a succession of zones, or narrow bands, that possess distinct luminescent characteristics and intensities. The emission intensity is usually homogeneous throughout each zone and reflects the chemical composition of that zone. The concentric arrangement of the zones corresponds to the different stages of crystal growth and gives information on the spatial distribution of the activator and quencher of luminescence at each phase of growth of the mineral (Oglesby, 1976).

Colour of luminescence

The luminescent emission of dolomite was found to be concentrated in a broad spectral band ranging from 620 to 690 nm (orange to deep red) with a peak at about 650 nm (Pierson, 1977). There is still confusion about the causes of the variety of colours of luminescence, and no specific luminescent spectral measurement of carbonates related to their chemical composition has been made. A few interpretations have been attempted, however, to relate the shift in wavelength to variations in crystalline structure and more precisely to the distance between atoms. According to Sommer (1972), the luminescent emission for the Mg solid-solution-series shifts to longer wavelengths with decreasing bond spacing caused by the emplacement of magnesium. The valence state of the manganese included in the crystal structure may also affect the emission wavelength (Kroger, 1948; Fonda, 1957). Osiko & Maksimova (1960) found that all green and yellow luminescence is caused by manganese with an average valence of 2, all orange-red

and red luminescence is due to some manganese with a valence of 2 and some with a valence of more than 2.

Arc spectroscopy and atomic absorption

Spectral analysis of the 245–350 nm region by arc spectroscopy revealed the presence of magnesium, manganese, iron, lead and titanium. The characteristic lines of lead and titanium, however, could not be measured within acceptable levels of confidence because of their low intensity, suggesting that these two elements were only present as traces in the analysed samples. Iron and manganese lines, on the other hand, were always present in various measurable intensities, but no distinction could be made between the different valence states of these two elements. The measurements reflect therefore the total content of iron and manganese.

The results of the arc spectroscopy analyses are not quantitative measurements of element concentration. They merely express the distribution of the analysed samples with respect to the relative abundance of Fe and Mn, using magnesium as the reference element (Fig. 2).

Quantitative analyses by atomic absorption show that the iron and manganese contents of the analysed dolomites are highly variable. Iron concentration ranges from less than 500 to 100,000 ppm (10 wt %). Manganese is present at concentrations ranging from

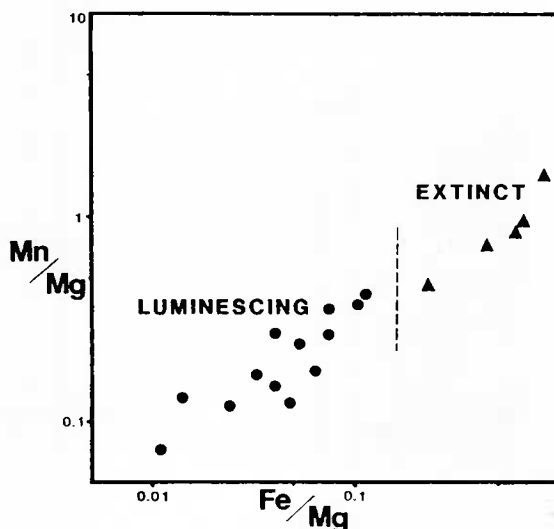


Fig. 2. Distribution of samples analysed by arc spectroscopy. Results expressed in terms of the relative intensities of the Mn and Fe lines using Mg as the reference element.

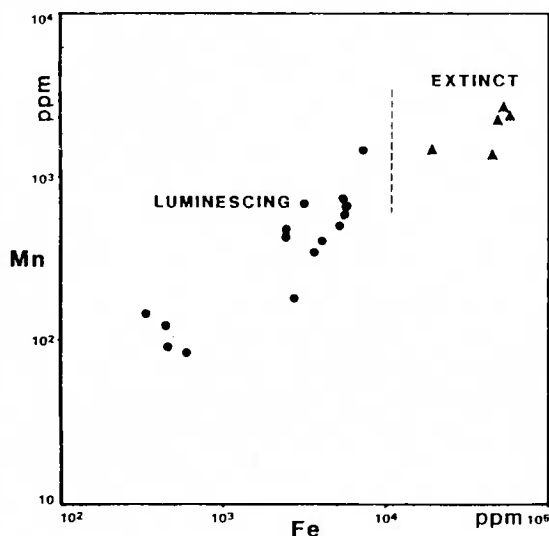


Fig. 3. Results of the atomic absorption analyses for iron and manganese. Note that the scale for iron is 10 times greater than for manganese.

less than 100 ppm to more than 2500 ppm. An anomalously low magnesium concentration is observed in samples that contain greater proportions of iron and manganese, suggesting that iron and manganese substitute preferentially for magnesium in the dolomite crystal structure.

Traces of lead, chromium, nickel, cobalt and strontium were found in most analysed samples. Their presence, however, does not provide any significant information concerning luminescent emission.

The distribution of the analysed samples relative to their iron and manganese contents is shown on Fig. 3. The results of the atomic absorption and of the arc spectroscopy analyses support each other by yielding similar information, i.e.:

(a) On a logarithmic scale, the samples show a fairly linear distribution, reflecting the parallel variation of both iron and manganese, with, however, greater variations in the iron content.

(b) Luminescing and extinct samples are clearly separated.

(c) The non-luminescing samples are all found at that end of the curve, where iron and manganese concentrations are highest, while luminescing samples contain lesser amounts of both elements.

Atomic absorption analysis (Fig. 3) yields additional information:

(d) A detectable luminescence is reached with

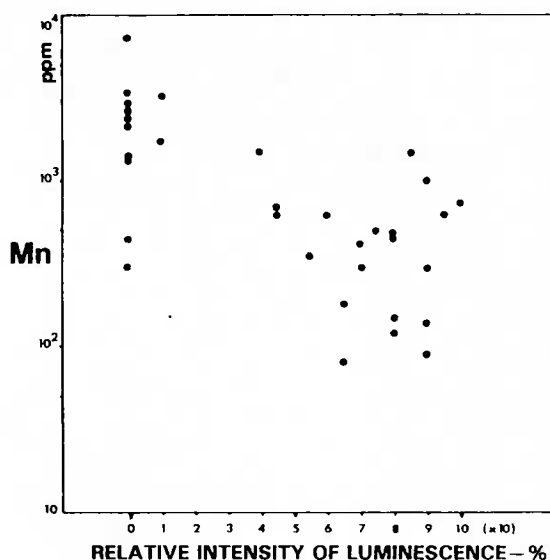


Fig. 4. Correlation between the manganese concentrations of dolomite samples and their relative intensity of luminescence. The random distribution of the points indicates a non-proportionality between luminescence intensity and manganese content.

surprisingly low manganese concentrations. Two highly luminescing samples contain less than 100 ppm Mn and, furthermore, the manganese concentration of the majority of the luminescing samples ranges from less than 100 to 1000 ppm. Few luminescing samples contain more than 1000 ppm Mn.

(e) All extinct dolomites contain more than 10,000 ppm (1 wt %) Fe, yet relatively large amounts of manganese are present in the same samples.

These observations contradict the assumption that the intensity of luminescence is simply proportional to the manganese concentration: samples showing a relatively high intensity of luminescence contain little manganese and extinct samples have Mn concentrations greater than 1000 ppm (Fig. 4).

A new lower limit for the manganese concentration is suggested at less than 100 ppm, since luminescing dolomite is found to contain such small amounts of manganese.

Electron microprobe analysis

The results of quantitative analyses by the electron microprobe show great variations in the iron and manganese concentrations, as in the atomic absorption analyses. Results for each crystal zone exhibiting distinctive luminescent characteristics and for

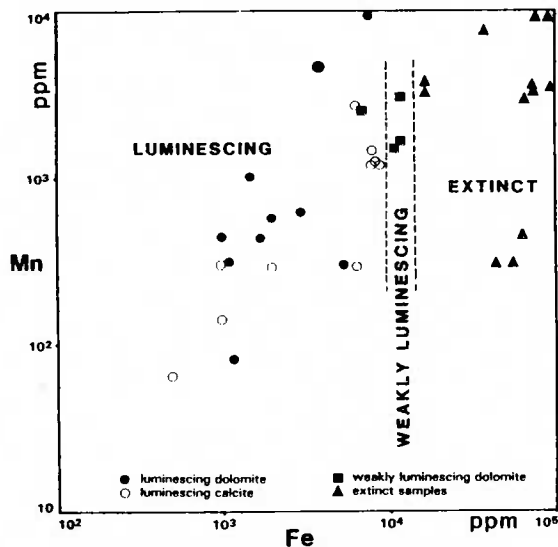


Fig. 5. Iron and manganese concentrations from electron microprobe analyses. Scale for iron is 10 times greater than for manganese. Crystals showing a zonation were analysed by the electron microprobe. Each point represents the data for an individual zone.

several calcite samples are reported on Figs 5 and 6, from which the following observations are made:

(a) Except for three extinct zones from one particular specimen (BP 22) located on the lower right portion of the graph, the distribution shows again a close coupling of the concentrations of iron and manganese although a linear trend is not as evident as on the previous figures (Figs 2 and 3). However, in spite of the scatter of the points on Fig. 5, the parallel variation of iron and manganese is still visible. It becomes even more evident when the different zones of each individual crystal are grouped into domains, as in Fig. 6. Each domain clearly follows a linear distribution pattern, suggesting once more that iron and manganese vary similarly, increasing or decreasing together in the same crystal.

(b) Luminescing and extinct samples and zones are clearly separated, but a gradual passage from luminescence to extinction appears on Fig. 5, as three samples producing a weaker luminescent emission (less than 40% relative intensity) define an intermediate zone between luminescing and extinct samples.

(c) Extinct zones contain greater amounts of iron than luminescing zones and, when considering each individual domain, or group of zones from the same crystal (Fig. 6), it becomes clear that lumin-

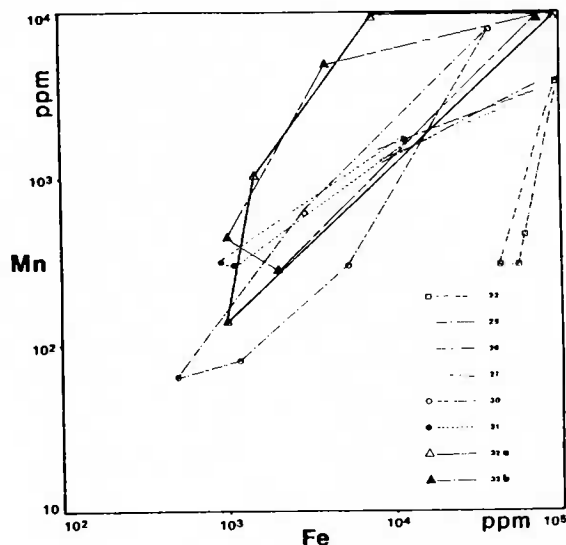


Fig. 6. Results of the electron microprobe analyses. The different zones of each individual crystal are grouped into domains delineated by a line pattern. Sample identification numbers are indicated for each line pattern.

escing dolomites as well as luminescing calcites contain lower concentrations of both manganese and iron.

(d) Manganese concentration in luminescing dolomite or calcite is often relatively low—less than 1000 ppm Mn, and even less than 100 ppm in a few instances—but several samples contain larger amounts, up to 10,000 ppm (1 wt %).

(e) Non-luminescing samples contain more than 10,000 ppm (1 wt %) Fe. A gradual passage from luminescence to extinction occurs in samples reaching and exceeding iron concentrations of 10,000 ppm. Above concentrations of about 15,000 ppm Fe^{2+} no sample produces a detectable luminescence.

Manganese and iron in dolomitic formations

The distribution of domains on Fig. 6 suggests that iron and manganese concentration ranges are specific to individual dolomite formations. The domains are subdivided into groups of samples characterized by a similar trend in the variation of Mn and Fe concentrations as well as by a similar luminescent behaviour. Samples 25, 26 and 27, showing a very narrow range of variation of the Fe and Mn content, were collected from the Devonian (Frasnian) red reefs of the Dinant Basin, in Western Belgium. Specimens 30, 31 and 32 form a separate

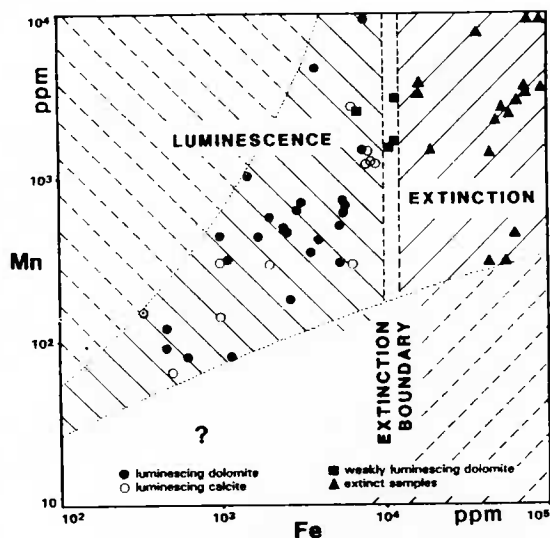


Fig. 7. Combination of the results of the atomic absorption analyses and the electron microprobe analyses, superimposed on the observations in cathodoluminescence.

group with a similar trend in the Mn-Fe concentrations and are all from the Lower Carboniferous of Campine, Belgium, collected from the Haalen borehole, at different depths (1163, 1165 and 1187.5 m respectively). Diagenesis not only leaves its imprint in the trace element content of dolomite, but also in the luminescent behaviour of the mineral. The potential use of dolomite chemistry and cathodoluminescent zonation in diagenetic correlations is suggested by the similarities in the trace element and luminescent characteristics of specific groups of samples.

Role of manganese

Since the valence state of manganese could not be determined, manganese is assumed to be included in the dolomite crystal lattice in its divalent state (Mn^{2+}), as suggested by previous workers (Long & Agrell, 1965; Sippel & Glover, 1965; Smith & Stenstrom, 1965; Martin & Zeeghers, 1969; Sommer, 1972). If manganese (Mn^{2+}) is the activator of luminescence, it seems reasonable to assume that a minimum amount of Mn^{2+} is required in order to produce a detectable luminescence. Martin & Zeeghers (1969) and Meyers (1974) suggested that this minimum amount was close to 1000 ppm Mn^{2+} . In the light of the analytical data presented in this study, it appears that the actual lower limit of luminescence is well below 1000 ppm Mn^{2+} . Results of lumines-

cence observations and chemical analyses appear to define the following zones of luminescence and non-luminescence (Fig. 7). The majority of the luminescing dolomite and calcite samples contain between 100 ppm and 1000 ppm Mn^{2+} , with a peak at 500 ppm. Although several luminescing samples contain more than 1000 ppm Mn^{2+} , a few specimens produce a relatively strong luminescent emission with as little as 100 ppm Mn^{2+} or less, a concentration 10 times lower than that previously suggested as the lower limit for luminescence.

None of the analysed samples were found to be extinct while containing small amounts of manganese. It is therefore impossible to establish, on the basis of the present study, a lower limit for the manganese concentration necessary for luminescence, but it is suggested that this threshold lies below 100 ppm Mn^{2+} . Subsequent investigations of Pliocene dolomite from the Bahamas have shown that the lower limit of manganese concentration is approximately 80 ppm (Pierson, 1981). Dolomites containing smaller amounts of manganese remain extinct.

Role of iron

The role of ferrous iron (Fe^{2+}) as a quencher of luminescence has been suggested by previous workers (Sommer, 1972; Meyers, 1974). The data presented here reinforce that hypothesis and yield specific information on the concentrations affecting cathodoluminescence in dolomite. Iron is consistently present in high concentrations in extinct samples or zones, although the same samples may also contain large amounts of manganese. Furthermore, all samples containing large concentrations of iron remain extinct.

Iron concentrations lower than 10,000 ppm (1 wt %) do not affect the luminescent properties of dolomite. At the critical concentration of 10,000 ppm iron, luminescence is weak. A similar observation was made for calcites by Machel (personal communication) who noted a colour change from yellow to red accompanying the decrease in luminescent intensity.

Samples with more than 15,000 ppm (1.5 wt %) Fe do not produce any luminescence, regardless of the concentration of manganese.

Several authors have suggested that luminescence of calcite is controlled by the ratio of ferrous iron to divalent manganese (Frank, 1979; Fairchild, 1978; Machel, personal communication). For a ratio greater than 10, extinction prevails in calcites. Although

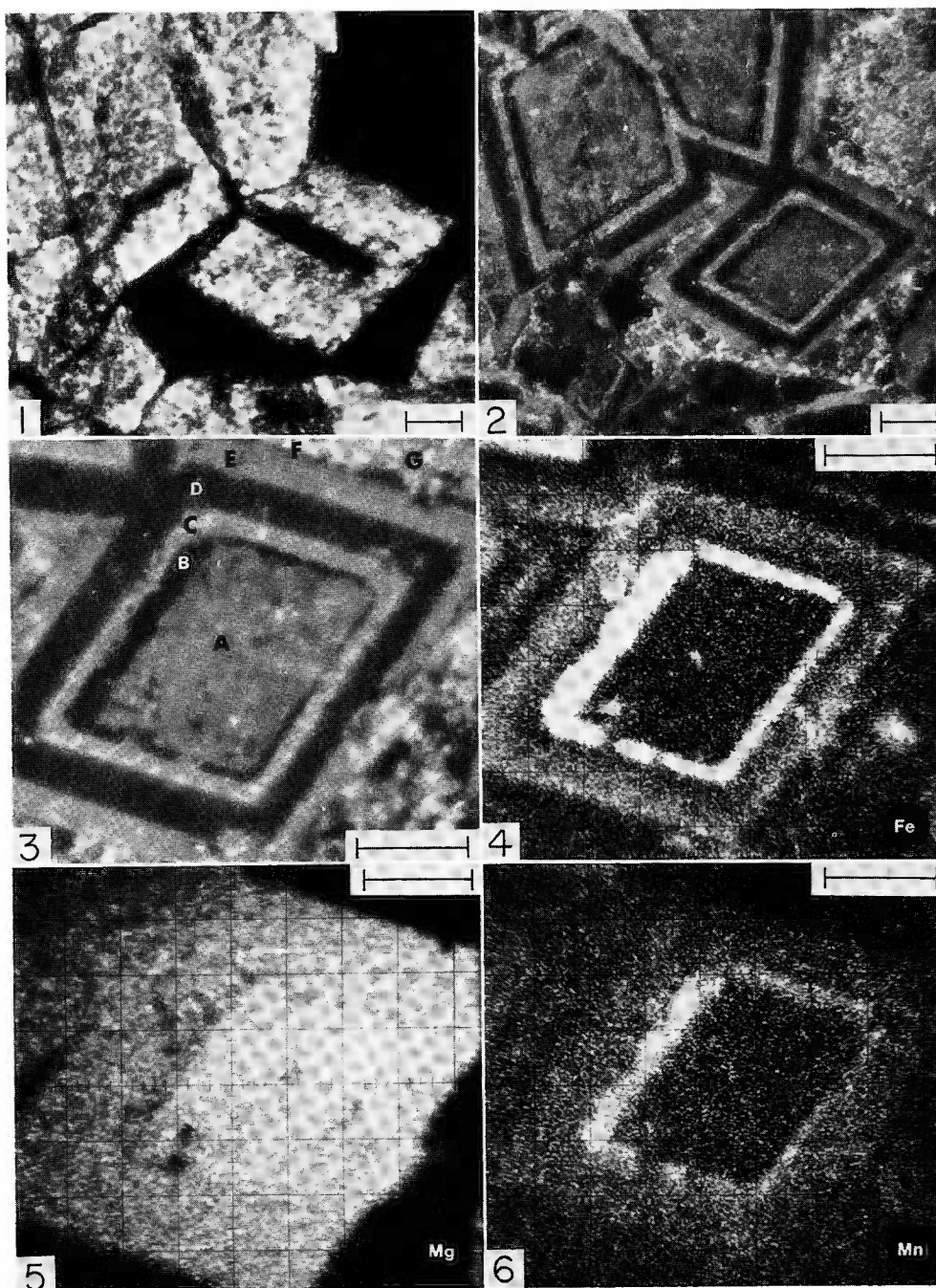


Fig. 8. Sample BP 32, from the Lower Carboniferous of Campine, Belgium. (Haalen core-boring, -1187.5 m.) Scale bar is 200 μm . (1) Euhedral rhombs of dolomite in a calcite matrix. Image in transmitted light. (2) Same as (1), in cathodoluminescence. (3) Crystal analysed by the electron microprobe. Designation of the crystal zones and the calcitic matrix in cathodoluminescence (A-G). (4) X-ray photomicrograph for iron ($\text{Fe } K\alpha$). The lighter areas correspond to zones of higher concentrations. (5) X-ray photomicrograph for magnesium ($\text{Mg } K\alpha$). (6) X-ray micrograph for manganese ($\text{Mn } K\alpha$).

Table 1. Electron microprobe analysis of sample BP 32

| Zone (Fig. 8) | wt % | | | | Relative intensity (%) |
|---------------|-------|-------|-------|-------|------------------------|
| | Ca | Mg | Fe | Mn | |
| Centre A | 21.04 | 11.96 | 0.168 | 0.043 | 80 |
| Zone B | 21.02 | 6.78 | 8.329 | 1.491 | 0 |
| Zone C | 22.69 | 10.46 | 0.766 | 1.004 | 95 |
| Zone D | 23.18 | 10.41 | 1.147 | 0.315 | 10 |
| Zone E | 24.50 | 10.98 | 0.144 | 0.100 | 90 |
| Zone F | 21.02 | 10.41 | 1.157 | 0.310 | 0 |
| Calcite G | 39.76 | 1.84 | 0.096 | 0.014 | 95 |

a similar trend is observed in dolomite, the Fe/Mn ratio does not seem to control the boundary between luminescence and extinction. Instead, extinction appears to be solely dependent on the iron content.

The role of iron in controlling cathodoluminescence in dolomite is clearly illustrated in Fig. 8, where the elemental zonation of a single crystal of dolomite is compared to the zonation in cathodoluminescence. The six zones (A–F) (Fig. 8(3)) appearing clearly in luminescence correspond exactly to the six zones visible in the distribution of iron in the crystal (Fig. 8(4)). The non-luminescing zones (zones B, D and F) contain larger amounts of iron as well as of manganese, demonstrating the parallel variation of the contents of both elements, and the quenching role of iron in spite of the high concentration of manganese (Table 1). The iron concentration of each of the non-luminescing zones exceeds 10,000 ppm.

The distribution of magnesium shows a depletion in that element in a thin zone corresponding to zone B, suggesting that Fe and perhaps Mn tend to occupy preferentially the Mg sites in the dolomite structure. When Fe and Mn concentrations are high, the Mg content falls dramatically, while calcium remains practically unaffected (see zone B, Fig. 8(5); Table 1) (Wilderman, 1970).

The overall mechanism of inhibition of luminescence by iron is not clear, although the pattern suggests a phenomenon of absorption of the energy produced by the activator (Mn^{2+}), or a stabilization of the crystalline configuration of dolomite by Fe, making luminescent transition very unlikely (Coy-III, 1970).

CONCLUSIONS

(1) Chemical analyses of dolomites indicate a positive correlation between the concentrations of iron and manganese on a log-log plot.

(2) Iron and manganese appear to occupy preferentially the magnesium sites in the dolomite crystal structure.

(3) As little as 100 ppm Mn (an order of magnitude less than previously assumed) are sufficient to produce a luminescent emission.

(4) There is no direct relationship between intensity of luminescence and manganese concentration.

(5) Iron (Fe^{2+}) is an important inhibitor of luminescence in dolomite when its concentration reaches 10,000 ppm or 1 wt % Fe^{2+} . Below 10,000 ppm iron has virtually no influence on luminescence. Above that value, luminescent properties are rapidly lost until complete extinction, regardless of the concentration of manganese. Dolomite containing more than 15,000 ppm (1.5 wt %) Fe^{2+} will not luminesce.

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