Geologie en Mijnbouw 64: 297-310 (1985).

Cathodoluminescence activation and zonation in carbonate rocks: an experimental approach

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Manuscript received 15 April 1985; accepted in revised form 19 August 1985

Abstract

Ten Have, T. & W. Heijnen 1985 Cathodoluminescence activation and zonation in carbonate rocks: an experimental approach – Geol. Mijnbouw 64: 297-310

Calcite crystals have been grown with the objective of studying the cathodoluminescence (C.L.) characteristics. No trace elements other than Mn^{2+} were needed to activate luminescence similar to that observed in natural carbonates. C.L. observations, combined with Mn and Fe analyses of synthetic crystals, natural calcites and dolomites, show that:

1. 15-30 ppm and 30-35 ppm Mn is sufficient to activate luminescence in calcites and dolomites, respectively.
2. The intensity of luminescence is controlled by the absolute amount of Mn^{2+} and not by the Fe^{2+}/Mn^{2+} ratio.

Both conclusions are valid provided Fe concentrations are low (< 200 ppm).

3. Luminescent zonation, common in synthetic and natural carbonates, reflects differential Mn^{2+} uptake during growth, caused by:
   a. changes in the Mn^{2+} concentration of the precipitating fluid, or
   b. changes in the rate of crystal growth independent of the Mn^{2+} concentration in the fluid.

The latter process has not been considered sufficiently in former C.L. studies, but will have important consequences for interpretation of luminescence features: e.g. definition of the geochemical history of pore fluids by characterisation of the rock's C.L., may not always be justified. Specifically, the concept of cement stratigraphy (i.e. correlation of similar luminescent colours or intensities) should be handled with care and only applied when it can be demonstrated that the zones are the result of bulk geochemical changes in the pore fluids and not merely of differences in crystal growth rate. Tentative criteria for such a differentiation are discussed.

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Introduction

Cathodoluminescence (C.L.) microscopy has become an extremely powerful and essential tool in the investigation of carbonate sedimentary rocks (Nickel 1978; Richter & Zinkernagel 1981; Amieux 1982; Miller, in prep.). Many petrographical and diagenetic features are revealed by cathodoluminescence, whereas they often remain invisible using conventional transmitted light microscopy. The method of cathodoluminescence microscopy involves electron bombardment of an uncovered thin section or rock slab in an evacuated sample chamber. This results in emission of electromagnetic radiation including visible light, characteristic for the material being bombarded. Luminescence in carbonate rocks generally exhibits yellow-orange-red colours (540-675 nm wavelength) and is caused by the presence of trace elements. Manganese is known to be the most effective activator of luminescence in calcites and dolomites, whereas Fe is regarded to be a quencher of luminescence (Long & Agrell 1965; Smith & Stenstrom 1965; Sommer 1972).

Interpretation of C.L. observations is, however, severely impaired by various uncertainties:

- What is the minimum Mn^{2+} concentration necessary to activate luminescence in carbonate minerals?
- Does the luminescence intensity depend on Mn^{2+} concentration only, or is it controlled by the Mn^{2+}/Fe^{2+} ratio?
- How does luminescence (i.e. trace element composition of the rock) relate to the trace element composition of the precipitating fluids?
- What is the cause of luminescent zonations so often observed in calcites and dolomites?

Various publications dealt with these uncertainties, all approaching them in a similar way by first establishing the luminescence of the rock and subsequently analysing its Mn^{2+}, Fe^{2+} content. However, no consensus exists and the minimum amount of Mn^{2+} necessary to activate luminescence is most commonly reported to be between 100-1000 ppm (Pierson 1981; Frank et al. 1982; Fairchild 1983). It is usually assumed that the luminescence of a rock reflects the trace element composition of the fluid from which it precipitated. This led many investigators to conclude that the geochemical history of pore fluids (e.g. redox potential) could be defined by studying the luminescent characteristics of the carbonate minerals (Carpenter & Oglesby 1976; Frank et al. 1982; Grover & Read 1983). This assumption has been specifically applied to the frequently observed luminescent zoning in carbonate minerals. This promoted the introduction of the concept of cement stratigraphy as one of the most promising applications of C.L. investigations (Meyers 1974, 1978): similar luminescent colours or intensities are correlated between samples over large distances to delineate regional cementation patterns.

Extensive C.L. investigations carried out at KSEPL (Koninklijke/Shell Exploratie en Produktie Laboratorium) on a variety of carbonate rocks, provided arguments to consider alternatives to various published interpretations of C.L. patterns. To enhance our understanding of luminescent features in carbonates, KSEPL and the Department of Crystallography of the Instituut voor Aardwetenschappen, University of Utrecht, engaged on a joint project to investigate, by experimentation, the existing interpretive uncertainties. Utrecht carried out some fifty calcite growth experiments in solutions with varying Mn^{2+} concentrations and KSEPL studied the resulting crystals by C.L. microscopy. The objective was twofold:

1. To gain a better insight into both cathodoluminescence activation and zonation in carbonate minerals.
2. To compare the experimental results with existing data of natural carbonates.

By using an experimental approach, our line of investigation differs considerably from previous studies. Additionally, it has the advantage of being able to control the geochemical composition of the precipitating fluid, therefore reducing the effect of other trace elements which possibly influence luminescence (Machel, in press).

Methods

Crystal growth

Two different experimental methods have been used to grow calcite crystals:

1. solution growth
2. gel growth

The *solution growth* experiments, numbering about 40, were carried out following Gruzensky's (1967) method which has been slightly modified. 4.8 g $CaCl_2 \cdot 4H_2O$ (Merck Suprapur) is dissolved in 200 ml water (deionised water purified by means of a Millipore Milli-Q2 system); 40 g NH_4Cl (Merck Suprapur) is added in order to increase the solubility of $CaCO_3$ in water. Manganese is in most cases introduced, by adding $MnCl_2 \cdot 4H_2O$ (Merck Zur Analyse). The initial Mn^{2+}/Ca^{2+} concentration ratio is varied in the range 0 - 0.002. This solution is filtered through a 0.22 μm Millipore filter to remove small particles, which might otherwise enhance nucleation. The filtrate is put into a 250 ml Erlenmeyer flask. A glass tube filled with ammonium carbonate (BDH AnalaR) is placed on top of this flask, separated from it by a tap. The assembly (Fig. 1a) is then transferred to a thermostatically controlled room kept at a constant temperature of 21.0 ± 0.2°C. The tap is slightly opened after a few hours, allowing vapour phase diffusion of partly dissociated ammonium carbonate to the unstirred solution. A few days later transparent crystals form, attached to the wall just below the surface of the solution. The crystals subsequently increase both in size and in number. In addition, a cluster of small crystals usually appears floating on the solution. The experiment is stopped when small white (hemi)spheres can be seen in the flask (in most cases after about 12 days). The solution is then filtered through a 0.45 μm Millipore filter. The precipitate is rinsed twice with water and once with ethanol. After drying, the crystals are observed by optical microscopy and separated into various groups by means of hand-picking.

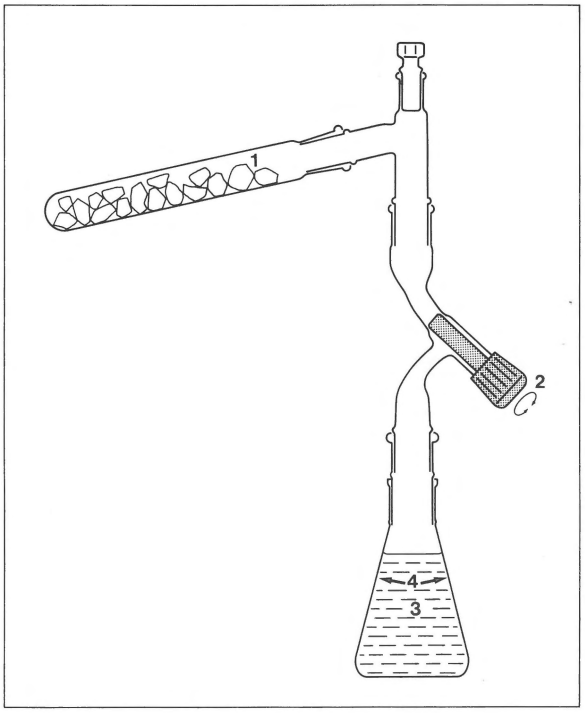


Fig. 1a. Apparatus for growing calcite crystals from solution; 1= ammonium carbonate; 2= tap; 3= aqueous solution containing $NH_4Cl + CaCl_2 \cdot 4H_2O \pm Mn\ Cl_2 \cdot 4H_2O$; 4= site where the first calcite crystals are formed.

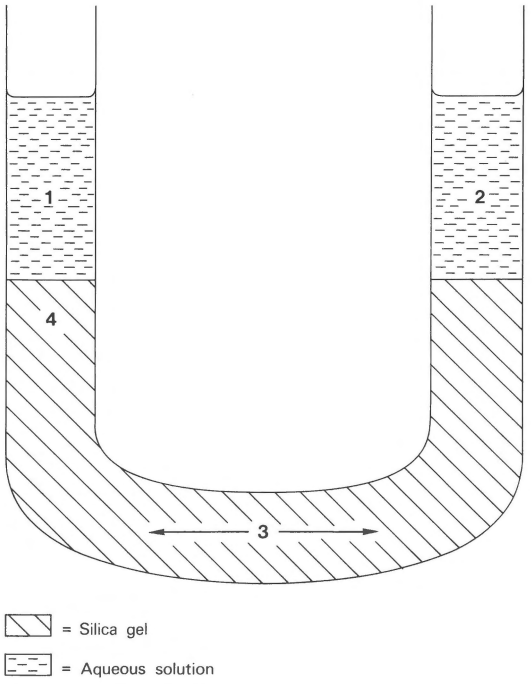


Fig. 1b. U-tube used in gel growth experiments; 1= calcium chloride solution; 2= ammonium carbonate solution; 3= portion of the tube where the first calcite crystals are formed; 4= site where secondary crystallization occurs.

The second experimental method used for the remaining 12 experiments is *gel growth* (Henisch 1970; McCauley & Roy 1974; Prieto et al. 1981; Garcia-Ruiz 1982). A sodium metasilicate $Na_2SiO_3 \cdot 9H_2O$ (Baker Analyzed Reagent) solution is acidified with 2M acetic acid (Merck Zur Analyse) to a final pH of 7-8. This solution, to which $MnCl_2 \cdot 4H_2O$ is in most cases added, is poured into a U-tube (Fig. 1b). After gelation a 0.16M calcium chloride solution is placed on top of the gel in one leg of the tube, while in the other leg a 0.16M ammonium carbonate solution is placed. The reaction takes place very slowly. After a few months the crystals were separated from the gel by handpicking and washed alternatingly in distilled water and 1N NaOH solution to remove adhering gel.

In order to investigate the effect of changes in the Mn^{2+} concentration of the precipitating fluid on the C.L. characteristics of synthetic calcite crystals, several twin growth experiments were performed. Two experiments, A and B, were carried out simultaneously, both starting off with the same Mn^{2+} concentration in the solution or gel. When visible crystals were formed, an extra amount of Mn^{2+} was added to experiment B. In the case of solution growth, we introduced 1 ml of a $MnCl_2 \cdot 4H_2O$ solution directly to the precipitating solution, whereas in gel growth experiments a Mn^{2+} containing solution was added to the leg containing the $CaCl_2$ solution. After this both experiments were continued as described above.

Characterisation

The following methods were applied:
- Guinier-De Wolff X-ray diffraction patterns were obtained (ENRAF-NONIUS Guinier IV) for a portion of the crystals of each experiment to enable identification of carbonate minerals.
- Mn and Fe analyses of calcite crystals were carried out using atomic absorption spectrometry (Perkin-Elmer 460) on circa 50 mg sample dissolved in 5 ml 1:19 HCl solution.
- Representative crystals of different morphologies were studied with a Cambridge Stereoscan 600M scanning electron microscope.
- About 8-10 representative crystals of every experiment were selected for C.L. investigation. They were split into two groups of which either one thin section and one impregnated block or two impregnated blocks were prepared. The blocks/thin sections were carefully cut until a good section through the crystals was obtained. Occasionally they were slightly polished. The samples were subsequently investigated in a Nuclide ELM-2BX luminoscope equipped with a SM Lux Pol microscope. The operating conditions were 14 kV accelerating voltage, 140 mtorr vacuum and 0.2-0.5 mA current. Photographs were taken with a Leitz photomultiplier system using both slides (Ektachrome 400 ASA) and prints (Kodacolor 1000VR). C.L. intensities were visually estimated, always by the same observer. A second indication of the intensities was derived from the exposure times used in making the photographs.

Crystal morphologies

The *solution-grown* crystals have been subdivided into three groups:

1. Very clear, transparent calcite crystals with shiny faces and a diameter of 0.3-0.7 mm. The cleavage rhombohedron is usually the only crystal form present (Fig. 2a).
2. White (hemi)spheres or globules, which only developed in the very last stage of crystal growth. XRD analyses showed these to be aggregates of very small aragonite and/or vaterite crystals. The vaterite spheres (Fig. 2b) consist of plates, whereas the aragonite spheres (Fig. 2c) are more massive and show a surface composed of needles. The (hemi)spheres often have one smooth plane, which was situated against the wall of the flask during growth.
3. The remaining material, i.e. aggregates of globules and rhombohedra grown together, and less perfect calcite crystals, some of which show non-singular crystal faces in combination with the rhombohedral faces (Fig. 2d+e). The latter type of similar morphologically curious crystals was also described by Prieto et al. (1981) as a result of growth in silica gel at very low concentration

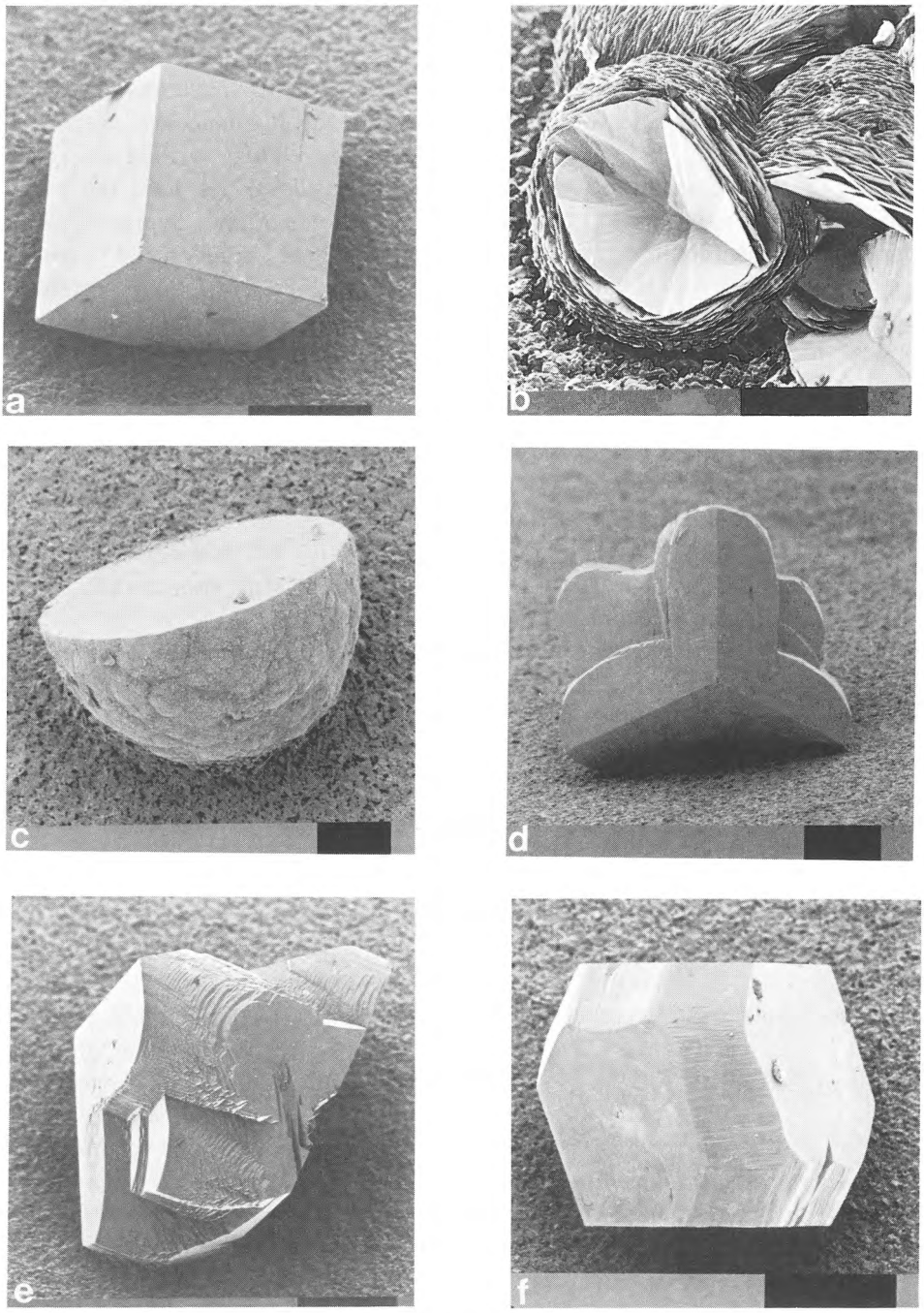


Fig. 2. a) solution grown calcite rhombohedron (scale bar is 200 μm)
b) solution grown vaterite globules (scale bar is 100 μm)
c) solution grown aragonite hemisphere (scale bar is 100 μm)
d,e) two views of the same solution grown calcite crystal showing curved faces (scale bar is 200 μm)
f) calcite crystal grown in gel with high Ca^{2+}/CO_3^{2-} concentration ratio (scale bar is 200 μm)

gradients. They could not preclude the presence of silica gel as a possible cause of the nonsingular crystal faces. We propose that this deviating morphology is a consequence of crystal growth in an unstirred solution with a complicated pattern of convection flow and diffusion flux.

The *gel-growth* experiments furnished two different types of calcite crystals:

1. Crystals grown in the middle and lowest part of the U-tube, indicated by the number 3 in Fig. 1b. They are bounded by cleavage rhombohedral faces only, but differ from solution-grown rhombohedra in size (being about 1 mm) and in being turbid when observed in optical microscopy. This turbidity is due to the inclusion of silica gel (Henisch 1970)
2. Crystals grown in the upper part of the leg containing a calcium chloride solution on top of the gel. That portion of the tube is indicated by the number 4 in Fig. 1b. They are smaller and show 18 faces (Fig. 2f). Their morphology is dominated by six large smooth faces defining the cleavage rhombohedron $\{10\bar{1}1\}$; six small smooth faces form the steep rhombohedron $\{02\bar{2}1\}$, whereas the remaining six striated faces constitute the hexagonal prism $\{11\bar{2}0\}$. The occurrence of $\{02\bar{2}1\}$ agrees with the observation of Kirov et al. (1972), who found this form present on calcite crystals grown from a solution with an excess of Ca^{2+} ions. The total amount of this type of calcite crystals formed is too small to allow analysis for Mn and Fe by means of AAS.

Cathodoluminescence results and discussion

Cathodoluminescence activation

Results

Each individual calcite crystal produced in a particular experiment is assumed to have the same average Mn and Fe content, as determined by means of AAS, using a large representative sample of crystals. This assumption is founded on two experimental measurements. Firstly, all 8-10 crystals in a thin section show similar C.L. intensities. Secondly, Mn analyses of several individual crystals from one experiment by means of instrumental neutron activation analysis (INAA) at I.R.I. (Delft) (Heijnen, in prep.), indicated that the variation in Mn content of different crystals remains within 25% of the average value.

The results of Mn-activated luminescence in the synthetic calcites are summarized in Fig. 3, which presents the luminescence characteristics of the crystals in relation to their Fe and Mn concentration. Although we used the purest chemicals available, the Merck Suprapur $CaCl_2 \cdot 4H_2O$ still contains about 3 ppm Mn and 7 ppm Fe, whereas in the Suprapur NH_4Cl no detectable amounts of these metals are present. Due to this contamination, even crystals grown from solutions to which no $MnCl_2 \cdot 4H_2O$ was added, still contain 4-10 ppm Mn and 10-50 ppm Fe, showing however no luminescence. Two conclusions can be drawn:

1. 15-30 ppm Mn^{2+} is sufficient to activate luminescence.
2. Intensity of luminescence increases with increasing Mn^{2+} concentration up till about 200 ppm.

Both conclusions are only valid for the low (< 200 ppm) Fe concentrations present in the synthetic crystals.

Discussion

The experiments were conducted in such a way that Mn^{2+} concentrations in the calcite crystals showed as wide a variation as possible (4-8646 ppm), whereas Fe concentrations were kept low (10-157 ppm). At these Fe concentrations no quenching effect has been observed. Hence, the suggestion of Frank et al. (1982) that luminescence is controlled by the Fe/Mn ratio rather than the absolute amounts of Mn^{2+} is not supported by the data obtained from synthetic calcites.

By using very pure chemicals, the influence of other trace elements was minimised. It has been argued that other trace elements such as Pb^{2+}, Ce^{2+} (as activators and/or sensitisors) and Ni^{2+} (as a quencher) influence luminescence in carbonates (Machel, in press). It should be pointed out that our experiments show luminescence to be exclusively activated by Mn^{2+}, with no other trace elements being present besides Fe. Calcite crystals grown from a solution to which Pb^{2+} instead of

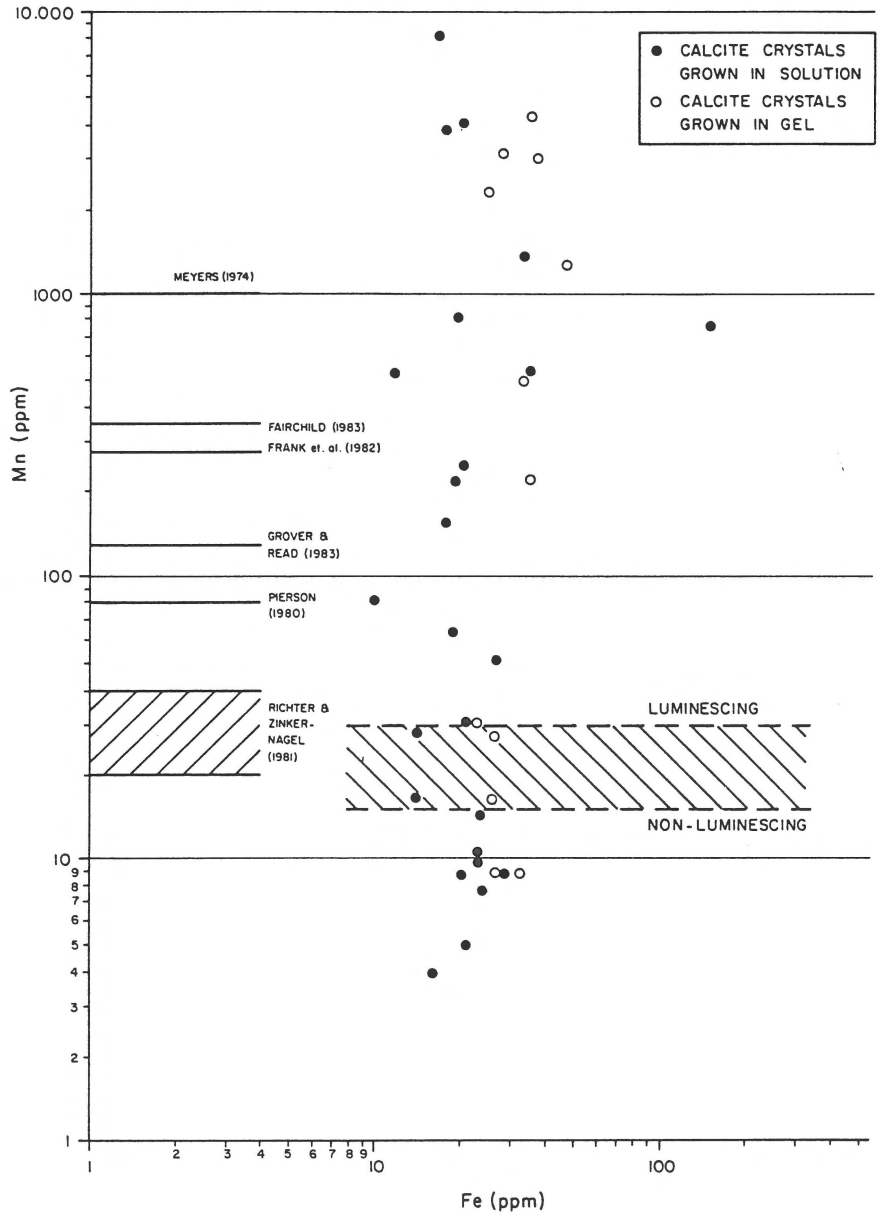


Fig. 3. Luminescence characteristics of synthetic calcite crystals. The minimum Mn concentration, necessary to activate luminescence, is 15-30 ppm. Solid lines, on the left, represent literature-derived minimum Mn concentrations for natural calcites.

Mn^{2+} was added, did not show any luminescence.

The minimum Mn^{2+} concentration necessary to activate luminescence varied slightly between the two types of crystals grown. Solution-grown crystals invariably showed luminescence when more than 15 ppm Mn was present, whilst gel-grown crystals needed higher Mn concentrations. This could be explained by some Mn^{2+} being attached to the silica gel which is incorporated in the crystals. Hence, this Mn^{2+} will be analysed and will add to the total measured Mn of the crystals, but it will not contribute to luminescence since it does not occupy a Ca^{2+} site in the calcite structure.

Two solution-grown crystals, containing 5 and 10 ppm Mn respectively, showed a zoned luminescence in spite of their very low (bulk) Mn content.

The zones comprise a non-luminescent core and a luminescent outer rim (Fig. 5a). Since the rim contributes only 1/3 to the bulk volume of the crystal, it wil actually contain some 15-20 ppm Mn, which corresponds well with the other data.

Comparison with natural carbonates

a. *Calcites.* Comparison of the results obtained from our synthetic calcites with published analyses of natural calcites shows that the minimum Mn content necessary to activate luminescence is generally considerably lower in the former than in the latter. The literature-derived lower limits are shown in Fig. 3 for comparison. The explanation for this discrepancy may be twofold:

1. the (unknown) effect of other trace elements in natural rocks; most natural calcites contain considerably more Fe^{2+} than our synthetic crystals;
2. differences in analytical methods which have been applied.

Most Fe, Mn determinations provided by literature were carried out by microprobe analyses, the detection limit of which is significantly higher than that of atomic absorption spectrometry, which has been used in the present paper. Interestingly enough, Richter & Zinkernagel (1981) – providing the only literature data on natural calcites which were in agreement with our data (Fig. 3) – also used AAS. Furthermore, KSEPL data on Pliocene calcites confirmed the results of synthetic calcites by showing luminescence when more than 20-25 ppm Mn (at low Fe concentrations) is present.

b. *Dolomites.* Results of two KSEPL data sets on dolomites are presented in Fig. 4. One set is from

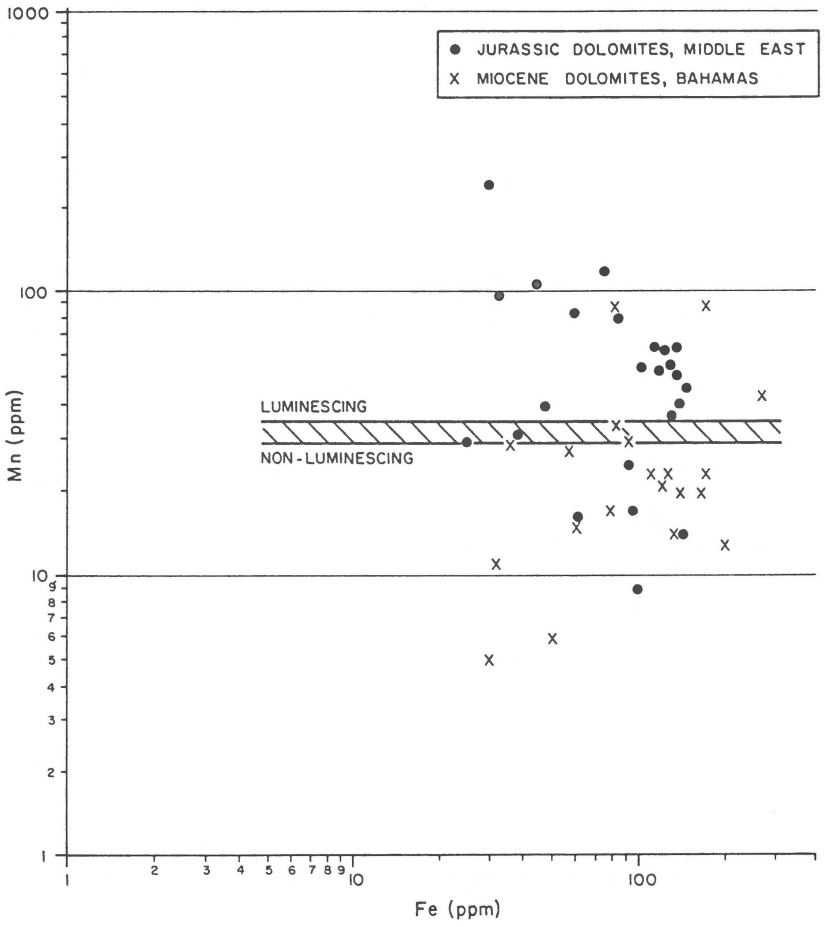


Fig. 4. Luminescence characteristics of two sets of natural dolomites. The minimum Mn concentration, necessary to activate luminescence in dolomites, is 30-35 ppm.

subsurface Miocene dolomites of the Bahamas and the other of subsurface Upper-Jurassic dolomites from the Middle East. Fe and Mn analyses were carried out by AAS, and luminescence investigations were performed with the same equipment as that used for the synthetic calcites. Fig. 4 shows that 30-35 ppm Mn is sufficient to activate luminescence in both dolomites. Comparison with the results of synthetic and natural calcites indicates two main differences:

1. Most existing data on dolomites suggest that a higher minimum Mn concentration is necessary to activate luminescence, e.g. 80 ppm (Pierson 1981) and 180 ppm (Fairchild 1983).
2. The lower limit of Mn-activated luminescence for dolomite (30-35 ppm) is slightly higher than for calcite (15-30 ppm). This could be explained by the observations of Sommer (1972), who demonstrated that Mn-activated luminescence in calcites is far more intense than in magnesite ($MgCO_3$). Manganese on the Ca site is a more efficient activator of luminescence than Mn on the Mg site. In dolomite, Mn^{2+} largely occupies the Mg^{2+} site and far less the Ca^{2+} site as shown by electron paramagnetic resonance studies (Wildeman 1970) and as theoretically explained by Kretz (1982). Hence, calcites need lower amounts of Mn^{2+} to produce luminescence than dolomites.

Experimental results showed that, if Fe^{2+} concentrations are very low, even small amounts of Mn^{2+} will be sufficient to activate luminescence. Consequently, cathodoluminescence in carbonates should be the rule rather than an exception, and occur more commonly than already observed. Indeed, one may be more justified in wondering why a calcite or dolomite does not show luminescence than why it does.

Cathodoluminescence zonation

Results

Many of the synthetic calcite crystals produced in the experiments display a luminescent zonation (Fig. 5) comparable to that commonly observed in natural carbonates. Microprobe analyses indicate that these variations in luminosity are possibly related to variations in the Mn content of the calcite crystals. Regrettably no further progress can be expected from microprobe analysis since the Mn concentrations occur near the detection limit of the instrument. In order to gain a better insight into the exact Mn distribution within a single crystal we are presently carrying out calcite growth experiments using solutions containing radioactive ^{54}Mn tracer; the resulting crystals can then be studied by both autoradiography and C.L. microscopy (Heijnen, in prep.).

Discussion

Assuming that differences in luminescence result from differences in Mn content within a crystal, we first have to consider the possible causes of differential Mn^{2+} uptake during growth. Meyers (1974), Pingitore (1978) and Frank et al. (1982) attribute variations in the Mn content of calcite solely to variations in the Mn^{2+} concentration or the Mn^{2+}/Ca^{2+} concentration ratio of the precipitating solution. A second significant factor influencing the Mn content of calcite, which has not been considered in past luminescence studies, is the crystal growth rate. Lorens (1981) measured the Mn distribution coefficient (D_{Mn}) in calcite as a function of calcite precipitation rate. His experiments showed that Mn^{2+} is preferentially incorporated in the calcite structure; so D_{Mn} is always greater than 1. D_{Mn} at very low growth rates appeared to be more than 10 times larger than at very high growth rates. Moreover, the most rapid changes in D_{Mn} occurred at comparatively low precipitation rates; rates which approximate the diagenetic reactions of calcite recrystallization and aragonite-to-calcite transformation.

Supposing that both the Mn^{2+}/Ca^{2+} concentration ratio in the fluid and the growth rate of the calcite crystals determine the Mn content of the growing calcite crystals, we now have to examine how these two variables evolve in the course of our experiments. In both solution and gel growth experiments the Mn^{2+} concentration in the fluid decreases with time, except in those experiments (hereafter called twin B experiments) to which an extra amount of Mn^{2+} is added after some initial crystal growth.

In order to get a quantitative impression of the

development of the Mn^{2+}/Ca^{2+} concentration ratio during an experiment, and of the average effective D_{Mn}, a representative example of a type A solution growth experiment is considered in more detail. It should be emphasized that crystal growth in our solution growth experiments takes place far from equilibrium at ill-defined conditions. We were, however, obliged to grow from unstirred solutions, since the calcite crystals obtained from stirred, well controlled aqueous solutions are not sufficiently large to be studied by means of C.L. microscopy.

From a solution with an initial Mn^{2+}/Ca^{2+} concentration ratio of 0.00019, 250 mg calcite precipitated containing 250 ppm Mn. This corresponds with a Mn^{2+}/Ca^{2+} concentration ratio of 0.00045 in the calcite crystals; about 23% of the initially present Mn^{2+} and 10% of the Ca^{2+} was incorporated in the crystals. As a result of the calcite precipitation, the Mn^{2+}/Ca^{2+} concentration ratio in the solution decreased to 0.00016 by the end of this experiment, which is 85% of the initial ratio. Rather than applying corrections to the concentrations in order to determine the activities, we have obtained the average kinetic D_{Mn} from the concentrations directly as 2.4 - 2.8.

The above described variations in D_{Mn} and Mn^{2+}/Ca^{2+} ratio in the fluid are too small to cause the variations in C.L. intensities shown by crystals grown in type A experiments. A direct proportionality of the Mn^{2+}/Ca^{2+} ratio in the growing crystal to that in the solution, i.e. a constant value of D_{Mn}, can therefore only explain the C.L. zonation observed in crystals grown in twin B experiments, in which the Mn^{2+}/Ca^{2+} ratio in the solution is suddenly increased. This can be traced in the C.L. pattern reflecting the Mn distribution in the crystals. Fig. 5b shows a C.L. photograph of a crystal formed in a twin B gel growth experiment. The nonluminescing core grew in the absence of Mn^{2+}, whereas the brightly luminescing overgrowth developed after the addition of a Mn^{2+} containing solution. In the more complex C.L. patterns of Fig. 5d and f the bright luminescence of the outermost rims results from the same mechanism. However, similar zonations (Fig. 5a, e and g) observed in crystals grown from a solution or gel with an approximately constant Mn^{2+}/Ca^{2+} concentration ratio cannot be explained by the direct proportionality of the Mn^{2+}/Ca^{2+} ratio in solution to that in the growing crystal; should that be the case, then the simultaneous occurrence of more or less constant values of both D_{Mn} and the Mn^{2+}/Ca^{2+} ratio in the fluid would have resulted in a more uniform C.L. pattern than observed.

To appreciate the second important factor determining the Mn content of calcite, we have to know the crystal growth rate as a function of time. Since our growth experiments take place in unstirred solutions or gels, in which considerable local

Fig. 5. (facing page) Cathodoluminescence photographs of synthetic calcite crystals

a) Solution grown crystal. Zonation is supposed to be due to an increasing Mn uptake during growth as a result of a decreasing crystal growth rate with time. The Mn^{2+} concentration in the solution remained approximately constant during the experiment.

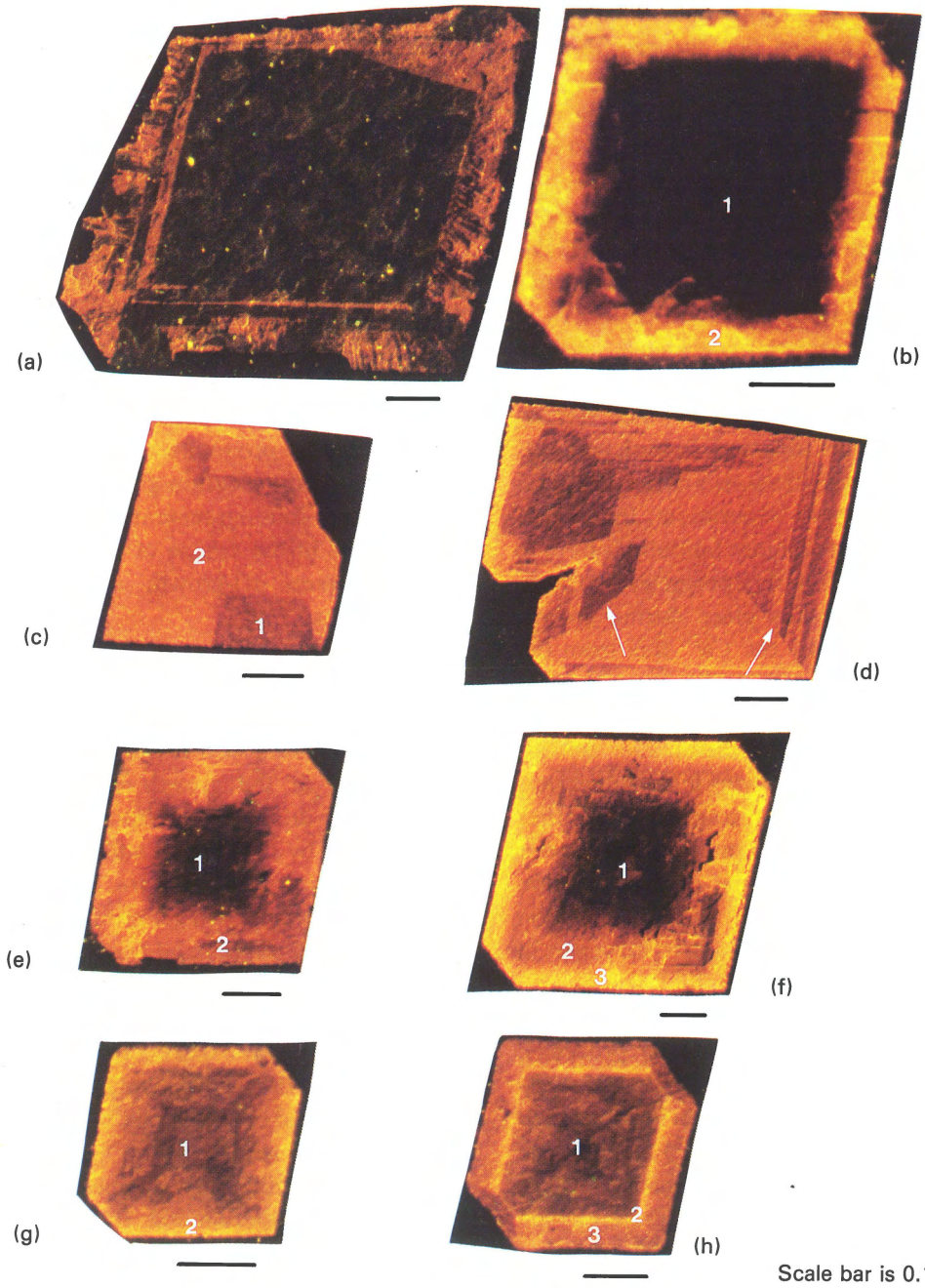
b) Gel grown crystal. Zonation is due to a change in the chemical composition of the gel. Zone 1 grew in a Mn-free gel. Subsequently a large quantity of Mn^{2+} was added and a brightly luminescing overgrowth developed (zone 2). Smearing is caused by polishing of the sample.

c) Solution grown crystal. Zone 1 probably represents the outline of the crystal in an earlier stage of growth. Zone 2 developed later, while zone 1 still was attached to the glass wall of the experimental flask. The Mn^{2+} concentration in the solution remained approximately constant during the experiment.

d) Solution grown crystal. Arrows indicate boundaries between growth sectors. C.L. variations within a growth sector are probably caused by growth rate variations resulting from convection and/or turbulence. A very thin, brightly luminescing overgrowth was formed after introduction of an extra amount of Mn^{2+}.

e,f) Calcite crystals bounded by cleavage rhombohedral faces only, grown in a twin gel-growth experiment. Both experiments had the same initial Mn concentration. To sample f (twin B) a large quantity of Mn was added after formation of the first visible crystals. Both crystals show similar zonations (zones 1 and 2) which are due to an increasing Mn uptake attributable to a decrease in crystal growth rate. Zone 3 is, however, only present in sample f and is interpreted to represent growth after addition of extra Mn, i.e. zone 3 is the result of a chemical change in the composition of the precipitating fluid.

g,h) Similar set of twin growth experiments as in 5e+f. However, these crystals show 18 instead of 6 faces and grew by a different mechanism and at a different position in the gel as compared to the crystals shown in Figs. 5e and 5f.



Scale bar is 0.1 mm.

variations in concentration of the reactants are admissible, it is impossible to present an exact quantitative description of the growth rate in the course of an experiment, but we can make an attempt to outline it. Assuming volume diffusion of the reactants to be the rate-controlling process in both growth methods, we can apply Frank's (1950) results. He considered systems in which the growth rate is limited only by volume diffusion and not in any sense by processes at the crystal surface itself. By solving the appropriate equation for diffusion in three dimensions he found that the radius r of a

growing phase is directly proportional to $t^{\frac{1}{2}}$, where t is time. It follows that the growth rate, dr/dt, is proportional to $t^{-\frac{1}{2}}$, i.e. growth rate decreases with time. Although this relation strictly holds in an idealized model only, Henisch (1970) and Garcia-Ruiz (1982) provided experimental arguments to support its application to gel growth systems. We suggest that it is reasonable to make use of this diffusion-controlled model in unstirred aqueous solutions as well.

Both the solution growth experiments and the gel growth experiments however, deviate from Frank's (1950) idealized model in which steady-state concentrations are assumed. In both methods such steady-state concentrations are not yet present at the beginning of an experiment. In the case of gel growth at least two more limitations have to be taken into account. Firstly a progressive exhaustion of the reagents takes place during growth (Henisch 1970). Secondly the Ca^{2+} flux from the $CaCl_2$-containing leg towards the horizontal part of the tube, where the large rhombohedra grow, diminishes from the moment the smaller crystals bounded by 18 faces start growing in the upper part of the leg. Both processes result in a further decrease of the crystal growth rate with time in our gel growth experiments. In the case of solution growth the condition of steady-state concentration is not satisfied either. The deviation is, however, in the opposite direction. The initial solution is undersaturated with respect to calcite. Supersaturation is built up as the experiment proceeds, resulting in nucleation and growth of calcite crystals. This increase in supersaturation is reflected in an increase of the pH from about 4 to 8. In the course of a solution growth experiment the overall supersaturation increases with time, attaining such a high value towards the end of an experiment, that the thermodynamically unstable aragonite and vaterite precipitate. The decrease in growth rate due to the dominance of the growth process by volume diffusion is assumed to be larger than the increase in growth rate due to the rising overall supersaturation.

Recapitulating we can state that, because volume diffusion is supposed to be the rate-controlling process, the crystal growth rate decreases with time during our experiments. Other processes seem to strengthen this trend in gel growth experiments, whereas it is weakened in solution growth experiments.

We will now combine the above theoretical considerations on the behaviour of the growth rate in our experiments with Lorens's (1981) experimental evidence on the dependency of D_{Mn} upon the growth rate. If we assume a constant Mn^{2+}/Ca^{2+} concentration ratio in the solution or gel, the decrease of the growth rate from the core towards the rim of the crystals results in an increasing luminosity from the centre outwards. This effect is observed more pronouncedly in gel-grown crystals (Fig. 5e) than in solution-grown crystals (Fig. 5a), which is in fair agreement with our postulated differences in the course of the growth rate with time between gel-growth and solution-growth experiments.

Solution-grown crystals (Fig. 5a, c, d) also differ from those grown in gels (Fig. 5b, e-h) in exhibiting a more complex and less homogeneous C.L. pattern. We suggest that this can be explained by differences in the growth methods. Firstly, in addition to diffusion, transport of reactants also takes place by convection and turbulence. These two processes play a more important role in solution-growth than in gel-growth experiments, in which they are suppressed (Henisch 1970). Hence the steady-state concentrations of Frank's (1950) volume diffusion model are more often disturbed in solution-growth experiments. These disturbances may give rise to relatively large variations in growth rate and consequently in Mn incorporation and luminescence (Fig. 5d). Secondly, the solution-grown calcites were formed attached to the wall of the experimental flask, whereas most gel-grown crystals were formed supported by the gel and thus in a more homogeneous surrounding than those growing in unstirred aqueous solutions (Fig. 5c, d), which again is reflected in the respective C.L. patterns.

From our experiments we may conclude that luminescent zonation can be caused by intrinsic (crystal growth rate) as well as external (geochemical changes in precipitating fluids) factors. We obtained C.L. patterns consisting of a dull- or

non-luminescing core and a bright luminescing overgrowth both from crystals grown in a solution (Fig. 5a) or gel (Fig. 5e) with an approximately constant Mn^{2+}/Ca^{2+} concentration ratio and from a solution or gel (Fig. 5b) to which an extra amount of Mn^{2+} was added after some initial crystal growth. Twin gel-growth experiments have shown that one crystal can exhibit the combined effect of changes in fluid composition and variations in crystal growth rate. C.L. patterns of the two morphologically different types of calcite crystals are presented in Fig. 5e-h for both the twin A and twin B experiments. The crystals grown in the twin A experiments (Fig. 5e, g) increase in luminosity, reflecting a decrease in growth rate, from the centre outwards; those grown in twin B experiments (Fig. 5f, h) show an additional luminescing outermost rim, which resulted from the introduction of an extra amount of Mn^{2+}.

The two morphologically different types of calcite crystals described in the section on crystal morphology, exhibit different C.L. zonations. The cleavage rhombohedron is the only form present on the crystals in Fig. 5e, f, whereas the crystals in Fig. 5g, h are bounded by 18 faces. These two types of crystals were formed by different growth mechanisms and at different positions in the U--tube (Fig. 1b), which could be responsible for the observed differences in C.L. zonation.

The present experimental observations imply that C.L. zonations may not necessarily always reflect variations in the trace element composition of the fluid as so often assumed. Consequently, correlation of luminescent zones over large distances (i.e. application of the concept of cement stratigraphy) is therefore only valid after having established that the zones do indeed reflect geochemical events in the pore fluids. Such luminescent zones may be identified by a sudden, marked colour (i.e. wavelength) change (cf. Amieux 1982) or they may be separated by a geological event such as fracturing or dissolution. Whenever a zonation consists of alternating non-, dull or bright luminescing zones of similar wavelength, an intrinsic cause (i.e. variation in crystal growth rate) is just as likely as an external cause (i.e. changes in trace element concentration in the fluid).

Conclusions

Cathodoluminescence studies of synthetic calcites compared with those of natural carbonates gave rise to the following tentative conclusions:

1. Luminescence in synthetic calcites has been exclusively activated by Mn^{2+}, yet is similar to that observed in natural carbonates. Hence, no other trace elements appear to be required as activators or sensitisors.
2. No Fe^{2+} quenching of luminescence occurs up to concentrations of 200 ppm.
3. At the current state of our instrumentation it has been established that 15-30 ppm Mn in the crystal structure is sufficient to activate luminescence in calcites, whereas 30-35 ppm Mn is necessary in dolomites; these minimum concentrations are significantly lower than currently reported. The slightly higher Mn concentrations required in dolomites reflect the less effective activation by Mn^{2+} incorporated on the Mg^{2+} site than on the Ca^{2+} site (cf. Sommer 1972).
4. Intensity of luminescence is controlled by the absolute Mn content and not by the Fe/Mn ratio, for Fe concentrations of, at least, up to 200 ppm.
5. Luminescent zonations in carbonates reflect differential Mn^{2+} uptake during crystal growth which can be caused by:
   a. changes in trace element composition of the precipitating fluid, or
   b. changes in the crystal growth rate independent of the Mn^{2+} concentration in the fluid.
6. The experimental results indicate that luminescence (i.e. a record of the trace element composition of the rock) does not necessarily reflect the trace element composition of the pore fluid. This highlights the need for very careful interpretation of C.L. patterns, particularly, when they are used to deduce the geochemical history of pore fluids (e.g. redox potential). Apparently great care is required to discriminate between compositional and saturation events of the formation fluids.

Acknowledgments

We thank M. Sweet (Utrecht) who did a substantial part of the experimental work, J. van Bergenhenegouwen for preparing Fig. 1, and T. Djie-Kwee, K.M. Stephan, G.P. Geelen and C.D. Laman (all Utrecht) for their analytical work. We are grateful to C. Passchier (KSEPL) for his skilful preparation of thin sections and impregnated blocks of the tiny crystals. We appreciate the constructive comments on the manuscript by P. Hartman and C.S. Strom (Utrecht) and S. Taylor (KSEPL). Special thanks are due to J.F. Lapré (KSEPL) for his seemingly endless motivation and interest in the subject and for the valuable comments and stimulating discussions throughout the entire project. Shell Research B.V. is acknowledged for permission to publish the data.

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