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# Cathodoluminescence activation and zonation in carbonate rocks: an experimental approach

## *Comment*

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## Introduction

Experimental data on cathodoluminescence activation and zonation in carbonates are badly needed. The few published data are partly contradictory, especially regarding activation of cathodoluminescence in carbonates (e.g. Fairchild, 1983; Machel, 1985). Therefore, any study that provides additional experimental data on this subject is welcome, and the paper by Ton ten Have & Wim Heijnen (1985) is no exception. However, several of their interpretations are not sufficiently supported by their data, and some of their conclusions are at variance with data published elsewhere, including Machel (1985). An earlier version of this paper was made available to Ten Have in 1984, and is quoted in Ten Have & Heijnen (1985) as Machel (in press)

## Activators other than manganese

Ten Have & Heijnen (1985: p. 302) claim that their experimental procedures 'show luminescence to be exclusively activated by $Mn^{2+}$, with no other trace elements being present besides Fe'. This conclusion is not substantiated by the data presented. Firstly, Ten Have & Heijnen (1985) never added any Fe compound, yet *all* their crystals contain Fe. One sample contains 157 ppm Fe, all other samples contain between 10 and 50 ppm Fe (their Figure 3). Apparently, even their 'purest chemicals' contained enough Fe to spike their crystals with up to 157 ppm Fe. How, then, can Ten Have & Heijnen be so sure that no elements other than Mn and Fe were involved in the luminescence of their samples? It might well be that their 'purest chemicals' were sufficiently impure to precipitate calcites which also contained other activator elements above their respective minimum effective concentrations. Secondly, and related to the first point, Ten Have & Heijnen (1985) did not analyze their calcites for elements other than Mn and Fe. Considering the low trace element concentrations under consideration, they should have analyzed *all* their chemicals and solutions for all elements suspected to be involved in the luminescence of calcites (see Machel, 1985) and should have shown the data. Based on these two points, I conclude that luminescence was *not necessarily* 'exclusively activated by Mn' in Ten Have & Heijnen's (1985) samples. There are many other elements, e.g. lead, other transition metals, and rare earth elements, which appear to be effective activators for cathodoluminescence at very low concentrations (below 30 ppm: Machel, 1985). Experimental evidence on binary and simple oxides provided qualitative and quantitative support for this point. Regarding cathodoluminescence in calcite in particular, Nichols et al. (1928) and Mukherjee (1948) determined spectra for transition and rare earth elements (Mukherjee first transformed his calcites to CaO to increase the elemental concentration), proving that activating rare earth elements are indeed contained in natural calcites. Larach (1968) then determined a range of 1–50 ppm for rare earth activation of cathodoluminescence in oxide and sulphide matrices, and Gies (1973) demonstrated this concentration range for activation in natural and artificial calcites with photoluminescence (other studies are cited in Machel, 1985). These findings are supported, and based on, general theories of solid state physics which permit (a) comparison of different modes of excitation (i.e. cathodoluminescence, photoluminescence, thermoluminescence), and (b) comparison of activators in different oxygen- dominated minerals such as binary and simple oxides (i.e. carbonates and CaO) (e.g. Curie, 1963; several articles in Goldberg, 1966; Lumb, 1978; Marfunin, 1979).

Furthermore, Ten Have & Heijnen (1985: p. 302/3) stated that 'calcite crystals grown from a solution to which $Pb^{2+}$ instead of $Mn^{2+}$ was added, did not show any luminescence', implying that there is no Pb-activation of cathodoluminescence in calcites. This implication is incorrect. The observation that the crystals spiked with Pb rather than with Mn 'did not show any luminescence' is no proof for the absence of Pb-activation. The luminescence caused by Pb is in the UV-part of the spectrum and thus invisible (Machel, 1985). Moreover, the possibility of Pb-sensitization in their Mn-activated samples has not been investigated.

I fully agree with Ten Have & Heijnen's (1985: p. 297) statement that 'no trace elements other than $Mn^{2+}$ are needed to activate luminescence similar to that observed in natural carbonates'. However, this kind of luminescence can be due to Mn, due to Mn *and* some other activator(s) and/or sensitizer(s), and possibly solely due to activators other than Mn (Machel, 1985; the last possibility has yet to be confirmed). Ten Have & Heijnen (1985) did not demonstrate the absence of the other activators (above their respective minimum effective concentrations) in their samples.

## Fe/Mn ratio and Fe-quenching

Ten Have & Heijnen (1985: p. 297) stated that 'the intensity of luminescence is controlled by the absolute amount of $Mn^{2+}$ and not by the $Fe^{2+}/Mn^{2+}$ ratio', ..., 'provided Fe concentrations are low (less than 200 ppm)', and they later extended this range to 'at least up to 200 ppm' (p. 309). These statements are not substantiated by the presented data. Ten Have & Heijnen's (1985) calcites contain only up to 157 ppm Fe (p. 302), and most samples have 10 to 50 ppm Fe (their Figure 3). Why is there a discrepancy in the Fe-concentrations of nearly 25% (157 versus 200 ppm) or more (at least up to 200 ppm')? Can the lower limit of the effect of Fe on luminescence really be determined on the basis of a single sample (157 ppm)? Establishing absolute concentration values for Fe-quenching requires consistency, better accuracy, and more data.

Secondly, the reader is left with the impression that authors such as Frank et al. (1982) were wrong 'suggesting that luminescence is controlled by the Fe/Mn ratio rather than the absolute amounts of $Mn^{2+}$, (Ten Have & Heijnen, 1985: p. 302). However, several authors have shown data indicating the dependence of luminescence intensity on the activator/quencher ratio (summarized in Machel, 1985). Supporting these findings, Meyers (unpub. data) found that the minimum Fe concentration needed to visibly quench Mn-activated luminescence in calcites is highly variable and generally increases with increasing Mn concent (see also Fairchild, 1983).

Thirdly, and related to the previous points, Ten Have & Heijnen (1985: p. 309) claim that 'no $Fe^{2+}$ quenching of luminescence occurs up to concentrations of 200 ppm' (this value was tentatively suggested by Machel, 1979). Regarding their insufficient data base (see above), this statement is not substantiated. Furthermore, if the minimum effective concentration of Fe-quenching is less than 200 ppm (which cannot be ruled out), Ten Have & Heijnen's 'occurs' should be changed to 'is visible'. Samples with up to 157 ppm Fe may be close to the onset of Fe-quenching, and there may be variations in luminescence depending on the Fe/Mn ratio that are too subtle to be visually detected and/or quantified. Furthermore, visual estimates of luminescence are imprecise and vary from observer to observer, from day to day for a single observer, and vary with instrument running condition. I therefore doubt that the subtle shifts in luminescence intensity and colour near the onset of Fe-quenching are visually quantifiable (although they may be detectable using internal standards). Ten Have & Heijnen (1985), however, estimated luminescence intensity merely visually without internal standards, and they did not measure the emission intensities nor the spectra.

Finally, Ten Have & Heijnen's (1985) samples display enormous luminescence variations from non-luminescent through bright yellow to dull red, in some cases with complex zonations (their Fig. 5). Ten Have & Heijnen (1985) measured only average Mn- and Fe-concentrations of these crystals. Who is to say that the luminescent zones (particularly the dull red ones) contain less than 157 ppm Fe? The luminescent zones are the ones of interest, and they probably contain more Fe than what was measured for the bulk crystals, considering that many crystals have large, non-luminescent nucleii (which presumably contain neither Mn nor Fe in significant amounts). Consequently, some zones may well contain more than 157 ppm or even more than 200 ppm Fe. In any case, at least some zones seem to contain Fe above the minimum effective concentration of Fe-quenching because the intensity and colour changes depicted in Figure 5 of Ten Have & Heijnen (1985) are typical for Fe-quenching in calcite (increasing amounts of Fe result in a decrease of the Mn-activated luminescence intensity and a colour shift from yellow-orange towards longer wavelengths: Fonda, 1957; Machel, 1985).Hence, and contrary to Ten Have & Heijnen's (1985) contention, I suspect that (a) their samples do display partial Fe-quenching, and (b) Fe-quenching in even these samples may depend on the Fe/Mn ratio. Ten Have & Heijnen (1985) did not offer any evidence to discard these possibilities.

## Mn-concentration

Ten Have & Heijnen (1985: p. 297) stated that '15–30 ppm and 30–35 ppm Mn is sufficient to activate luminescence in calcites and dolomites, respectively'. These Mn-limits are not substantiated by the presented data. Firstly, individual crystals are chemically heterogeneous, as indicated by their internal luminescence variations (Ten Have & Heijnen, 1985; Figure 5). Yet, only bulk crystal analyses were conducted. Secondly, 'circa 50 mg' were analyzed per sample (which must be 150 to 300 crystals per sample, taking the indicated crystal size range), which were 'observed by optical microscopy and separated into various groups' (Ten Have & Heijnen, 1985: p. 299). This implies that the crystals were not separated on the basis of their luminescence, and that all crystals of a particular 'group' (precipitation experiment?, crystal shape?) were assumed to contain the same amount of Mn. However, crystals from a single flask, regardless of their shape, probably did *not* all contain the same amount of Mn because the solutions and gels were not stirred. Ten Have & Heijnen (1985: p. 306/7) themselves stated that in their unstirred growth experiments 'considerable local variations in concentration of the reactants are admissible'. Therefore, Ten Have & Heijnen's (1985) bulk sample analyses are not suitable to establish absolute activator concentration limits. The activator concentrations should have been determined for those parts of individual crystals that actually did show luminescence (which requires the use of a microprobe if the crystals are small). Alternatively, only those crystals should have been analyzed (by AAS, ICP, or neutron activation analysis) that had homogeneous luminescence, or a homogeneously luminescent part and a non-luminescent part (presumed to contain no activator). This would permit calculation of the trace element concentration in the luminescent part. Ten Have & Heijnen's (1985) paper contains no evidence that these kinds of analytical approach have been taken.

Although Ten Have & Heijnen's (1985) determinations of the minimum effective Mn concentration for cathodoluminescence in calcite and dolomite are inconclusive, their concentration ranges for Mn are, perhaps fortuitously, fairly accurate (Richter & Zinkernagel, 1981; Machel, 1985). However, based on the above arguments and a comparison with natural calcites from the Lake Valley Formation in New Mexico, Meyers (1986, pers. comm.) suggested that Ten Have & Heijnen's (1985) Mn limits are too low.

## Zonation

Ten Have & Heijnen's (1985) experimental precipitation of calcite were free runs of up to about 12 days in closed flasks. Under these conditions, some of the observed zonation patterns probably are due to variations in growth rate, as Ten Have & Heijnen rightly pointed out. However, at least two other partitioning phenomena are also involved: closed-system partitioning and sector zoning, both possibly modified by ionic gradients within the unstirred solutions and gels.

Regarding closed-system partitioning, Ten Have & Heijnen (1985: p. 306) concluded that the change in bulk solution composition was 'too small to cause the variations in C.L. intensities shown by crystals grown in type A experiments'. This conclusion is not justified, however, because of two points: (a) they attempted to calculate the Mn-decrease through time on the basis of equilibrium partitioning (p. 306), yet on the same page they stated that their experiments took place 'far from equilibrium under ill-defined conditions'; and (b) they calculated *average* distribution coefficients for their inhomogeneous crystals. The distribution coefficients of Fe and Mn are greater than 1 (about 1–20 for Fe and 5–30 for Mn at diagenetic temperatures). Therefore, closed-system precipitation of calcite, at least in aqueous solution, does successively deplete the solution in both elements (and change the Fe/Mn ratio). Hence, the composition of the fluids must have evolved during Ten Have & Heijnen's experiments in such a way, that their crystals contain much less Fe and Mn in younger growth zones (disregarding those experiments where additional Mn was added at a later time). Meyers (poster session at the SEPM Midyear Meeting 1985 in Golden, Colorado) showed Mn-spiked calcites grown in similar solution experiments, and his crystals do show the expected decrease in Mn and cathodoluminescence in younger growth zones (no additional Mn was added). However, none of Ten Have & Heijnen's (1985) photographs displays clear evidence of such a zonation. Presumably, concentration gradients caused by convection and diffusion in their unstirred solutions and gels interfered with the closed-system partitioning effect.I therefore contend that Ten Have & Heijnen's (1985) conclusion regarding the evolution of the bulk solution composition is partially incorrect. Their data do not rule out a significant closed-system partitioning effect.

Why did Ten Have & Heijnen not measure the composition of the fluid(s) and crystal growth rate(s) through time? In this case, it would have been possible to relate the composition of individual growth zones to the fluid composition present at that time. As it stands, the observed zonation patterns cannot be related to the fluid composition nor the crystal growth rate. This is reflected in the discussion of zonation by Ten Have & Heijnen (1985) which is clustered with questionable assumptions, circular reasoning, and contradictions. For example, based on the assumption that volume diffusion is the rate-controlling process, Ten Have & Heijnen (1985: p. 308) deduced that the crystal growth rate decreased with time. Yet they also stated that supersaturation increased with time, which would tend to increase crystal growth rate. Recognizing this problem, Ten Have & Heijnen (1985: p. 308) introduced yet another assumption, i.e. that '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'. Hence, because volume diffusion is assumed to be the rate-controlling process, the decrease in growth rate due to volume diffusion is assumed to be dominant. This is circular reasoning. The assumption that the growth rate is limited only by volume diffusion is, in itself, highly questionable because it excludes crystal surface phenomena (p. 307). The observed intricate and complicated zonation patterns themselves are ample evidence for crystal surface phenomena (whose exact nature remains elusive). No bulk solution equilibrium or disequilibrium model, or steady-state diffusion model, can explain these zonations (particularly those that are laterally discontinuous).

This is related to the second partitioning phenomenon mentioned above: sector zoning. Although positive identification is not possible using Ten Have & Heijnen's (1985) photographs, the crystals in their Figures 5 (d), 5 (g), and 5 (h), perhaps also 5 (c), 5 (e) and 5 (f), show indications of compositional sector zoning similar to the examples depicted by Reeder & Prosky (1986). Ten Have & Heijnen (1985) apparently recognized sector zoning in at least one of their samples (5 (d)), but misinterpreted its origin. This type of sector zoning is not due to 'growth rate variations resulting from convection and/or turbulence' (p. 306), but due to crystal surface phenomena, probably similar to the protosite model (i.e. Nakamura, 1973; see also the excellent discussion of compositional sector zoning in carbonates by Reeder & Prosky, 1986).

In summary, I contend that Ten Have & Heijnen's (1985) experiments were not conducted under rigorous enough conditions to justify their explanation of the resulting zonation patterns. On the other hand, I wholeheartedly support Ten Have & Heijnen's (1985: p. 297) statement that 'the definition of the geochemical history of pore fluids by characterization of the rock's cathodoluminescence may not always be justified', and that the 'concept of cement stratigraphy should be handled with care' (p. 297). I made a similar statement on the basis of other criteria (Machel, 1985).

## Conclusions

This comment is not meant to discredit any of Ten Have & Heijnen's (1985) work. Instead, it intends to provoke discussion to clarify the points I raised.

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# *Reply*

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## Introduction

When we submitted our paper (Ten Have & Heijnen, 1985) for publication, we clearly realized that some of our interpretations were not completely supported by the presented data. Especially the homogeneity of the incorporation of $Mn^{2+}$ both on the scale of different crystals grown in one experiment and on the still smaller scale of different regions within an individual crystal remained uncertain at that moment. Necessary additional experimental research on the distribution of $Mn^{2+}$ was in progress as indicated on p. 302 and 305 of our paper (Ten Have & Heijnen 1985). Meanwhile, the results of these investigations have been published (Heijnen 1986). A number of the critical remarks raised by Machel have already been dealt with in that paper. In order to avoid needless duplication in the present reply we will mainly turn our attention to the other arguments put forward by Machel.

## Activators other than manganese

We agree with Machel that there is ample evidence that elements other than manganese can effectively activate cathodoluminescence in carbonates. However, the approach of our study was to minimize the influence of the others and concentrate on Mn and Fe, being recognized as the main activator and quencher respectively. Having this object in view, the solution growth experiments were arranged in series.

Each series was composed of 2–4 simultaneous growth experiments and contained one blank experiment to which no $MnCl_2 \cdot 4H_2O$ was added. The 2–4 solutions were always prepared together from the same lots of $CaCl_2 \cdot 4H_2O$, $NH_4Cl$ and deionised water. Hence all 2–4 solutions contained similar amounts of impurities, e.g. Fe, Mn and rare earth elements. The quantities of $MnCl_2 \cdot 4H_2O$ introduced to 1–3 solutions of a series of experiments were too small to be responsible for the presence of sufficient amounts of elements other than Mn to affect the luminescence of the growing crystals.

Since none of the calcite crystals grown in blank experiments showed any visible luminescence, the absence of all possible activator elements, including Mn, above their respective effective concentrations was demonstrated. It follows that the same holds for all possible activator elements, except Mn, in the calcite crystals grown in the experiments to which $MnCl_2 \cdot 4H_2O$ was added. The luminescence observed in these crystals was therefore concluded to be exclusively activated by $Mn^{2+}$. The above described experimental design of our investigations makes the rigorous chemical analyses, as required by Machel, redundant.

Later radiochemical investigations (Heijnen 1986) moreover showed a clear one to one relation between C.L. intensity and Mn distribution within individual solution grown calcite crystals. These results strongly supported the conclusion that the luminescence observed in our synthetic calcite crystals was exclusively activated by $Mn^{2+}$.

## Fe/Mn Ratio and Fe-Quenching

Due to a contamination of an origin unknown to us, one single sample of our synthetic calcite crystals showed an Fe content of 157 ppm, whereas all other samples contained 10–50 ppm Fe. We considered it a matter of scientific integrity to include this determination in our paper. It was also regarded as self-evident not to attach any significant conclusions to this exception. Machel, however, based his objections on this single determination twice, and moreover in a dualistic way. On the one hand he emphasized its importance in order to demonstrate the possible presence of considerable amounts of impurities in our synthetic crystals. On the other hand he minimized its value, stating that more data are required to determine the lower limit of the effect of Fe on luminescence. We agree with the latter argument, which is why our conclusions on Fe quenching of luminescence did not only rest on synthetic crystals containing 10 to 50 ppm Fe, but, as indicated on p. 304 of our paper (Ten Have & Heijnen 1985), also on data from natural Pliocene calcites, Jurassic and Miocene dolomites, which contained up to 200 ppm Fe.

We did not dispute that Fe can quench luminescence, but merely stated that, at such low Fe concentrations as observed in our natural and synthetic carbonates, quenching was not visible. Most natural carbonates contain more Fe and hence the quenching effect can be better quantified (e.g. Fairchild 1983). We did not present 200 ppm as the absolute limit value for Fe quenching.

Machel is certainly right when he remarks that in order to characterize luminescence, measuring the emission spectra is to be preferred to visually estimating colours and intensities. Unfortunately we did not have a suitable spectrometer at our disposal, but we admit that our investigation would have benefited from its application.

Returning to the accidental Fe concentration of 157 ppm in one sample, we consider it very unlikely that some zones in our synthetic calcite crystals may well contain more than 200 ppm Fe, as suggested by Machel. Of course, none of the cathodoluminescence photographs in Fig. 5 (Ten Have & Heijnen 1985) showed a crystal of this particular sample. The six crystals depicted in Fig. 5a–f contain between 17 and 38 ppm Fe. The Fe content of the gel-grown crystals in Fig. 5g–h was not determined, because the amount of crystals obtained was too small to allow analysis for Fe and Mn by means of AAS. Moreover, the whole discussion of Fe/Mn ratio and Fe quenching of luminescence did not apply to these crystals, since they probably grew by an exceptional mechanism as explained on p. 306 and 309 (Ten Have & Heijnen 1985).

## Mn-Concentration

As described on p. 300 and 302 (Ten Have & Heijnen 1985), the crystals grown in each experiment were separated into groups on the basis of their outward appearance and not on the basis of their luminescence. Only the group composed of clear calcite rhombohedra was subjected to further investigations with respect to cathodoluminescence. About 8–10 of these crystals were used for the preparation of thin sections, while the remaining morphologically indistinguishable crystals were analyzed by means of XRD, SEM and AAS. Since in every growth experiment the 8–10 arbitrarily selected crystals showed similar C.L. intensities, they were assumed to contain the same average Mn and Fe content as determined by means of AAS analysis of about 50 mg of the corresponding crystals. This assumption was supported by later radiochemical investigations (Heijnen 1986), which we already anticipated on p. 302 of Ten Have & Heijnen (1985).

Two growth experiments yielded extremely zoned calcite crystals, one of which was shown in our Fig. 5a. Although no extra amount of $Mn^{2+}$ was introduced during these experiments after some initial crystal growth, the resulting crystals showed a nonluminescing core and a luminescing rim. The bulk Mn content of these crystals was 5 and 10 ppm respectively. Following a similar reasoning as suggested by Machel we concluded on p. 302 and 304 (Ten Have & Heijnen 1985) that the luminescent parts of these crystals contain more than 5–10 ppm Mn.

The fact that the ranges we quoted in our paper are comparable to those in Machel (1985) does not imply that they are (fortuitously or not) accurate. The important point is that they are significantly lower than generally published, including those of Meyers (1974) on Lake Valley, and that our experimental data compare very well with the results of a large number of analyses on natural (sub)surface carbonates (see p. 304 of Ten Have & Heijnen 1985 and Richter & Zinkernagel 1981).

## Zonation

Machel correctly remarks that zonation can be caused not only by variations in growth rate, but also by closed-system partitioning and sector zoning. With regard to closed-system partitioning we presented a calculation (p. 306 Ten Have & Heijnen 1985) of the $Mn^{2+}/Ca^{2+}$ concentration ratio of the initial solution in comparison with the final solution. On the basis of the resulting 15% decrease we concluded that this effect was too small to be responsible for the observed large differences in $Mn^{2+}$ incorporation. Moreover, a depletion of $Mn^{2+}$ from the solution would cause a luminosity decreasing from the core towards the rim of the crystals, which is just the reverse of what was encountered. For that reason we concluded that the closed-system partitioning effect can be neglected with respect to the effect of the decreasing growth rate with time during our experiments. Machel wrongly states that we carried out our calculations on the basis of equilibrium partitioning. Instead we calculated *average kinetic* distribution coefficients, which, as expected, turned out to be significantly lower than the usually applied equilibrium distribution coefficients.

Regarding Machel's question why we did not measure the composition of the fluid(s) and the crystal growth rate(s) through time, our answer can be very brief. We simply do not know of any experimental method to perform such measurements in free-run precipitation experiments in unstirred solutions. We were condemned to this type of experiments by the requirement of growing sufficiently large crystals to allow C.L. investigations.

The second important partitioning phenomenon according to Machel is sector zoning. The presence of nonequivalent faces on a growing crystal is a prerequisite to the possible occurrence of compositional sector zoning (Nakamura 1973; Reeder & Prosky 1986). Since the observed crystal faces were almost exclusively cleavage rhombohedral, all crystal faces showed the same atomic surface configuration and thus the same mechanism and rate of incorporation of impurities. Therefore compositional sector zoning according to the models formulated by Nakamura (1973) and Reeder & Prosky (1986) was quite impossible in our calcite growth experiments; only sector zoning due to local growth rate variations occurred, which was already mentioned on p. 306 of Ten Have & Heijnen (1985).

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