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## CATHODOLUMINESCENCE OF SOME SYNTHETIC CALCITE CRYSTALS. INVESTIGATION ON THE ROLE PLAYED BY CERIUM

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### Abstract

Cathodoluminescence (CL) from undoped and cerium-doped synthetic calcite is examined at room temperature and at liquid nitrogen temperature, using a scanning electron microscope. At room temperature, all of the samples exhibit a CL emission in the near ultraviolet (UV), centered at approximately 370 nm with some possible shoulders at 345 nm. At low temperature, the samples show an emission of CL in the near UV but with two well defined maxima for the Ce-doped crystals (460 ppm and 4600 ppm) peaking at 345 and around 380 nm. The third Ce-doped crystal (1.74%) presents a maximum at 375 nm and a shoulder at 345 nm. The undoped crystal shows a maximum at 370 nm and a shoulder at 345 nm similar to the others. In this case, inductively coupled plasma mass spectrometry (ICP-MS) measurements have been carried out to determine the eventual presence of cerium: 1 ppm was detected (other elements such as iron, manganese and lanthanum were also detected). Thus, the near UV emission bands are interpreted as due to the presence of Ce<sup>3+</sup> substituting at calcium sites as already shown in the literature using photoluminescence results. Other emission bands have been detected in the rest of the spectrum for which some bibliographical data or some hypotheses are given. This work is dedicated to further applications in cathodoluminescence interpretation of archaeological marble. One example is described.

**Key Words:** Cathodoluminescence, calcite, cerium, marble.

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### Introduction

The cathodoluminescence (CL) emission of calcite provides a powerful tool for investigating the nature of defects in minerals. It has already been widely investigated with numerous applications in geology [14, 16, 17, 20, 21, 23] and archaeology [2, 19] where the search for signs indicating the provenance, or origin, of calcium carbonates is still of great interest. Today, it is generally accepted that the main emission of natural calcite, when excited with an electron beam, is situated in the orange part of the spectrum (600-620 nm) and is due to the manganese Mn<sup>2+</sup> impurity. Years ago, when trying to interpret this emission, some researchers investigated manganese-doped crystals [12, 18, 22] to demonstrate the relationship between the presence of manganese as trace element and the orange luminescence. This emission is now well understood: the emitting level of Mn<sup>2+</sup>, a d<sup>5</sup> ion, is the first excited state <sup>4</sup>G(T<sub>1g</sub>) in octahedral coordination [9] when Mn<sup>2+</sup> is substituting for Ca<sup>2+</sup>, giving an emission at around 610 nm in calcite according to a specific value of the crystal field strength [11]. Depending on the nature and the structure of the host crystal, the crystal field may change, leading to variations of the emission wavelength (e.g., calcite versus dolomite); this particularity has been largely developed in the field of phosphors, which presents a very high emission efficiency [13].

For the other emission bands detected in calcite from ultra-violet (UV) to near infrared (IR) (notably 300, 370 and 450 nm), one of them has been interpreted using the same method as for manganese, i.e., doping a synthetic crystal with the suspected impurity to observe the evolution of the luminescence signal as a function of the added amount of impurity. In this way, the 300 nm emission band was found to be related to the presence of lead Pb<sup>2+</sup> [12].

However, for the blue emission at 450 nm, which is often observed [12, 22], no conclusive model is available at present. The remaining emission in the near UV (370 nm), may be explained using photoluminescence results obtained with natural calcite. Initially, the Mn

**Table 1.** CaCO<sub>3</sub> synthetic calcite crystals, laboratory references and trace element concentrations determined with ICP-MS or flame spectrometry\*.

Reference	Ce	Mn	Fe	La
BDX 1667	1 ppm	4 ppm	3%	1.2 ppm
BDX 1670	460 ppm*	—	—	—
BDX 1672	4600 ppm*	—	—	—
BDX 1668	1.74%	4.7 ppm	2.4%	97 ppm

impurity was suspected to act as an emitting centre in this part of the spectrum [1]; however, later, this band was ascribed to Ce<sup>3+</sup> [3].

Taking into account these facts, we performed some CL measurements on Ce-doped synthetic calcite crystals in an attempt to understand the relationship between cerium and the CL emission around 370 nm.

One example of an application to a natural sample, an archaeological marble, shows that nearly all emission bands can be explained or at least good hypotheses can be presented. This is fundamental in regard to the problem of provenance of calcium carbonate which underlies this investigation.

#### Materials and Methods

The synthetic samples consist of approximately 10 μm powders. They were synthesized using aqueous solutions of (NH<sub>4</sub>)HCO<sub>3</sub>, CaCl<sub>2</sub> and CeCl<sub>3</sub> as needed. The chemical reaction of precipitation is controlled by a diffusion process through a porous barrier of agar-agar (temperature: 21°C; at atmospheric pressure). Table 1 gives the laboratory references, the contents of cerium and other elements which were also revealed.

Quantitative data were obtained with inductively coupled plasma mass spectrometry (ICP-MS) for the undoped and one of the Ce-doped samples. Two values concerning cerium concentrations were given by the researchers who supplied the samples (determination made by flame spectrometry). In all cases, X-ray diffraction (XRD) confirmed the calcite structure.

Cathodoluminescence measurements were performed in a JEOL 820 scanning electron microscope (SEM) operated at an accelerating voltage of 20 keV and electron beam current of 10 nA, at room temperature (RT) and at a low temperature, using a liquid nitrogen (LN) cooled unit (Oxford Instruments, Oxford, U.K.). The CL emission was collected with an ellipsoidal mirror (Oxford Instruments) and guided through a UV type fibre (pure fused silica) to a Jobin-Yvon HRS2 scanning monochromator {focal length 600 mm, aperture f/5.7, grating 1200 (grooves per millimeter, gr/mm) blazed at 500 nm, resolution 0.2 nm at 500 nm, entrance and exit slits set at 180 μm width} followed by a photomultiplier (RTC 56TUVVP with S20 type photocathode) and appropriate amplification.

**Figure 1 (on the facing page).** Cathodoluminescence emission spectra of synthetic calcite, undoped and doped with cerium. (a), (c), (e) and (g) were taken at room temperature, while (b), (d), (f) and (h) were taken at liquid nitrogen temperature (LNT). See text for details.

Calibration was set using mercury lines. The time required to do a spectral scan was 25 minutes. Spectra were not computer-collected and no peak deconvolution analysis could be performed but the peak positions were thoroughly controlled with repeated scanings. Taking into account all the experimental parameters, the precision was defined to be ± 5 nm. We add that spectra were not corrected for the spectral response of the whole signal detection system, but one must note that the photocathode used is well adapted to this kind of near UV emission. Another set of equipment (Nuclide Lumino-scope system) was used which has a broad (3 mm diameter or more) 10 keV electron beam which impinges on to the sample at an angle close to 45°; the CL emission is then directed through the objective of a video-camera to take a colour photograph of the surface of the sample. Only the marble sample was studied this way.

Electron spin resonance (ESR) measurements were also carried out using a Varian V-4502 spectrometer operating at a frequency of 9.5 GHz without any previous irradiation of the sample.

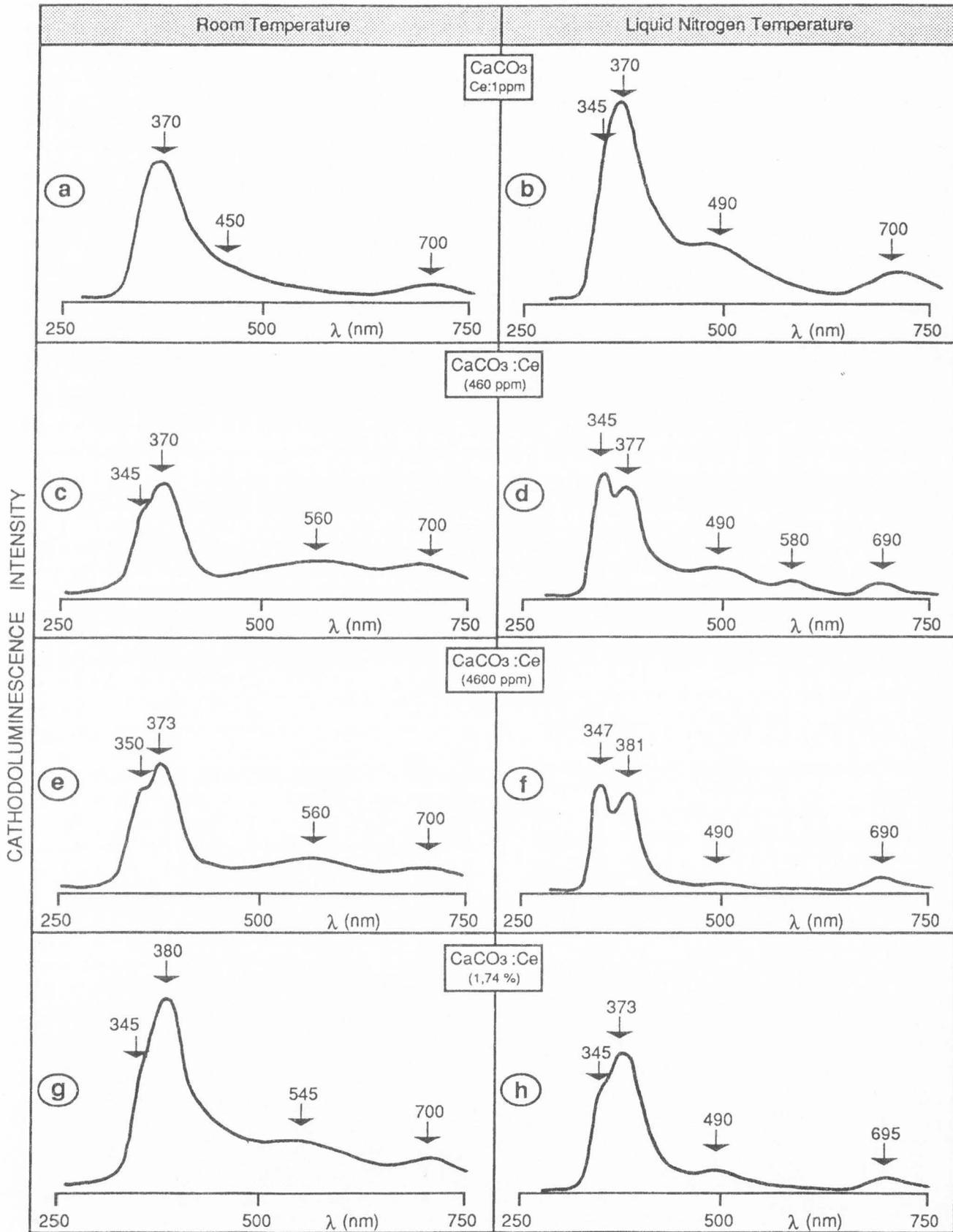
#### Results and Discussion

##### Cathodoluminescence results

The CL emission spectra are presented in Figure 1. This figure is a comparison between the samples according to their Ce content and the conditions of recording the spectra {i.e., room temperature or liquid nitrogen temperature (LNT)}.

The undoped sample of CaCO<sub>3</sub> shows a large emission band centered at 370 nm at RT (Fig. 1a) and some weak and very broad band whose maximum seems to be located in the blue around 450 nm. We also note a weak emission in the red part of the spectrum at 700 nm. At LNT (Fig. 1b), the near UV band is still centered at approximately 370 nm with a possible shoulder at 345 nm, while the blue emission is more clearly emitting around 490 nm as is the red at 700 nm.

CL of synthetic calcite crystals



In the first Ce-doped calcite (460 ppm), the RT spectrum (Fig. 1c) is almost identical to the undoped sample spectrum with a maximum at 370 nm and a shoulder at around 345 nm. The difference is in the blue region where almost no emission is detected, and only a very weak one appears in the red at 700 nm. A new broad, weak, band appears centered at around 560 nm. At LNT (Fig. 1d) the spectrum appears slightly different: two separate emission bands show up at 345 and 377 nm. In the blue region, the wide emission is centered at 490 nm, and the red one still appears around 690 nm. The green emission is shifted to 580 nm.

The RT spectrum (Fig. 1e) from the second Ce-doped sample (4600 ppm) is quite similar to the first Ce-doped sample: emissions peak at 350 and 373 nm; no emission shows up in the blue. In the red, the emission is very weak at 700 nm. A broad emission centered around 560 nm is apparent. The LNT spectrum (Fig. 1f) again shows two separate, narrow bands centered at 347 and 381 nm. The blue emission around 490 nm still exists as well as the red one at 690 nm.

The last highly Ce-doped calcite (1.74%) at RT (Fig. 1g) gives maxima at 380, 545 and 700 nm with a shoulder around 345 nm. The LNT spectrum (Fig. 1h) is very close to the RT one in the UV part showing a maximum at 373 nm with a 345 nm shouldering. The blue emission at 490 nm and the red one at 695 nm are again detected.

#### Electron spin resonance (ESR) results

ESR observations were recorded on only two of the samples: the undoped crystal and the highly Ce-doped crystal (Fig. 2). In an attempt to interpret the CL results, ESR was used to detect the presence of cerium in the undoped calcite which shows a strong UV emission without a specific impurity being voluntarily added. A comparison of ESR spectra from undoped and highly doped calcite shows that they differ because of the signal due to cerium in one of the samples (Fig. 2b). The broad typical signal of  $\text{Ce}^{3+}$  is easily recognized [10] along with a weak signal from  $\text{Mn}^{2+}$  ions. This latter signal is easier to identify in Figure 2a where the six characteristic hyperfine rays show up indicating the presence of  $\text{Mn}^{2+}$  substituting at  $\text{Ca}^{2+}$  sites in octahedral symmetry [9, 11]. In this case, a lack of cerium signal suggests that its amount is below the detection limit, estimated at 0.05% using ESR. As already mentioned, the very small amount of cerium here was demonstrated and determined with the ICP-MS measurements.

#### Discussion

Before starting any discussion concerning the assignment of cerium to the UV emission, we should note that

lanthanum is not known to be at the origin of any luminescence in calcite and that the manganese concentration is too low to contribute (moreover, Mn provides a well known orange emission which is not detected here). Iron participation to CL of calcite may be evoked, but it concerns the red part of the spectrum as discussed below. Lead, also known as an emitting center, was not detected.

When we examine the CL results, the main problem relates to the identification of the cerium impurity as being responsible for the near UV emission. While, methods such as ESR and wavelength dispersive X-ray spectrometry analysis (with an electron microprobe analyzer), failed to detect cerium in such low concentration in the undoped sample, ICP-MS demonstrated the presence of cerium in this sample and established its concentration (i.e., 1 ppm).

The study of the different Ce-doped samples has enabled us to confirm the implication of cerium as a luminescent centre in  $\text{CaCO}_3$  matrix. The CL results also show the presence of this near UV emission, even in the undoped calcite sample. This result is in good agreement with the prediction of the presence of cerium in extremely low concentration in such matrix [3] if we believe that cerium is responsible for this CL emission band. The fluorescence of  $\text{Ce}^{3+}$  activated compounds is well known [4 and references therein]: the emission consists generally of a broad band with two peaks in the near UV region. In  $\text{CaCO}_3$ , these emissions were located at 345 and 367 nm (measurements recorded at LNT) [1]. Since the  $\text{Ce}^{3+}$  has a  $4f^1$  configuration, the ground state consists of a doublet ( $^2F_{5/2}$  and  $^2F_{7/2}$ ). The lower excited states are the crystal field components of the 5d configuration. The  $\text{Ce}^{3+}$  emission is due to  $5d \rightarrow 4f$  transition, which is an allowed electric dipole transition with a very short fluorescence decay time ( $< 10^{-7}$  sec.) [4]. In our case, decay time measurements have not been carried out because of the lack of sample in sufficient quantity but such results might lend additional support to our proposal.

Nevertheless, the observation of a large CL emission band in all cases (Fig. 1) with at least two peaks more or less well defined and located in between 345 and 381 nm is rather clear. Depending on the temperature at which the experiment is carried out, the maxima may slightly change in position. We also note the small shift of the second band maximum which is located at 378 nm for  $\text{CaCO}_3:\text{Ce}$  (460 ppm) and at 381 nm for  $\text{CaCO}_3:\text{Ce}$  (4600 ppm). This is within the error limits of the measurements, but can also be attributed to some instability in the temperature-controller device. The maxima of emission may also change in intensity depending on the amount of cerium. It seems that the intensity ratio (345 nm/370 nm) is in favor of the second

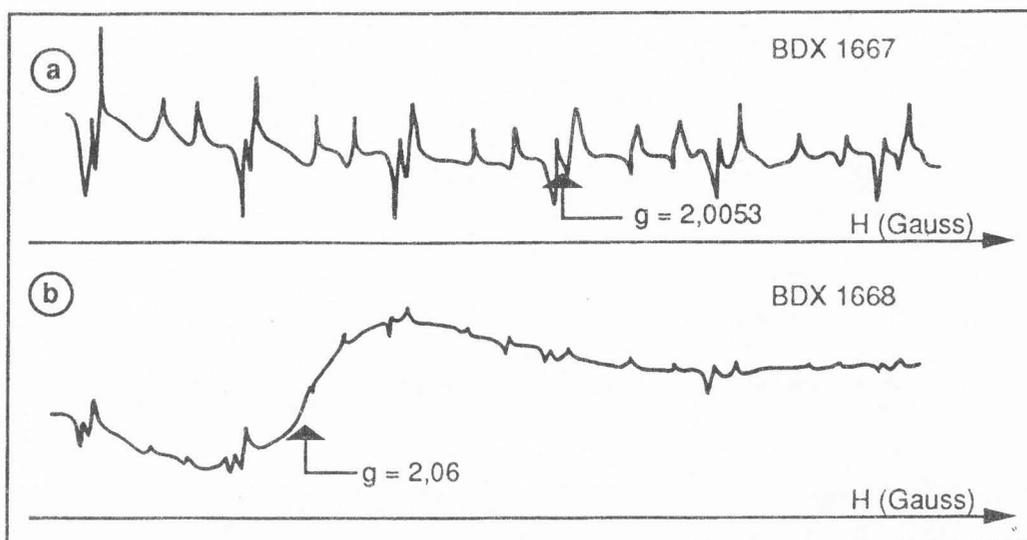


Figure 2. ESR spectra from (a) undoped (BDX 1667) and (b) 1.74% Ce-doped (BDX 1668) calcite crystals.

peak for the lowest concentration (1 ppm), then is nearly equal to one for the second and third sample (respectively 460 and 4600 ppm Ce-doped) and comes back to the former situation for the highly Ce-doped (1.74%) sample. This can be explained by either self-absorption or energy transfer phenomenon [4]. Concerning the UV region of the spectra, it is without any doubt the contribution of cerium  $\text{Ce}^{3+}$  substituting at calcium sites. Also interesting is the possibility of cerium to be a luminescent centre in as low amount as 1 ppm, which makes CL a good method for detecting this element.

The cerium emission can be interpreted rather straightforwardly but this is not the case for the other emissions. The blue emission around 450 nm at RT and 490 nm at LNT is the most difficult one to explain. It has been previously observed, but no interpretation has been put forward until now. A matrix defect was suggested [22], as also the presence of impurities such as  $\text{Mn}^{2+}$  or  $\text{Eu}^{2+}$ . To our knowledge, no blue emission coming from manganese has been detected thus far. This suggests that one of the absorption levels of  $\text{Mn}^{2+}$  would lead to a blue emission. The probability of such an event is low, that is why most of the emitting processes happen through the  $^4\text{G}(\text{T}_{1g})$  level giving rise to the 610 nm emission. The other trace element to be evoked is  $\text{Eu}^{2+}$ . This ion is known for its luminescent properties in phosphors, giving generally a blue contribution [5]. In our case, no trace of europium was detected using ICP-MS for which the detection limit is less than a ppm.

Again, it is cerium that is proposed for its capacity of showing an eventual third emission due to another

level from the 5d excited state. This has already been observed and interpreted this way in some phosphors [4]. Moreover, in our case, the LNT measurement shows a displacement of this blue emission from 450 to 490 nm which could be explained by either the fact that the lowest 5d level lies exceptionally low, or by a large Stokes shift.

Another hypothesis which can be proposed does not concern any impurity ion but, on the contrary, the matrix itself. The group  $\text{CO}_3^{2-}$  has been evoked in the interpretation of thermoluminescence (TL) results on natural calcite [6 and references therein] where it was concluded that electrons could be trapped to form  $\text{CO}_3^{3-}$  centers and that these centers could be involved in the TL emission process. Our experience on silicates [7, 8] leads us to think that this hypothesis has to be developed since it is well known that both TL and CL involve similar processes [17, 19]. For silicates, it is one oxygen ion from the  $\text{SiO}_4^{4-}$  group which is implicated, and of course, one could think of using an analogous approach for the  $\text{CO}_3^{2-}$  group.

The emissions detected at 545 and 560 nm at RT (Figs. 1c, 1e and 1g) and 580 nm at LNT (Fig. 1d) have found no interpretation yet. One can think that the higher excited level of cerium, the one suggested for the blue contribution at 450-490 nm, could be a candidate if not involved in the blue emission, however, this is highly speculative.

Finally, for the red emission 690-700 nm, the only reasonable proposal that can be put forward, comes from the presence of iron which was detected using ICP-MS (3% in  $\text{CaCO}_3$  undoped and 2.4% in  $\text{CaCO}_3:\text{Ce}$  1.74%). This hypothesis of a red emission due to  $\text{Fe}^{3+}$

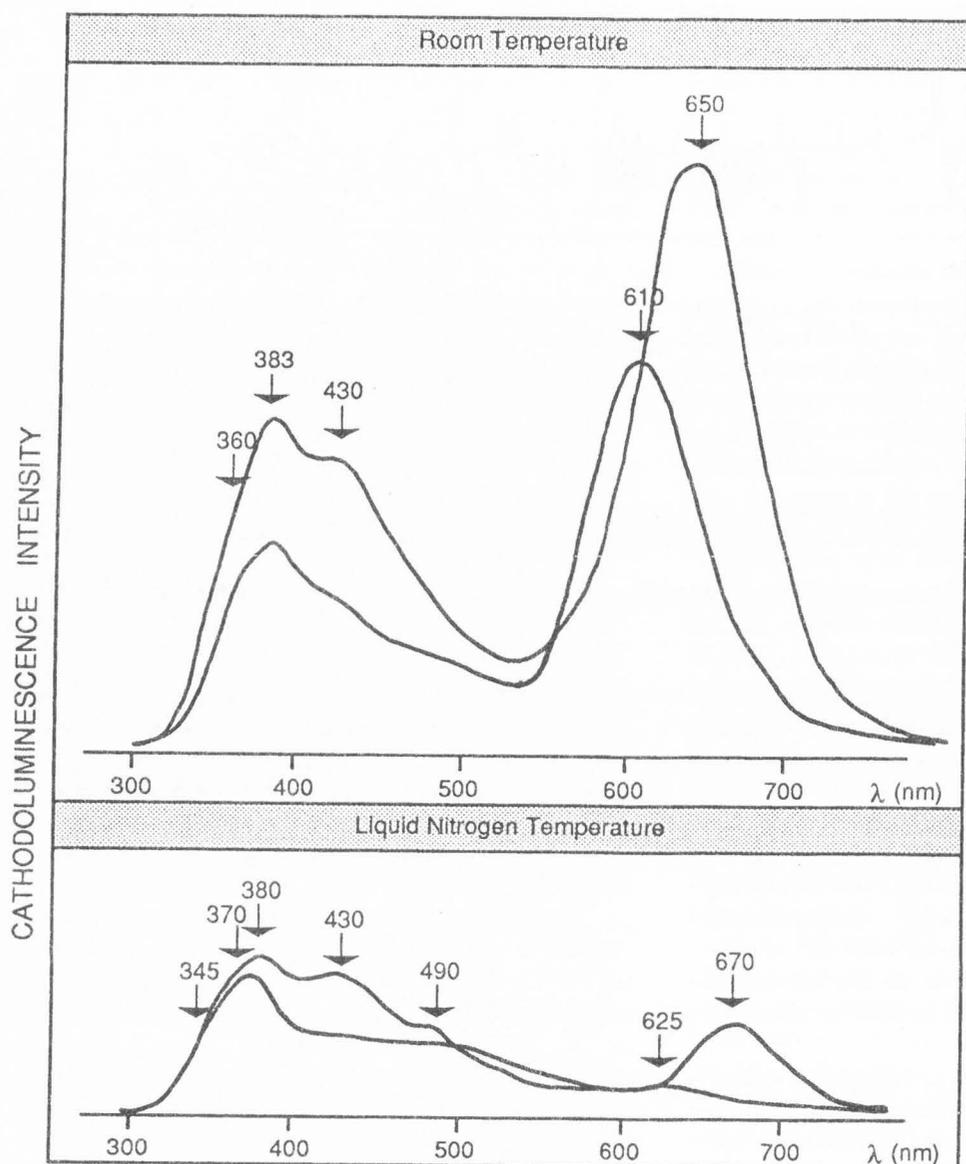


Figure 3. CL spectra from a sample of marble (BDX 4433) recorded at RT and LNT; (1) indicates a calcitic area, (2) indicates a dolomitic area.

has been suggested in other natural materials [15 and references therein]; we add that in our case, we reached the detection limits of our CL equipment in this part of the spectrum.

With this level of understanding, we tried to interpret the CL from a natural sample of marble.

#### Cathodoluminescence of a Sample of Marble

The sample to be investigated is a piece of marble coming from Thasos-Vathy in Greece (reference: BDX 4433). XRD analysis and X-ray fluorescence with the SEM indicated a dolomitic marble with well localized calcitic areas. Cathodoluminescence imaging shows a soft colour in between pink and violet. The spectra (Fig. 3) were also recorded at both RT and LNT. From

this initial work, we can attempt to apply the results previously developed in this study.

On that basis, all the emission bands may be explained. At RT the near UV bands (360–383 nm) may be due to the presence of cerium; the blue emission (430 nm) could be either due to cerium or to the matrix centre  $\text{CO}_3^{2-}$  or both; the emission in the orange (610 nm) for the calcitic zone and red (650 nm) for the dolomitic zone, comes from manganese substituting at calcium and magnesium sites [11], respectively. These results show a slight modification when recorded at LNT. Concerning the calcitic area (curves 1 in Fig. 3), the UV bands are more clearly defined at LNT (345 and 370 nm); the blue band is shifted at around 490 nm and the orange emission is moved to 625 nm with a consequent decrease of intensity due to the low

temperature condition and for which we do not have any explanation as yet. For the dolomitic area (curves 2 in Fig. 3), at LNT, the UV band is peaking at 380 nm, the blue emission still at 430 nm and the red one is shifted to 670 nm and shows also a consequent decrease of intensity. Interpretation would be the same as for the synthetic calcite crystals: the UV bands would be due to  $Ce^{3+}$ , the blue ones to either cerium or a matrix defect associated with an oxygen ion, the orange-red ones to the presence of  $Mn^{2+}$ .

### Conclusion

This work provides new data for the interpretation of CL spectra of calcite. Considering the first experiments using photoluminescence carried out on natural calcite, it is clear that the CL results go in the same direction at least for the near UV part of the spectrum: cerium emits at around 370 nm at RT and shows a second band at 345 nm better defined at LNT. For the rest of the spectrum, it seems obvious that the comparison of results obtained from different methods will help in the interpretation. The application to a sample of marble is of great importance in view of provenance of calcium carbonates. In this first example, one can observe the difficulty of such approach but, nevertheless, all the possibilities a set of methods can bring. Once again it is shown that one method is not enough to give a definite conclusion.

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