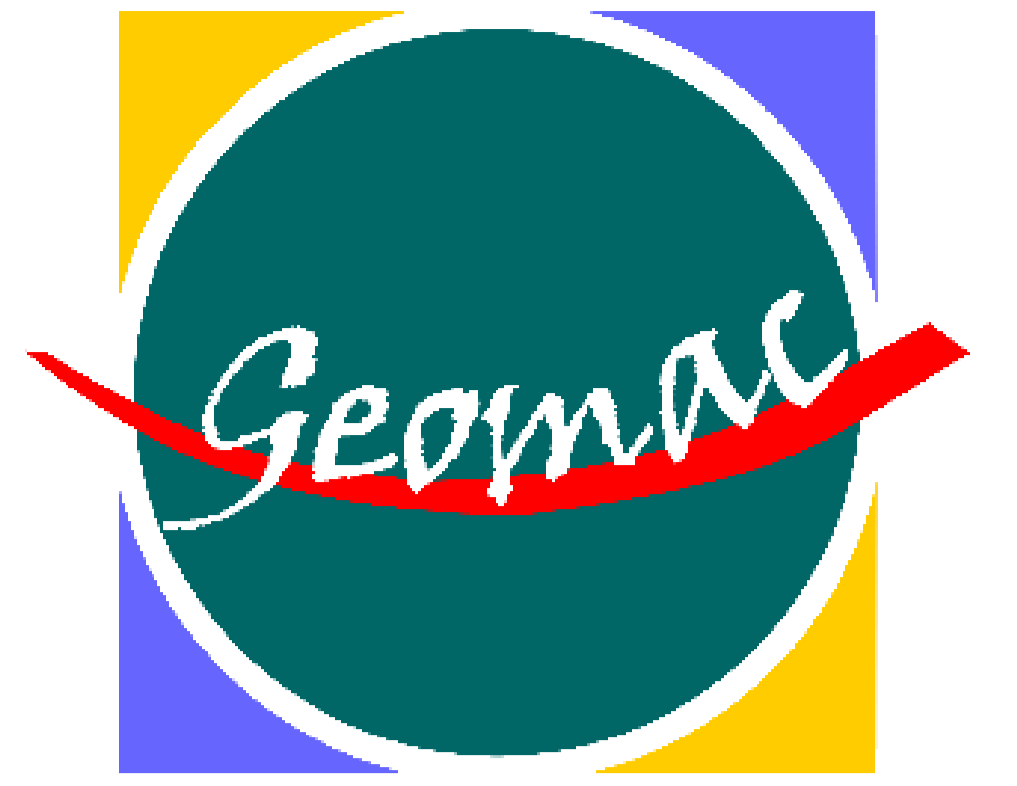


# Multispectral Imaging in cathodoluminescence Microscopy



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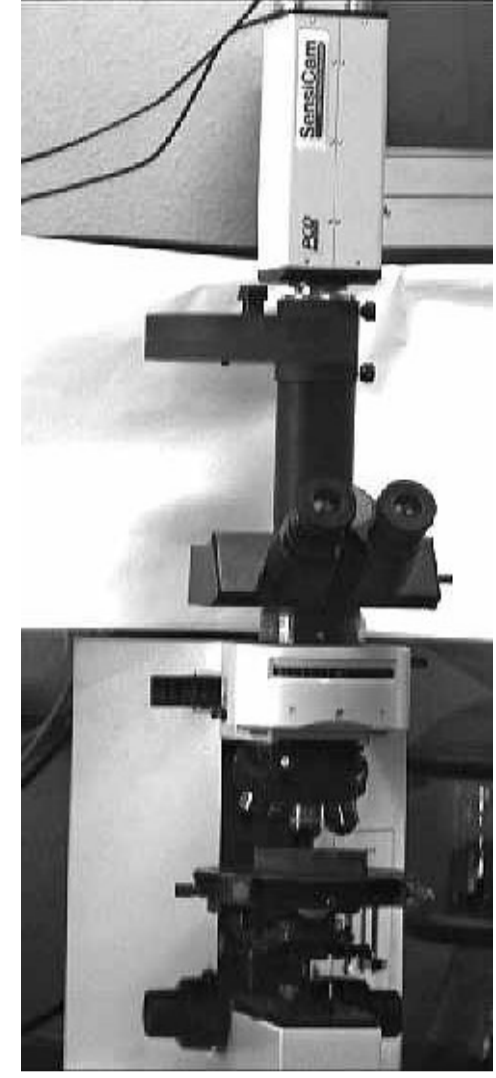
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The Cold Cathode CL 8200 MK4 with various sample stages and gun geometries (doc. CITL)



An Olympus BX 60 Reflected Light Microscope fitted with a multispectral filter wheel and coupled to a high-resolution / long exposure PCO Sensicam.



360 nm  
438 nm  
489 nm  
591 nm  
692 nm  
870 nm

## 1. INTRODUCTION

Cathodoluminescence (CL) microscopy is a common tool in geology and particularly in the description of sedimentary rocks (especially carbonates) (see the reviews of Barbin & Schwoerer, 1997 and Pagel et al. (Eds.), 2000). Basically, petrologists take advantage of variations in colour in order:

- to distinguish different mineral species and to quickly estimate their abundance (for example calcite vs. aragonite; K-feldspar vs. plagioclase...);
- to interpret different mineral paragenetic sequences and different mineral generations (characterised by different crystallisation conditions so by different trace elements resulting in different luminescence);
- to detect zoning in minerals because CL contrasts may be generated in some favourable cases by chemical contrasts of only a few ppm in activator elements such as Mn<sup>2+</sup>, REE, Fe<sup>3+</sup>, Ti<sup>4+</sup>, etc. (such small variations of trace elements content would not be detected by EPMA);
- to characterize microfracturing, defect centre, fluid migration, alteration...

Although CL observations are widely used, imaging associated with quantitative analysis of emission spectra keep still poorly documented. Current mineralogical usages are often qualitative with visual (or photographic) analysis of luminescence. That's why we have investigated imaging of selected spectral bands (Multispectral Imaging) with a CCD camera associated with CL, a new association of techniques which may open new way to a better understanding of crystallochemistry, compositional zonings and growth conditions of minerals.

## 2. PRINCIPLES OF CATHODOLUMINESCENCE

CL is a luminescence phenomena induced by the interaction between energetic electrons and a material surface. Most studies are restricted to the spectra field from 200nm to 900nm. This luminescence is produced by activator trace elements present in minerals. These ones are essentially transition elements (Fe, Mn...) and REE (Rare Earth Elements). The CL spectra are associated with two types of transitions: f-f and f-d transitions (Rémond et al., 1992). Two types of CL systems are available: a cold cathode CL and a hot cathode CL. The first one has been developed for easy observations with optical microscopes and the second one is essentially devoted to spectral analysis when coupled to a spectrometer. Both systems present advantages and inconveniences summarized in the following table.

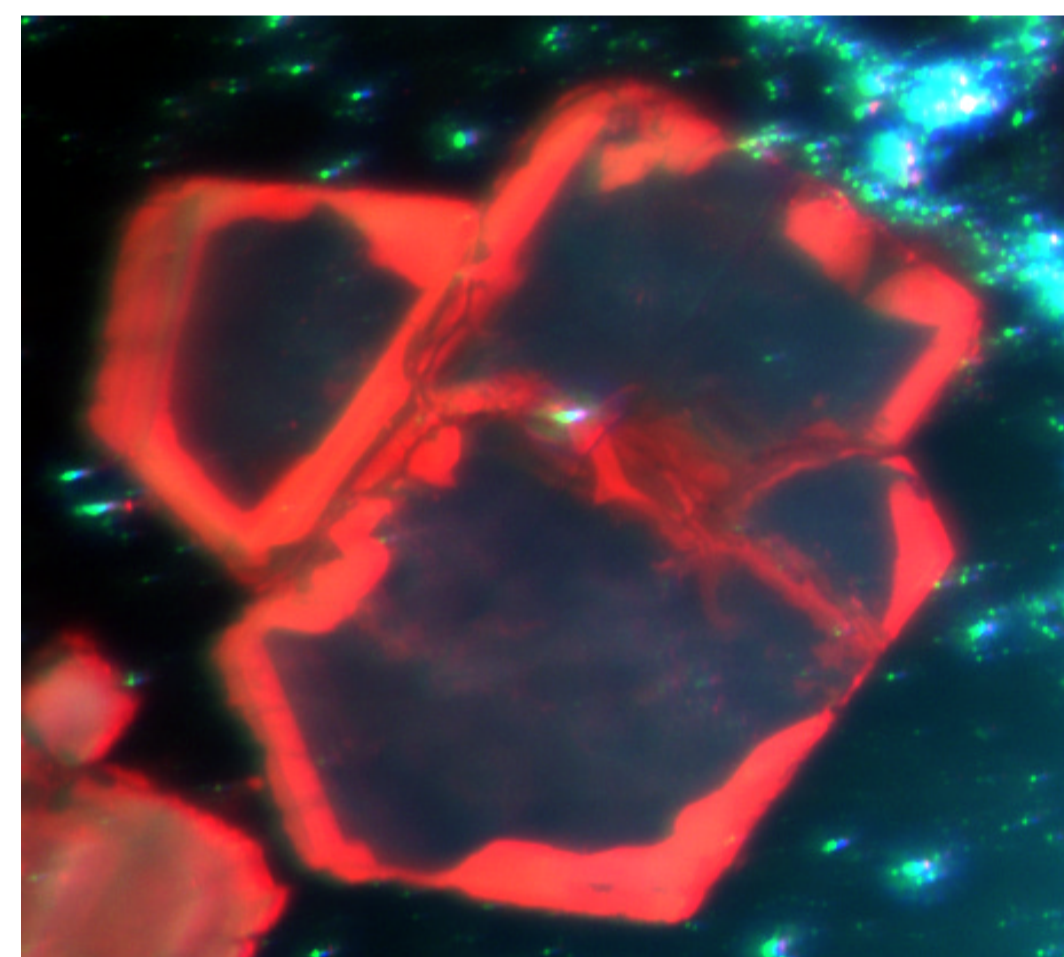
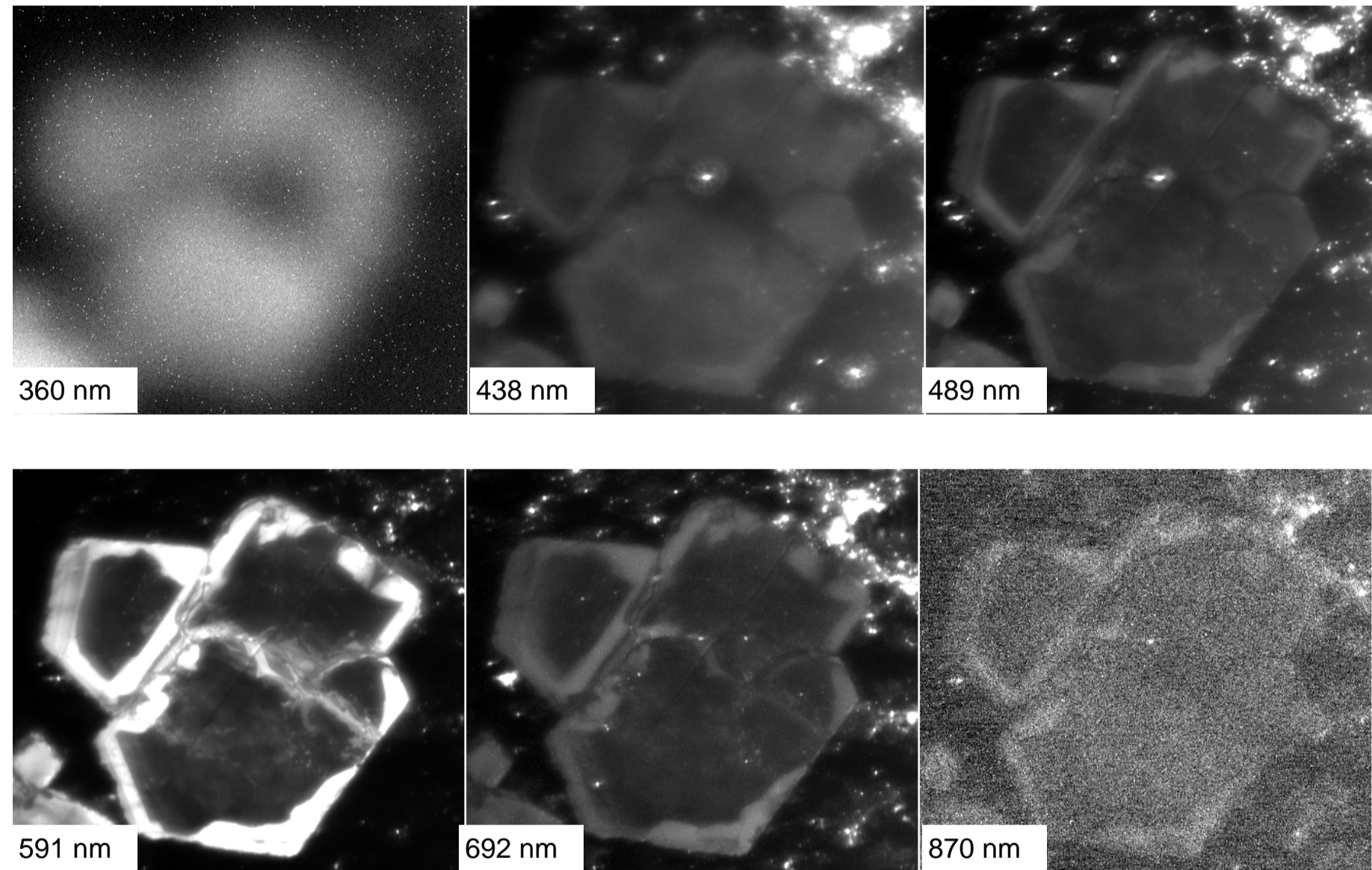
Cold cathode	Hot cathode
Electrons produced by an electric discharge between two electrodes under a low gas pressure	Electrons produced by heating a filament (2000-3000°)
<b>Advantages:</b> <ul style="list-style-type: none"> <li>• Low cost</li> <li>• Fits to an optical microscope</li> <li>• Easy low vacuum system</li> <li>• Large field of observation (about 2 cm)</li> <li>• No coating required</li> </ul>	<b>Advantages:</b> <ul style="list-style-type: none"> <li>• Good spatial resolution (due to a narrow electron beam)</li> <li>• High magnification</li> <li>• Higher current density (so higher luminescence intensity)</li> <li>• High stability of luminescence</li> <li>• Can be coupled with BSE and EDX mapping</li> </ul>
<b>Inconveniences:</b> <ul style="list-style-type: none"> <li>• Low spatial resolution</li> <li>• Instability of luminescence (due to variation of the gas pressure)</li> </ul>	<b>Inconveniences:</b> <ul style="list-style-type: none"> <li>• Coating recommended</li> <li>• A high vacuum is necessary</li> <li>• High cost</li> </ul>

## 3. MATERIALS AND METHODS

A cold cathode CL equipment from CITL (model CCL 8200 mk3) mounted on an Olympus BX 60 microscope has been used for this study. The CL stage consists of a vacuum chamber containing the X-Y stage control and the electron gun. A control unit allows for precise control of the vacuum conditions and kV beam intensity.

The imaging device is a PCO SensiCam camera with a Peltier cooling stage allowing for a continuous adjustment of the integration time (exposure) from 1 millisecond to 1000 seconds. The connection tube between the PCO camera and the microscope is fitted with a rotating wheel holding nine different 25mm Ø filters. Interference filters with a 10 nm bandwidth have been selected with reference to known excitation bands such as 360nm (Ce<sup>3+</sup>), 390nm (Nd<sup>3+</sup>), 410nm (Eu<sup>2+</sup>), 560nm (Mn<sup>2+</sup>), etc.

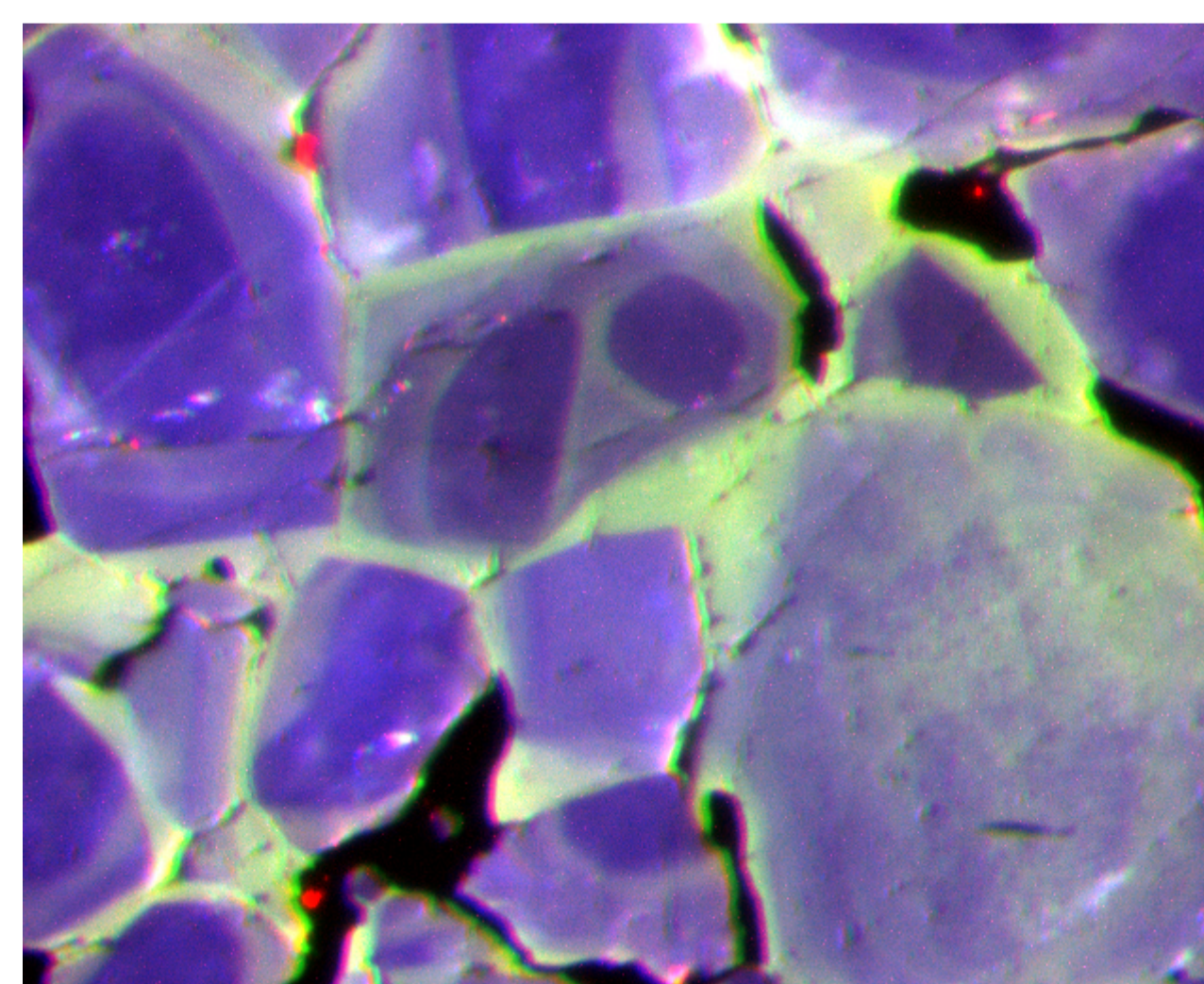
Polished samples are introduced in the vacuum chamber. Analytical conditions are between 0.05 to 0.1 torr, 15 to 20 kV and about 200 mA. Due to very low light levels imposing long exposures (from 1 to 300 seconds), optimal imaging conditions may be hard to achieve. By taking advantage of the binning capabilities of the camera, it is possible to combine the photonic response of neighbouring cells and to obtain reasonable refreshing rates (ex. one image every two seconds) at reduced spatial resolution.



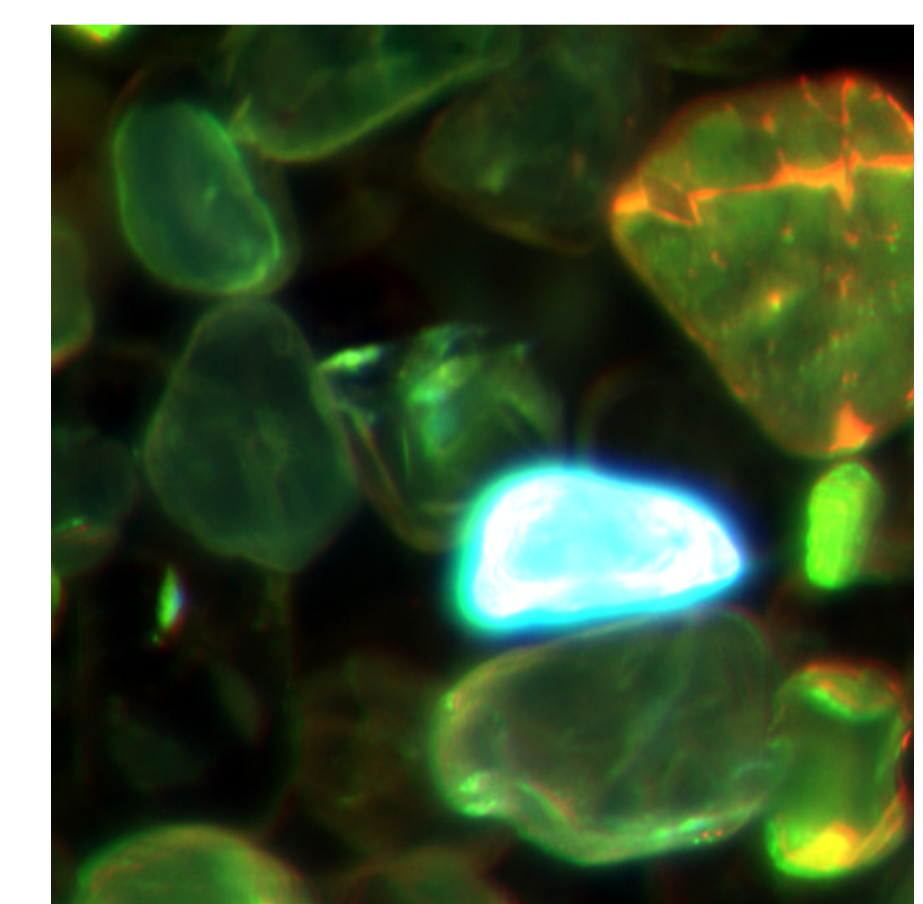
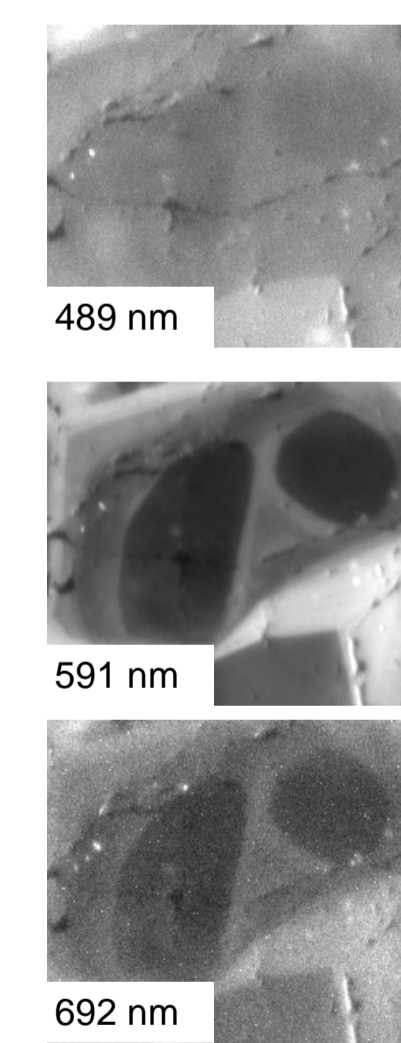
Colour composite visualisation of zoning in a scheelite from the Costabonne skarn deposit. (Red = 591 nm, Green = 489 nm and Blue = 438 nm)

## 4. APPLICATIONS OF MULTISPECTRAL IMAGING IN CATHODOLUMINESCENCE

Our investigations concentrated on four intensively luminescent minerals: apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,OH,Cl)), zircon (ZrSiO<sub>4</sub>), monazite (CePO<sub>4</sub>) and scheelite (CaWO<sub>4</sub>). Figure 1 displays images of zoned apatite crystals coming from drill cores in the Topuchowo nelsonite (Fe-Ti-P rich rocks) situated in the Suwalki anorthosite (Poland). These images have been taken at 489nm, 591nm and 692nm. It can be seen that the zoning is best revealed by the image at 591nm which displays the higher luminosity contrast. This is interpreted to result from variable amounts of Mn<sup>2+</sup>. The higher luminescence intensity toward the border implies a growing Mn<sup>2+</sup> content from the centre of the mineral to the border.



Zoning in apatites from the Suwalki anorthosite correspond to variable Mn<sup>2+</sup> contents. Colour composite (Red = 692 nm, Green = 591 nm and Blue = 489 nm)



A strongly luminescent monazite within the zircon concentrate from Richard's Bay (Rep. South Africa) Colour composite (Red = 591 nm, Green = 489 nm and Blue = 438 nm)

## 5. CONCLUSIONS - PERSPECTIVES

Multispectral imaging of CL emissions in contrast to RGB colour imaging opens the way to quantitative image analysis of selected bands. Preliminary results show the interest to explore this technique in more detail. However, technical problems such as luminescence instability during image capture should be taken into account. Possible scenarios include time averaging of sequential video images or real-time multispectral imaging using gratings instead of filter wheels. The use of hot cathodes instead of cold ones could improve the overall image quality.

Another problem is the availability of standard luminescing materials for CL systems. Recently, the Society for Luminescence Microscopy and Spectroscopy (SLMS) has decided to encourage the development of standards for CL systems with spectral acquisition capabilities and for CL systems with photographic recording (Marshall & Kopp, 2000).

Although microchemical data are not available at the moment to compare the trace element contents of minerals with the CL emission intensities and wavelengths, the next step will be to map variable activator element concentrations in minerals with in-situ high-resolution analytical techniques such as Laser Ablation ICP-MS or SIMS. The ultimate goal would be to map and to quantify the trace element content of minerals with CL multispectral imaging.

## 6. REFERENCES

- Barbin V. & Schwoerer M., 1997. Cathodoluminescence et géosciences. C. R. Acad. Sci. Paris (Sciences de la Terre et des Planètes), 325: 157-169.
- Pagel M., Barbin, V., Blanc, P. & Ohnenstetter, D. (Eds.), 2000. Cathodoluminescence in Applied Geosciences. Springer-Verlag, Berlin, 2000.
- Marshall D.J. & Kop O.C., 2000. The status of the standards program of the Society for Luminescence Microscopy and Spectroscopy. In: Pagel M., Barbin, V., Blanc, P. & Ohnenstetter, D. (Eds.) Cathodoluminescence in Applied Geosciences. Springer-Verlag, Berlin, 2000.
- Rémond G., Cesbron F., Chapoulié R., Ohnenstetter D., Roques-Carnes C. & Schwoerer, 1992. Cathodoluminescence applied to the microcharacterization of mineral materials : a present status in experimentation and interpretation. Scanning Microscopy, 6: 23-68.