Application of Cathodoluminescence to The Study of Feldspars: Imaging and Spectrometry

Rute Fonseca 1, Helena Couto 1, 2
1 Universidade do Porto, Faculdade de Ciências, Departamento de Geociências, Ambiente e Ordenamento do Território,
2 Instituto de Ciências da Terra, Rua do Campo Alegre 687, 4169-007 Porto, Portugal
fonsecarute@hotmail.com

Abstract. Cathodoluminescence (CL) studies were carried out on polished thin sections of different feldspar samples (from migmatites, granites, aplite-pegmatites and granitic aggregates) using a hot cathode CL equipment HC3-LM coupled to an optical microscope and to a spectrometer (SpectraPro 2300i and a CCD Pixis 400B detector and the software Winspec32) from the Faculty of Sciences of University of Porto. The system was operated at 14kV and a filament current of 0.18 mA. The samples were coated with a thin gold film using a Cressington 108 Auto device. Luminescence images were acquired during the CL analysis with an adapted digital video-camera (KAPPA PS 40C-285 (DX) with dual stage Peltier cooling) and an acquisition time between 3.5 and 3.52 s. The CL study, including imaging and spectrometry, proved to be an important tool to complement the feldspar petrography as it contributes to the identification of features not observed under optical microscope. The application of the Cathodoluminescence to feldspar allows distinguishing between potassic feldspar and plagioclase, differentiating generations of feldspar and displaying internal zoning and growth areas, among other. The spectrometry complements the CL imaging. It allows obtaining a qualitative level of emission intensity, which permits the interpretation of the nature of this luminescence in each feldspar. Bands shown in the spectra are related to the existing activator elements. In the present study, it was found an association of each feldspar to different spectra and respective colour. The plagioclases exhibit yellow or green luminescence. The activator element is Mn$^{2+}$, showing a broad emission band between 550 – 570 nm specially detected on this type of feldspars, due to the replacement of K$^+$ for Mn$^{2+}$. The potassium feldspars have more or less intense blue colour associated with various activators elements: the activator element is Cu$^{2+}$ showing a broad emission band between 420±5 nm. This emission band can be detected either in potassium feldspar or in plagioclases, but when associated with the blue colour, it indicates that it is a potassium feldspar. Spectra with a wavelength of 460±10 nm, associated to the element activator/synthesizer Ti$^{3+}$, which is initially deposited as Ti$^{4+}$, replacing Al, as temperature rise. The emission band with a wavelength of 860 nm correspond to the activator element Pb$^+$, and occurs specially in potassium feldspar like adularia and orthoclase. The activator element Al - O - Al, show a broad emission band between 450-480 nm. This emission in CL is caused by the replacement of Al$^{3+}$ and Si$^{4+}$ in feldspars.

1. Introduction
Cathodoluminescence (CL) is a method used for the study of minerals that takes advantage of the luminescence of those minerals. The emitted luminescence can be studied by imaging or spectroscopy. Imaging delivers information on different phases, zoning and internal structure, defects. Spectrometry allows the acquisition of different spectrums referent to each specific mineral, indicating, through the peak wavelength, which is the activator element that makes the mineral take that specific colour and helping to understand its origin.
It is perceptible that this technique allows a deeper knowledge about minerals, feldspars in this particular case.

The main objective was to proceed to the feldspar identification with the Cathodoluminescence and to compare the different obtained imaging and spectrums with the pre-defined ones, to understand how the cathodoluminescence can contribute to the identification of the feldspar and its genesis. Feldspars are the most important and abundant minerals that occur in igneous, metamorphic and sedimentary rocks. The basic structural compounds of feldspars are SiO$_4$ and AlO$_4$ tetrahedrons intercalated with K, Na or Ca cations of, being the replacement by other compounds possible. These are designated as trace elements, which become activator elements of the mineral, causing luminescent emissions that are detected with CL [1].

Feldspars are included in the aluminosilicates class and can be classified, accordingly to its chemical formula as: potassium feldspars (sanidine, orthoclase, microcline), with KAlSi$_3$O$_8$ as its general formula; or can correspond to solid solutions of plagioclase (from the albite, with NaAlSi$_3$O$_8$ as its formula, till the anorthite with the formula CaAl$_2$Si$_2$O$_8$); in summary, the majority of the minerals can be encountered in the series K – Na – Ca (orthoclase – albite – anorthite) [1]. Feldspars formed under different conditions, have different luminescent characteristics, depending on the crystallization environment and the presence of activator elements.

This last factor gives to the feldspars a certain luminescence (light blue, yellowish-green, violet or red), allowing an interpretation and quick distinction between the different phases, composition, interpolating processes occurred and giving information about its textural level, making it easier to distinguish between the distribution of potassium feldspars and plagioclase.

Secondary weathering and alteration processes that can occur in feldspars (mostly the potassium ones), causing defects on its structure, are also detectable by CL, by registering an alteration in the colour, turning from blue to brownish. [1]

The CL application to the feldspars allows a most correct interpretation about the specific conditions of formation and the alteration suffered by the rocks containing feldspars [1]. This way CL makes it possible to: differentiate between potassium feldspars and plagioclase; detect different feldspars generations; visualize internal zoning and growing areas; determination of the alteration caused by weathering and radiation; detect the secondary autigenic growing; quickly differentiate between quartz and feldspar, due to the luminescence emission in CL. Spectrometry is used as a supplement to CL imaging, by permitting the acquisition of qualitative levels of the emission intensity that admits an interpretation about the luminescence nature of each feldspar. The peaks present in the spectrums are related to the existing activator elements.

2. Methodology

Thin polished sections of different samples were studied previously with the optical microscope in order to understand the distribution of feldspars to choose the different areas that would be analysed with the cathodoluminescence (in the Faculty of Sciences of University of Porto). After the observation of the feldspars in cathodoluminescence, the images from each sample and its spectrum were obtained. These were then compared with standard spectrums, leading to the identification of each activator element, being this way possible to proceed to the individual identification.

• CL Study

The samples to be used in the Cathodoluminescence equipment correspond to polished thin sections, that were submitted to C coating in order to become conductors, once if this proceeding is not performed it will occur charge accumulation at the polished surface, leading to errors on the observation due to the excess of electrons exposure that are produced on the cathode incident on the slide. For the coating the equipment Cressington sputter Coater 108 auto was used. For the Cathodoluminescence study it was used the Lumic HC3 – LM equipment. This equipment is constituted by an optical microscope to which is linked an electrons cannon and a vacuum chamber. The electron cannon is designated by hot cathode, because the filament can reach temperatures between 2000º and 3000º C, creating an electron beam that will incise on the sample.
Next, the electric tension filament must be turned on, verifying that it has the value of 14Kv (pre-established value in manual mode), without letting it exceed 0,7 A, because above this value the filament can be damaged. Now it is possible to observe the sample in cathodoluminescence, bearing in mind that the laboratory must remain completely in the dark, so there are no interferences on the observation. The images registry was performed through the software Kappa, that is installed on a computer to which the camera is connected, being this way possible to adjust the conditions for the observation of each sample.

The spectrometry the equipment used was the SpectraPro 2300i with the software Winspec32 which is installed on another computer connected to the spectrometer, where it is possible to control the exposure time and spectrum propagation velocity, in a way to obtain the best results.

3. Results
The studied samples were, from Migmatitic band located on the oriental coast of northern of Portugal [2], namely a migmatite (FM22), an aplite – pegmatite (VC17b) and a two mica granite (VC27a), a sample of Porto granite considered a two mica leucogranite, sin tectonic relatively to the third Variscan phase [3], a sample of Régua bridge cinder block with thin grain two micas granite [4].

- Migmatite (FM22)
On this migmatitic sample, four feldspars have been analyzed. In Cathodoluminescence, it is possible to observe blue and yellow luminescence colour. Feldspars with the blue colour are posterior to the feldspars with yellow colour, appearing as a filling of fractures, resulting from fluids.

Plagioclase:
On this mineral, the presence of polysynthetic macla characteristic of the plagioclase is evident, confirmed by the yellowish-green luminescence, with inclusions of feldspar with blue luminescence in CL (Figure 1). On the inner, non-luminescent quartz inclusions occur. On the spectrum it is observed a peak (Figure 2) corresponding to, approximately 560 nm (within the interval 550-570 nm), indicating that the activator element is Mn$^{2+}$ [5]. This peak is specially detected on plagioclases, being less common in potassium feldspars due to the difficulty of occurring the replacement of K$^+$ by Mn$^{2+}$ on this kind of feldspar.

![Figure 1. Mineral with yellowish-green luminescence, with inclusions of feldspar with blue luminescence in CL](image1.png)

![Figure 2. The mineral’s spectrum with its peak approximately at 560 nm with indication of activator element](image2.png)

Three more plagioclases were observed, with a spectrum of the same type, and occurrence of more intense luminescent areas (clearer and brilliant colours) along the fractures, indicating recrystallization. These differences show that there are two distinct generations on the same mineral.
**Potassium Feldspar**

In CL, it is visible the blue luminescence, surrounded by yellowish luminescence, that indicate the presence of two different feldspar generations (Figure 3). The spectrum (Figure 4), shows a peak between 420±5 nm, so, its activator element is the Cu²⁺ [6]. This peak can be detected either in potassium feldspars or plagioclases, but its intense blue colour indicates that it is a potassium feldspar. The occurrence of Cu²⁺ as an activator element indicates that the feldspar is located in an area where many impurities have occurred, caused by the excess of this element.

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**Two Micas Granite (VC27a)**

In Cathodoluminescence, it is possible to observe some feldspar with the blue luminescence and others with the green one. This difference in colouration indicates that these feldspars are from different generations and, being evident that the blue feldspars are later than the green feldspar.

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**Potassium feldspars**

On this sample it was observed three crystals of potassium feldspars. The first one presents a completely blue luminescence colour (figure 5). By analysing its spectrum (Figure 6), it is clear that it has a peak that detaches from the rest of the spectrum, at 469 nm. Considering this peak and the blue colouration of the mineral, it is understandable that the peak is in the interval 460±10 nm, so, the activator element corresponds to Ti³⁺ [6].

By analysing the spectrum, it is possible to verify that there are other peaks co-existing in this mineral, and it is possible to realize that there are many interferences by other mineral on the sample. The presence of this Ti³⁺ activator element is more evident in potassium feldspars than in plagioclases (that corresponds to this case, due to its high intensity). This element is initially deposited as Ti⁴⁺, replacing the Al, making the electrons present on the deposition spot to release during heating [6].

Due to this fact, it is not possible to be certain that this is an activator element, it might be a CL’s synthesizer. The second potassium feldspar, in CL has blue colour, meaning that there is only one generation. Its spectrum has a peak that corresponds to a very elevated wavelength, approximately 870 nm. This peak may be due to the presence of Pb⁺ that occurs mostly in potassium feldspars such as adularia and orthoclase. Having this high intensity, it is not possible to consider that the cause of this peak is exactly this activator element, because its pre-defined wavelength is 860 nm [7] occurring in rocks formed at high temperatures.

The third one, in CL has a blue colour, with quartz inclusions (non-luminescent areas). It is possible to see that on the left corner there is a green colour that in natural light, corresponds to a “dirty” area, which may indicate that it belongs to a more altered feldspar. Its spectrum reaches a peak between 450 – 480 nm that corresponds to the Al – O⁻ - Al activator element [8]. This CL’s emission is a result of
the replacement of $\text{Al}^{3+}$ by $\text{Si}^{4+}$ in feldspars [8]. This activator element may be linked to a structural alteration or to impurities related to the rocks formation environment. Despite this activator element occurs both in potassium feldspar and in plagioclases, it is more intense on the first case and it is associated with the blue luminescence.

![Figure 5. Mineral with the colour blue](image)

![Figure 6. The mineral’s spectrum with its peak at 469nm with indication of activator element](image)

**Plagioclase**:  
A plagioclase was also observed with a yellowish-green luminescence and the fractures are filled by shinier colours than the rest of the mineral, which indicates the existence of recrystallization.  
Its spectrum has a peak between the values $550 – 570$ nm, indicating that its activator element is the $\text{Mn}^{2+}$ [5], the same observed on the anterior plagioclases.

- **Aplite – pegmatite (VC17b)**  
On this sample two different feldspars were analyzed. In other feldspars with a darker luminescence colour, the spectra did not allow correct analyses.  
With the CL, it is possible to observe yellow feldspar near feldspar with an intense blue colour. This fact indicates that these feldspars are from two different generations, the one with the blue colour appears to be posterior to the yellow luminescence feldspar. In both cases is detectable the recrystallization in fractures.

**Plagioclase**  
In CL, it is noticeable a recrystallization, with a brighter colour. It is also possible to observe a polysynthetic macla in the CL image. By analyzing the spectrum, it is verified that the peak occurs at approximately $560$ nm, corresponding to the $\text{Mn}^{2+}$ activator element, belonging to the interval of $550 – 570$ nm, that is also a characteristic of the plagioclases [5], (like in two Micas Granite -VC27a).

**Potassium feldspars**  
In CL, it is possible to visualize the bright blue feldspar surrounded by the plagioclase described above. The darker areas on the image, non-luminescent, are from quartz.  
Relatively to the obtained spectrum to this blue feldspar, it is noticeable the existence of irregularities and secondary peaks, being two of them easily distinguished.  
The main peak corresponds to approximately $465$ nm, and once it is in the interval of $460\pm10$ nm, it has high intensity and presents a blue luminescence, being possible to conclude that the activator element corresponds to $\text{Ti}^{3+}$ [6], the same as in the previous sample (VC27a).
• **Porto Granite**
  On this sample three different crystal feldspars were analyzed. It is verified, all over the sample, the existence of a lot of apatite and micas, the first one having a huge influence on the obtained spectrums. The observed feldspars on this sample have blue and yellowish – green luminescence.

  **Potassium feldspar**
  On this sample two potassium feldspars with the same activator element were observed. In CL image (Figure 7), it is shown that the feldspar has an intense blue colour, and that there are apatites and fractures, which will have a direct influence on the spectrum.
  It is confirmed that this spectrum (Figure 8), is very inconstant, having many irregularities and secondary peaks that can be caused by the apatite in the inner of the feldspar. Its peak is reached, approximately, at 460 nm, that is on the interval of 450 – 480 nm, which indicates that the activator element is the Al - O’ - Al [8]. This CL emission is caused by the replacement of Al³⁺ by Si⁴⁺ in feldspars [8]. This activator element may correspond to a structural alteration or to impurities related to the rock formation environment.

  ![Figure 7](image1.png) **Figure 7.** Mineral with an intense blue color, with apatites and fractures

  ![Figure 8](image2.png) **Figure 8.** The mineral’s spectrum with its peak at 460nm with indication of activator element

• **Plagioclase**
  Observing this mineral in CL, it is perceptible the existence of an intense blue colour, interrupted by darker luminescence (almost completely non-luminescent) and green colours, that can correspond to the existence of minerals on the interior of the fractures and even to the presence of apatite that have a huge influence on the spectrum, as explained previously.
  By analysing the spectrum, it is observed the existence of irregularities and secondary peaks that, like in the other situations, occur due to the presence of apatite. It is also visible a more intense peak, with a higher wavelength, approximately at 504 nm, that detaches from the rest of the spectrum and may be an exterior interference.
  Other analyzed peak, which is framed on the spectrum, has its approximate value at 565 nm, corresponding to the interval 550 – 570 nm [5], which indicates that Mn²⁺ is the activator element, like on the previous plagioclases.

• **Régua bridge sample**
  On this sample of a granite cinder block, two different feldspars were analyzed, which present fracturing, although not as intense as in the previous cases. In CL the sample presents blue and yellow colours.

  **Potassium feldspar**
  In CL the feldspar has an intense blue colour without any colour alteration that predicts the existence of only one generation. It is also observed the existence of apatites, which can interfere on the
spectrum. By observing the spectrum, the existence of a main peak is verified at the approximate value of 455 nm, so the peak is in the interval of 450 – 480 nm, corresponding to the Al – O – Al as the activator element [8].

Plagioclase

In CL it is visible that the plagioclase has a green colour at the core and a blue colour on the borders, indicating an alteration and the possible existence of two different generations. It is observed, once more, the presence ofapatite, within the plagioclase. Its spectrum, despite the irregularities and presence of secondary peaks resulting from the apatite has its main peak at approximatly 564 nm. This is in the interval of 550 – 570 nm, indicating that Mn$^{2+}$ as the activator element, which is characteristic of the plagioclases [5], like the other studied plagioclases.

4. Discussion

Spectra are disturbed by dispersed light from strongly (apatite and K-feldspar), a problem related to the low spatial resolution of HC3-LM, what explain the problems we have with some spectra [9]. The observed plagioclases on the FM22 sample are those that present more clearly the polysynthetic macla. Despite this, in every analyzed plagioclase it is verified the same type of spectrum, always associated with the activator element Mn$^{2+}$ that corresponds to a wavelength of 550 – 570 nm [5]. This peak indicating and activator element is specially detected in plagioclases, being less common in potassium feldspars due to the difficulty to, on these minerals, occur the replacement of K by Mn$^{2+}$, having always, in CL, the yellowish-green colour. However, some of the plagioclases present inclusions of other feldspars, usually with blue luminescent colour, showing that these are posterior to the plagioclase or even to the apatites.

In general, according to the CL’s results, all of the potassium feldspars have a blue luminescence colour, more or less intense. These minerals have very distinct characteristics from each other, in what concerns the spectrums, mostly due to the presence of other minerals, such as apatite and quartz. Several potassium feldspars were studied, associated to the different types of spectrums:

- Spectrum that reaches its peak between 420±5 nm having the Cu$^{2+}$ as activator element [6], can be detected both in potassium feldspars and plagioclases, but the colour intense blue indicates a potassium feldspar.

- Spectrums with a very prominent peak, corresponding to a high intensity, are associated to the activator/synthesizer element Ti$^{3+}$, with a wavelength of 460±10 nm [6]. The presence of this activator element is much more evident in potassium feldspars than in plagioclases.

- Spectrums with a peak corresponding to the activator element Pb$^{+}$ that has a value of 860 nm [7], occurs especially in potassium feldspars such as adularia and orthoclase.

- The most observed spectrum was the one associated to the activator element Al – O – Al, which peak is reached in the interval 450 – 480 nm [8].

This CL’s emission is caused by the replacement of Al$^{3+}$ and Si$^{4+}$ in feldspars. Despite in numerous different types of spectrums have been observed, some present more than one main peak, which wavelength interval value corresponds to only one activator element. The feldspar distinction was made having the spectrum peaks as an informative base and combining this with the colour of each feldspar captured with the CL.

5. Conclusions

Imaging and spectra CL allows distinguishing potassium feldspars from plagioclases. Activator elements were distinguished by spectrum, determined by the main peak wavelength, being also observed secondary peaks possibly related to interferences on the observation, due to the presence of dispersed light from strongly emitting minerals like apatite.

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