

High-resolution spectrometric analysis of rare earth elements-activated cathodoluminescence in feldspar minerals

Jens Götze ^{a,*}, Dirk Habermann ^b, Rolf D. Neuser ^c, Detlev K. Richter ^c

^a Department of Mineralogy, Freiberg University of Mining and Technology, Brennhaugasse 14, D-09596 Freiberg, Germany

^b Department of Experimental Physics, Freiberg University of Mining and Technology, D-09596 Freiberg, Germany

^c Department of Geology, Ruhr-University Bochum, D-44780 Bochum, Germany

Received 14 January 1998; accepted 6 July 1998

Abstract

Cathodoluminescence (CL) investigations of igneous, metamorphic and sedimentary feldspars indicate that rare earth elements (REE)-activated CL in feldspars is more common than previously assumed. Hot-cathode CL microscopy combined with high-resolution spectrometric analysis of CL emission allow to detect some REE below the detection limits of electron microprobe and proton-induced X-ray emission analysis (PIXE) and reveal variations in the REE distribution within single feldspar crystals. Differently luminescing zones can reflect changes during feldspar crystallization and/or element fluctuations during secondary alteration processes which are not discernible using conventional polarizing microscopy. The results of the study document Eu^{2+} , Sm^{3+} , Dy^{3+} , Tb^{3+} , and Nd^{3+} -activated CL in feldspars of different origin. The influence of the crystal field on shape and position of REE luminescence spectra significantly differs for divalent and trivalent REE ions. Whereas Eu^{2+} shows a broad band emission (~ 420 nm) which is influenced by the local crystal field, trivalent ions of the rare earth show narrow emission lines which reflect the transitions between excited state wave functions lying inside closed electronic shells. The positions of these peaks and the characteristic energies are described for the different REE^{3+} . © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hot-cathode CL microscopy ; High-resolution spectrometric analysis; Rare earth elements; Cathodoluminescence; Feldspar

1. Introduction

Feldspars are the most important rock forming minerals occurring in igneous, metamorphic and sedimentary rocks. Cathodoluminescence (CL) of feldspars is an important tool in interpreting genetic conditions of rock formation and alteration. Feldspars formed under different conditions can show different

luminescence emission characteristics, depending on crystallization environment and trace-element uptake during growth or recrystallization. Thus, different CL colours permit rapid visual distinction of different feldspar phases, compositional zoning, fine-scale structures, and mineral intergrowth.

Most of the feldspars in samples from igneous and metamorphic rocks exhibit luminescence with CL colours of bright blue, greenish-yellow, violet and red (Marshall, 1988). The CL emissions generally consist of three broad emission bands in the blue

* Corresponding author. Fax: +49-3731-39-3129; E-mail: goetze@mineral.tu-freiberg.de

(around 450 nm), green (560 nm), and red on the edge of the infra-red (~ 700 nm). The blue emission has been related to structural defects (e.g., oxygen related defects such as Al–O[−]–Al, Marfunin, 1979), whereas the most abundant activator elements Mn²⁺ and Fe³⁺ cause the green and red emission in feldspars, respectively (Geake et al., 1973). Other elements which can probably act as activators of CL in feldspar are Tl, Pb, Cu, Cr, and REE (Mariano et al., 1973; Marshall, 1988; Gorobets et al., 1989; Götze et al., 1998).

Rare earth element (REE) activation responsible for CL is known since Mariano et al. (1973) have synthesized doped plagioclase. The REE ions Eu²⁺, Sm³⁺, Ce³⁺ were found to be effective as activators in synthetic feldspar samples (Laud et al., 1971; Mariano and Ring, 1975). Furthermore, Ce³⁺ activation was reported from feldspars of regional metamorphic rocks showing variations of intensity in dependence on PT conditions of rock formation (Rokatschuk et al., 1989; Kusnetsov and Kramarenko, 1995).

In general, however, the REE are assumed to occur rarely in sufficient amounts in natural feldspars to be CL activators (Marshall, 1988). The contents of REE and Y are generally up to 10 ppm in plagioclases (La, Ce, Eu up to 100 ppm) which is significantly higher compared to K–feldspar. High concentrations of REE were especially reported from Y, REE-enriched pegmatites (Černý, 1994). The REE and Y occur as trivalent ions in feldspars except Ce⁴⁺ and Eu²⁺. The partition of Eu²⁺ into plagioclases is more efficient than the trivalent REE because of the similarity to Sr²⁺. The Eu²⁺/Eu³⁺ ratio increases from ca. 1 in anorthite to ca. 100 in albite mainly depending on oxygen fugacity and temperature (Smith and Brown, 1988).

The present study should illustrate whether hot-cathode CL microscopy combined with high-resolution spectrometric analysis of CL emission allows to detect some REE with very low detection limits and to reveal variations in the distribution of REE within single feldspar crystals.

2. Materials and methods

The sample material consists of well characterized feldspars of the orthoclase–albite–anorthite ternary

system (Götze et al., 1998). Chemical composition of the feldspars was determined by microprobe analysis using a CAMECA Camebax SX 50 and natural feldspar standards. Trace elements were analyzed by ICP-MS (Perkin-Elmer Elan 5000) and proton-induced X-ray emission analysis (PIXE) using a 3-MeV proton beam generated by a dynamitron tandem accelerator (for details, see the work of Meijer et al. (1994)).

The CL examinations were carried out on polished thin sections of the samples using a ‘hot-cathode’ CL microscope at 14 kV and with a current density of $\sim 10 \mu\text{A}/\text{mm}^2$ and an operating vacuum $< 10^{-6}$ Torr. To prevent the build-up of electrical charge during CL operations, the thin sections were coated with carbon. Luminescence images were captured ‘on-line’ during CL operations by means of an adapted digital video-camera (KAPPA 961-1138 CF 20 DXC with cooling stage).

High-resolution spectral analysis was carried out to detect the REE-activated CL emission and to provide identification of activator elements and structural information. CL spectra were obtained using an EG&G digital triple-grating spectrograph (resolution of 0.5 nm at 600 nm) with liquid nitrogen cooled, Si-based charge-coupled device (CCD) detector. The CCD camera was attached to the CL microscope (transmission of the glass optics > 380 nm) by a silica-glass fibre guide (Habermann et al., 1996). CL spectra were measured in the range 380 to 800 nm and also 380 to 1100 nm using standardized conditions (calibration by a Hg lamp, accumulation time 10 s, spot width 30 μm ; for details of specification and correction, see the work of Habermann (1997)). To prevent any falsification of the CL spectra due to electron bombardment, all spectra were taken on non-irradiated sample spots.

3. Results and discussion

The investigation of more than 50 feldspar samples from different parent rocks showed that REE-activated CL in feldspars is more common than assumed in previous investigations (e.g., Marshall, 1988). Using high-resolution spectral CL very low intensities of REE-activated CL emission are detectable.

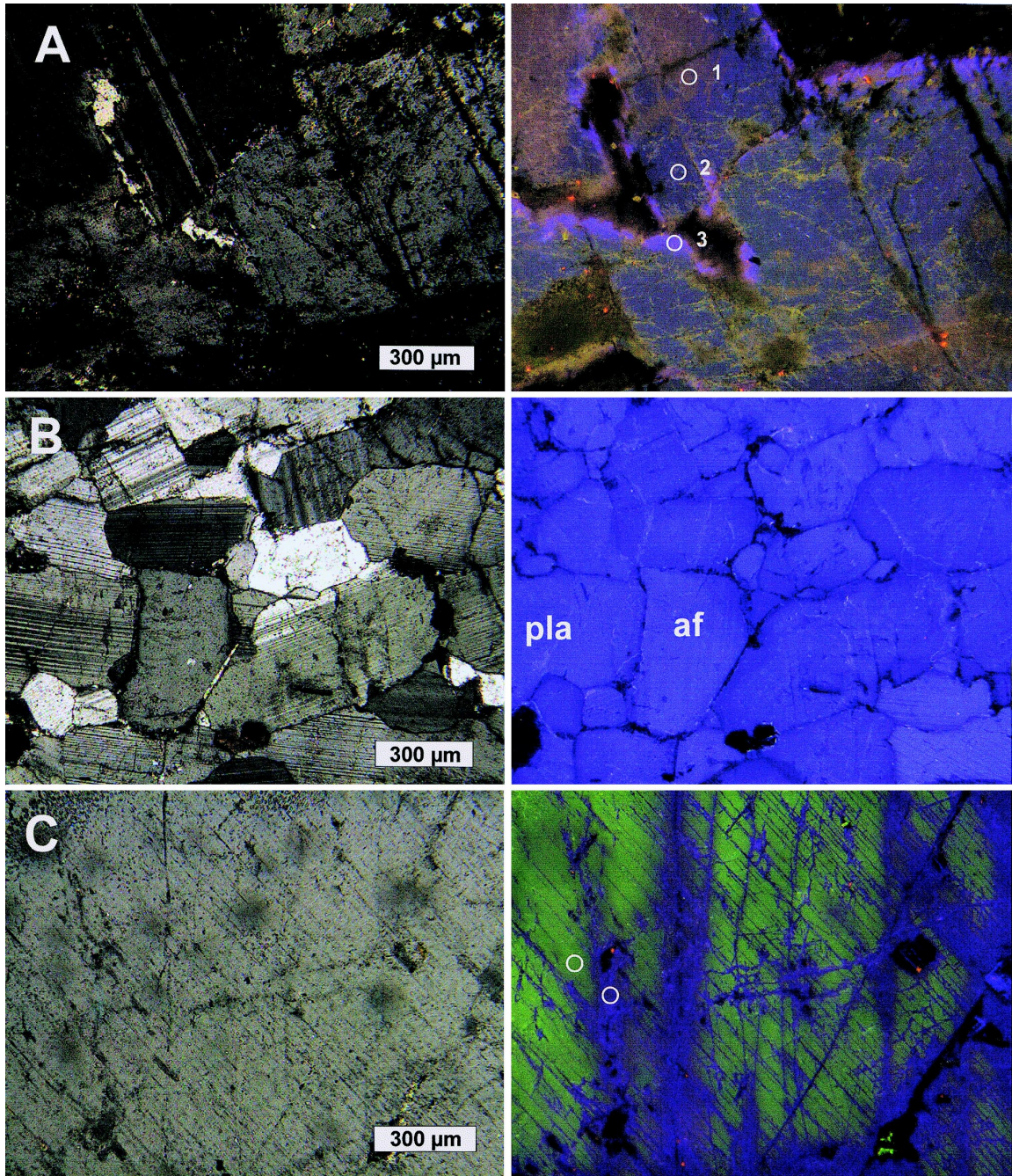


Fig. 1. Crossed polars (left) and CL image (right) pairs of micrographs of selected feldspar samples. (A) Labradorite (An67) from Bautzen, Germany showing CL zonation with reddish-green (1), blue (2) and violet (3) luminescence (CL spectra, see Fig. 2); (B) alkali feldspar (Or18-af) intergrown with oligoclase (An20-pla) in a granulite sample from Waldheim, Germany showing homogeneous deep blue CL (CL spectrum, see Fig. 3); (C) albite (Or13) from Spruce Pine, NC, USA with primary green CL and strong REE-activated blue-violet CL colours in secondary fissures probably resulting from hydrothermal alteration (CL spectra, see Figs. 5 and 6).

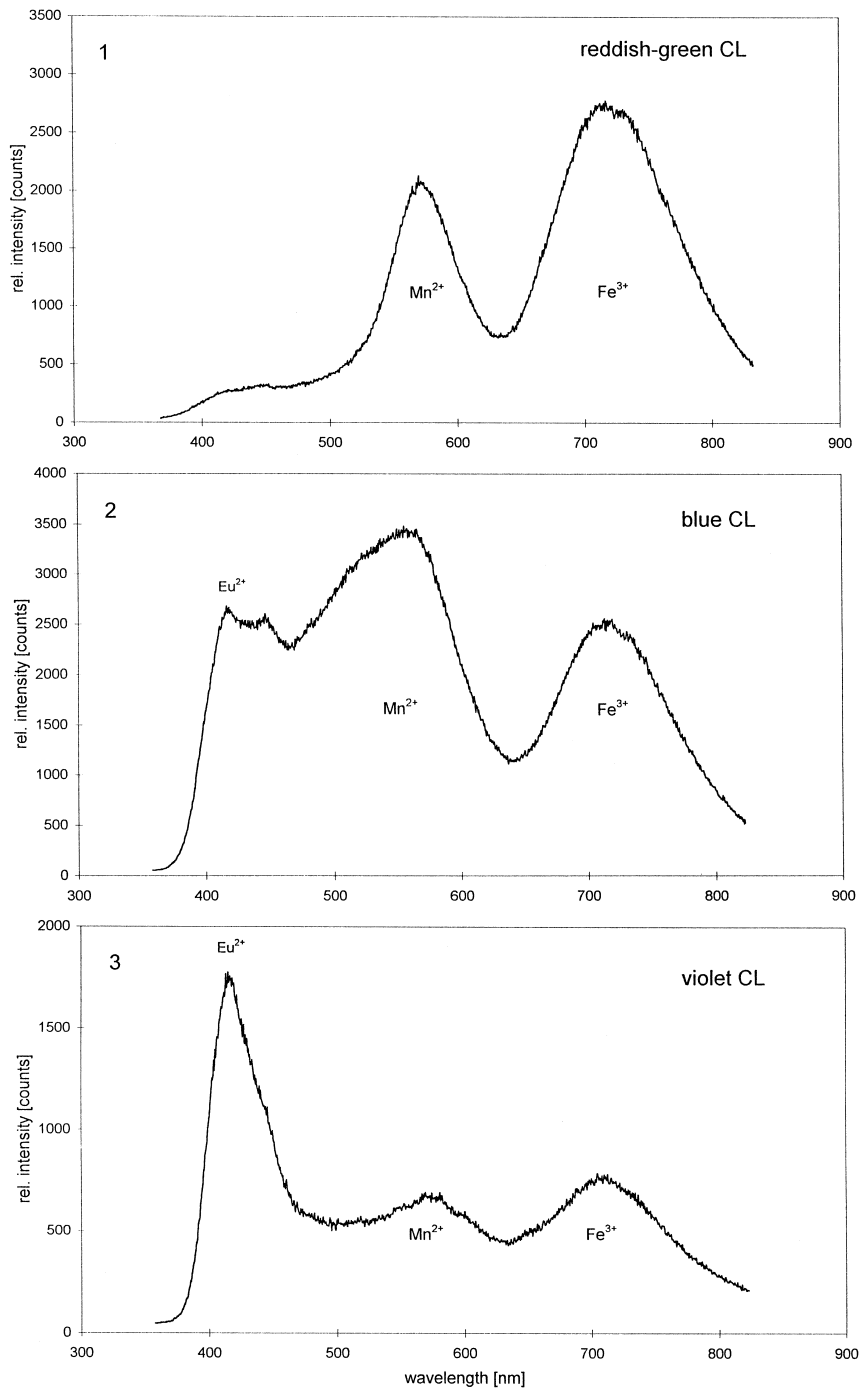


Fig. 2. CL emission spectra of differently luminescing zones (1–3) in a labradorite sample from Bautzen, Germany (compare Fig. 1A); the violet luminescing zone shows an intense emission band at ~ 420 nm due to Eu^{2+} activation.

REE³⁺ and REE²⁺ especially substitute Ca²⁺ in the structural M-site of plagioclases (Gorobets et al., 1989). Europium is one of the elements which is accepted for substitution in the feldspar structure because of similar ionic size and charge to calcium. Most of the natural alkali feldspars and plagioclases, however, rarely contain more than a few parts per million of europium. Accordingly, visible CL emission is often not detectable, especially when covered by strong emissions caused by other activator elements or defects. In such case Eu²⁺ can be detected using high-resolution spectral CL.

Mariano et al. (1973) reported a broad band emission of Eu²⁺ at approximately 420 nm in a doped (200 ppm Eu) synthetic anorthite showing deep blue luminescence. In natural samples, the blue-violet

Eu²⁺-activated luminescence was especially detected in plagioclases of hydrothermal and Greisen deposits, and regional metamorphic rocks. Gorobets et al. (1989) concluded that it is rare in plagioclases of granitoids, crustal pegmatites and REE formations.

Our studies showed that the concentration of Eu can be heterogeneous within a single feldspar crystal. The investigation of visible CL zonings by spectral measurements with a spatial resolution of about 30 μm revealed that the emission spectra of such distinct zones can vary significantly. Fig. 1(A) shows a CL micrograph of a labradorite (An67) from Bautzen, Germany exhibiting at least three zones with red-dish-green (1), blue (2) and violet (3) CL, which are not discernible using conventional polarizing microscopy. The associated CL spectra in Fig. 2 illus-

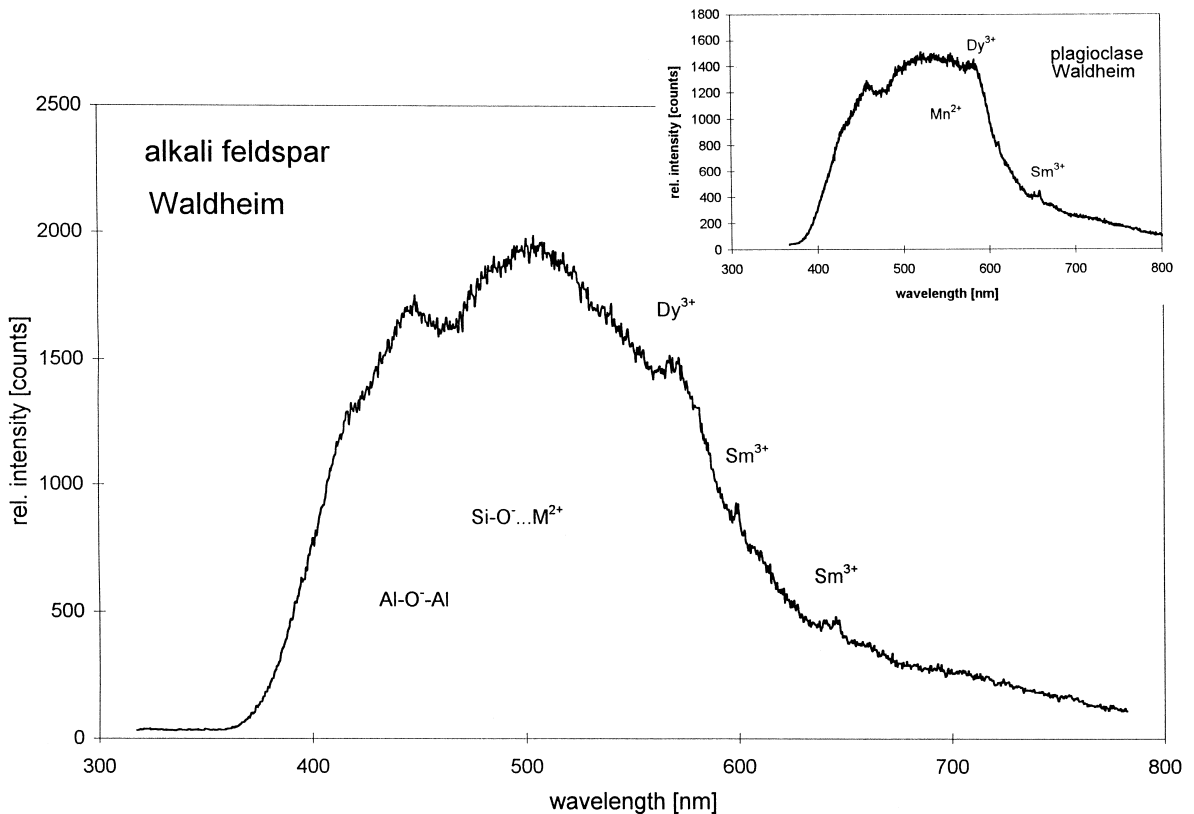


Fig. 3. CL emission spectrum of a blue luminescing alkali feldspar (Or18) from Waldheim, Germany (compare Fig. 1B); the spectrum is dominated by two emission bands at 450 and 500 nm which can be related to structural defects (Al–O[–]–Al and Si–O[–]...M²⁺ centres, respectively), but also reveals additional low-intensity CL activation by Dy³⁺ and Sm³⁺. The CL spectrum of the plagioclase (inset) also shows strong emissions in the blue but a broadening of the band between 500 and 600 nm due to an additional emission of Mn²⁺ at ca. 560 nm. The visible CL colour of alkali feldspars and plagioclases is very similar (compare Fig. 1B).

trate that the spectrum of the violet luminescing zone (outer rim) is dominated by a broad band emission at ~ 420 nm which can be related to Eu^{2+} activation. This emission band is caused by the transition between the $4f^65s^25p^65d^1$ excited state configuration and the $^8S_{7/2}$ level of the $4f^75s^25p^6$ ground state configuration (Mariano and Ring, 1975). In the other crystal areas Mn^{2+} - and Fe^{3+} -activated CL dominates and Eu^{2+} -activated CL emission is weak or absent.

Although the presence of REE in feldspars is not always indicated by the visible CL colour, these elements are clearly detectable by high-resolution spectral CL. Fig. 3 shows the CL emission spectrum of a homogeneously blue luminescing alkali feldspar (Or18) originated from the granulite of Waldheim, Germany (compare CL image in Fig. 1(B)). The presence of very low CL intensity activated by trivalent REE is proved in the CL spectra by distinct narrow-band peaks which can be assigned to Dy^{3+} and Sm^{3+} . The REE are inherited in concentrations below the detection limit of electron microprobe or PIXE. The criterion for distinguishing the peaks in the CL spectra from the background was used according to Homman et al. (1994). The minimum acceptable CL peak area is $3(N_b)^{1/2}$, where N_b is the amplitude of the background at the peak.

The influence of the crystal field on shape and position of REE luminescence spectra significantly differs for divalent and trivalent REE ions. The broad band emission of Eu^{2+} (~ 420 nm) is influenced by the local crystal field. This influence on the energy levels can cause wavelength shifts of this Eu^{2+} -activated CL emission. In contrast, trivalent ions of the rare earth show narrow emission lines which reflect the transitions between excited state wave functions lying inside closed electronic shells. These transitions are more or less shielded from the local crystal field and thus, the positions of the emission lines are relatively constant. This enables to identify rapidly the different REE $^{3+}$ emission peaks.

In certain feldspar samples strong REE-activated CL was observed which could be related to Sm^{3+} , Dy^{3+} , Nd^{3+} , and Tb^{3+} . In these feldspars REE accordingly play an important role in controlling CL. An albite sample (Or13) from Spruce Pine, NC, USA (see Fig. 1(C)) was selected for detailed presentation of REE $^{3+}$ -activated emission line positions

and to reveal variations of REE activation within a single feldspar crystal.

Using CL microscopy, two clearly different areas are distinguishable in the CL image which are not discernible by polarizing microscopy: (1) green CL, representing the CL characteristics of the primary crystal and (2) violet luminescing zones, which are probably due to secondary alteration processes. Trace element analysis by ICP-MS was carried out on the bulk sample to obtain more information about the chemical characteristics of this albite sample. The results of trace element analysis (Table 1) and the chondrite-normalized REE distribution patterns in Fig. 4 show a strong negative Eu anomaly and a relative enrichment of the heavy REE Ho–Lu.

Combined analyses by high-resolution spectral CL and PIXE were carried out separately on the green and violet luminescing crystal zones to explain this REE distribution pattern. The CL spectra are compared in Fig. 5. The CL emission spectrum of the

Table 1

Trace element composition (ppm) of the albite sample (Or18) from Spruce Pine, NC, USA determined in the bulk sample by ICP-MS and in differently luminescing crystal zones by PIXE

	Albite bulk sample ICP-MS	Albite 1 green CL PIXE	Albite 2 violet CL PIXE
Ga	25.2	50.4	45.7
B	3.5	nd	nd
Fe	126	124	99
Mn	8.0	18.3	1.3
Pb	37.0	52.4	50.1
Sr	nd	16.6	13.2
Y	6.38	8.4	7.8
La	27.4	95.7	61.6
Ce	49.5	140	122
Pr	6.02	nd	nd
Nd	18.38	33.5	39.8
Sm	3.28	(8.8)	(5.3)
Eu	0.06	5.9	< 0.1
Gd	2.01	(0.0)	3.0
Tb	0.26	(1.4)	(1.6)
Dy	0.98	(2.4)	(4.2)
Ho	0.14	nd	nd
Er	0.38	nd	nd
Tm	0.06	nd	nd
Yb	0.43	2.0	8.8
Lu	0.07	nd	nd

nd—Not determined.

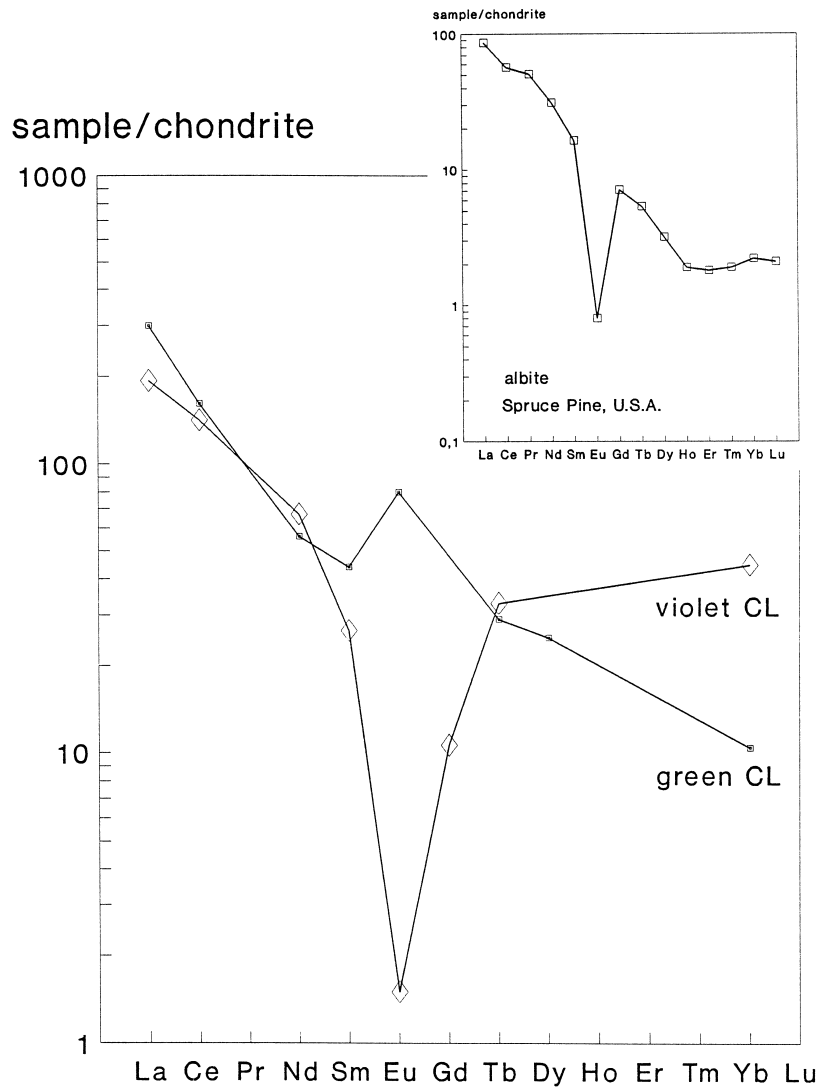


Fig. 4. Chondrite-normalized REE distribution pattern of the bulk albite sample from Spruce Pine, NC (inset) and the green and violet luminescing zones. Trace element analyses were obtained by ICP-MS (bulk sample) and PIXE (separate zones).

green luminescing grain area is dominated by Mn^{2+} -activated CL with a broad band around 560 nm. The Mn concentration was determined by PIXE to be 18.3 ppm. This confirms earlier results of Mora and Ramseyer (1992) and Götze et al. (1998) that Mn concentrations < 20 ppm can activate the green CL emission in feldspars. The REE-activated CL in this zone is hidden by the dominant Mn^{2+} and partly by the Fe^{3+} emission. Only small peaks of Dy^{3+} and Sm^{3+} are detectable.

The luminescence bands caused by the transition elements Mn^{2+} and Fe^{3+} are due to electron transitions of the outer, partially filled 3d shell (Marfunin, 1979). In this case, the energy levels are influenced by the crystal field and the peak positions can vary. Although the wavelength of the green peak (~ 560 nm) cannot directly be correlated with the feldspar composition, Mora and Ramseyer (1992) reported a shift toward shorter wavelength with increasing anorthite content. The red peak shifts from 688 to 740

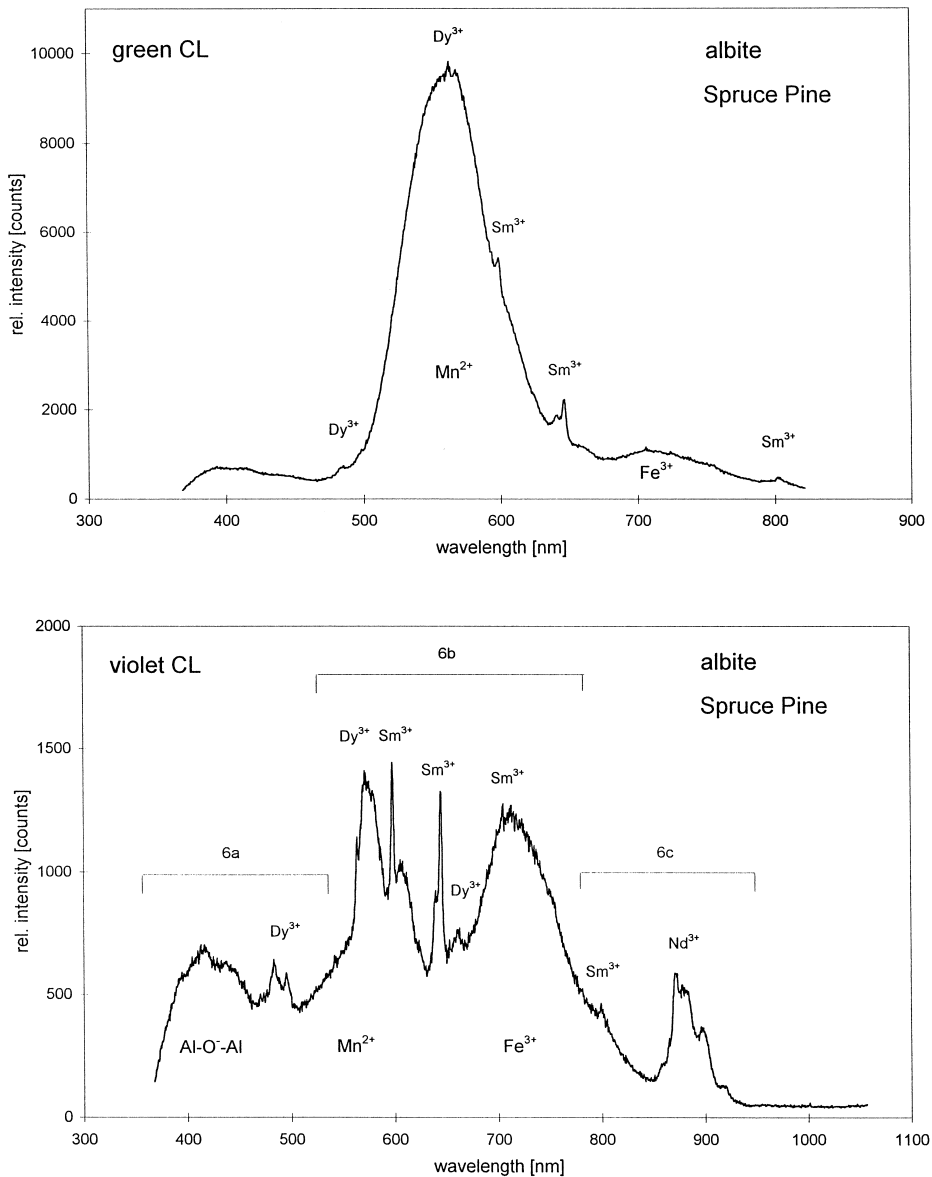


Fig. 5. CL emission spectra of an albite (Or18) sample from Spruce Pine, NC, USA characterizing the primary green luminescing crystal and the alteration zones showing blue-violet CL (compare Fig. 1C). The resolved spectra are shown in Fig. 6a–c.

nm over the range An_{98} – An_5 (Götze et al., 1998). Both the structural state of the plagioclase and the tetrahedral site occupancy of Fe^{3+} can affect the position of the red peak (Telfer and Walker, 1978; Petrov et al., 1989). Furthermore, the existence of incommensurate structures within the plagioclase series can influence the position of the red peak. In the

intermediate composition around An_{50} plagioclases exsolve and can form lamellar intergrowths (Putnis, 1992). Probably, these structural peculiarities can explain the existence of a slight splitting of peaks around 700 nm (cf. Fig. 2(1) and (2)).

The CL emission spectrum of the violet luminescing zone shows strong REE³⁺-activated CL, espe-

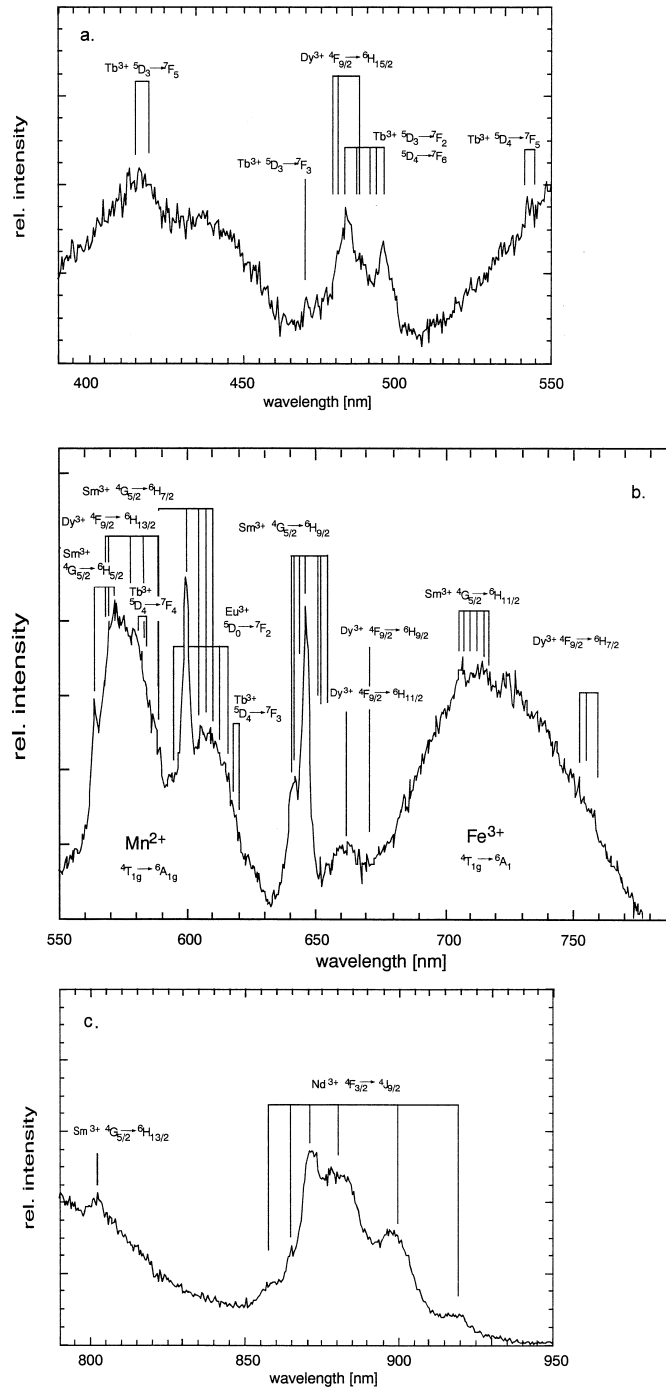


Fig. 6. Resolved CL emission spectra a–c of the albite from Spruce Pine, NC, USA with characteristic electron transition energies of the specific REE³⁺ ions.

cially of Dy³⁺, Sm³⁺ and Nd³⁺. These narrow-band emissions can be related to transitions of electrons of the partly filled 4f shell which is shielded by the filled 5s and 5p orbitals. Thus, the positions of these peaks and the characteristic energies can be described for the different REE (Marfunin, 1979). In Fig. 6 (resolved spectra a–c) the narrow lines are attributed to the specific electron transitions which are more or less constant in all feldspars.

The significant differences in the CL emission spectra of the green and violet luminescing zones of the albite are also reflected in the specific trace element compositions of these zones. The chondrite normalized REE contents determined by PIXE (see Table 1 and Fig. 4) show that the primary green luminescing albite has a common pattern with high LREE, low HREE and a distinct positive Eu anomaly. The supposed alteration processes in the violet luminescing zone have caused a strong negative Eu anomaly and a relative enrichment of HREE. Moreover, the contents of Mn and Fe are depleted. Accordingly, the REE distribution pattern of the bulk sample (Fig. 4) reflects the overlapping of the characteristic features of these two crystal zones. Using combined optical and spectral CL and spatial resolved trace element analysis by PIXE these characteristics are clearly distinguishable.

4. Conclusions

The investigation of more than 50 feldspar samples of the orthoclase–albite–anorthite ternary system by high-resolution spectral CL showed that REE-activated CL in feldspars is more common than concluded from previous studies. Although the REE concentrations in many natural samples are below the detection limits of spatial resolved analytical methods such as microprobe or PIXE, specific REE are detectable by distinct narrow-band emission peaks using a highly sensitive spectrometer.

In certain feldspar samples the visible CL colour appears to result from a combination of the characteristic broad-band emissions in the blue (~ 450 nm due to Al–O[–]–Al), yellow (~ 560 nm due to Mn²⁺) and red (~ 700 nm due to Fe³⁺) with a broad-band emission at ~ 420 nm due to Eu²⁺ or several nar-

row-band emissions which can be related to specific REE³⁺ ions. The resulting CL colour depends on the intensity ratios of these emission bands and thus, is not an unambiguous characteristic of one element.

In some cases optical CL revealed zones with different CL colours within separate feldspar grains which show significantly different REE contents. The different zones reflect changes during feldspar crystallization and/or element fluctuations during secondary alteration processes. Here, CL spectroscopy is a powerful method which reveals small-scale changes in the REE distribution often below the detection limit of common microprobe.

References

- Černý, P., 1994. Evolution of feldspars in granitic pegmatites. In: Parsons, I. (Ed.), *Feldspars and Their Reactions*. NATO ASI Ser. C 421. Kluwer, Dordrecht, 501–540.
- Geake, J.E., Walker, G., Telfer, D.J., Mills, A.A., Garlick, G.F.J., 1973. Luminescence of lunar, terrestrial, and synthesized plagioclase, caused by Mn²⁺ and Fe³⁺. *Proceedings of the Fourth Lunar Sci. Conf. Geochim. Cosmochim. Acta* 3 (Suppl. 4) 3181–3189.
- Gorobets, B.S., Gaft, M.L., Podolskiy, A.M., 1989. *Luminescence of Minerals and Ores*. Ministry of Geology USSR, Moscow, 53 pp., in Russian.
- Götze, J., Krbetschek, M.R., Habermann, D., Wolf, D., 1998. High-resolution cathodoluminescence of feldspar minerals. In: Pagel, M., Barbin, V., Blanc, Ph., Ohnenstetter, D. (Eds.), *Cathodoluminescence in Geosciences*. Springer-Verlag, Berlin, in press.
- Habermann, D., 1997. *Quantitative hochauflösende kathodolumineszenz-spektroskopie von calcit und dolomit*. PhD Thesis. Ruhr-University Bochum, 152 pp.
- Habermann, D., Neuser, R.D., Richter, D.K., 1996. REE-activated cathodoluminescence of calcite and dolomite: high-resolution spectrometric analysis of CL emission (HRS-CL). *Sed. Geol.* 101, 1–7.
- Homman, N.P.O., Yang, C., Malmquist, K.G., 1994. A highly sensitive method for rare-earth element analysis using ionoluminescence combined with PIXE. *Nucl. Instr. Methods Phys. Res. A* 353, 610–614.
- Kusnetsov, G.V., Kramarenko, N.K., 1995. Kinetic luminescence characteristics of Ce³⁺ in plagioclases as a guide for facial classification of granitoids. *Miner. J.* 17 (2), 86–90, in Russian.
- Laud, K.R., Gibbons, E.F., Tien, T.Y., Stadler, H.L., 1971. Cathodoluminescence of Ce³⁺ and Eu²⁺-activated alkaline earth feldspars. *J. Electrochem. Soc.* 118, 918–923.
- Marfunin, A.S., 1979. *Spectroscopy, Luminescence and Radiation Centres in Minerals*. Springer-Verlag, Berlin, 352 pp.

- Mariano, A.N., Ito, J., Ring, P.J., 1973. Cathodoluminescence of plagioclase feldspars. *Geol. Soc. Am. Abstr. Prog.* 5, 726.
- Mariano, A.N., Ring, P.J., 1975. Europium-activated cathodoluminescence in minerals. *Geochim. Cosmochim. Acta* 39, 649–660.
- Marshall, D.J., 1988. *Cathodoluminescence of Geological Material*. Allen & Unwin, London, 146 pp.
- Meijer, J., Stephan, A., Adamczewski, J., Bukow, H.H., Rolfs, C., Pickart, T., Bruhn, F., Veizer, J., 1994. PIXE microprobe for geoscience applications. *Nucl. Instr. Methods Phys. Res. B* 43, 229–232.
- Mora, C.I., Ramseyer, K., 1992. Cathodoluminescence of coexisting plagioclases, Boehls Butte anorthosite: CL activators and fluid flow paths. *Am. Miner.* 77, 1258–1265.
- Petrov, I., Yude, F., Bershov, L.V., Hafner, S.S., Kroll, H., 1989. Order-disorder of Fe^{3+} ions over the tetrahedral positions in albite. *Am. Miner.* 74, 604–609.
- Putnis, A., 1992. *Introduction to Mineral Sciences*. Univ. Press, Cambridge, 457 pp.
- Rokatschuk, T.A., Tscherbakov, I.B., Steschin, V.A., 1989. Genetic interpretation of the distribution of centres in plagioclases. *Miner. J.* 11 (5), 60–67, in Russian.
- Smith, J.V., Brown, W.L., 1988. *Feldspar Minerals: 1. Crystal Structures, Physical, Chemical and Microtextural Properties*, 2nd edn. Springer-Verlag, Heidelberg, 828 pp.
- Telfer, D.J., Walker, G., 1978. Ligand field bands of Mn^{2+} and Fe^{3+} luminescence centres and their site occupancy in plagioclase feldspars. *Mod. Geol.* 6, 199–210.