Application of cathodoluminescence microscopy and spectroscopy in geosciences

Jens Götze, TU Bergakademie Freiberg

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History of Cathodoluminescence in geosciences

1879  CROOKS
Luminescence studies on crystals after bombardment with a cathode ray

1965  SIPPEL, LONG & AGRELL
First application for thin section petrography

1965  SMITH & STENSTROM
Cathodoluminescence studies with the microprobe

1971  KRINSLEY & HYDE
Cathodoluminescence studies with the SEM

1978  ZINKERNAGEL
First CL microscope in Germany
Introduction

CL in geosciences - literature
Basics of luminescence
Bioluminescence
Photoluminescence
(UV excitation)

Agate (SiO$_2$)
Idar-Oberstein, Germany

Agate (SiO$_2$)
Montana, USA
Basics of luminescence

Primary electron beam

- Back scattered electrons
- Secondary electrons
- Auger electrons
- Specimen current
- Unscattered electrons
- Scattered electrons
- X-rays
- Cathodoluminescence

Electron beam interaction with a solid

Yacobi & Holt (1990)
Basics of luminescence

Luminescence = transformation of diverse kinds of energy into visible light

... results from an emission transition of anions, molecules or a crystal from excited electronic states to the ground state or a state with lower energy.
(Marfunin 1979)

(1) absorption of excitation energy and stimulation of the system into an excited state

(2) transformation and transfer of the excitation energy

(3) emission of light and relaxation of the system into an unexcited condition
Basics of luminescence

How can we use the luminescence signal??

Visualization of the defect (real) structure of solids by CL

Luminescence centres

lattice defects
(broken bonds, vacancies)

trace elements
(Mn$^{2+}$, REE$^{2+/3+}$, Cr$^{3+}$, etc.)
Basics of luminescence

How can we use the luminescence signal??

(1) CL microscopy
- contrasting of different phases
- visualization of defects, zoning and internal structures of solids

(2) CL spectroscopy
- determination of the real structure
- detection of trace elements, their valence and structural position

Apatite $\text{Ca}_5[F/(\text{PO}_4)_3]$
Basics of luminescence

CL emission

Influence of the crystal field

= local environment of the activator ion

- type of the activator ion (size, charge)
- type of the ligands
- the interaction distance
- local symmetry of the ligand environment, etc.
Basics of luminescence

Influence of the crystal field on CL emission spectra
(2) influence of the crystal field = weak

CL spectra of narrow emission lines (e.g. REE\(^{3+}\))

CL emission spectra are specific of the activator ion
**Basics of luminescence**

**Influence of the crystal field on CL emission spectra**

(2) influence of the crystal field = strong

- **calcite** yellow-orange (~615 nm)
- **aragonite** green (~560 nm)
- **magnesite** red (~655 nm)

CL spectra of broad emission bands (e.g. Mn$^{2+}$)

CL emission spectra are specific of the host crystal
Basics of luminescence

Influence of the crystal field on CL emission spectra

(2) influence of the crystal field = strong

Position of the Fe$^{3+}$ activated CL emission band in plagioclase solid solutions in relation to the anorthite content
Instrumentation

→ all electron beam instruments
Scanning Electron Microscope JEOL 6400 with OXFORD Mono-CL detector
Instrumentation

Hot-cathode luminescence microscope HC1-LM

CL microscope with attached CCD based video camera

Computer aided image analysis

electronic steerage

vacuum pumps
Cold-cathode luminescence microscope (CITL) (Cambridge Instruments)

Instrumentation

Electron beam generated by an ionized gas
### Cathodoluminescence Techniques

<table>
<thead>
<tr>
<th>SEM-CL</th>
<th>CL Microscopy</th>
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<tbody>
<tr>
<td>polished sample surface</td>
<td>polished thin (thick) section</td>
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<tr>
<td>focused electron beam, scanning mode</td>
<td>defocused electron beam, stationary mode</td>
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<tr>
<td>heated filament 20 kV, 0.5-15 nA</td>
<td>heated filament („hot cathode“) 14 kV, 0.1-0.5 mA ionized gas („cold cathode“)</td>
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<td>mirror optics: 200-800 nm (UV - IR)</td>
<td>glass optics: 380-1200 nm (Vis - IR)</td>
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<td>analytical spot ca. 1 µm</td>
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<td>true luminescence colours</td>
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<td>resolution &lt;&lt; 1 µm</td>
<td>resolution 1-2 µm</td>
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<td>SE, BSE, EDX/WDX, cooling stage</td>
<td>polarizing microscopy, (EDX)</td>
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Götze & Kempe (2008)
**Sample preparation**

**Polished thin section**

- 28 x 48 mm
- Sample thickness ca. 30 µm

**Sample holder for fluid inclusion preparations**

- 28 x 48 mm
- Sample thickness 100 - 300 µm

→ application for all CL equipments

**Polished section**

- Pressed tablet (powder)

→ application for SEM-CL
### Cathodoluminescence techniques

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Instrumentation

Götze & Kempe (2008)
Comparison of CL spectra from SEM-CL and OM-CL measurements, respectively; note the differences in the UV region.
## Cathodoluminescence Techniques

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Instrumentation

Götze & Kempe (2008)
Instrumentation

Cathodoluminescence imaging

SE

zircon

BSE

quartz

CL

Cathodoluminescence microscopy
CL properties of selected minerals
Mineral groups and minerals showing CL

- in general all insulators and semiconductors

- elements: diamond

- sulfides: sphalerite

- oxides: corundum, cassiterite, periclase

- halides: fluorite, halite

- sulfates: anhydrite, alunite, baryte

- phosphates: apatite

- carbonates: calcite, aragonite, dolomite, magnesite

- silicates: feldspar, quartz, zircon, kaolinite, forsterite

- technical products (synthetic minerals, ceramics, glasses !)

- no luminescence of conductors, iron minerals and Fe-rich phases
Mineral groups and minerals showing CL

- in general all insulators and semiconductors

  elements          diamond
  sulfides          sphalerite
  oxides            corundum, cassiterite, periclase
  halides           fluorite, halite
  sulfates          anhydrite, alunite, baryte
  phosphates        apatite
  carbonates        calcite, aragonite, dolomite, magnesite
  silicates         feldspar, quartz, zircon, kaolinite, forsterite

  close relationship between specific conditions of mineral formation, real structure and CL properties may provide important genetic information

  = typomorphic properties
Quartz ($\text{SiO}_2$)

12.6% of the Earth's crust
Quartz

Cathodoluminescence (CL) of quartz (SiO₂)

CL properties of quartz from different geological environments
Defects mainly caused by:

- Vacancies of silicon and/or oxygen
- Oxygen excess
- Structural incorporation of trace elements

Real structure of quartz

- SiO$_4$ tetrahedron
- Silanol groups
- Oxygen vacancy
- Peroxy linkage
- Hole trapped on nonbridging oxygen
- Nonbridging oxygen
- Substitutional isoelectronic cation
- Substitutional heteroelectronic and interstitial cations
- Peroxy radical