Basics and potential of cathodoluminescence in metamorphic petrology

Jens Götze

Institute of Mineralogy
TU Bergakademie Freiberg, Germany

Content

1. Basics of luminescence

- physical basics
- instrumentation
- general applications

2. Application of CL in metamorphic petrology

- identification of minerals, mineral distribution
- primary growth structures
- secondary features

  (deformation - recrystallization - fluid flow - alteration - mineral neoformation)
- examples of technical processes

3. Conclusions

Basics of luminescence

Literature

Literature

Unwin-Hyman
Boston

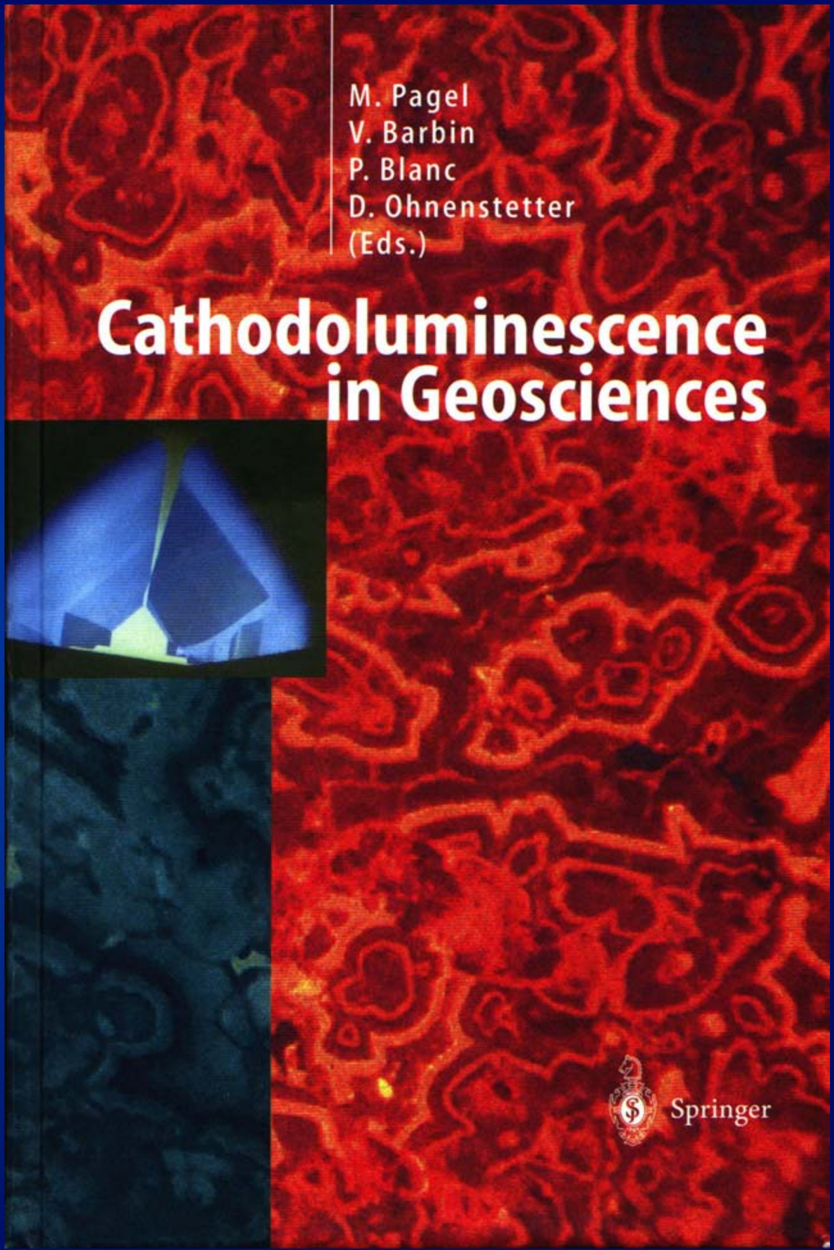
1988

Cathodoluminescence of geological materials

D.J. Marshall

Unwin-Hyman Ltd.

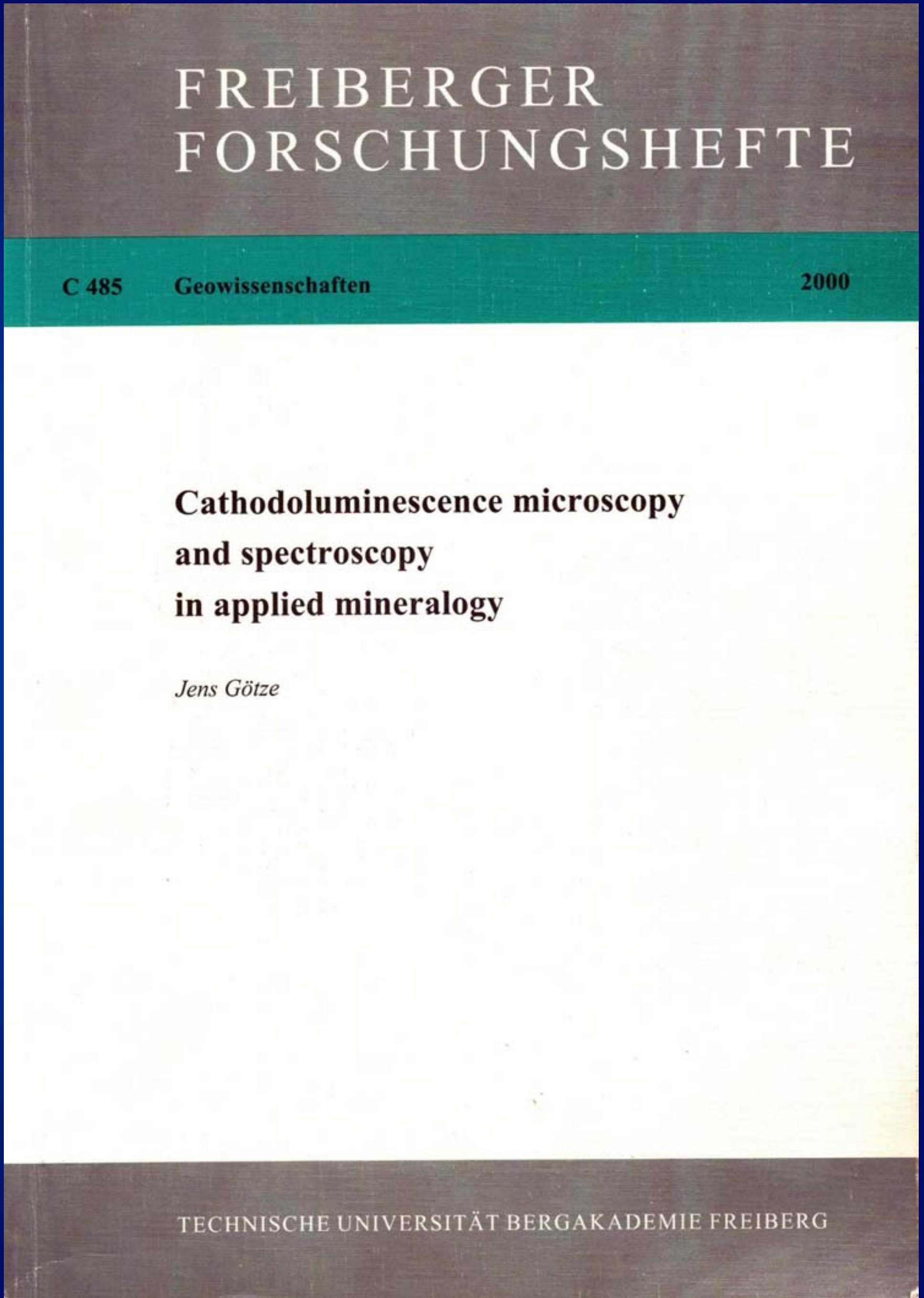
Literature



Springer-Verlag
Berlin, Heidelberg, New York
2000

ISBN 3-540-65987-0

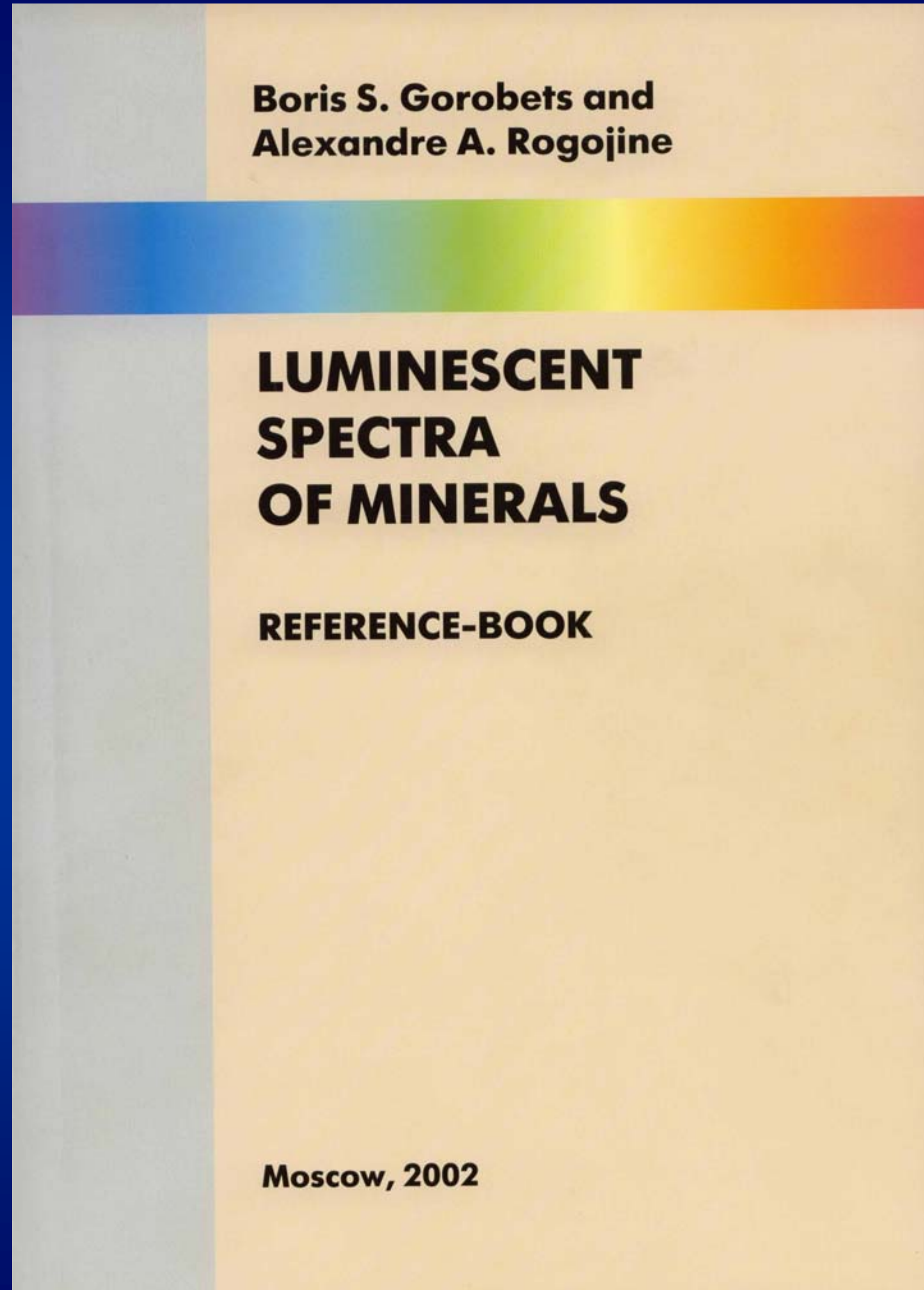
Literature



TU Bergakademie Freiberg
Akademische Buchhandlung
Merbachstraße, PF 203
D-09599 Freiberg

ISBN 3-86012-116-2

Literature



All-Russia Institute of Mineral Resources (VIMS)
Moscow
2002

ISBN 5-901837-05-3

History of cathodoluminescence

History of Cathodoluminescence

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

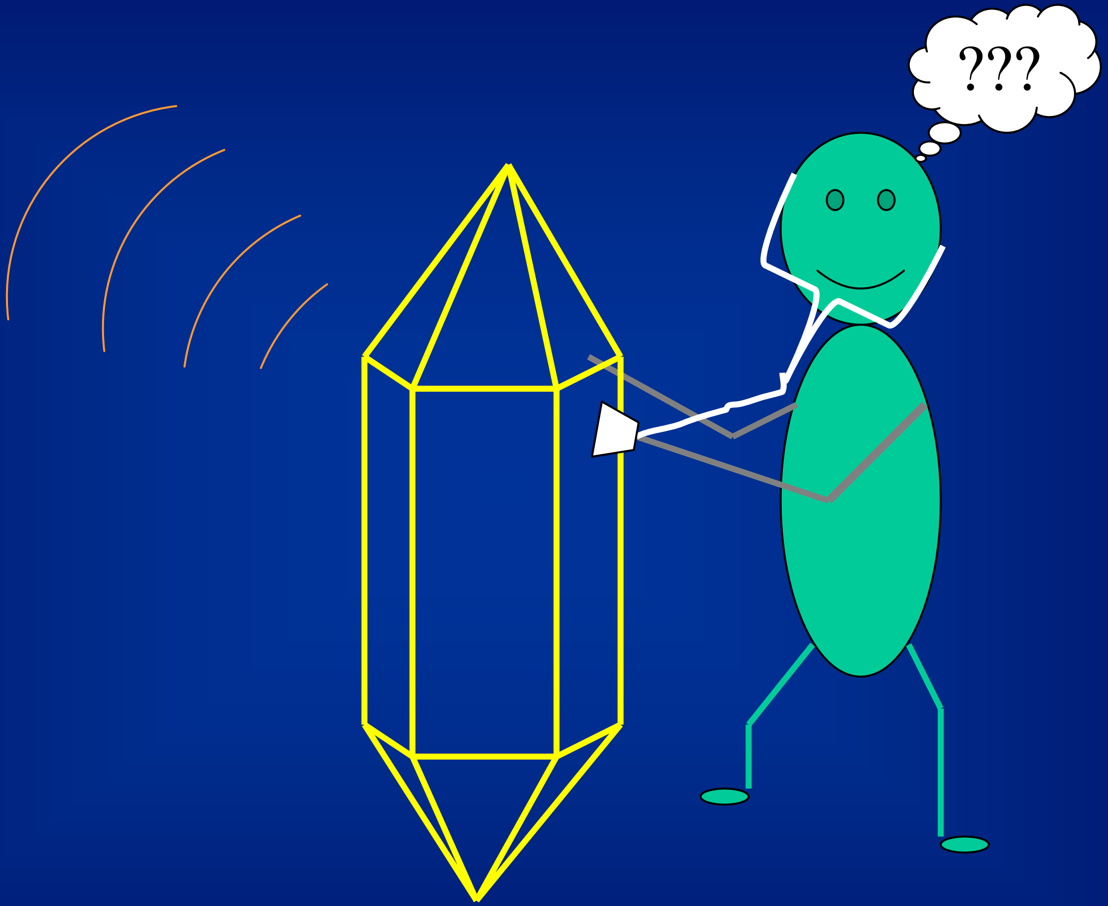
1965 ***SIPPEL, LONG & AGRELL***
First application for thin section petrography

1965 ***SMITH & STENSTROM***
Cathodoluminescence studies with the microprobe

1971 ***KRINSLEY & HYDE***
Cathodoluminescence studies with the SEM

1978 ***ZINKERNAGEL***
First CL microscope in Germany

Basics of luminescence



Luminescence

= transformation of diverse kinds of energy into visible light

Luminescence of inorganic and organic substances results from an emission transition of anions, molecules or a crystal from an excited electronic state to a ground state with lesser energy.

(Marfunin1979)

***Fluorescence* =** **luminescence emission with a lifetime $\leq 10^{-8}$ s**

***Phosphorescence* =** **luminescence emission with a lifetime $> 10^{-8}$ s**

Main processes of luminescence

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

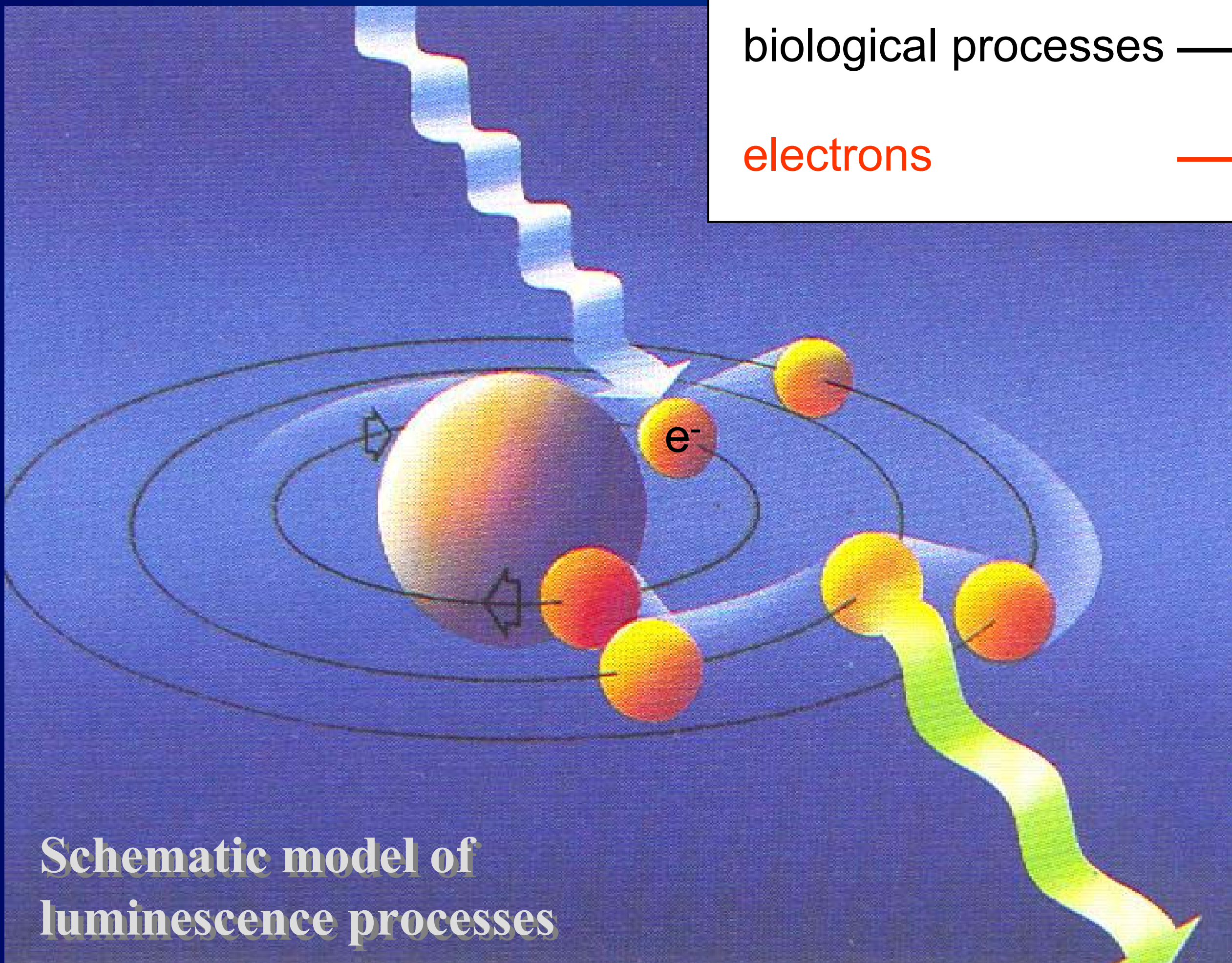
(2) transformation and transfer of the excitation energy

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

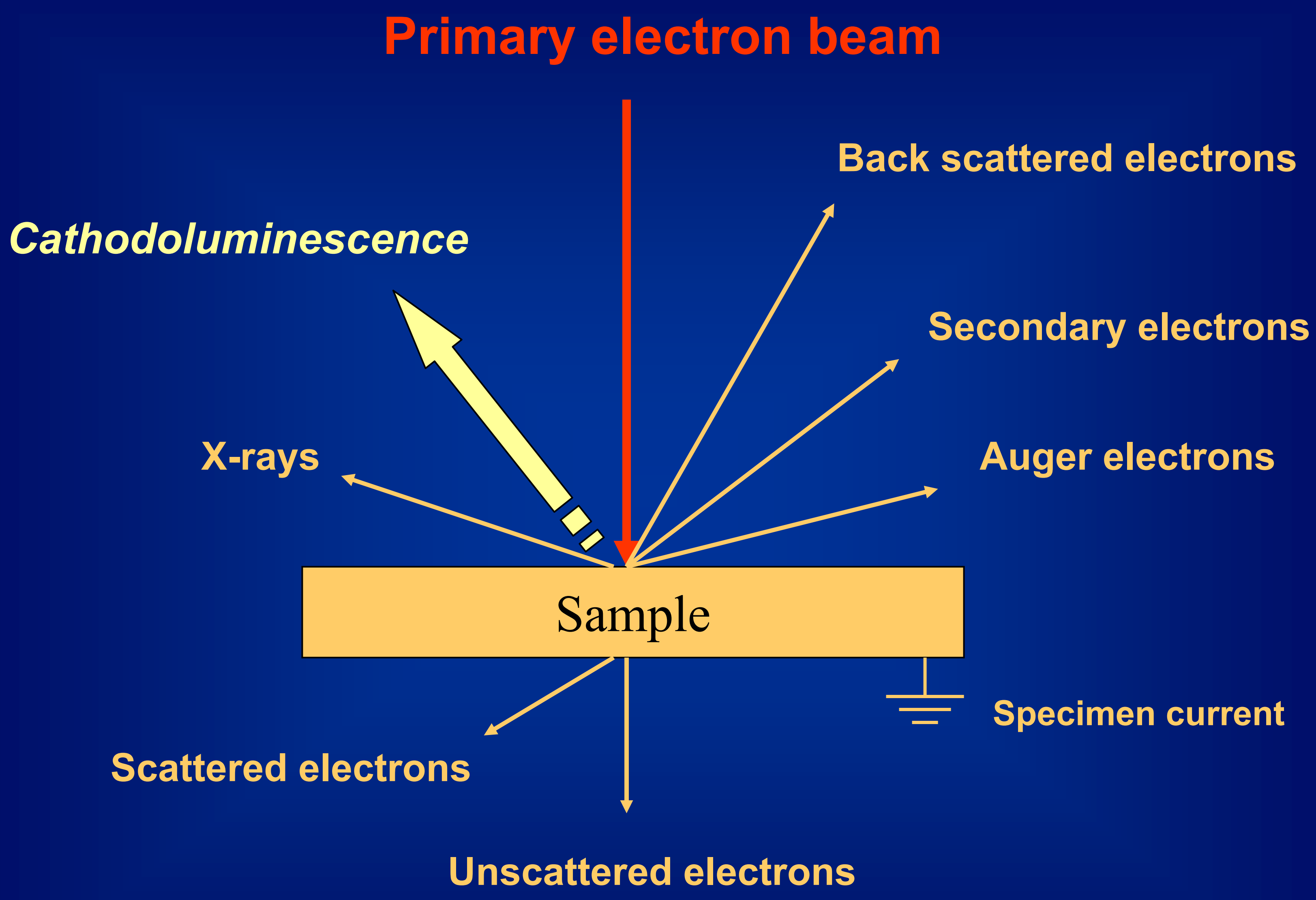
Basics of luminescence

UV	→	photoluminescence
thermal excitation	→	thermoluminescence
biological processes	→	bioluminescence
electrons	→	cathodoluminescence

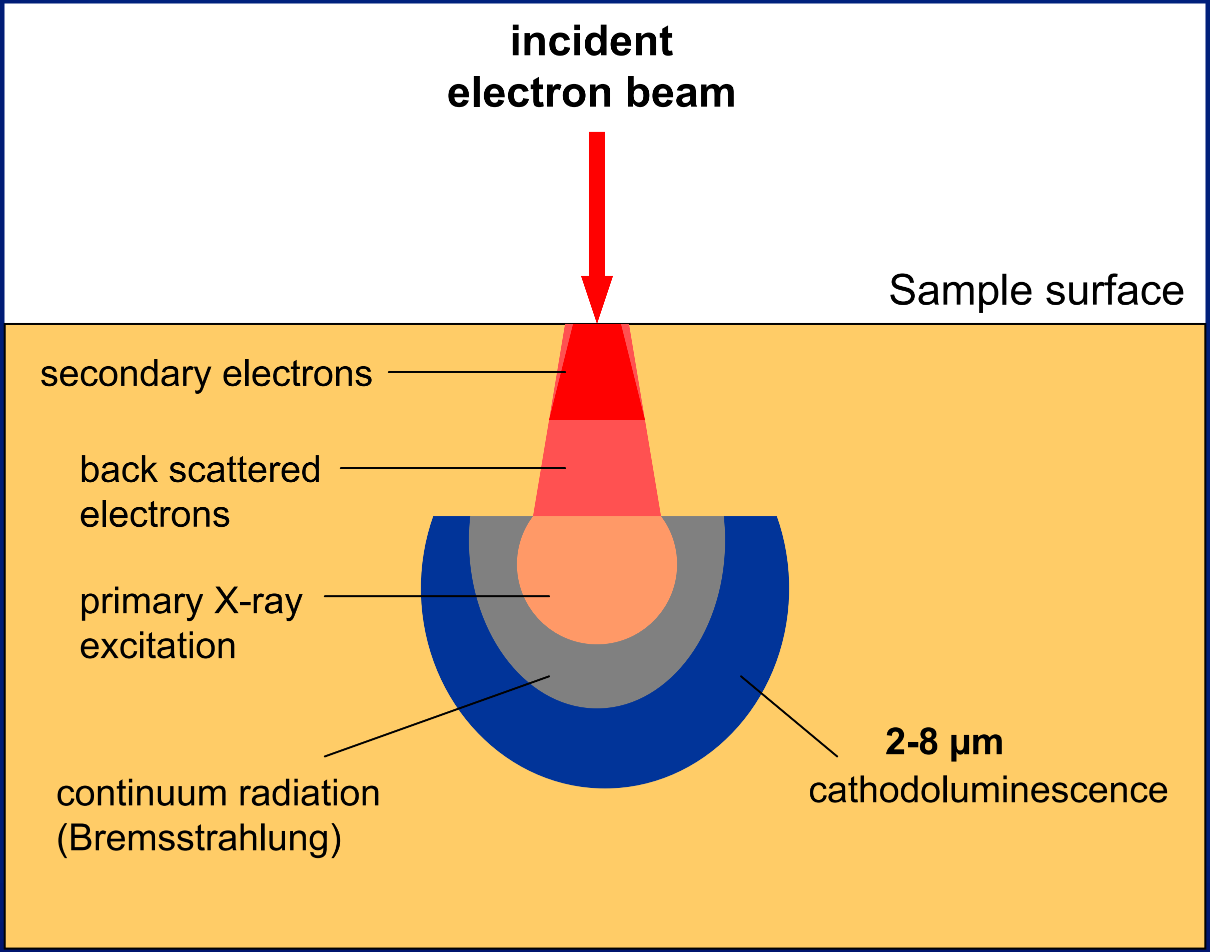
Excitation by energy



Emission of light

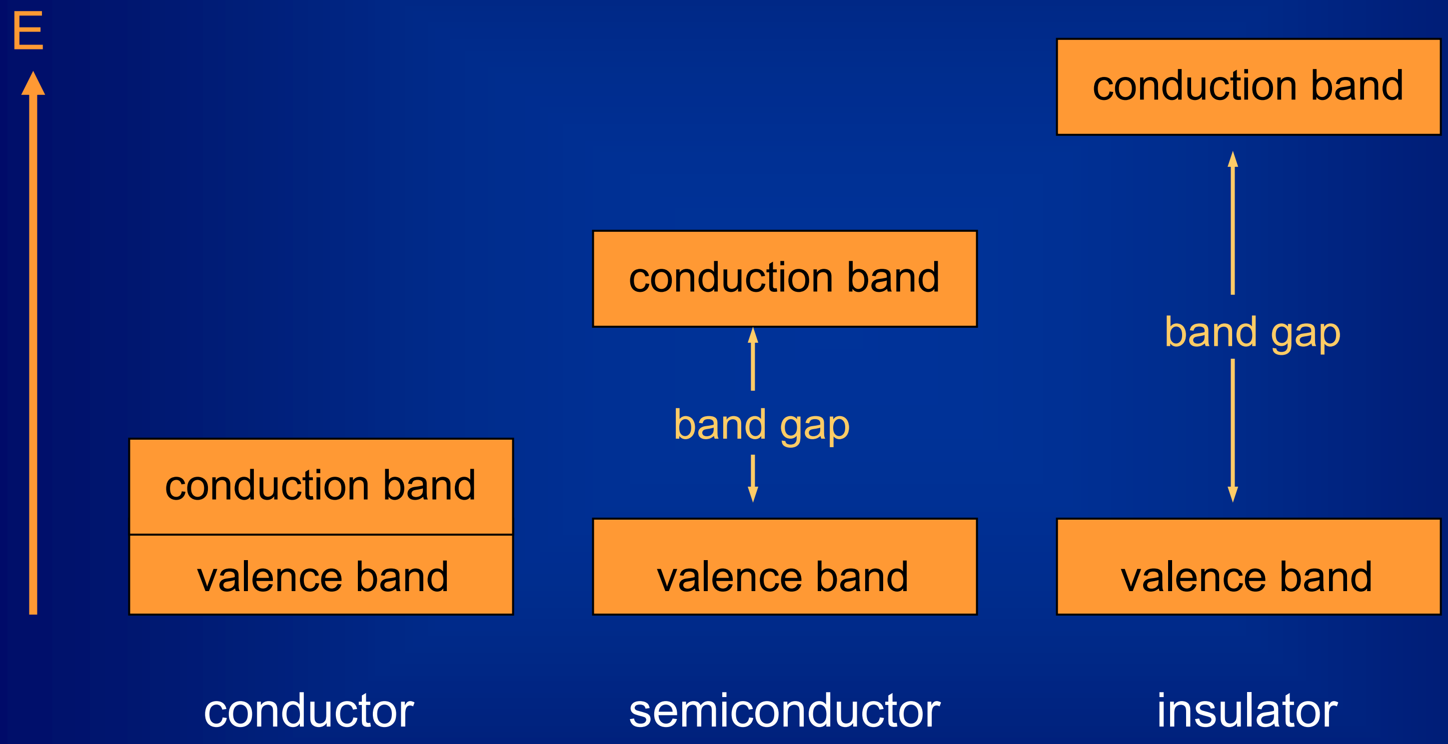

Primary electron beam
Back scattered electrons
Cathodoluminescence
Secondary electrons
X-rays
Auger electrons
Sample
Specimen current
Scattered electrons
Unscattered electrons

Electron beam interaction with a solid

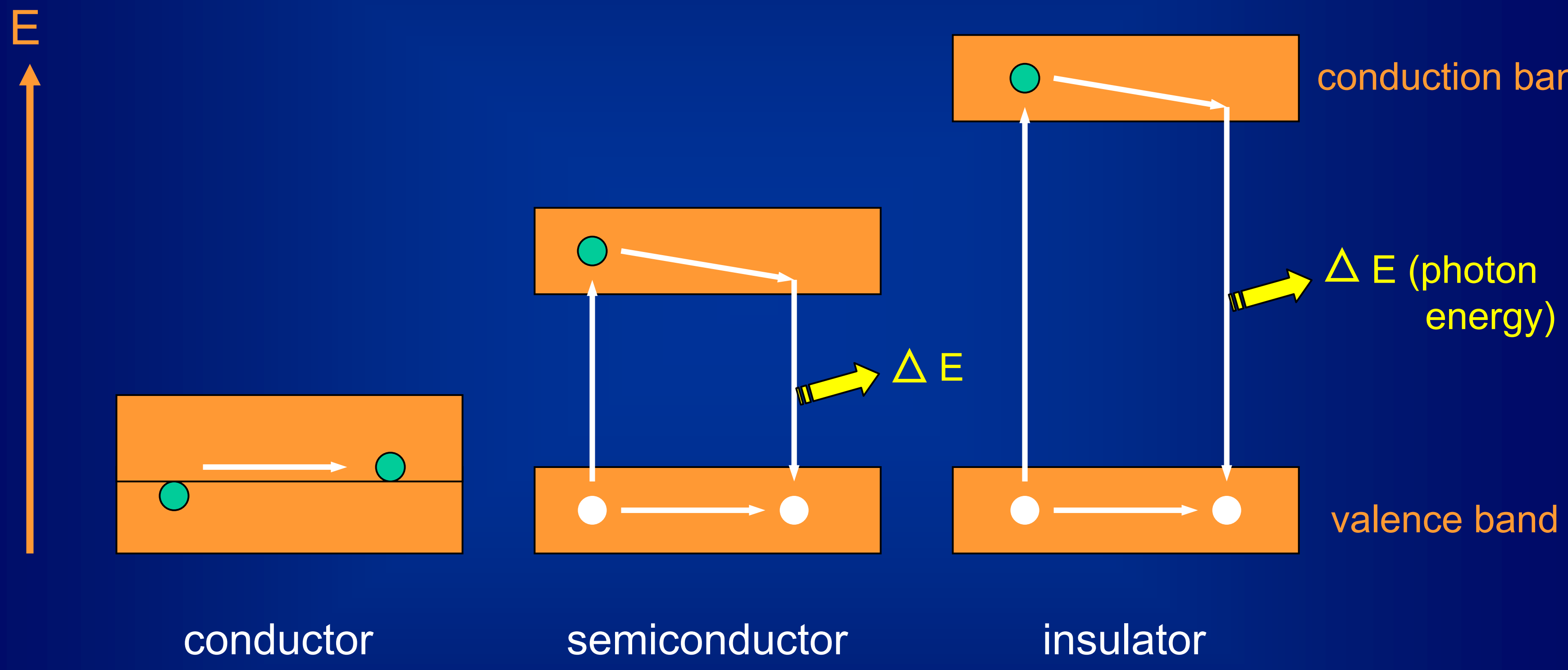


The band model

Basics of luminescence

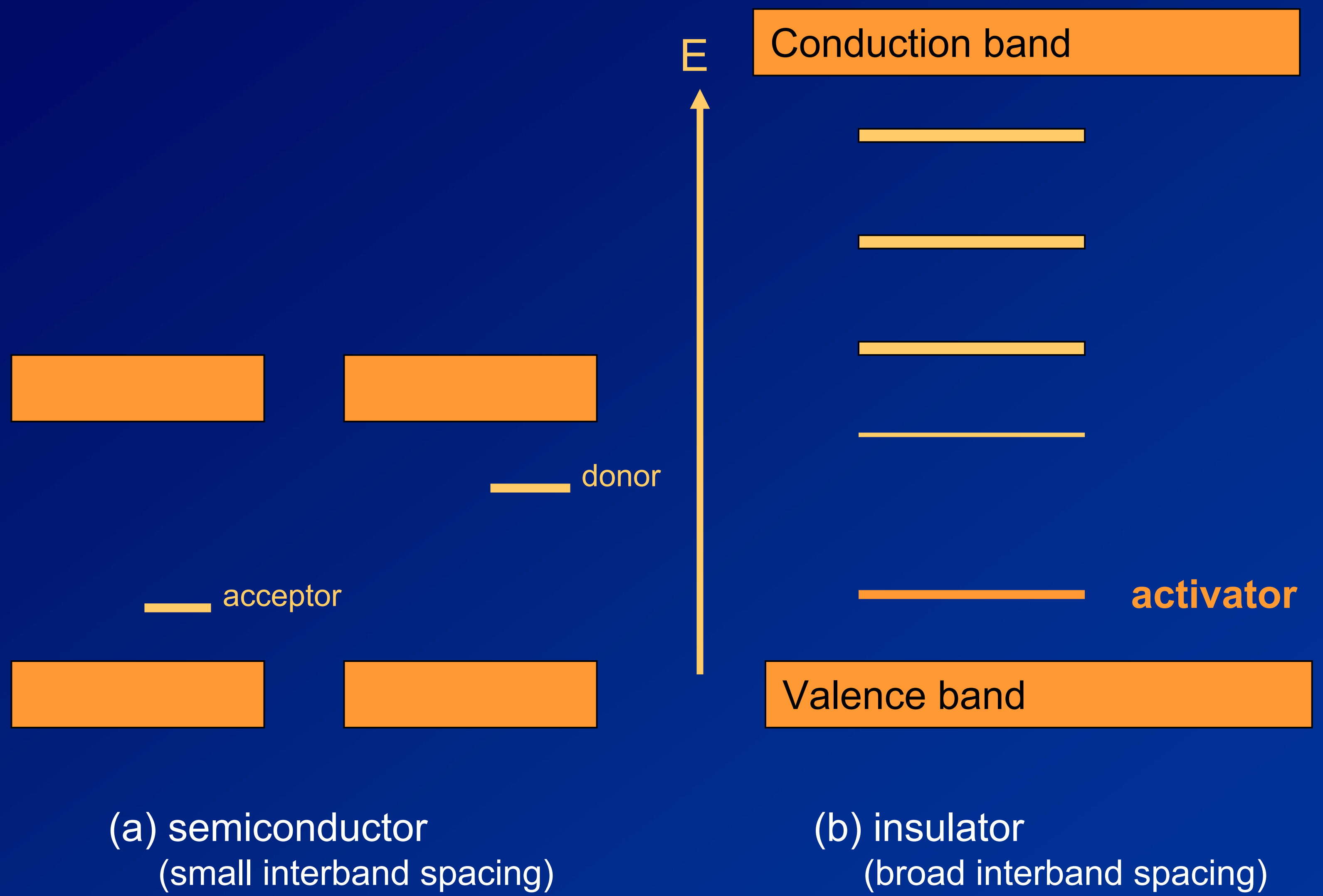


Energy levels in a band scheme for different crystal types



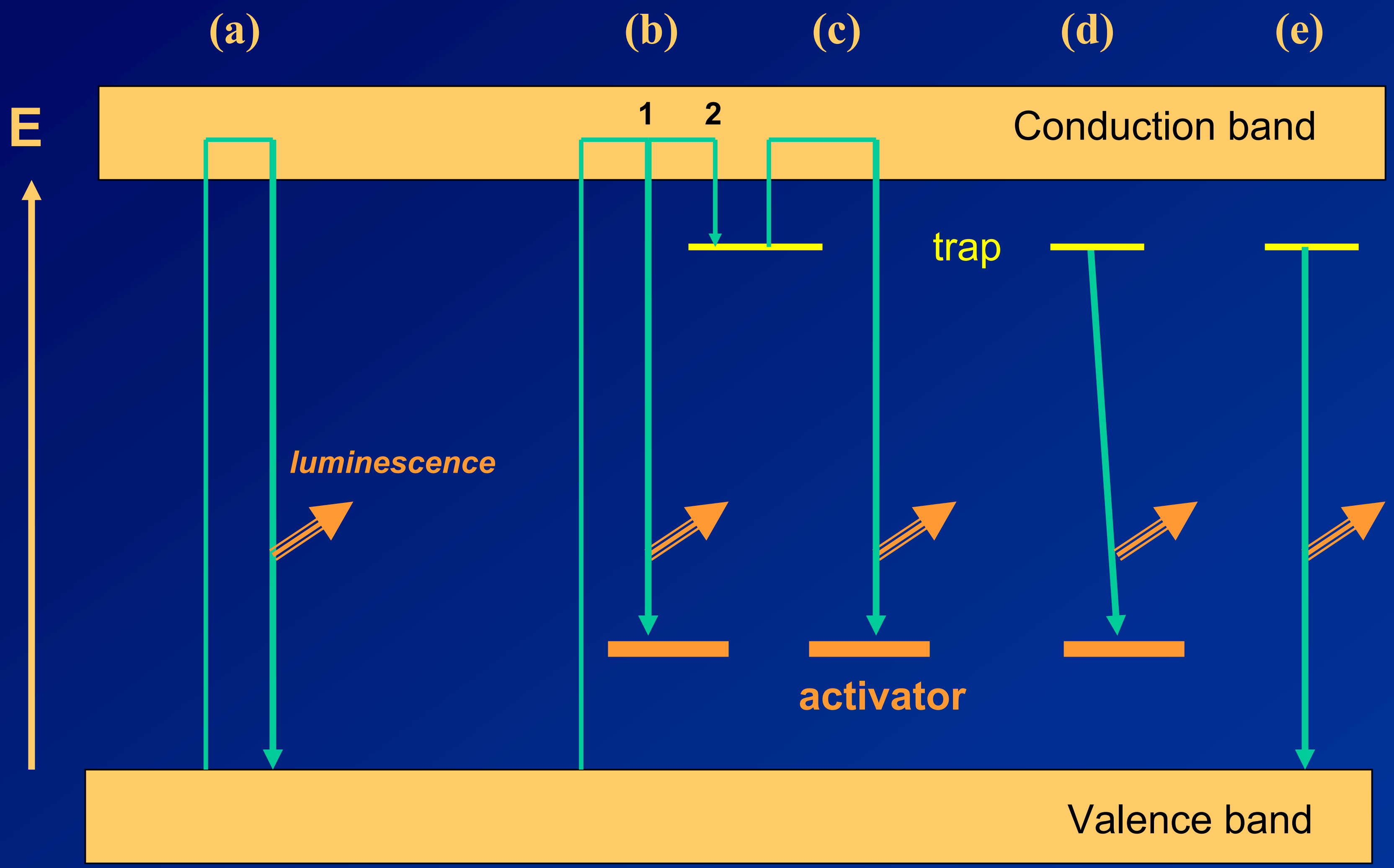
Electron transitions in a band scheme for different crystal types

Basics of luminescence

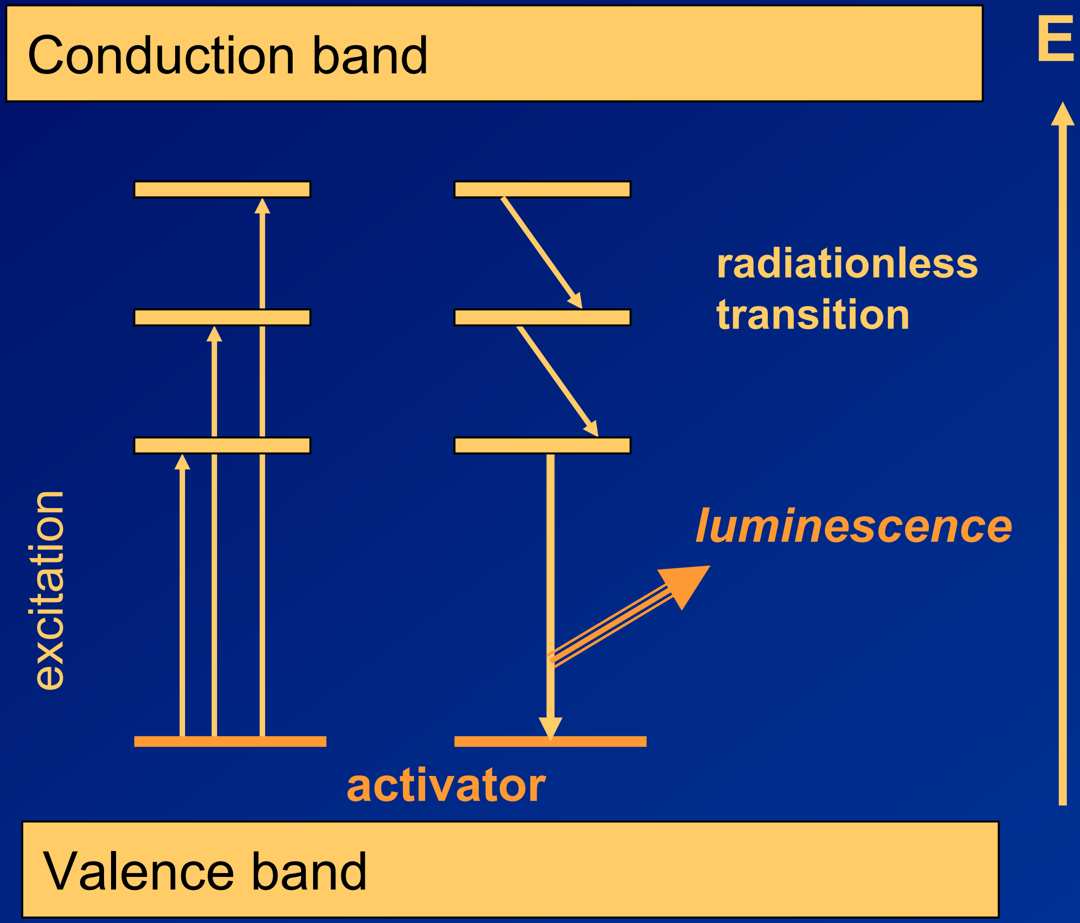


Positions of ion activator energy levels in a band scheme for different crystal types

Basics of luminescence

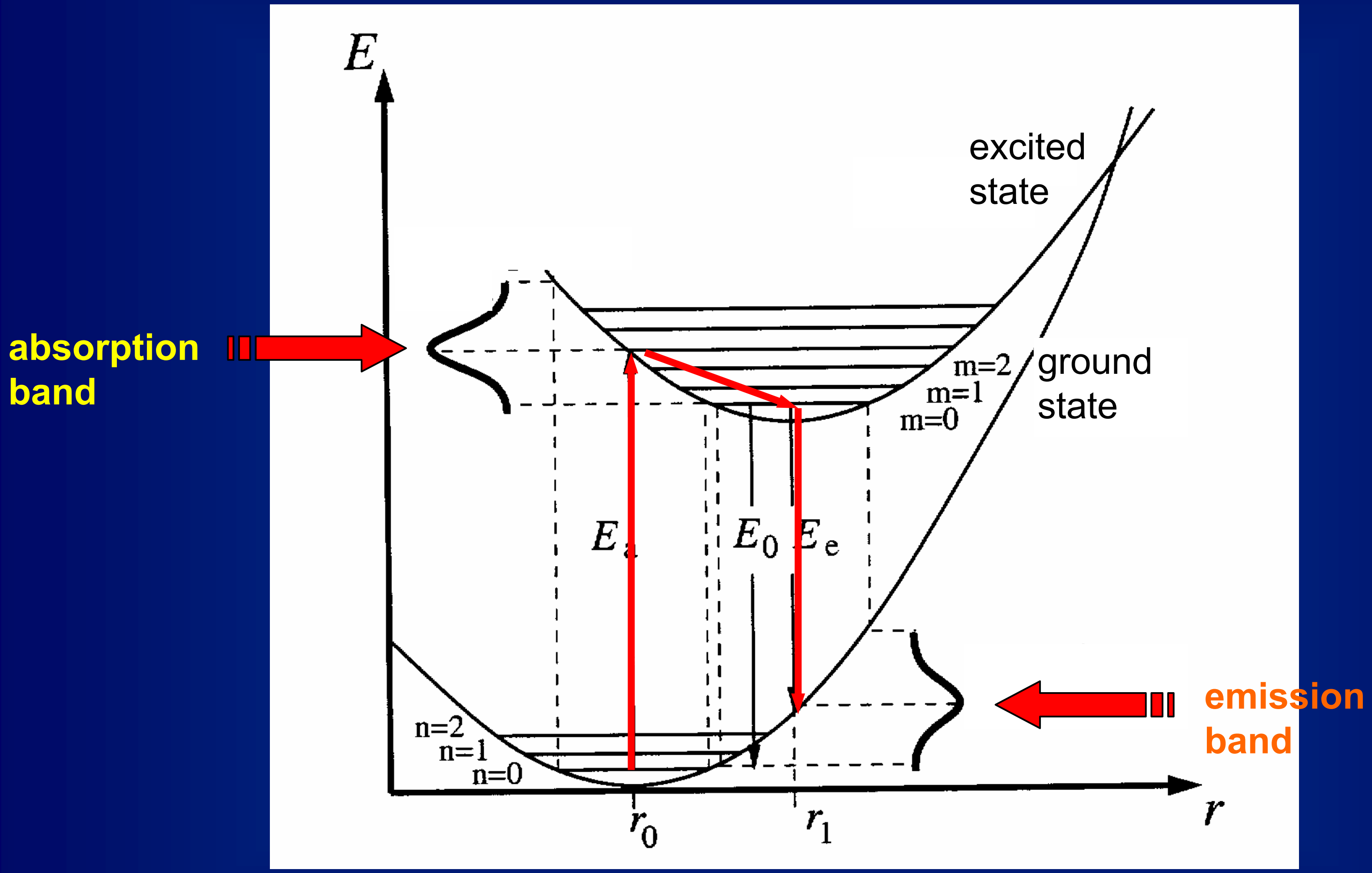


Electron transitions and luminescence processes in a solid

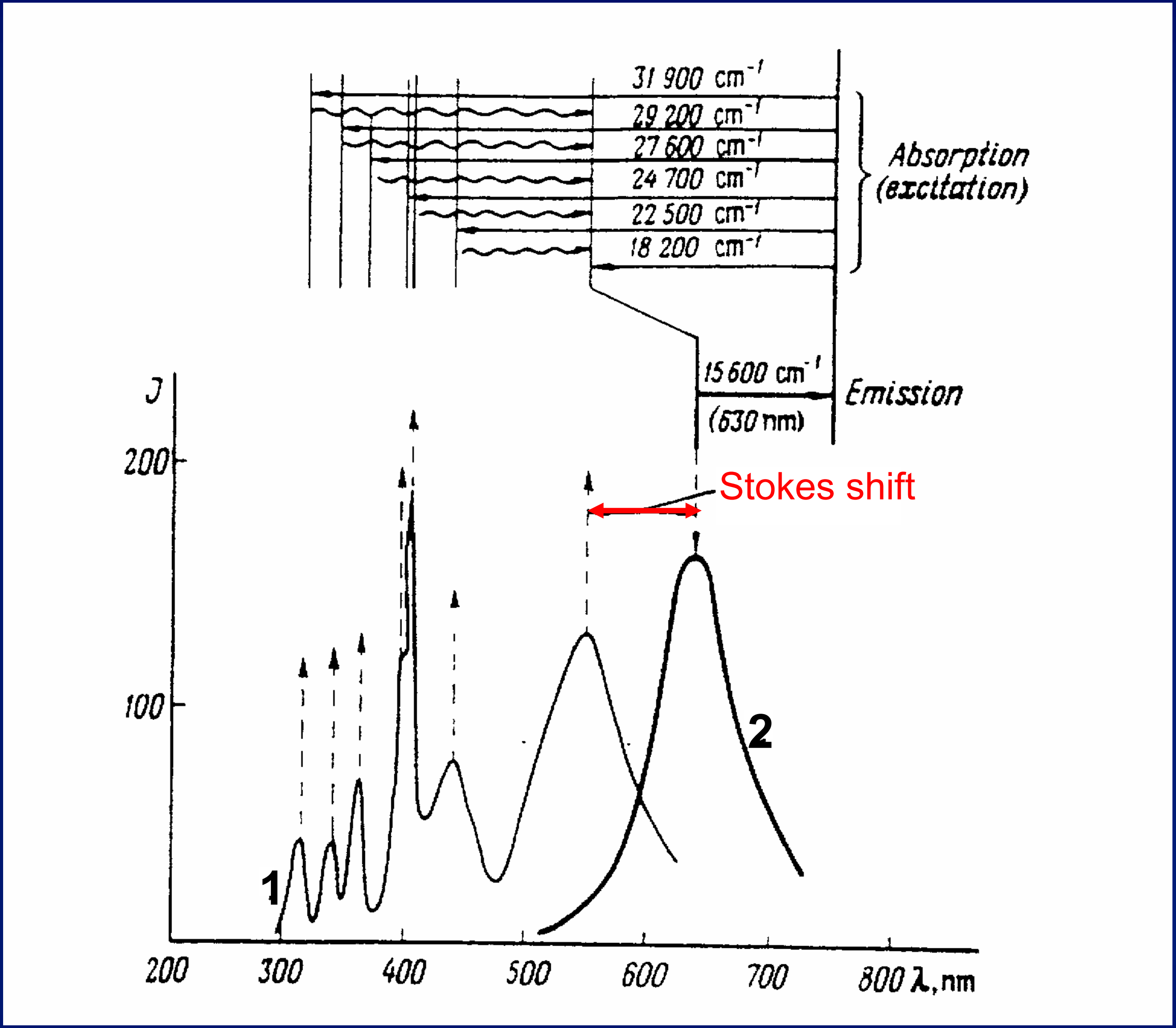


Electron transitions and luminescence in a solid with ion activation

The configurational coordinate model

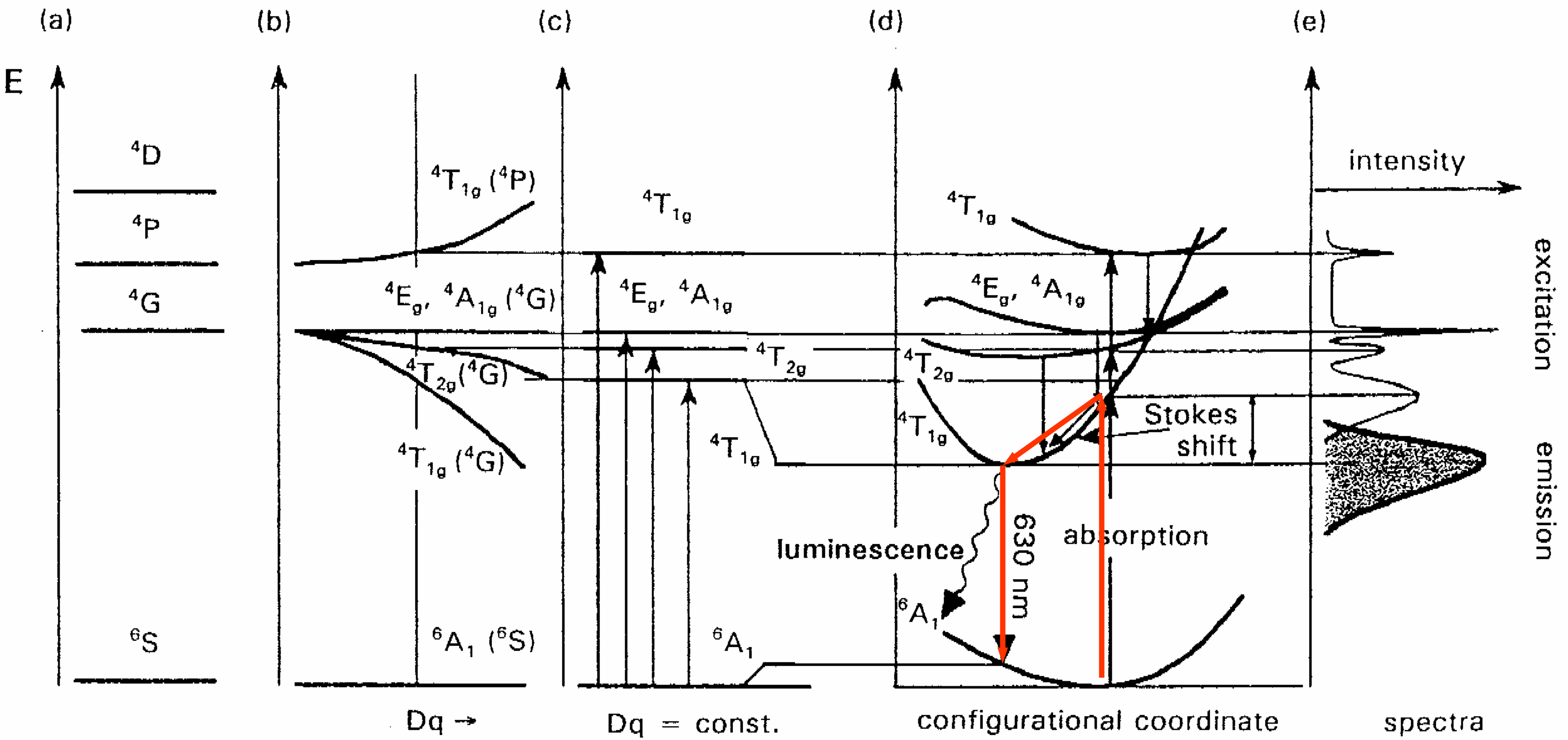


Configurational coordinate diagram for transitions according to the *Franck-Condon* principle with related absorption and emission bands, respectively.
(modified after Yacobi & Holt 1990)



Excitation (1) and emission (2) spectra of Mn^{2+} in calcite (after Medlin 1964)

Basics of luminescence

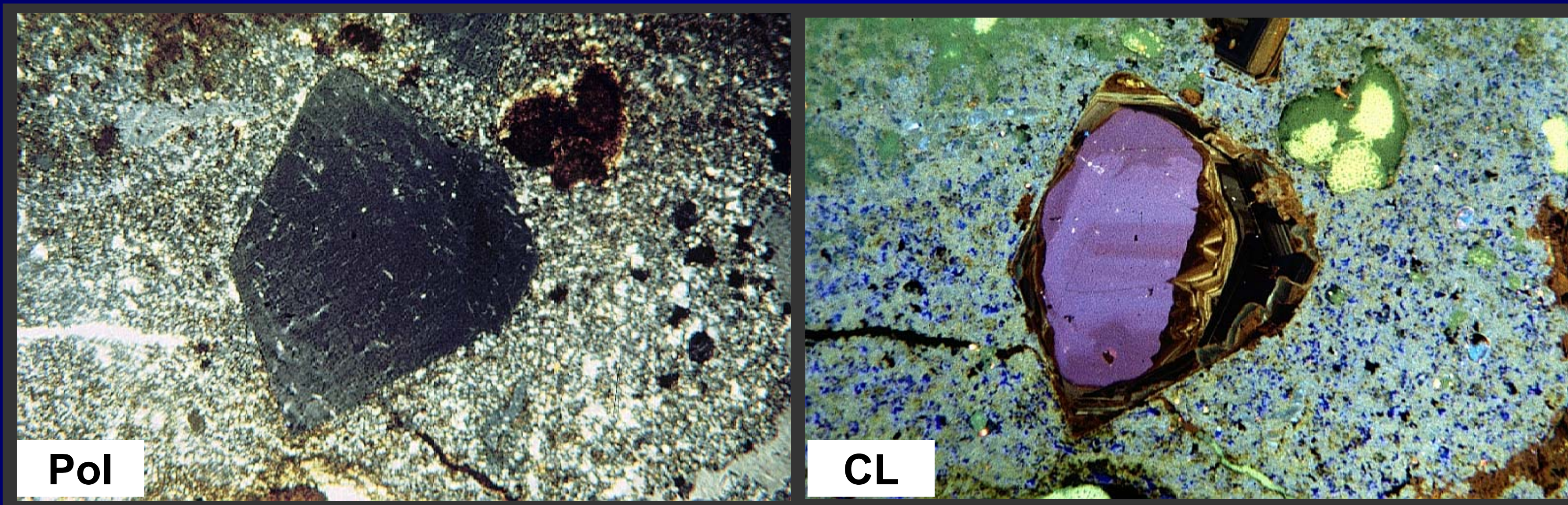


The sensitivity of the electronic states of the Mn^{2+} ion in octahedral coordination to changes in the intensity of the crystal field splitting Dq and representation in a configurational diagram (modified after Marfunin 1979 and Medlin 1968)

How can we use

the luminescence signal ??

Visualization of the real structure of solids by CL



Luminescence centres

intrinsic

lattice defects
(broken bonds, vacancies)

extrinsic

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

Types of luminescence centres

- transition metal ions (e.g., Mn^{2+}, Cr^{3+}, Fe^{3+})
- rare earth elements ($REE^{2+/3+}$)
- actinides (especially uranyl UO_2^{2+})
- heavy metals (e.g., Pb^{2+}, Tl^{+})
- electron-hole centres (e.g., S_2^-, O_2^-, F-centres)
- crystallophosphores of the ZnS type (semiconductor)
- more extended defects (dislocations, clusters, etc.)

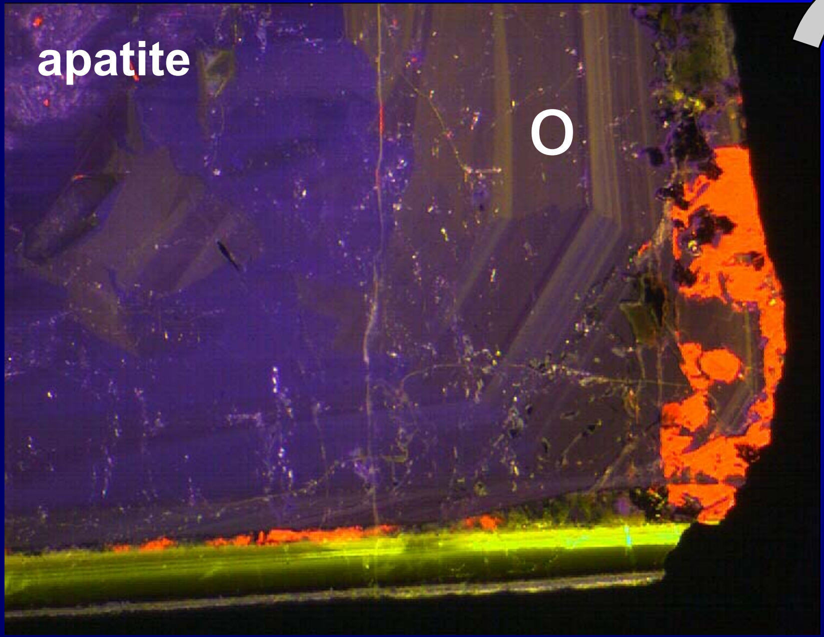
Detection of the cathodoluminescence emission

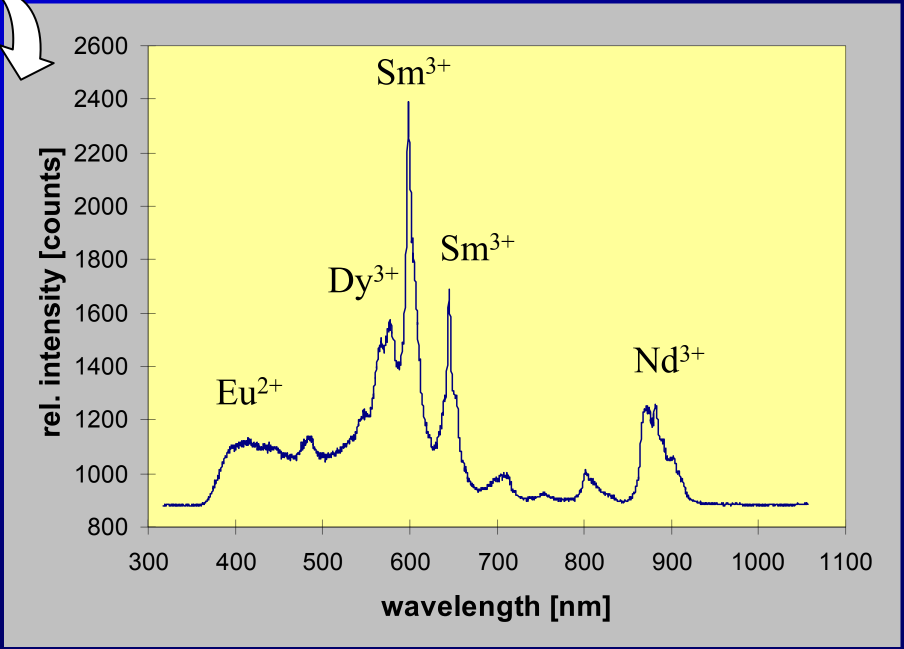
(1) CL microscopy

- 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





CL emission spectra

The crystal field theory

(Burns, 1993)

→ local environment of the activator ion

- The activator-ligand distances in the different excited states and the slope of the energy levels depend on the intensity of the crystal field
(expressed as crystal field splitting $\Delta = 10Dq$)

- The stronger the interaction of the activator ion with the lattice, the greater are the Stokes shift and the width of the emission line.

The crystal field theory

→ local environment of the activator ion

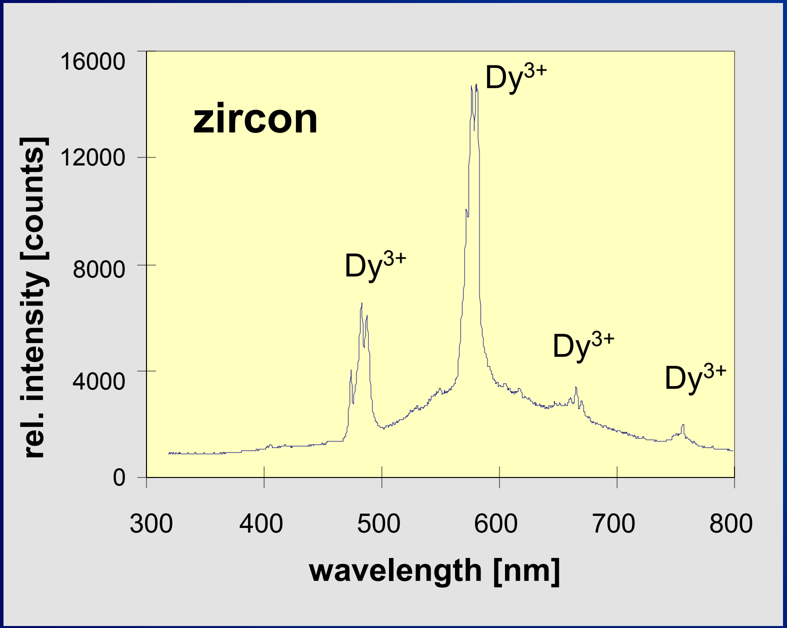
Factors influencing values of Δ or 10Dq are:

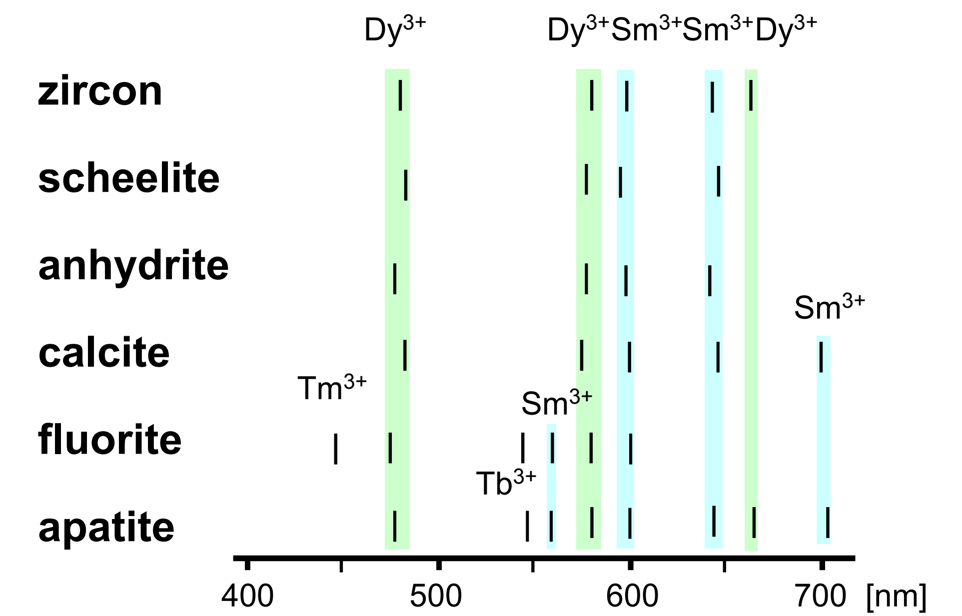
- type of the activator ion (size, charge)
- type of the ligands
- the interaction distance
- local symmetry of the ligand environment

etc.

Influence of the crystal field on CL emission spectra

(1) influence of the crystal field = weak

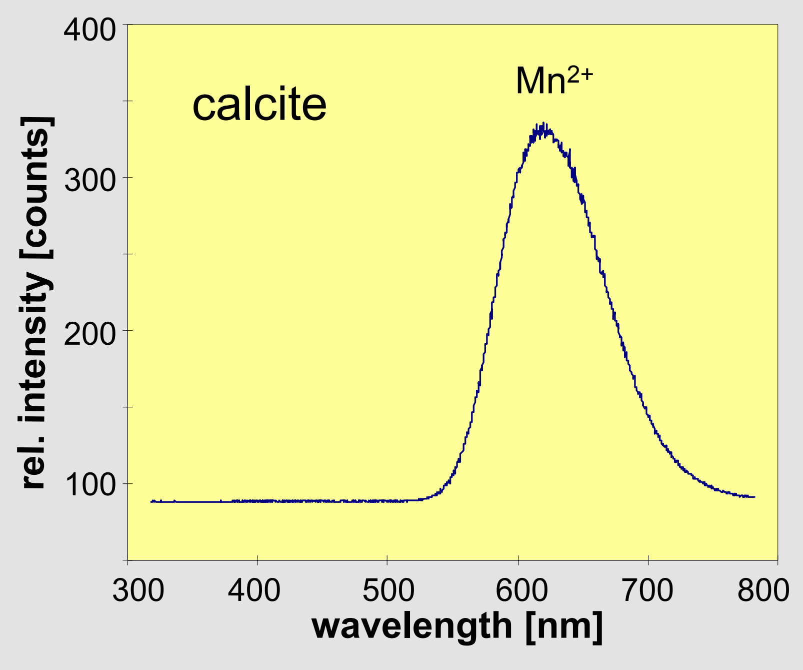




- CL spectra of narrow emission lines (e.g. REE^{3+})
- CL emission spectra are specific of the activator ion

Influence of the crystal field on CL emission spectra

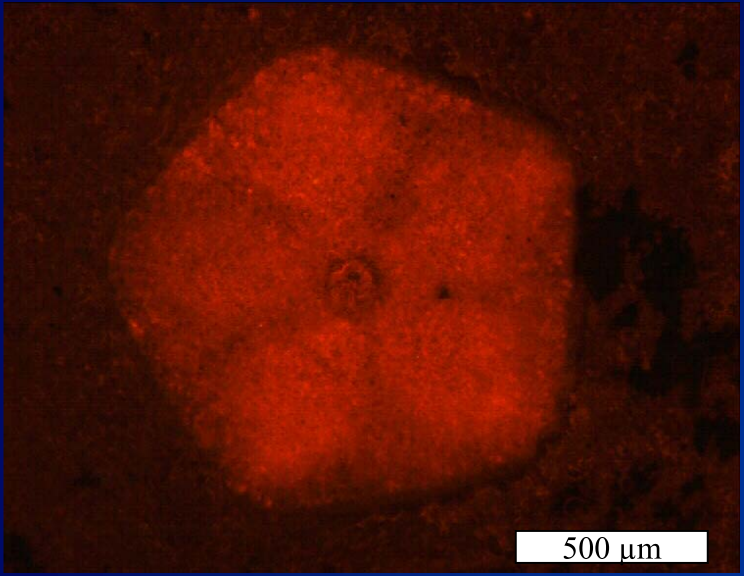
(2) influence of the crystal field = strong



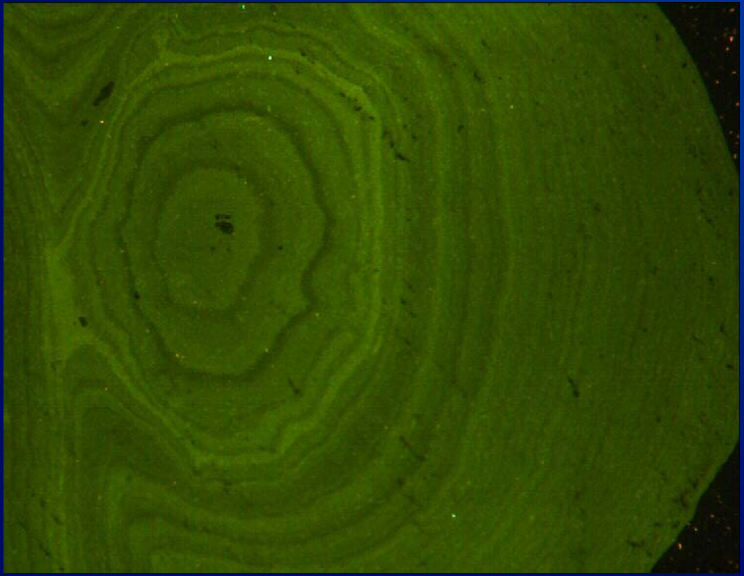
Mn^{2+} activated CL of $CaCO_3$:

aragonite	**green**	**(~560 nm)**
calcite	**yellow-orange**	**(~610 nm)**
magnesite	**red**	**(~655 nm)**

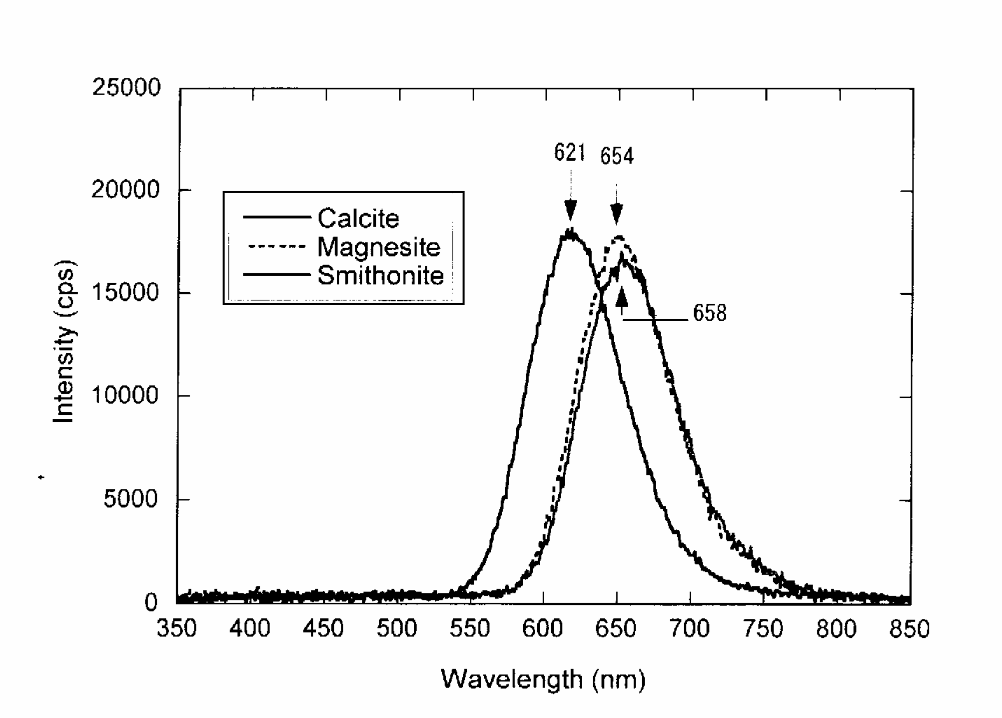
- CL spectra of broad emission bands (e.g. Mn^{2+}, Fe^{3+})
- CL emission spectra are specific of the host crystal



sea lily stalk (calcite $CaCO_3$)

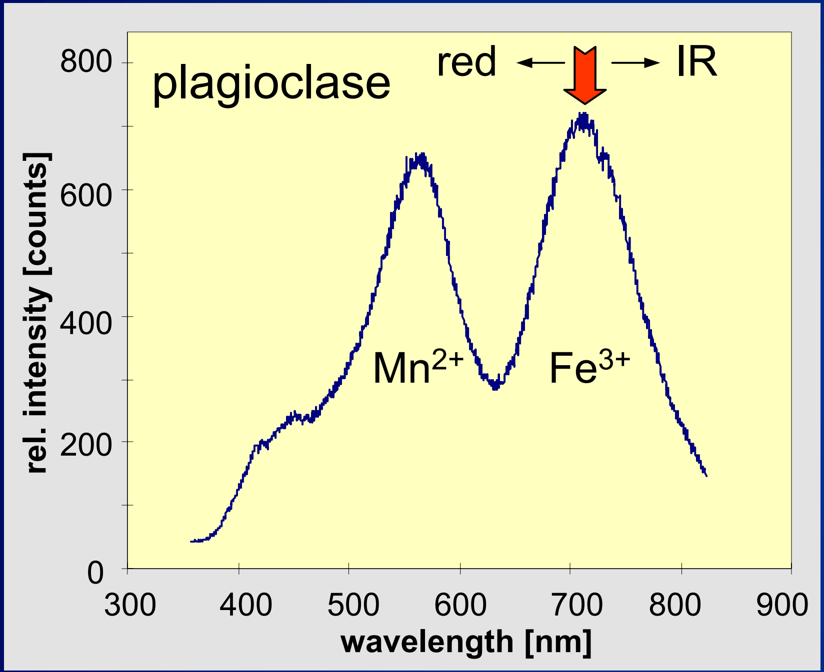


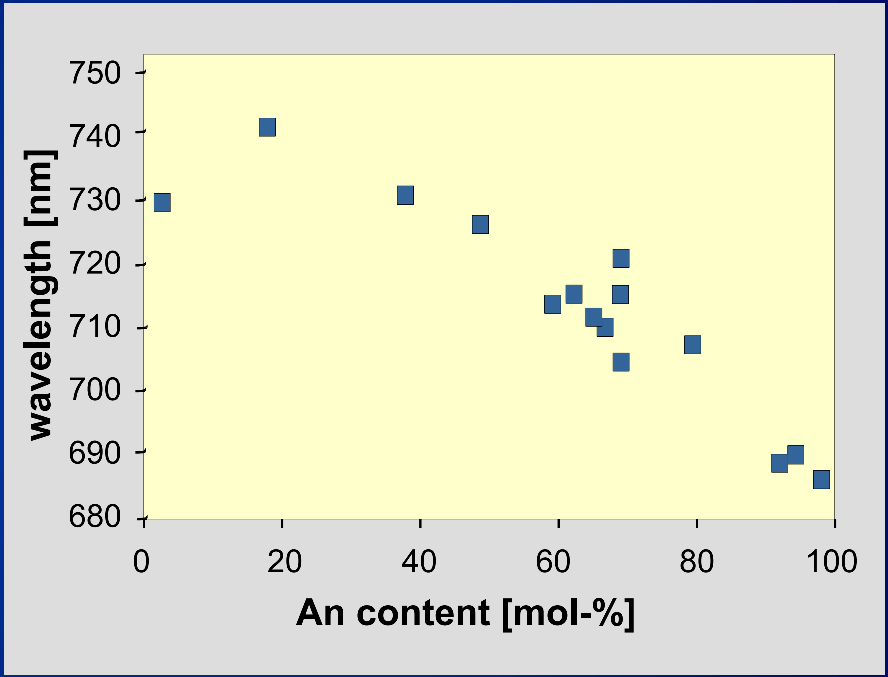
perl (aragonite $CaCO_3$)



Visual and spectral detection of Mn^{2+} activated CL in natural carbonates

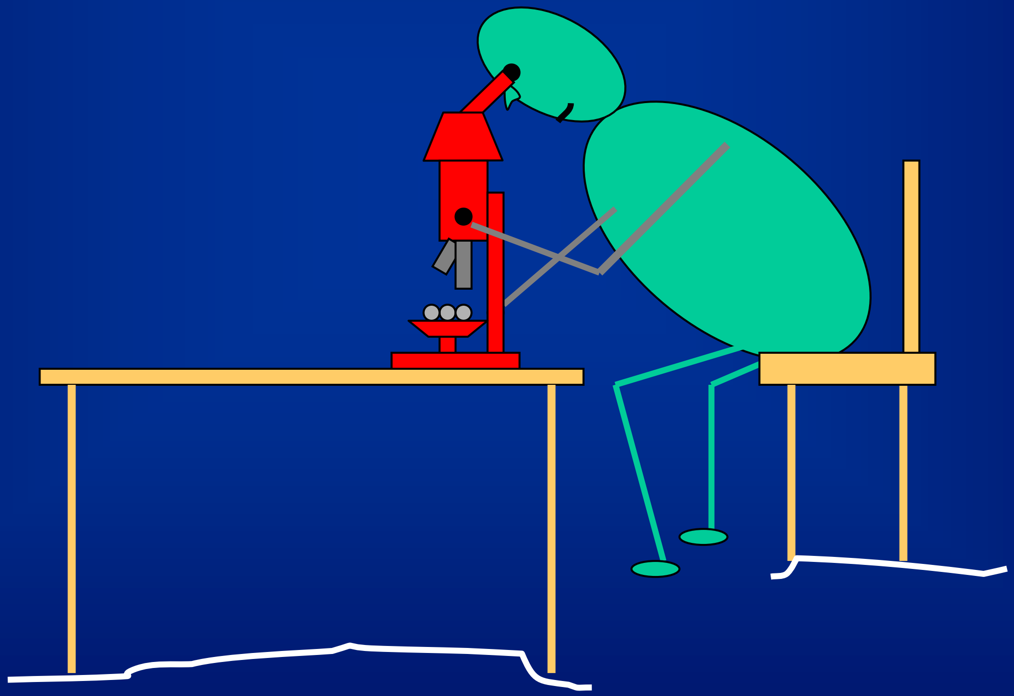
Influence of the crystal field on the broad CL emission bands in solid solutions



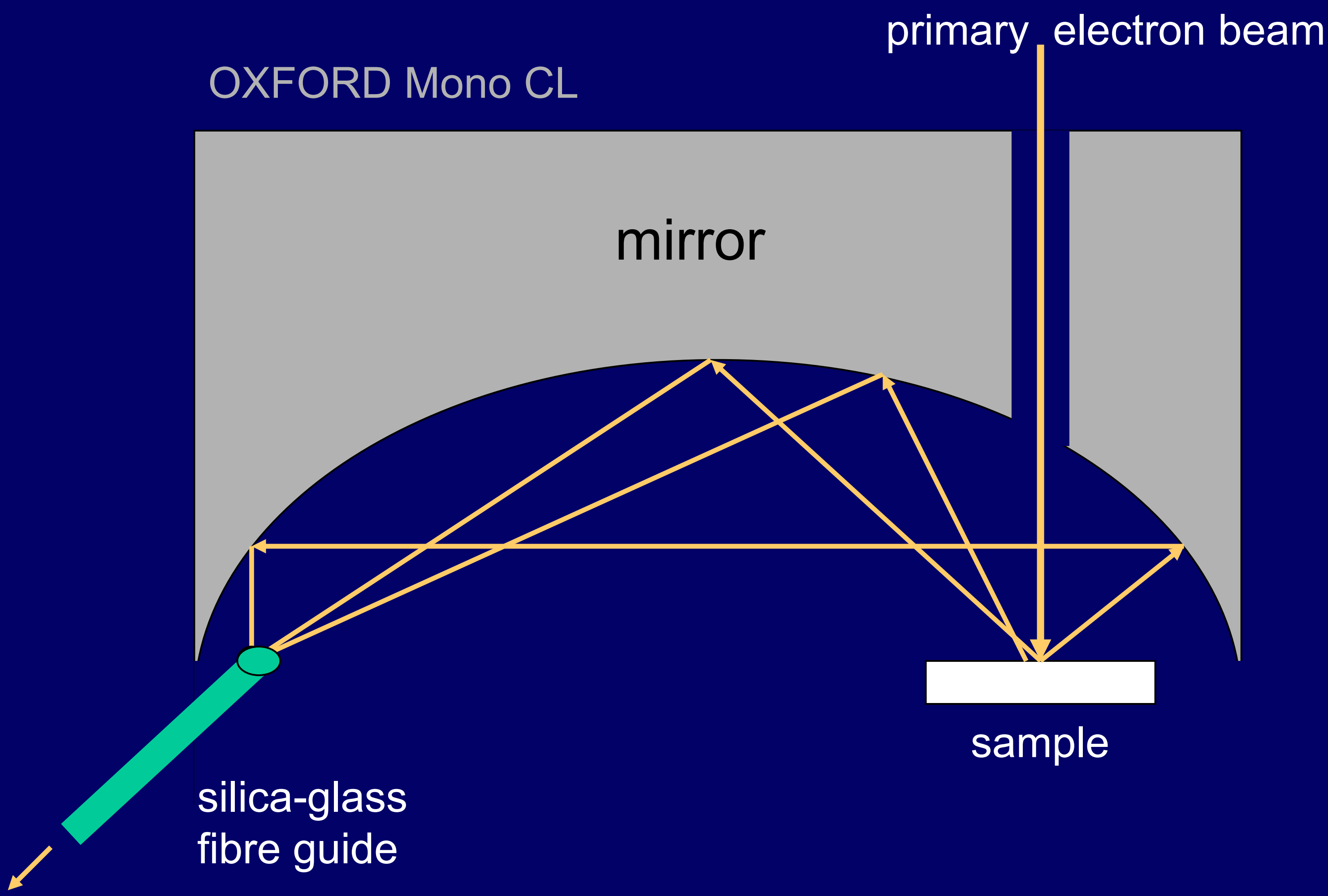


Position of the Fe^{3+} activated CL emission band in plagioclases in relation to the anorthite content

Instrumentation

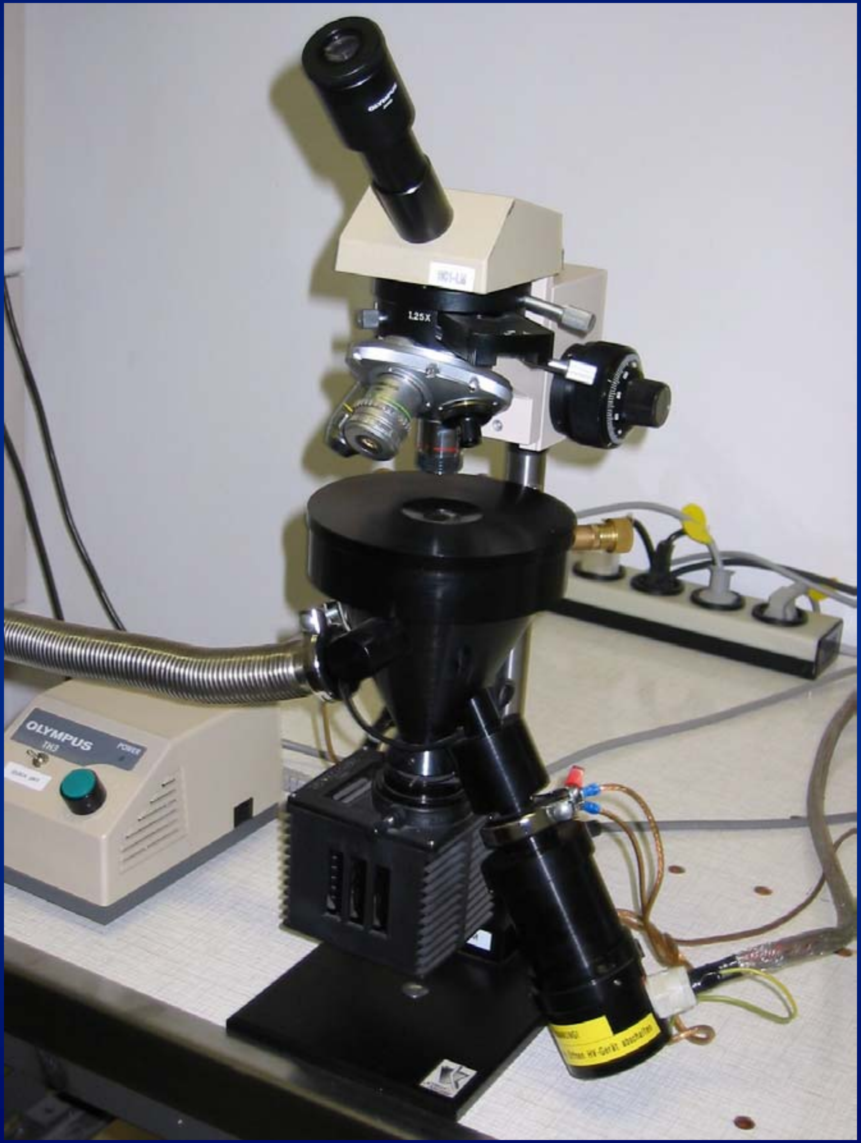


Scanning Electron Microscope JEOL 6400 with OXFORD Mono-CL detector

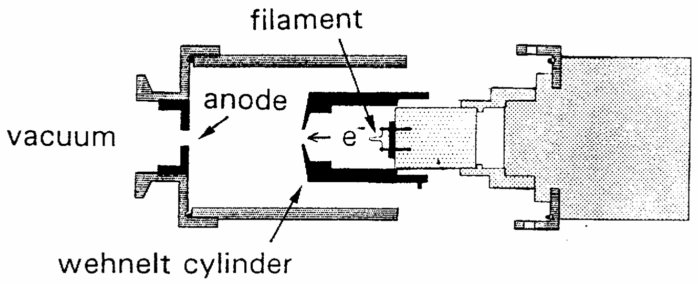


Cathodoluminescence detector on a scanning electron microscope

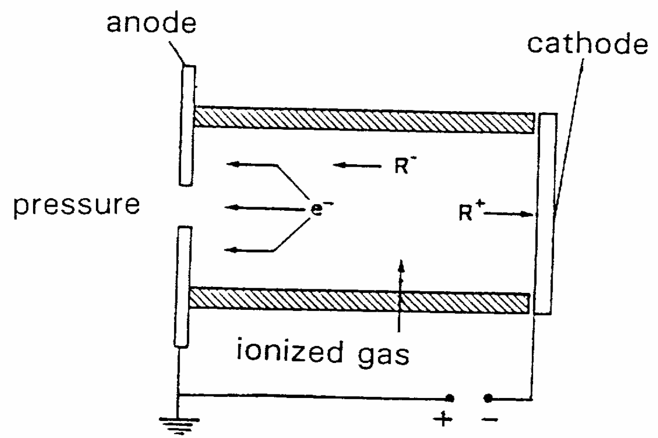
Hot-cathode luminescence microscope HC1-LM
(designed by Rolf Neuser, Bochum)



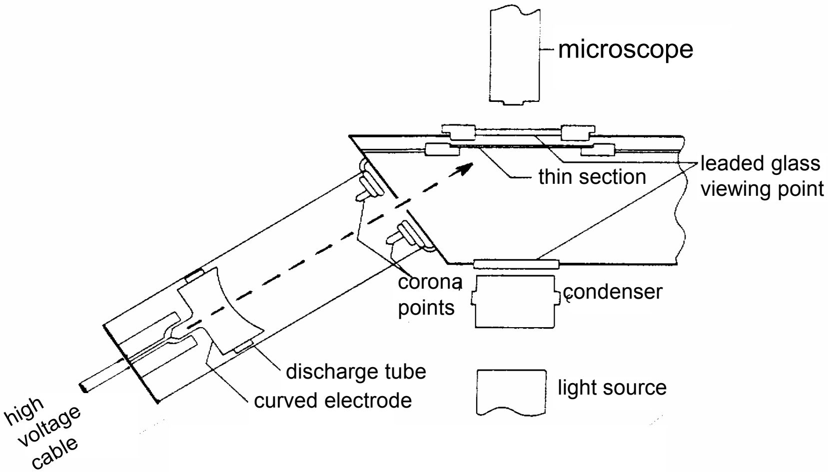
Instrumentation

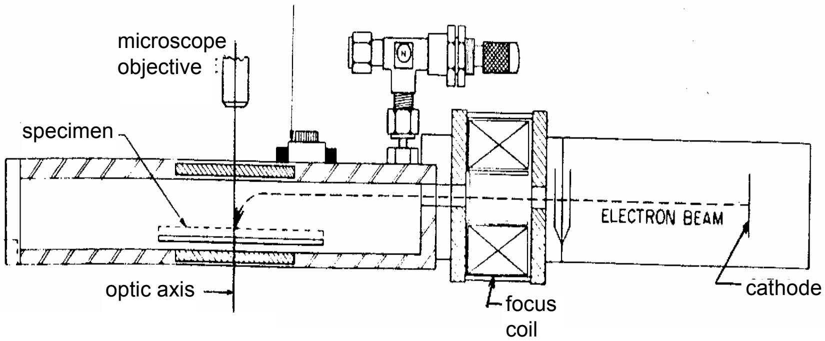


hot-cathode microscope



cold-cathode microscope

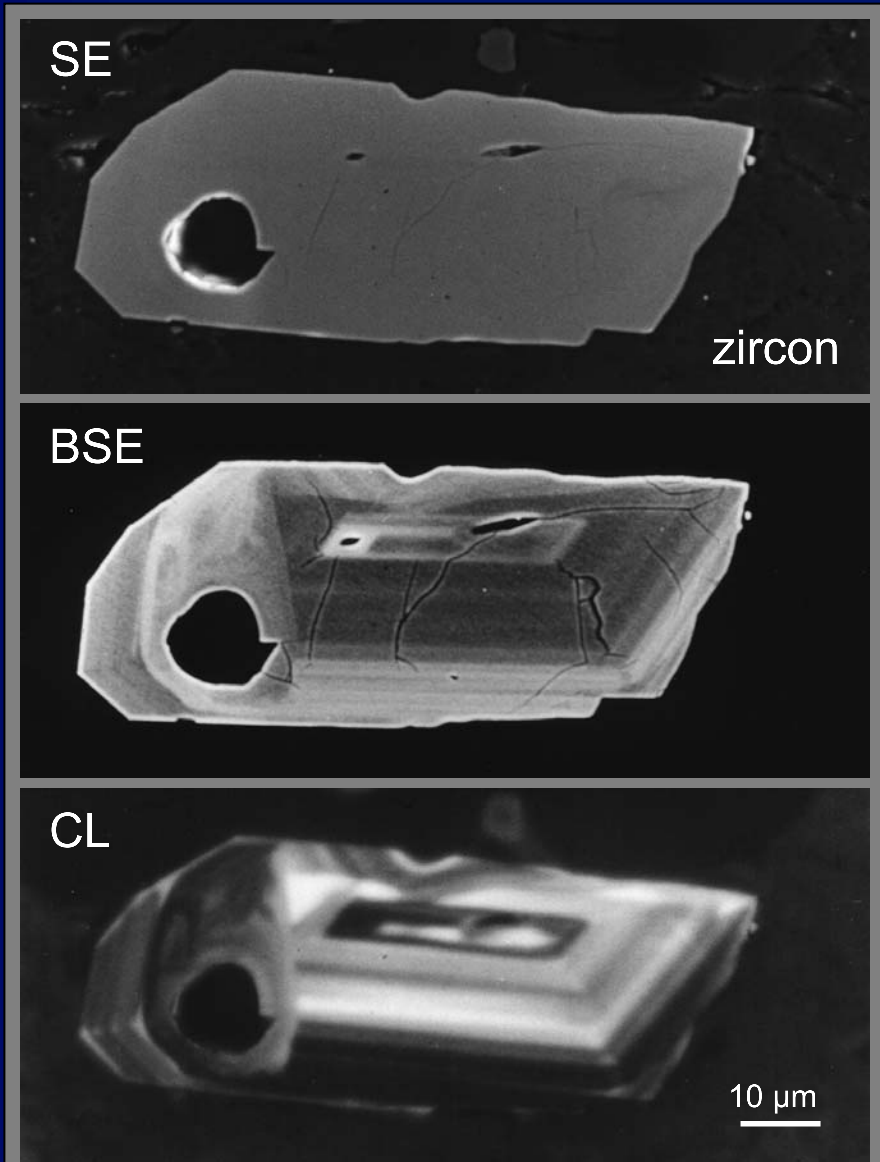




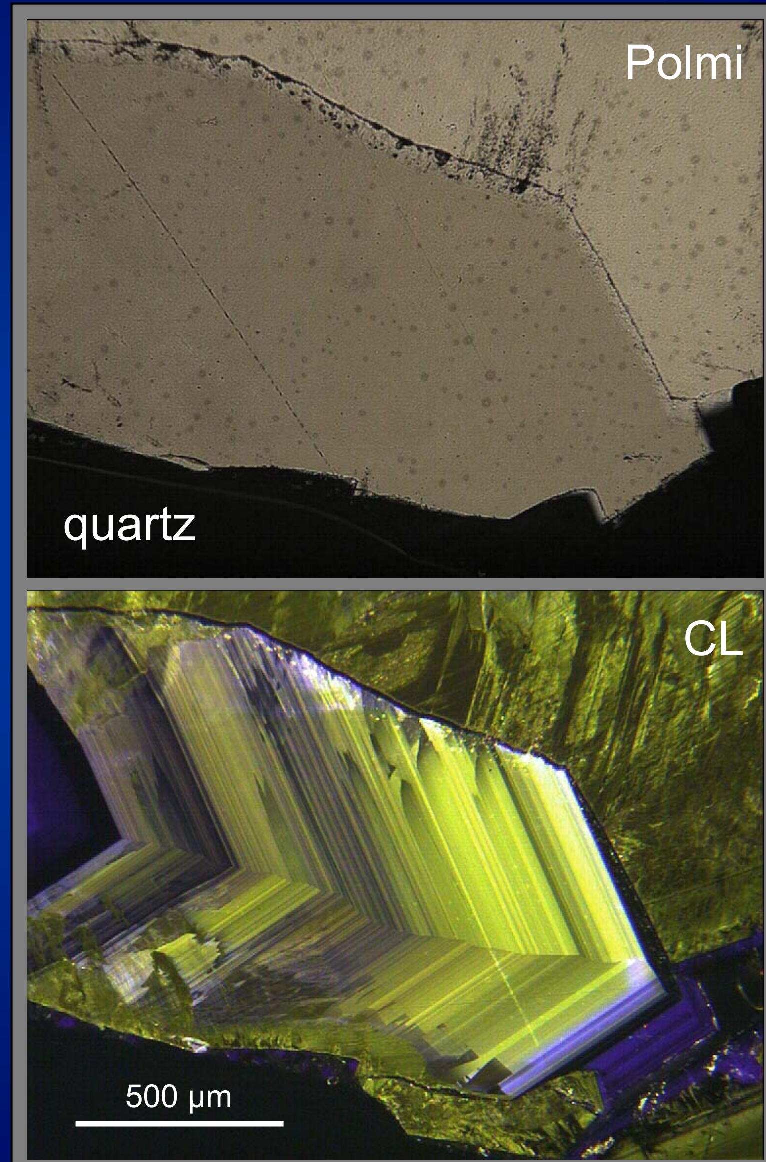
Cathodoluminescence techniques

SEM-CL	CL microscopy
polished sample surface	polished thin (thick) section
focused electron beam, scanning mode	defocused electron beam, stationary mode
heated filament 20 kV, 0.5-15 nA	heated filament („hot cathode“) 14 kV, 0.1-0.5 mA ionized gas („cold cathode“)
mirror optics: 200-800 nm (UV - IR)	glass optics: 380-1200 nm (Vis - IR)
analytical spot ca. 1 µm	analytical spot ca. 30 µm
panchromatic CL images (grey levels)	true luminescence colours
resolution << 1 µm	resolution 1-2 µm
SE, BSE, EDX/WDX, cooling stage	polarizing microscopy, (EDX)

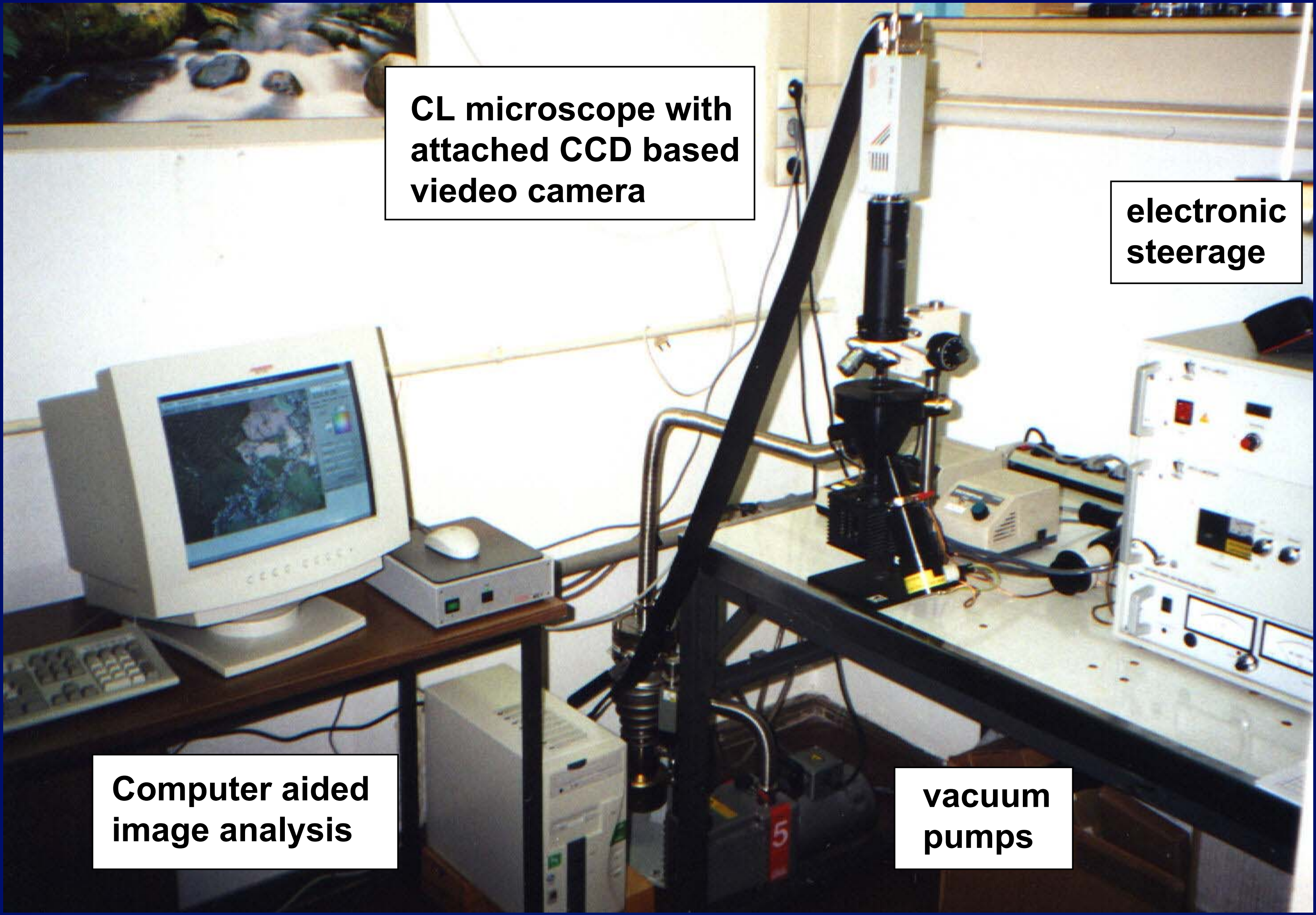
Cathodoluminescence imaging



SEM cathodoluminescence

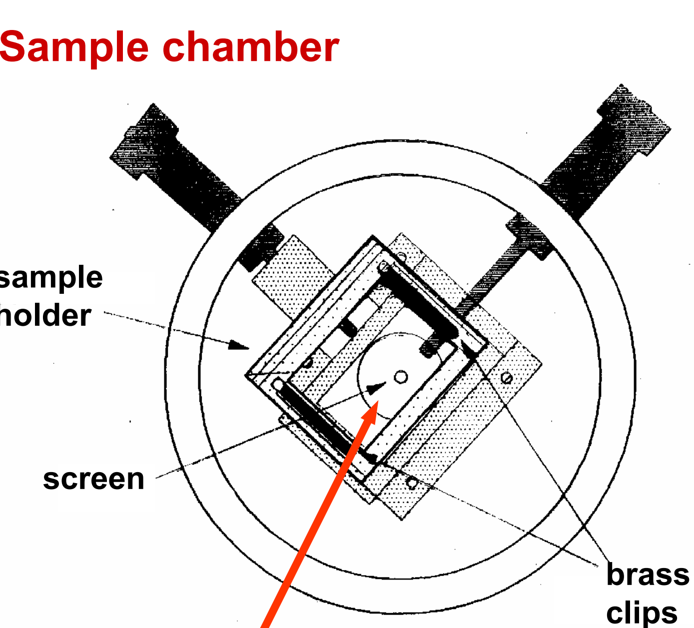


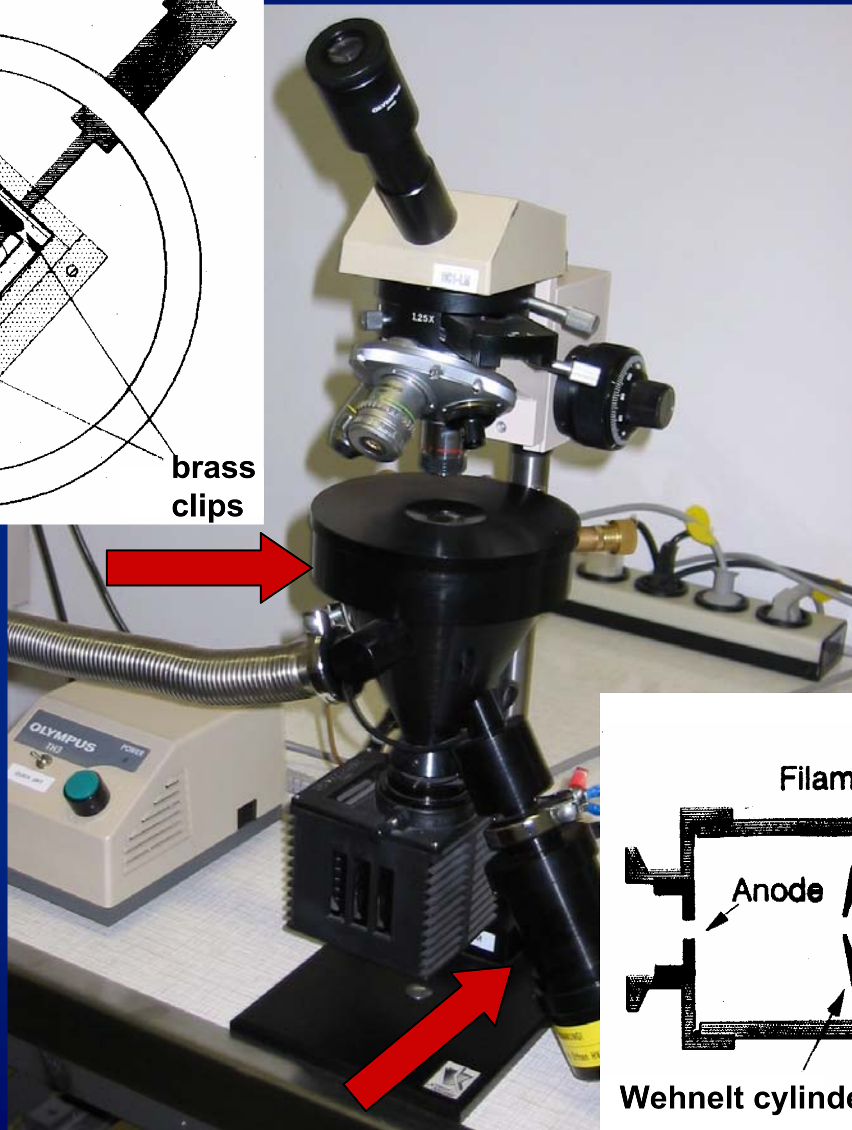
Cathodoluminescence microscopy

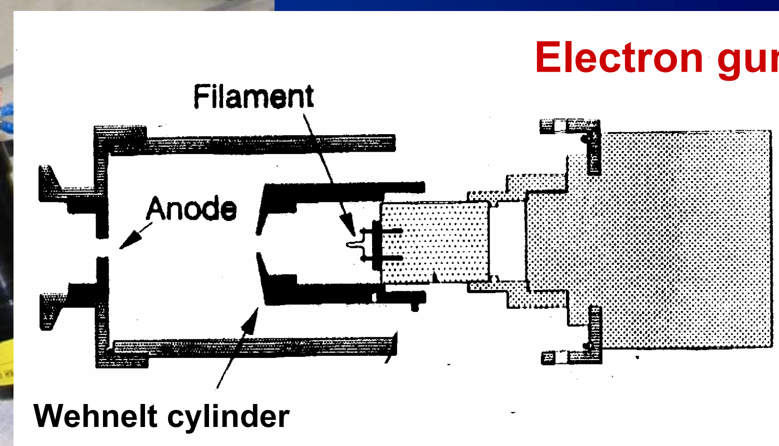


Cathodoluminescence microscope HC1-LM

Hot-cathode luminescence microscope HC1-LM





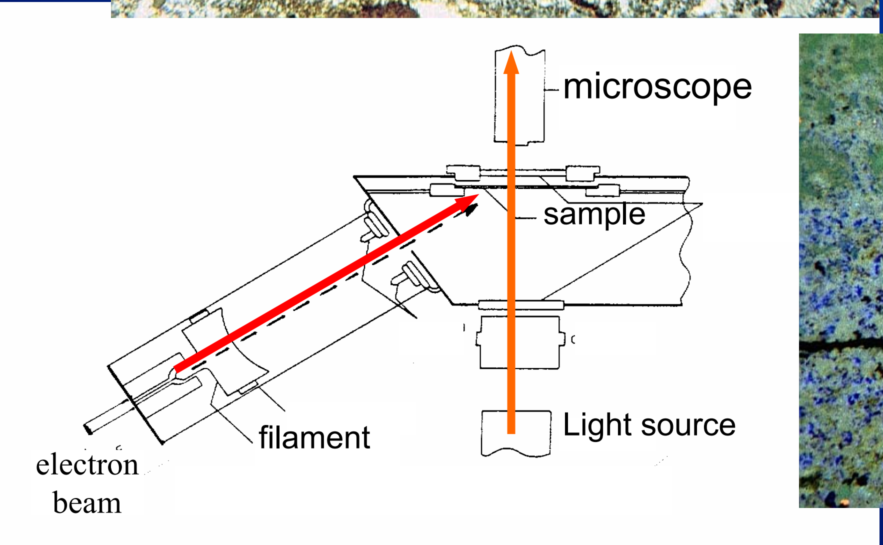


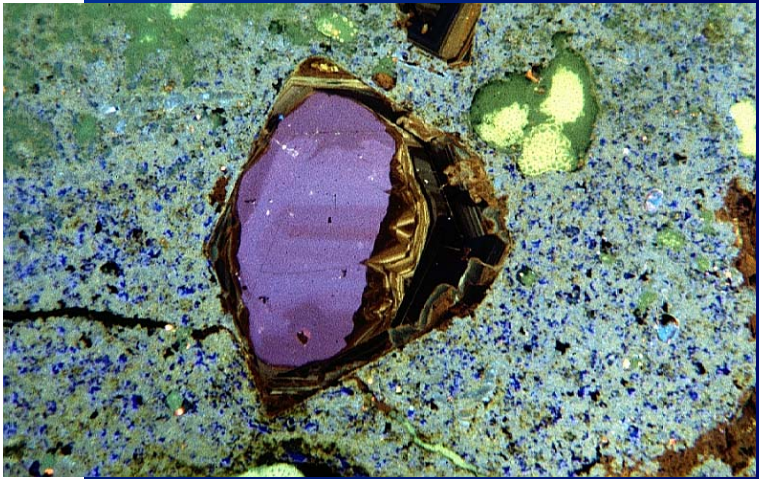
sample is fixed upside down in the sample holder

→ transparency !

Cathodoluminescence microscopy

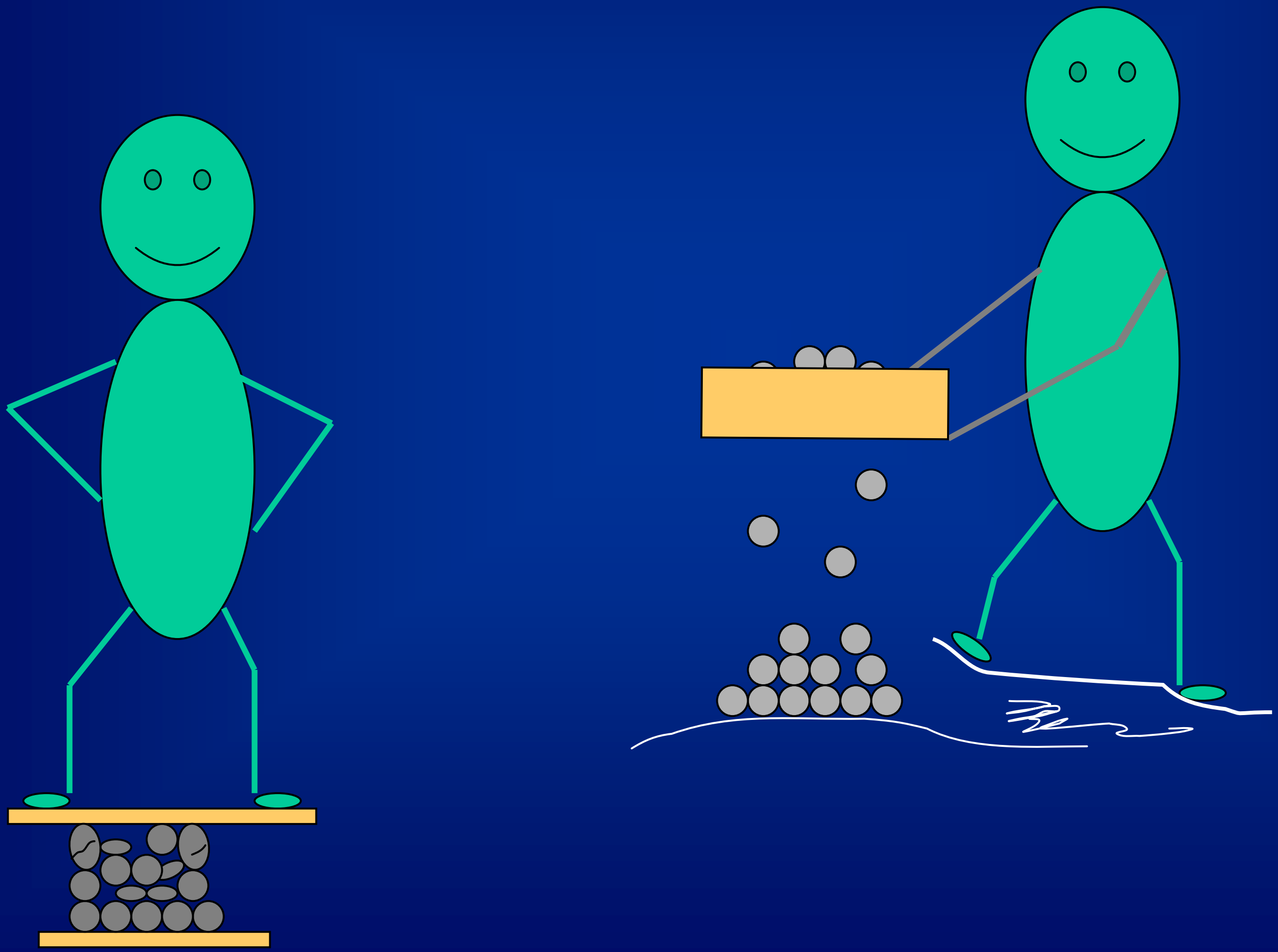
Polarising microscopy





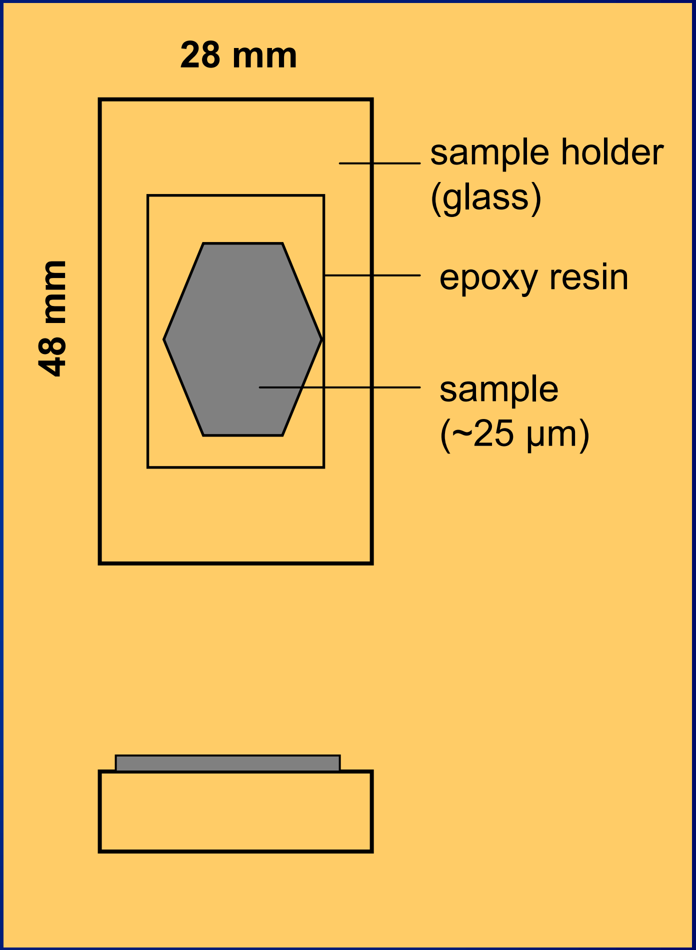
Cathodoluminescence microscopy

Sample preparation



Sample preparation

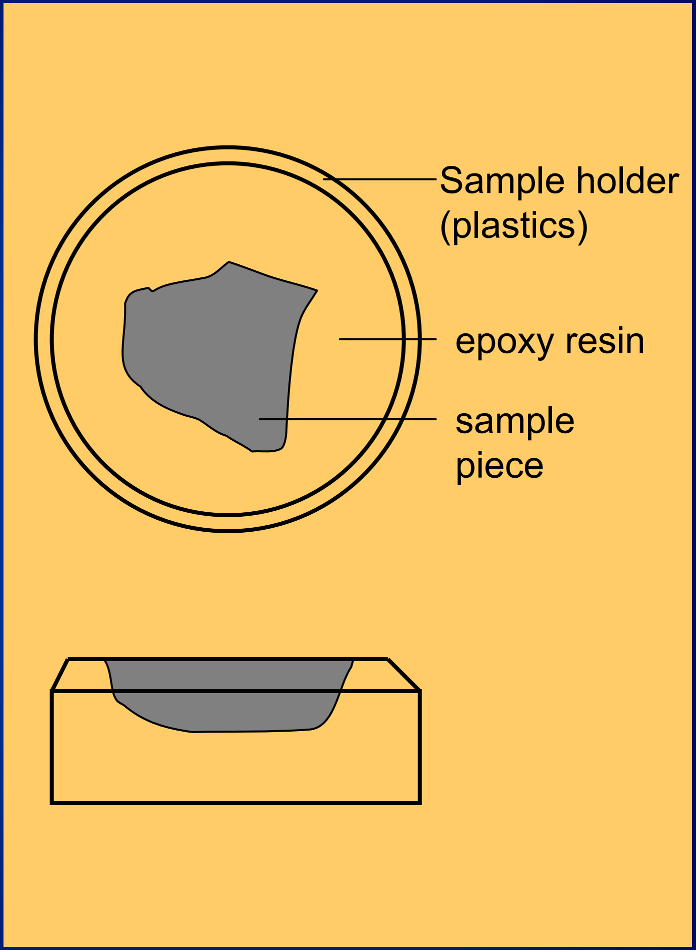
1. Polished thin section



→ application for all CL equipments

Sample preparation

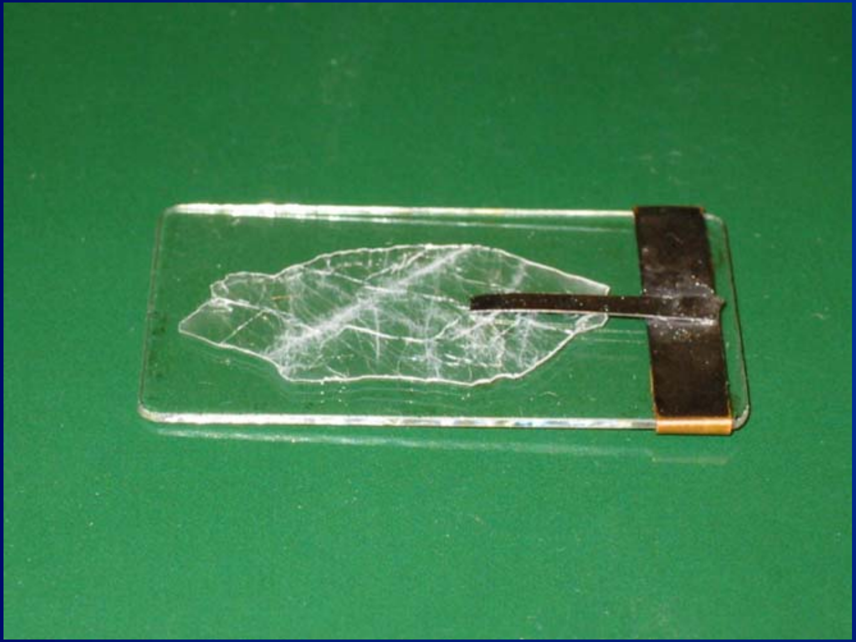
2. Polished section

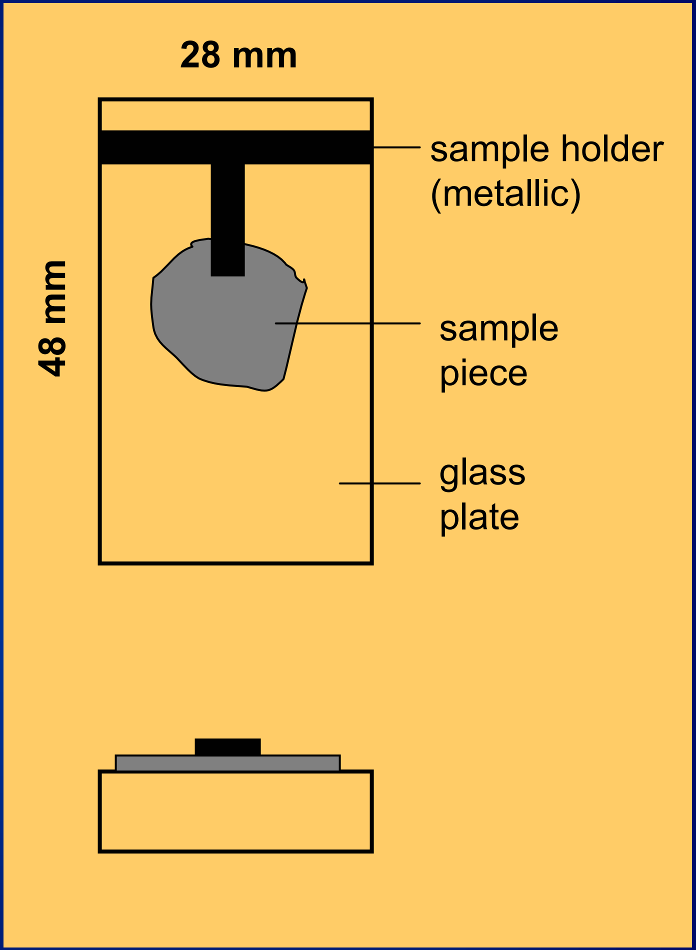


→ application for SEM-CL („cold-cathode“ microscopes)

Sample preparation

4. Sample holder for fluid inclusion preparates

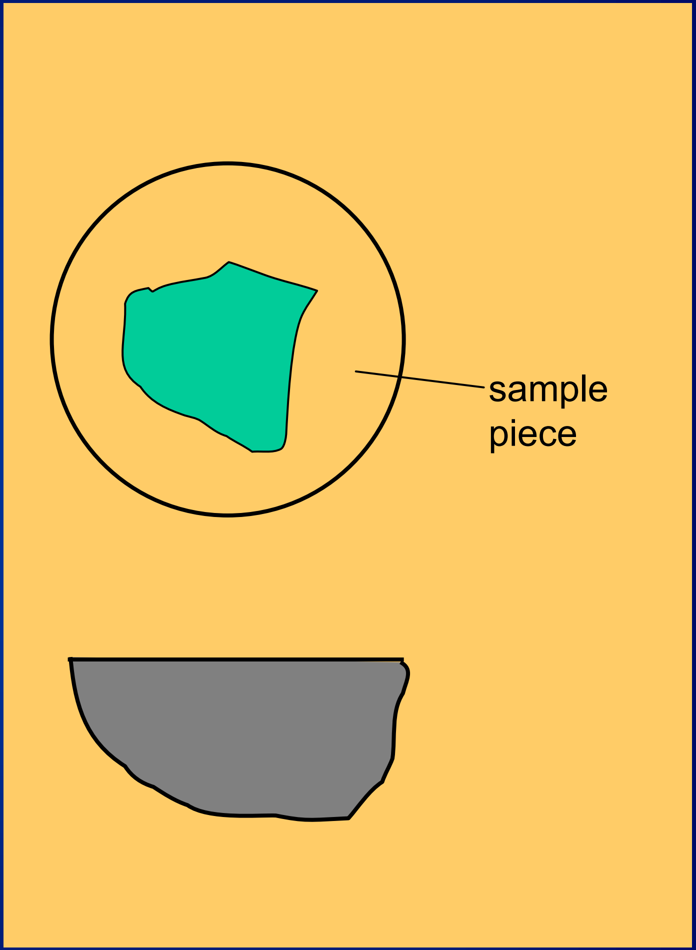




application for all CL equipments

Sample preparation

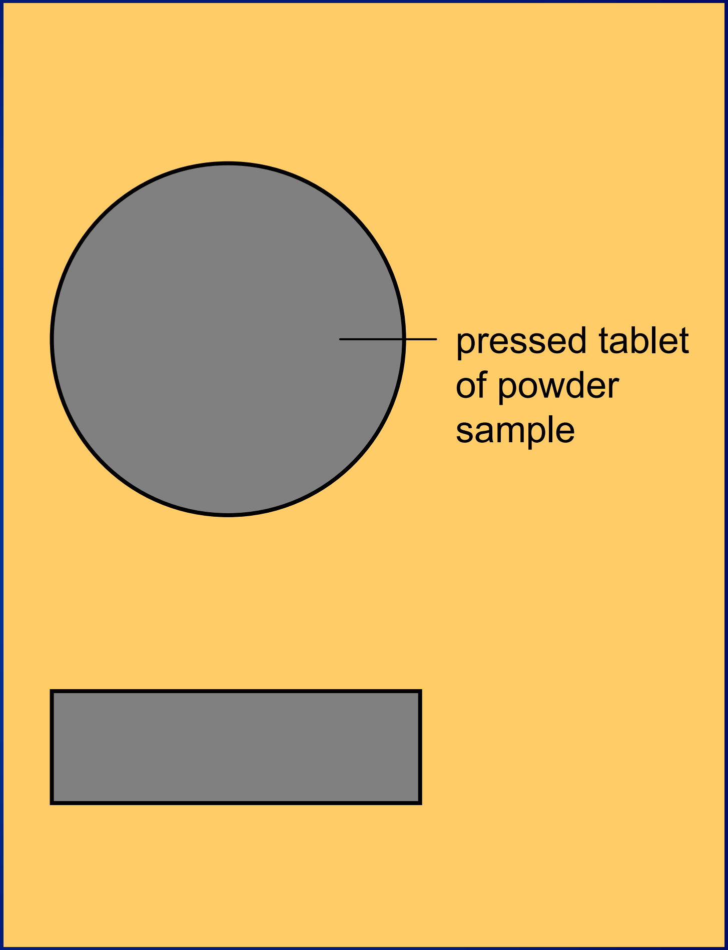
3. Polished sample piece



➡ application for SEM-CL („cold-cathode“ microscopes)

Sample preparation

5. Pressed tablet (powder samples)



➡ application for SEM-CL („cold-cathode“ microscopes)

Sample preparation

<u>Coating with conducting material</u>

- to prevent the built up of electrical charge during electron irradiation

- coating material: **C**, **Au**, Al, Ag, Cu

→ for SEM-CL and „hot-cathode“ CL microscopes

Documentation

Documentation

<u>Convetional photos/slides</u>

- Nikon photo camera
  Kodak Ektachrome 400 HC

<u>Digital micrographs</u>

- Digital video camera
  KAPPA 961-1138 CF 20 DXC

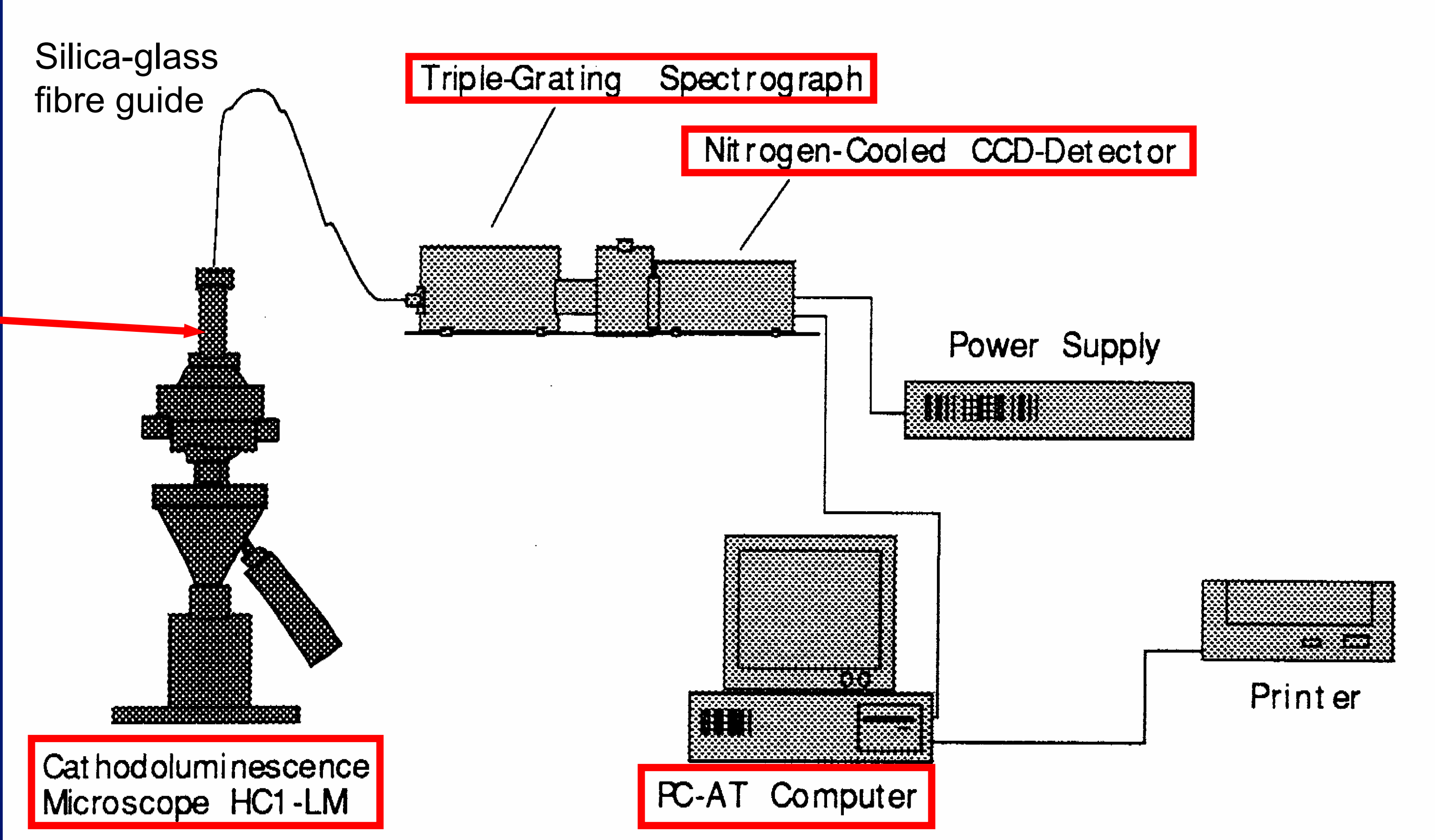
Advantages of CCD:

- high spatial resolution
- high sentsitivity
  - analysis of minerals with very low CL intensities
  - low accumulation time
- direct combination with image analysis

Spectral CL measurements

High-resolution CL spectroscopy

150, 600, 1200 lines/mm 0.4 nm resolution



daptation
30µm screen)

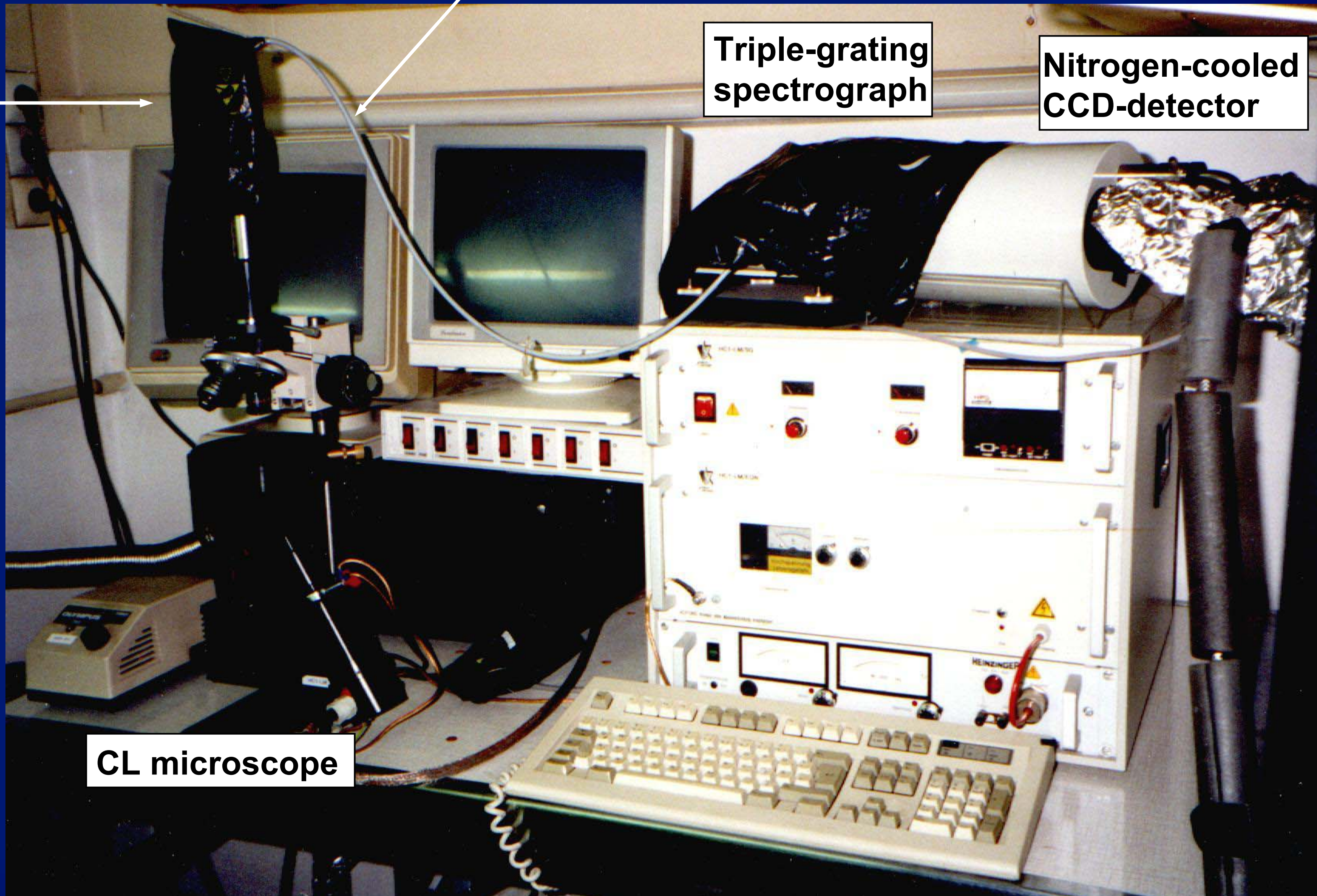
14 kV, 0.2 mA
< 5s accumulation time

data processing

High-resolution CL spectroscopy

Silica-glass fibre guide

daptation

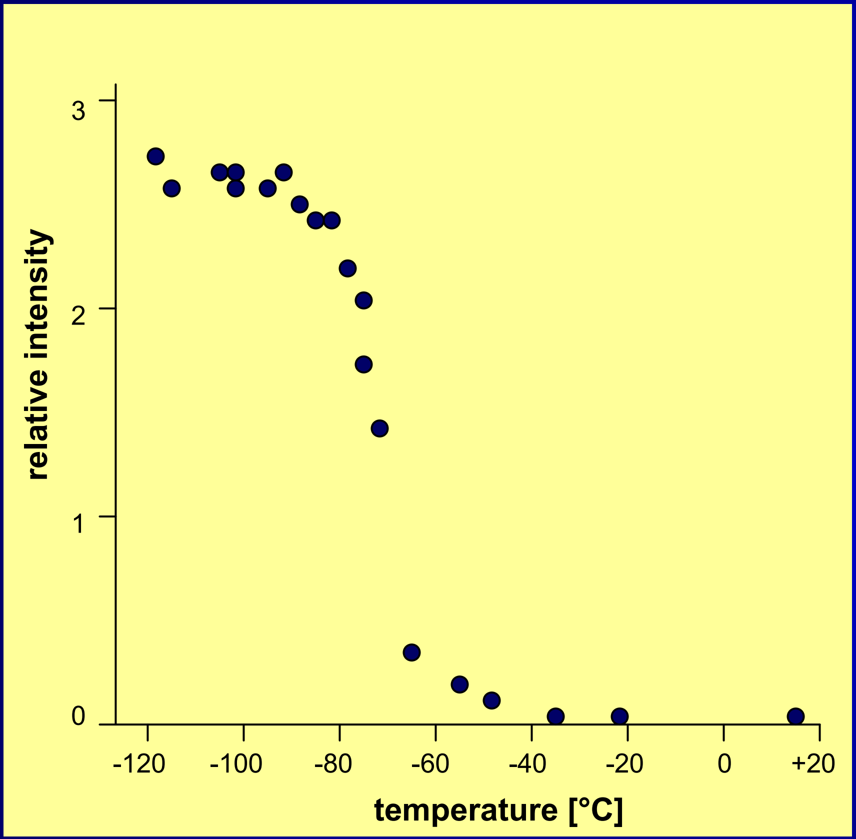


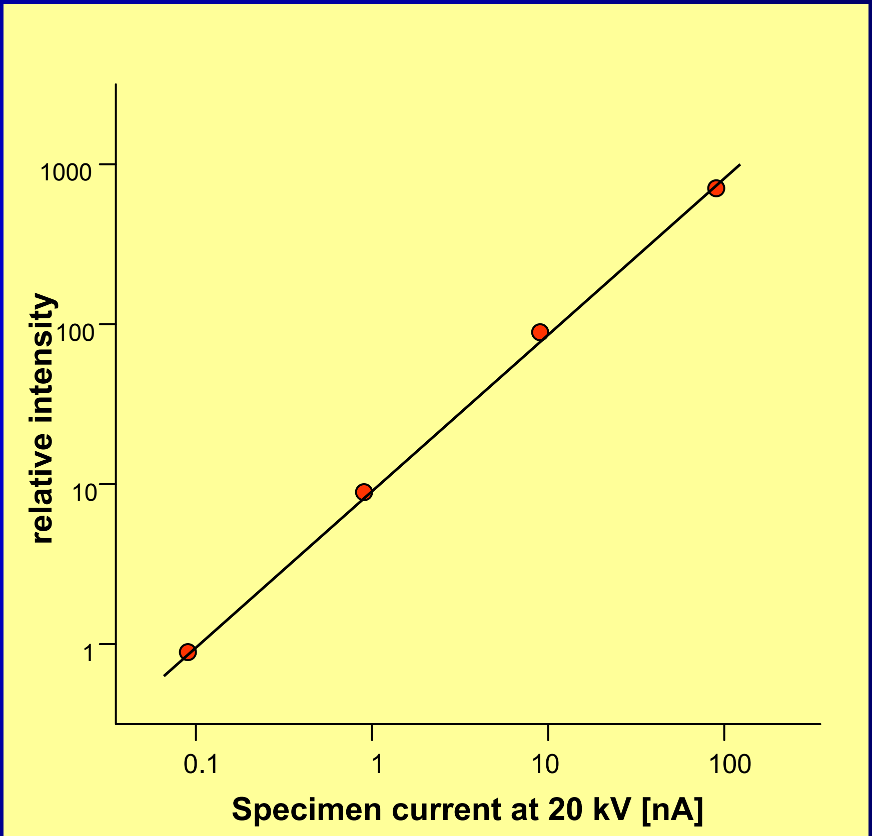
Factors influencing CL properties/intensity

Factors influencing the CL intensity

- sample preparation
  (sample surface, thickness, etc.)
- sample coating
  (quality, thickness, material, etc.)
- temperature
- analytical conditions
  (acceleration voltage, beam current, vacuum, etc.)
- time
  (especially transient CL)

Analytical parameters influencing cathodoluminescence





Variation of CL intensity with sample temperature for quartz
(modified after Hanusiak & White 1975)

Variation of the intensity of quartz CL with beam current
(modified after Hanusiak 1975)

Sensitizing and quenching

Interaction between two or more ions with transfer of ecitation energy from one ion to another resulting in changes of their luminescence.

***Sensitizing of luminescence*:**

(1) emission-reabsorption („cascade“ luminescence)

(2) resonance radiationless

(3) nonresonance radiationless

***Quenching of luminescence*:**

(1) concentration quenching (self quenching)

(2) quenching by ions with intense charge transfer bands (e.g. Fe^{2+}, Co^{2+})

(3) quenching due to lattice defects

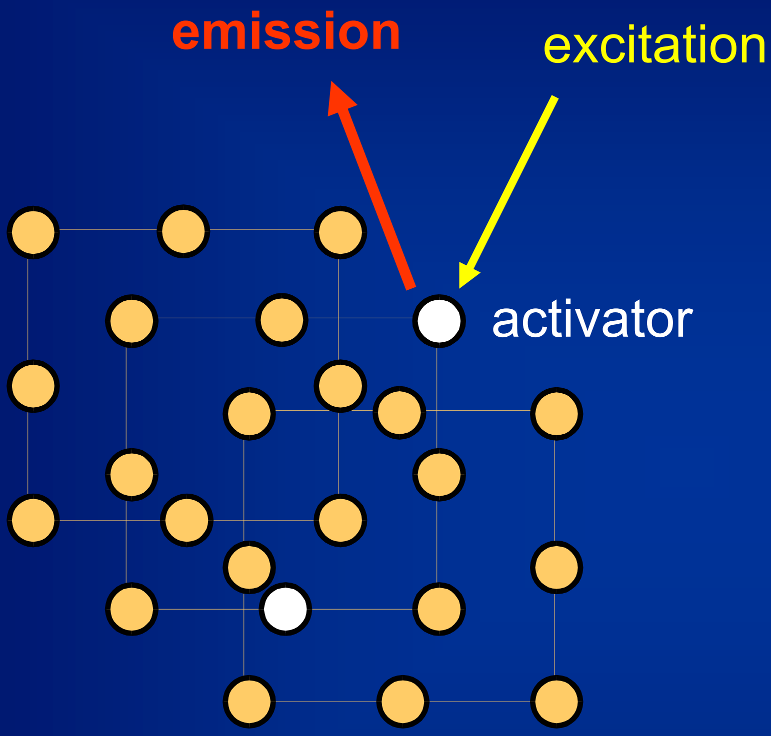
(4) thermal quenching

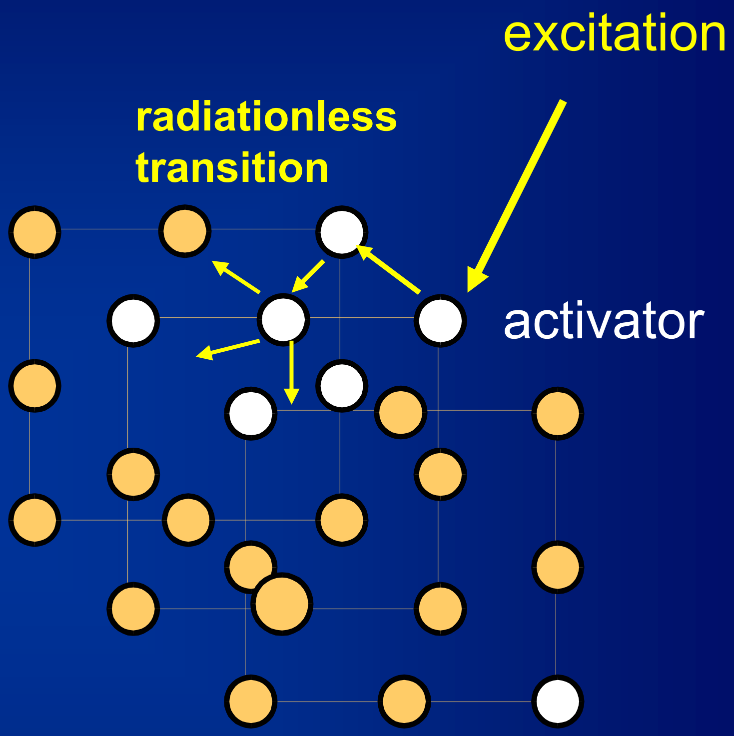
typical sensitizer ions:

(1) ions with intensive absorption bands in the UV (e.g. Tl^{+}, Cu^{+}, Pb^{2+}) for sensitization of Mn^{2+}

(2) ions of transition metals (e.g. Mn^{2+}) for sensitization of REE^{3+}

(3) $REE^{2+/3+}$ for sensitization of REE^{3+}

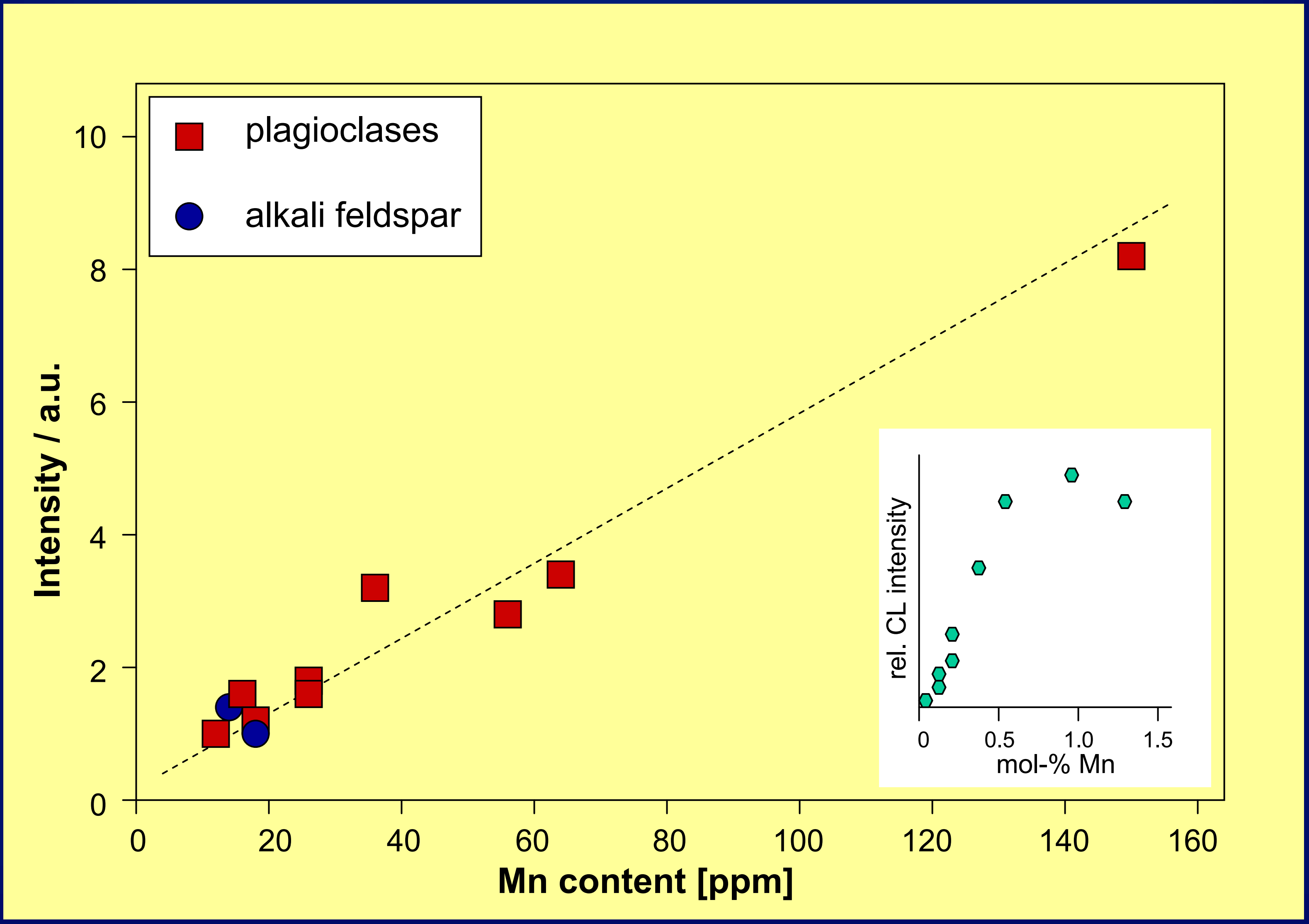




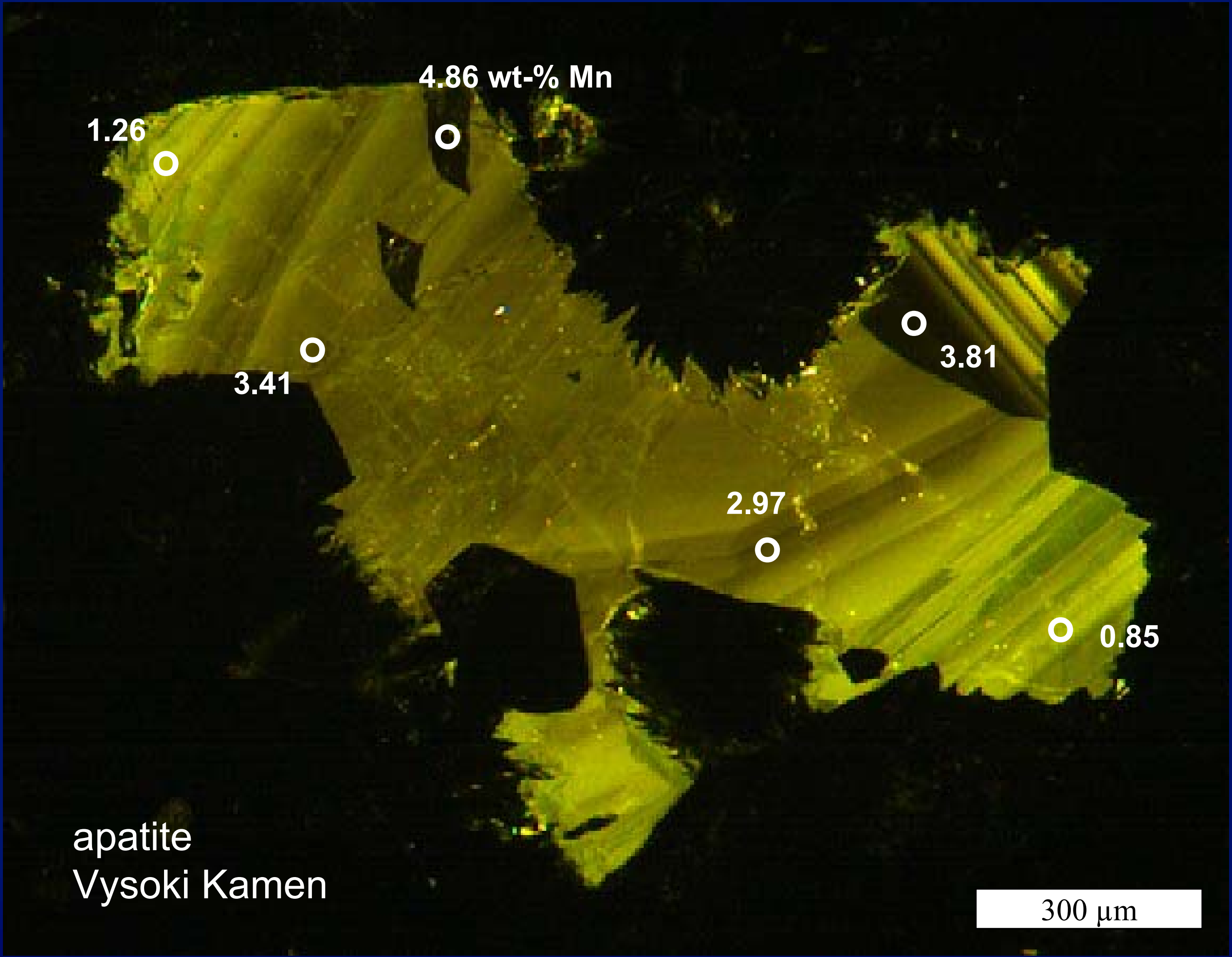
luminescence emission

concentration quenching

Intensity of the Mn^{2+} activated CL (ca. 560 nm) in dependence on the Mn content in feldspar



Concentration quenching („self quenching“) of Mn^{2+} activated CL in apatite



from Kempe & Götze (2002)

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*
phosphates	*apatite*
carbonates	*calcite, aragonite, dolomite, magnesite*
silicates	*feldspar, quartz, zircon, kaolinite*

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

- **no luminescence of conductors, iron minerals and Fe-rich phases**

General applications of CL in geosciences

- identification of minerals, mineral distribution and quantification
- typomorphic properties
  (CL colour, CL behaviour, spectral characteristics)
- crystal chemistry
  (trace elements, internal structures, zoning)
- reconstruction of geological processes
- characterisation of technical products
  (also non-crystalline phases !)