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20 YEARS OF EXPERIENCE IN CATHODOLUMINESCENCE RESEARCH AT THE PGI-NRI

20 LAT DOŚWIADCZEŃ W BADANIACH KATODOLUMINESCENCJI W PIG-PIB

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Abstract. The use of catholuminescence analysis in scientific research at the PGI-NRI has a 20-year history. The method, combined with other analytical techniques, has become an effective tool in widely understood mineralogical and petrographic investigation reported in numerous publications.

Key words: cathodoluminescence studies, CL images, CL spectra.

Abstrakt. Wykorzystanie analizy katodoluminescencyjnej w badaniach naukowych w PIG-PIB ma już 20-letnią historię. Metoda ta, w połączeniu z innymi technikami analitycznymi, stała się skutecznym narzędziem w szeroko pojętych badaniach mineralogiczno-petrograficznych. Potwierdzają to liczne publikacje.

Słowa kluczowe: badania katodoluminescencyjne, obrazy CL, widma CL.

The cathodoluminescence analysis is a microscopic method of petrographic research. It uses the phenomenon of luminescence of minerals, induced by electron beam bombardment. The prerequisite for mineral luminescence is the presence of luminescence centres in crystals (crystal lattice defects).

Simplifying, there are two basic sources of luminescence in minerals: admixtures of trace elements and internal defects in the crystal lattice structure of minerals.

The worldwide development of CL research in geology took place in the 1960s. It appeared that the analysis of the characteristic features of luminescence (cathodoluminescence) of individual minerals is a new research tool in broadly understood petrology (*e.g.*, Zinkernagel, 1978; Matter, Ramseyer, 1985; Marshall, 1988; Sikorska, 1994; Adams, MacKenzie, 1998; Götze, 2000; Machel, 2000; Richter *et al.*, 2003; Pahl, Sikorska, 2004). In the course of time, CL analysis has been successfully used in many other fields of science, ranging from palaeontology to archaeology and medicine (Götze, 2000, 2002; Sikorska, 2000a).

The most commonly used equipment (being the simplest, cheapest and extremely effective) is the so-called standard cold cathode, in which electrons are released between the cathode and the anode in ionized gas. It is combined with a polarizing microscope, and the observed research effects are represented by colour images (with preserved natural, original CL colours) subsequently recorded on photographs (Fig. 1).

A leap to a completely different quality of CL tests was the adaptation of the electron microscope (SEM) for cathodoluminescence analysis. In this case, the tungsten filament is used as a source of electrons. The SEM-CL method provides a black-and-white image, but its major advantage is the possibility to obtain much greater magnifications as compared to optical microscopy. In addition, it is possible to compare CL images with SE and BSE images and to perform chemical microanalysis (EDS).

The use of spectrometers for cathodoluminescence studies created completely new research prospects (Sikorska, 2005). Analysis of CL spectra provides the possibility to determine the factors causing luminescence in a given mineral, and even in its various areas differing in luminescence. We can determine whether the given emission band of the CL spectrum results from the presence of internal defects in the

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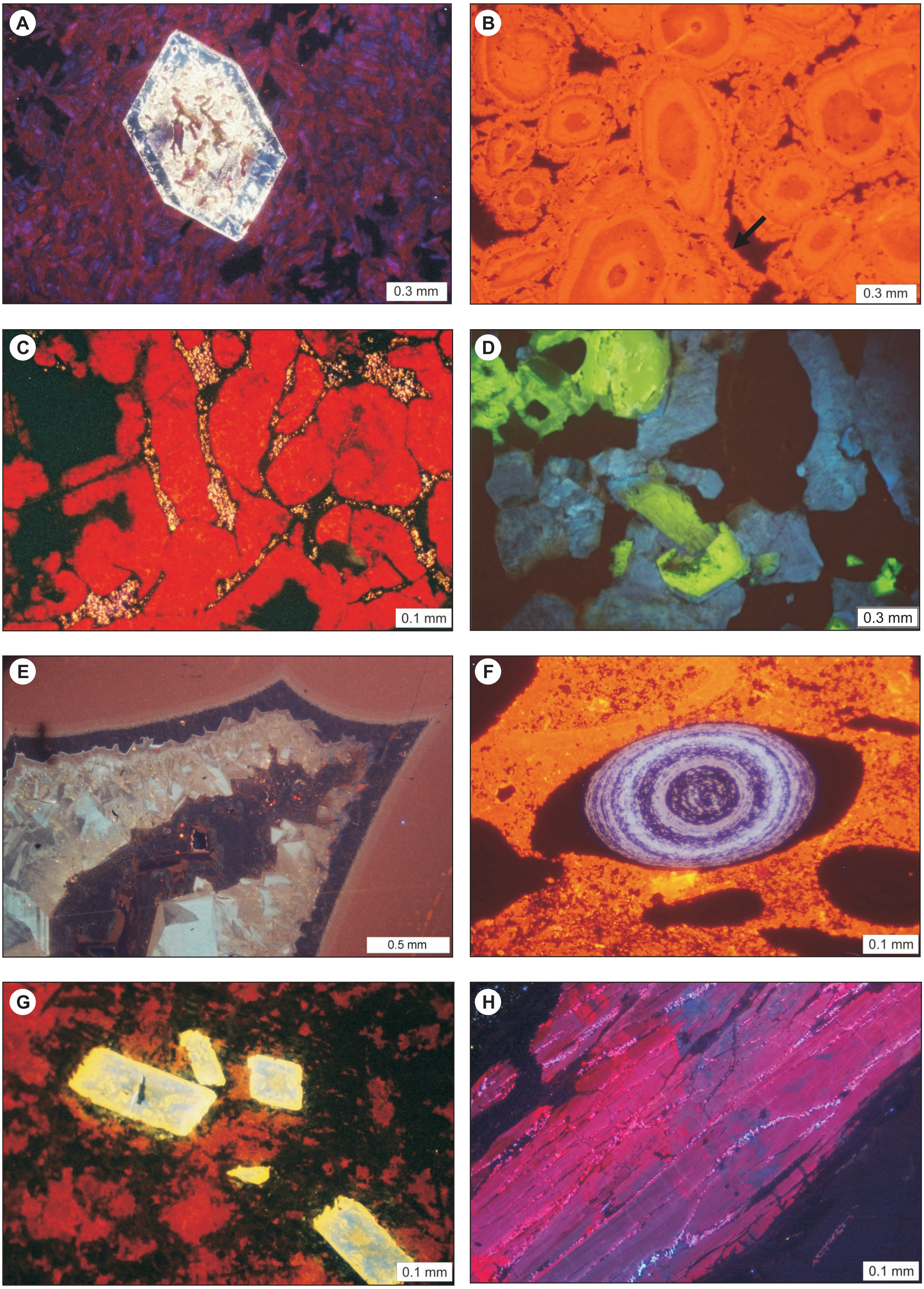
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Fig. 1. CL images

A – zircon in mariupolite; **B** – Cambrian limestone; **C** – diamonds (yellow CL) in a meteorite; **D** – feldspars in the Karkonosze granitoid; **E** – quartz druse in agate; **F** – phosphatized chamosite ooid; **G** – sellaite (yellow CL) in dolomite rock; **H** – kyanite in mica shale

Obrazy CL

A – cyrkon w mariupolicie; **B** – wapień kambryjski; **C** – diamenty (żółta CL) w meteorycie; **D** – skalenie w granitoidzie karkonowskim; **E** – druza kwarcowa w agacie; **F** – sfosfatyzowany ooid szamozytowy; **G** – sellait (żółta CL) w skale dolomitowej; **H** – dysten w łupku mikowym

crystal lattice or defects resulting from admixture (impurity) of a chemical element (Fig. 2).

Obviously, the interpretation of CL spectra is possible thanks to the wide range of scientific publications presenting results of highly specialized research on the crystal structure (*e.g.*, electron paramagnetic resonance, ionic microbe analysis) in combination with CL spectral analysis (Gorobets, Rogojine, 2002; Gaft *et al.*, 2005).

In recent years, attempts have been made to use CL spectral analysis for quantitative determination of trace elements (activators) in minerals (Gillhaus *et al.*, 2001).

The Polish Geological Institute was the first scientific institution in Poland to purchase, in 1996, the CCL 8200 mk3 equipment combined with a polarizing microscope. Since then, the author has been conducting cathodoluminescence research using the instruments for both her own scientific projects and those conducted by other researchers from many scientific centres. Since 2002, when the PGI purchased the new VIS-View 900 cathodoluminescence equipment with a CL spectrometer, these studies have been complemented with CL spectral analyses of minerals.

The author's own work focused mainly on Cambrian sedimentary rocks of the East European Craton, and covered an entire range of diagenetic processes (Sikorska, 1998a). Particularly important were CL investigations of quartz cementation and its impact on reservoir properties of sandstones (Sikorska, Pacześna, 1997; Sikorska, Jaworowski, 2007). Various forms of phosphate occurrences in Cambrian and Ordovician deposits (Fig. 1F) could be examined due to their unique cathodoluminescent properties (Sikorska, 1998b). To analyze the silicification process, Cambrian sandstones from the Wiśniówka area in the Holy Cross Mountains were also studied (Sikorska, 2000b).

CL observations of detrital material proved of special importance for speculations about its origin in uppermost Vendian and Cambrian deposits in the foreland of Pomeranian Caledonides (Sikorska, 2000c).

CL analysis was a meaningful tool in studying the origin of Upper Cambrian limestones in the Baltic Depression (Sikorska, 2007). Atypical forms of CL structures in calcite crystals, in particular their origin, are currently the subject of studies by Polish and foreign specialists (Fig. 1B).

Thanks to the CL research, it was possible to discover and describe the first occurrence of sellaite MgF_2 in Poland (Fig. 1G). It is a very rare mineral, although it occurs in various types of rocks. Sellait was found in boreholes of NW Poland in the Zechstein dolomites with abundant anhydrite cement (Sikorska, 2008). Diagenetic processes and the sequence of crystallization of cements were the subject of many cathodoluminescence studies in both Zechstein formations (Ca2) (Słowakiewicz *et al.*, 2008, 2010) and Jurassic rocks (Kozłowska *et al.*, 2010).

CL analysis proved to be an indispensable tool in comprehensive studies of clay shales for shale gas exploration, allowing a quick estimation of the proportions of feldspars and carbonates, and the presence of microfractures in fine-grained rocks (Sikorska-Jaworowska *et al.*, 2016).

The CL instruments, particularly when combined with spectral analysis, have been used in scientific projects implemented in cooperation with other scientific institutions. Their research results have been published in many Polish and foreign journals.

Several papers are devoted to detailed mineralogical investigations, using various analytical methods combined with CL (SEM, EDS, EPMA, ICP-OES, ICP-MS, Raman spectroscopy), in the syenite Mariupol Massif and the Oktyabrsky Massif, Ukraine. The studies dealt with dissolution and recrystallization of zircon (Fig. 1A), origin of REE-rich phosphate minerals, transformation of nepheline and albite into sodalite, and fenitization manifested by a CL colour change of feldspars (Dumańska *et al.*, 2010, 2011, 2012, 2015a, b).

CL analysis was also employed to study rocks from the Kola Peninsula: vein mineralization by prehnite-albite-calcite in metamorphic rocks from the Lapland Granulite Belt and Ca-Mg-Sr carbonates from the Kovdor Massif (Huber *et al.*, 2007, 2018).

Results of CL analyses proved helpful in the investigations of magmatic processes in the Tatra granite, petrogenesis of granitoid rocks from the Western Tatra Mts., which are extremely rich in apatite, and hydrothermal alterations in the Karkonosze granitoid (Fig. 1D) (Ciesielczuk, Sikorska, 2007). To better understand the post-orogenic processes and mobility of chemical elements, the formation of a fluoroapatite-rich dike on Mount Baraniec in the Slovak Tatra Mts. was investigated. Unique CL images and CL spectra were obtained for kyanite (Fig. 1H) from mica shales of the Slovak Tatra Mts. (Gawęda, Sikorska, 2010; Szopa *et al.*, 2013; Pyka *et al.*, 2014; Gawęda *et al.*, 2016).

Lower Silesian trachyandesites were examined for a better understanding of albitization process of feldspars, which is manifested by a change in CL colours. The presence of luminescence centres (structure defects) Al-O^--Al and Al-O-Ti bridges, causing blue luminescence in feldspars, was discussed (Powolny *et al.*, 2018).

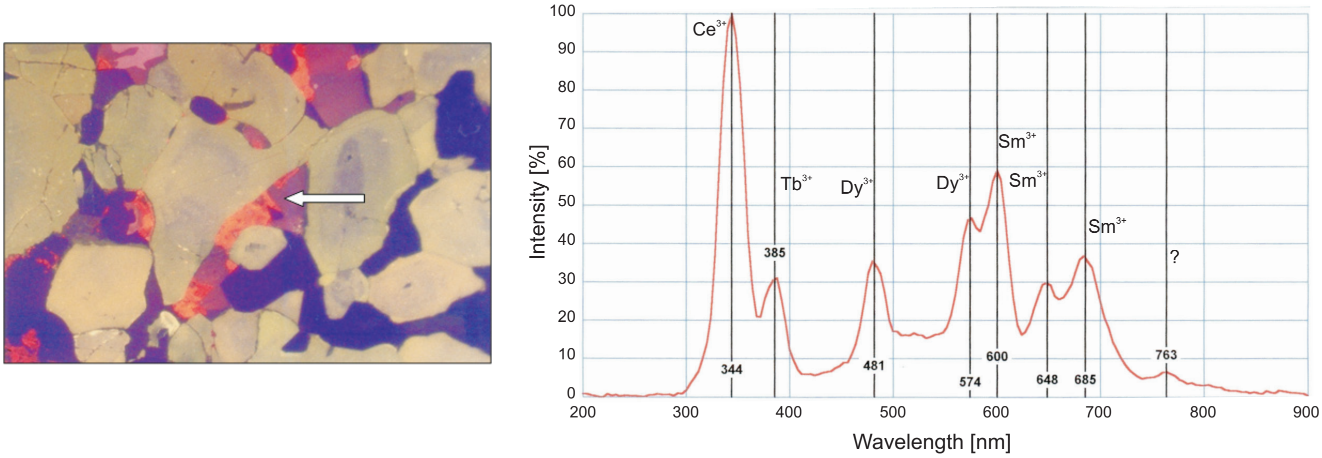

Fig. 2. CL image and CL spectrum of anhydrite

Obraz CL i widmo spektralne CL anhydrytu

To the extremely interesting and rarely conducted CL projects belong studies of meteorites. In the PGI-NRI, we succeeded in taking interesting CL photos and obtaining CL spectra of fine diamond grains in ureilite meteorites (Fig. 1C). Three CL types of diamonds have been identified: pink, green-blue and yellow, showing characteristic CL spectra that allowed classifying them as type Ia diamonds (Sikorska *et al.*, 2011).

An interesting experience was the combination of the effects of CL research and fluid inclusion analysis to determine conditions of the formation of REE-rich carbonatites from the Tajno Massif in the Suwałki region (Kozłowski *et al.*, 2005).

Many different research projects include: carbonate cements in Cambrian conglomerates from Australia, processes ofcultivated pearl formation in shells of breeding clams (China), Paleogene amber-bearing sands (Ukraine), untypical bitumen-containing agates from Nowy Kościół (Fig. 1E) and agates from Płóczki Górne (Lower Silesia), carbonate and sulphate mineralization in ore-bearing dolomites (Silesian-Cracow district), carbonate veins in Neogene volcanites (Pieniny Klippen Belt), and nelsonites – apatite rocks from the Anorthosite Suwałki Massif. In the latter rocks, anhydrite of unusual violet CL was identified, and the spectral image shows the trivalent rare earth elements: terbium, dysprosium and samarium, to be the activators (Fig. 2).

Currently, there are ongoing cathodoluminescence studies of feldspars in the Ashua limestones (Peru), which shed new light on their origin. CL images revealed the processes of both feldspar albitization (at the magmatic stage?) and growing authigenic albite rims.

Cooperation in the field of archaeology and art history involved, among others, research on sandstone elements of sculptures and a gate at the royal residence of Wilanów, architectural fragments stolen during the Swedish Deluge and excavated from the Vistula River, and diagenetic processes in Neogene and Cretaceous sandstones of Lower Silesia with respect to their use in Romanesque buildings.

CL photographs were taken of the Carrara marbles, beach sands, aragonite otoliths (ear organs of fish), and shell fragments of contemporary and fossil snails as part of palaeontological studies on the ontogenesis of these organisms.

During all these scientific projects, CL analysis was a complementary method in comprehensive mineralogical and petrographic studies, sometimes playing a key role in the final solution to a given problem.

In the light of the author's experience, the question whether it is worth using the CL analysis in scientific research becomes a rhetorical question.

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STRESZCZENIE

Analiza katodoluminescencyjna jest mikroskopową metodą badań petrograficznych, która wykorzystuje zjawisko luminescencji minerałów.

Najpopularniejsza jest standardowa aparatura z tzw. zimną katodą, która współpracuje z mikroskopem polaryzacyjnym, a obserwowane efekty badań są w postaci kolorowych obrazów (fig. 1). Spektralna analiza CL pozwala uzyskać widma CL i wnioskować o czynnikach wywołujących luminescencję danego minerału (fig. 2).

Aparatura CL, w szczególności w połączeniu z analizą spektralną, była i jest wykorzystywana w projektach naukowych realizowanych w PIG-PIB oraz we współpracy z innymi ośrodkami naukowymi, a wyniki badań publikowano w wielu polskich i zagranicznych czasopismach naukowych.

Przedmiotem badań były wszystkie rodzaje skał: od osadowych (piaskowce, wapienie, dolomity, łupki), przez magmowe i metamorficzne (granity, sjenity, mariupolity, karbonatyty, łupki mikowe), po meteoryty (diamenty w ureilitach). Obserwacje CL są kluczowym elementem w badaniach procesów diagenetycznych w osadach oraz przeobrażeń minerałów, zachodzących w procesach pomagmowych. Dzięki luminescencji udaje się ujawnić obecność niespotykanych wcześniej faz mineralnych (sellait w cechsztyńskich skałach dolomitowych). Analiza CL okazała się nieodzownym narzędziem w kompleksowych badaniach łupków ilastych w aspekcie poszukiwań gazu łupkowego (oszacowanie udziału skaleni, węglanów oraz obecności mikrospękań)

We wszystkich wymienionych w artykule projektach naukowych analiza CL stanowiła dopełnienie kompleksowych badań mineralogiczno-petrograficznych, odgrywając niekiedy kluczową rolę w ostatecznym rozwiązaniu danego problemu.