Application of Combined Cathodoluminescence and Energy-dispersive X-ray Spectroscopy for Analysis of Mineral Raw Materials

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ABSTRACT: Energy-dispersive X-ray spectroscopy (EDS) attached to the cathodoluminescence (CL) equipment enables the analyst to identify minerals and other components readily and simultaneously with CL and polarising microscopy. It is especially helpful when rapid analysis has to be carried out of samples of rocks or mineral raw materials with complex composition. Moreover, the instrumentation described here, can be used as a microprobe for easily mounted pellets of finely ground powders. The results rapidly obtained by this method represent reproducible data and are comparable to those obtained by EDS systems of scanning electron microscopes. The analytical procedure was successfully tested on thin sections, rock specimen and powders of various sedimentary raw materials and hydrocarbon reservoir rocks, containing transparent and opaque, as well as luminescent and non-luminescent minerals and rock fragments.

1 INTRODUCTION

The importance of thin section analysis carried out by means of polarising microscopy combined with cathodoluminescence (CL) microscopy has been proven for many years. For example, in applied industrial research related to mineral raw materials and hydrocarbon exploration (e.g. Houseknecht 1991, Götte 2000, He et al. 1997). A significant progress in this area can been in the possibility to combine this technology with simultaneous energy dispersive spectroscopy (EDS). Results obtained by combined CL-EDS analysis from a series of sandstone samples were recently published (Vortisch et al. 2003). The present publication is focusing on the application of this technology to the study of raw materials, including hydrocarbon reservoir rocks.

2 ANALYTICAL PROCEDURES

For simultaneous CL-EDS analysis of uncoated thin sections, rock slabs and powder pellets a cold cathode equipment combined with an energy dispersive X-ray detector was applied for the present study (manufacturer: CITL – Cambridge Image Technology Ltd.; for technical details see Vortisch et al. 2003). Powder pellets were produced by pressing finely ground rock powder mixed with a small amount of distilled water on a glass slide. The CL-EDS equipment is used together with a standard polarising microscope. Thus polarising microscopy, CL and EDS can be carried out simultaneously. The EDS results are comparable to those obtained by an EDS system (with Be window) attached to a scanning electron microscope (SEM), except for the larger spot size (< 100 µm). Advantages, compared to the SEM (non-environmental), are the much easier handling (no coating, no high vacuum system) and the possibility of simultaneous light optical and CL observation, and also the lower price of the equipment.

3 SAMPLES ANALYSED

3.1 Clinoptilolite (thin section, Figs. 1, 2)

This sample was taken from a Slovakian economic sedimentary clinoptilolite deposit of Cenozoic age. The sodium content of this clinoptilolite deposit is very low (XRF whole rock analysis: 0.29% Na₂O). Considerable sodium concentrations were only found in feldspar grains (essentially plagioclase, potassium feldspar very rare) which represent almost
all luminescing grains in Figure 1. Quartz occurs only in trace amounts. The CL colour of the plagioclase grains is very uniform (between "moderate yellow green" and "moderate yellowish green" according to the "Rock-Color Chart" of Goddard et al. 1984). No CL could be observed on the very fine-grained clinoptilolitic matrix of this sample. EDS spectra of the clinoptilolitic matrix and a plagioclase grain are shown in Figure 2 (spectra 1 and 2). For comparison the EDS powder spectrum of another clinoptilolite sample (used as standard) with 3.60% Na₂O (XRF) is shown as well (Fig. 2, spectrum 5). With exception of sodium and calcium the chemistry of the Slovakian clinoptilolite is very similar to the one of the standard as is shown by the EDS spectra. Proportions of main elements by XRF: Slovakian clinoptilolite – 66.4% SiO₂, 12.2% Al₂O₃, 3.33% K₂O; standard – 66.8% SiO₂, 11.3% Al₂O₃, 3.74% K₂O.

Figure 1. Optical (A, C; plane polarized light) and CL images (B, D) of thin sections (width of all images c. 3 mm). A: Clinoptilolite with feldspar grains (essentially plagioclase) which correspond to nearly all brightly translucent grains. B: CL image of A, showing essentially plagioclase (see text). C: Lower Cambrian heavy mineral placer, consisting mainly of quartz (detrital and cement, low relief, medium grey), detrital zircon (high relief, dark grey, example: arrow 3) and authigenic anatase (opaque in black and white copy, example: arrow 4). D: CL image showing mainly zircon grains. Anatase (originally greenish CL) in black and white copy only faintly visible. Very short exposure time in order to prevent overexposure of zircon, CL of quartz therefore not visible (detrital quartz and quartz cement can easily be differentiated in these sandstones by CL, see e.g. Vortisch et al. 2003, Fig. 2).
3.2 Heavy mineral placer (thin section, Figs. 1, 2)

The heavy mineral suite of this Lower Cambrian heavy mineral placer from South Sweden consists essentially of detrital zircon and diagenetically formed anatase, a wide-spread TiO_2 polymorph (Vortisch 1975). Zircon shows mainly light bluish CL colours with zoning in some grains, as noted by other authors (see e.g. Marshall 1988), whereas the anatase luminescence is greenish. Typical EDS spectra of these minerals are shown in Figure 2 (spectra 3 and 4), minerals optically similar to those identified here (e.g. monazite that might be similar to zircon) can easily be excluded by means of EDS.

3.3 Red brick clay (powder, Fig. 2)

Main elements of this clay from a German economic clay deposit are Si, Al, Fe and K (see spectrum 6). Proportions of oxides according to X-ray fluorescence analysis (XRF): 64.25% SiO_2, 17.60% Al_2O_3, 5.93% Fe_2O_3, 4.29% K_2O, 4.35% LOI. The
3.4 Red ceramic clay (powder, Fig. 2)

This clay is used for the production of traditional indigenous ceramics in a Costa Rican village. Main chemical components are only SiO₂, Al₂O₃ and Fe₂O₃. The relatively high content of aluminium besides dominant silicon as well as the absence of alcalies and alcali-earths clearly indicate the main mineralogical components: kaolinite (dominant), quartz, and some hematite. This mineralogy was confirmed by XRD.

3.5 Black ceramic stain (powder, Fig. 2)

This material is applied for the staining of the indigenous ceramics mentioned above. It consists predominantly of manganese (Fig. 2, spectrum 8). As further elements with considerable proportions occur silicon, potassium, calcium, and with minor proportions titanium, iron (indicated FeKα peak superimposed on MnKα peak), aluminium and magnesium. Corresponding to the EDS spectrum the manganese minerals cryptomelane and bixbyite were identified by XRD as dominant mineral components. Moreover, quartz and traces of zeolite are visible in the diffractionograms.

3.6 High grade iron ore (hand specimen, Fig. 3)

This hand specimen from an itabirite mine in Minas Gerais is almost purely composed of hematite. The analysed slab was cut off by means of a diamond saw. For analysis no further treatment was necessary. The combined CL-EDS analysis proved the existence of a variety of non-hematite components. Minute lenses of whitish material revealed bluish CL (e.g. Houseknecht, 1991, Plate 5) and EDS spectra typical for clay minerals of the kaolinite subgroup: Si:Al ratios of 1:1, no measurable amounts of aluminas and alcali-earths were observed. The CL-EDS features presented in Figure 3 indicate the admixture of finely dispersed quartz + clay minerals within the predominantly hematite matrix. Besides these components, others containing sulfur or phosphorus were observed. More research will be carried out on this type of iron ore samples.

3.7 Hydrocarbon reservoir sandstones

CL-EDS analysis was applied for various reservoir sandstones. It proved to be extremely helpful for rapid petrographic analysis of sandstone thin sections. Both, clastic grains as well as cements are readily determined and quantifiable. In the case of carbonate cements the analytical conditions for establishing a cement stratigraphy are considerably improved.

4 CONCLUSIONS

The potential of combined CL-EDS analysis was tested for various raw materials and sedimentary rocks. Thin sections, unpolished rock slabs as well as easily mounted powder pellets, were studied without further treatment. Based on this test it can be stated that mineral raw materials as well as rocks in general can be analysed faster and with more accuracy by means of this technology. Moreover, it helps the analyst to understand more rapidly the samples he has to study, thus shortening the time of individual training.

5 REFERENCES


