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Electron Microprobe Analyser (EPMA) – the Principles and Applications in Modern Geology

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Introduction

The principle of electron microprobe analysis was firstly described in 1947 by Hillier, (U.S. patent). He defined it as a chemical analysis using characteristic X-ray spectra excited by a focussed electron beam. In 1951 R. Castaing, under the supervision of Professor A. Guinier at the University of Paris, wrote his Ph.D. thesis, where he presented the foundations of the theory and practice of quantitative electron microanalysis. He described the successful development of a new instrument destined to have an impact in many fields of science and technology. The instrument originated by join of classical electron optics and electron microscope with fitted X-ray spectrometer. It was called *the electron microprobe* or *the electron microprobe analyser (EPM - EPMA)*. The first commercial instrument was developed in Paris, France by the Cameca Company, in 1958 (Reed, 1997).

The methods of electron microprobe analysis have its important place also in Slovak geology. The first EPMA JEOL - 733 Superprobe was bought in 1981. It was used 20 years, since 1981 to 2001, at Geological Survey of Slovak Republic (GÚDŠ, GSSR) Bratislava. This instrument was rebuilt and modernised in 1992 - 1995.

JEOL JXA - 733 SUPERPROBE was the electron microanalyser with four WDS spectrometers with crystals TAP, PET and LIF, controlled by KEVEX SESAME system and KEVEX DELTA+ EDS spectrometer with software package QUANTEX+. There were produced plenty of WD and ED analyses, BEI and SEI images.

In 2001, this old instrument was replaced by the CAMECA SX-100 electron microanalyser, which represents one of the most modern instruments used for the investigation of geologic, but not only geologic materials. In almost two years of full service, it persuades about its important place in the Slovak geology.

Principle of electron microprobe analysis

Electron microprobe analysis is a non-destructive analytical method for chemical analyses of small volumes of solid samples. Accelerated electrons in the form of a finely focused electron beam (probe) bombard a polished sample. X-rays are excited by the interaction of this electron beam with atoms of the sample. The place of this interaction is very small (usually some μm) so we can name it as the *analysed point*.

The versatility of this method among material sciences is based on its simplicity. X-ray spectrum is mostly independent on a physical and chemical state of studied material and it directly depends only on the atomic number of the present elements. The X-ray spectrum contains lines which are characteristic of the elements present, hence an analysis is easy to obtain by identifying the lines from their wavelengths or photon energies.

Electron microanalysis can be performed with two systems. In ***Wavelength dispersive method*** *(WD)* X-ray of defined *wavelength* corresponds to certain element. Generated X-rays are diffracted on crystals and then detected by a detector. The position of crystal and detector on Rowland circle follows Bragg´s law. In ***Energy dispersive method*** *(ED)* X-ray with defined *photon energy* corresponding to certain element is detected by so called Si(Li) detector. Since 1968 the solid-state Li-drifted silicon detector is known and widely used for detection of low energy X-rays.

Qualitative analysis serves for identifying of elements present in the sample. In this case X-ray spectrometer records the whole spectrum over the range of wavelengths (WD method) or energies (ED method). Lines and energies of present elements in acquired spectrum are identifiable by the reference to tables.

In *quantitative analysis* the intensities of X-rays correspond to the concentrations of elements present in studied material. In the case of WD method, the intensities are detected in counts per time. In ED method, the intensities are detected also in count per time, but for the certain energy window (in eV).These intensities are compared with intensities from standards of known composition (pure elements, natural and synthetic compounds). According to known standard composition we can calculate composition of the studied material. We need to make number of corrections to the measured data to obtain a precise analysis, e.g. substraction of background, "matrix corrections". ZAF correction which takes into account correction factors depend on atomic number, absorbtion and fluorescence is widely used (Reed, 1997).

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Other applications of EPMA

EPMA yields not only information about the composition of samples but also image observations. Images from EPMA are comparable with those acquired from classical scanning electron microscope, but with less magnification and resolution. Images are created by the scanning electron beam in a television-like raster and displaying a collected signal from the detector on the screen. Scanning electron beam interacts with sample surface to produce various types of signals (Fig. 1). A specific type of image corresponds to specific type of signal (secondary electrons, back-scattered electrons, cathodoluminescence).

Secondary electron images (SEI) give us information about sample surface. Secondary electrons are weakly bounded electrons released from the surface of the sample. ***Back-scattered electron images*** (BEI) give us approximate information about the composition of the sample, darker places at these images contain elements with lower atomic number and vice-versa. The back-scattered electrons are electrons of beam scattered out from the sample after interaction with atom core. The higher atomic number of element, the more of interactions which produce these electrons. ***Cathodoluminescence*** is based on the detection of visible light which is also generated by interaction of electron beam with the sample. Cathodoluminiscence is observable only in some materials e.g. quartz, feldspars etc. Cathodoluminescence images are used for identification of inner texture, small veins, cracks, growth zonation.

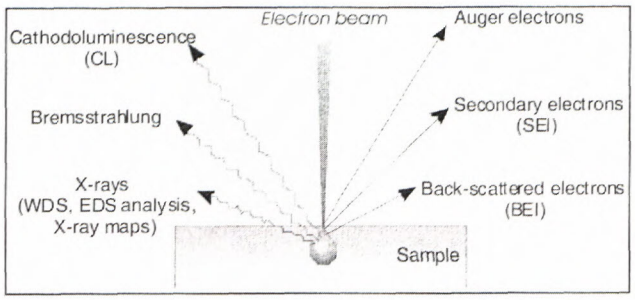

Figure 1. Interaction between electron beam and sample gives an origin to the various types of signals, which can be detected and used in electron microscopy and microanalysis. The space of interaction has an onion shape. (Compiled by V . Kollárová according to Energy - Dispersive X-ray microanalysis. An Introduction. Kevex Instruments, Inc., 1989, 52 p.)

The main construction principles of EPMA

An electron microprobe (Fig. 2) consists of the main frame with column and spectrometers, then of block of electronics, cooling system, vacuum system and controlling computer.

The electron beam is generated and corrected in the vertical column positioned on the main frame. It consists of electron gun, alignment coils, condenser lens, probe current detector, aperture, scanning coils, stigmator and objective (final) lens. The electrons are produced thermoionically from heated tungsten filament in the top of the column. They pass through Wehnelt (focusation elect-

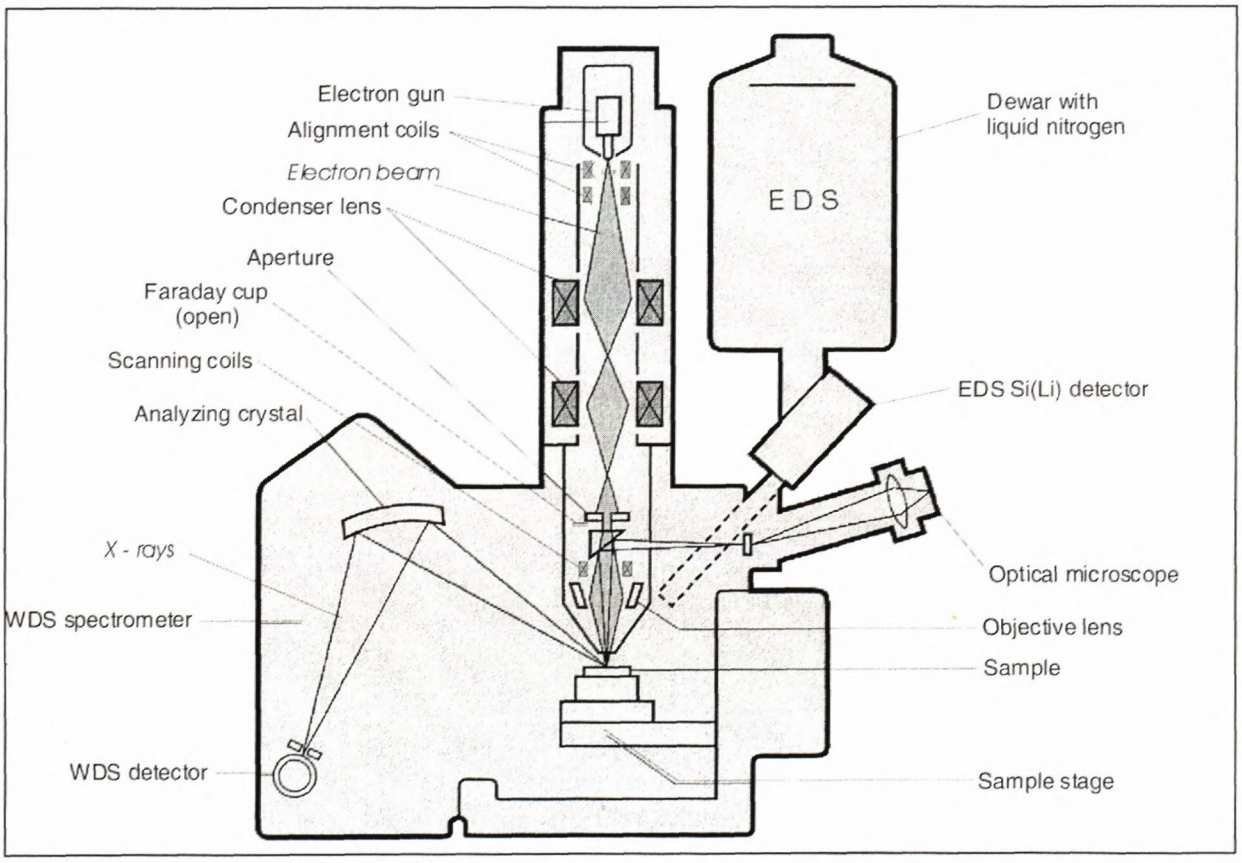

Figure 2. Schematic diagram of electron probe microanalyser. Electron gun consists of filament, Wehnelt and anode. (Compiled by V. Kollárová and P. Siman according to propagation materials of fy. JEOL).

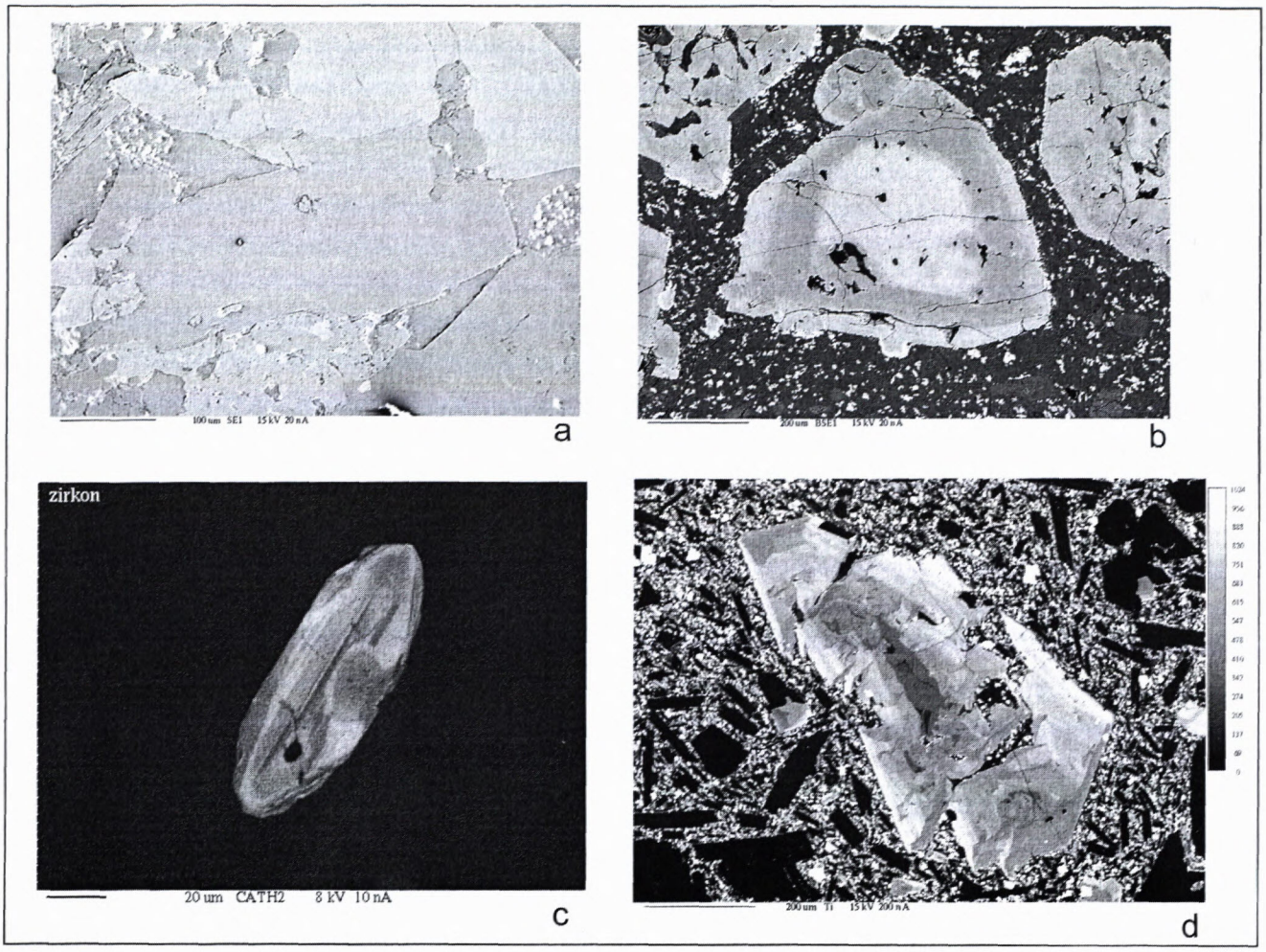

Figure 3. - Images taken by electron microprobe CAMECA SX-100 at Slovak Geological Survey, Bratislava
a - secondary electron image, porphyric quartz diorite, Javorie Mts., b - back-scattered electron image, zoned clinopyroxene, basaltic andesite, Kremnické vrchy Mts., c - cathodoluminescence image, zircon in stromatitic migmatite, Slovenské rudohorie Mts. d - X-ray map, distribution of Ti in zoned clinopyroxene, alkaline basalt, Banská Štiavnica

rode) and grounded anode. Electrons are speeded up by accelerating voltage 5 to 40 kV applied between a filament and anode. The electron beam is then collimated and focused by a system of magnetic lenses, apertures and coils. Prepared electron beam with specific beam diameter is used for analysing. Scanning coils are used for electron beam deflection to produce various types of images. The sample stage for fitting standards or samples is placed in the bottom of the column. Up to 5 WD spectrometers can be attached to the column. Inside we find the moving analysing crystals and detectors. Optionally we can add an ED detector. The sample inside in the column can be observed by optical microscope, usually with CCD camera. The block of electronics control the whole instrument including cooling system, vacuum system, electron optics etc. In advanced instrument all data are collected in computer.

EPMA in the laboratory of Geological Survey of Slovak Republic

The Department of Electron Microanalysis in the Geological Survey of Slovak Republic is equipped with electron microprobe analyser CAMECA SX-100. This instrument is a representative of the new generation of microprobe in the most modern and unique laboratory of this type in Slovakia. Here are some basic parameters:

- three built-in vertical spectrometers with large analyzing crystals LLIF, LPET, LPCO and TAP, PC2
- energy-dispersive (ED) spectrometer KEVEX with ultra-thin window Moxtek AP 1.3
- SEI, BEI and cathodoluminescence detector for images
- very stable electron beam (beam stability 0.3% in 12 hours)
- very precise system of movement of the versatile specimen stage
- optoelectronics, which controls stage, detector and crystals
- coaxial optical zoom microscope with autofocusing colour CCD camera, field of view 0.25 – 1.7 mm, polarized light
- SUN microsystem operating basis

The analytical possibilities are summarised as follows:

- wavelength-dispersive (WD) analyses from *boron* to *uranium* with routine precision 0.01 wt. %

- semiquantitative and quantitative energy-dispersive (ED) analyses from *fluorine* to *uranium*
- line profiles with stage or beam movement
- X-ray mapping
- high-quality BEI and SEI images with resolution up to 2048x1536 pixels
- cathodoluminescence images
- all results available in digital and printed form

Geological applications of EPMA

Methods of microanalysis and image analysis are commonly used in geology, basic and applied research. It is a non-destructive method for analysing samples of rocks and minerals with maximum spatial resolution of ~ 0.7 mm. Rock samples must be perfectly polished. We can mount thin sections (2.5 x 4.5 cm) and cross sections (diameter of the cylinder 2.5 cm) in the sample holder. The polished samples must be carbon coated under the high vacuum. Individual mineral grains can be analysed in situ, with their structural and textural relationships. Samples can be observed in an optical microscope as well as under scanning electron beam which enables us to localise the mineral phases, relationships among them and finally, a position of the suitable place for the microprobe analysis. SEI, BEI, CL, optical images (Fig. 3) and all measured data can be easily saved in computer in digital form or directly printed or sent by E-mail.

The accuracy of analysis is routinely under ~0.01 wt % depending on the concentration of the element in the sample. 1s error (wt %) is directly listed in the analysis report. In special cases the detection limit ~ 50 ppm (100--10 ppm) is possible to achieve. All elements with atomic number above 9 (F) can be determined with uniform accuracy and sensitivity. Measurement of lighter elements requires a special care and conditions.

Sample exchange is very easy and requires a relatively short time. Also one silicate analysis (10 elements) is completed quite quickly, in ~ 3 minutes. It is enabled by special large analysing crystals that are approximately 8-times more sensitive then the classical ones.

All above mentioned microprobe analyses and image pictures including X-ray maps are well usable in the mineralogy, for finding a mineral composition, growth profiles, diffusion profiles, potentially for a finding of new mineral species, then in descriptive and experimental petrology for the geothermobarometry calculations, rare phase location, investigations of mineral successions and relations among minerals and approximate modal analysis.

Our possibilities and experience with electron microprobe analysis

During 20-year history of electron microanalysis methods usage in our Institute, we have attained many experiences with chemical analyses. Our possibilities and experiences can be summarised as:

- basic chemical compositions of the rock-forming, clay and accessory minerals
- ore and silicate deposit minerals, including composite sulphosalts and sulphides
- micro, trace and rare earths element measurements
- environmental problems - wastes, heavy metal and asbestos distribution
- different kinds of geological problems
- analyses of the crushed stones, construction and decoration stones

References

Reed, S. J. B., 1997: Electron microprobe analysis. Cambridge Univ. Press, Cambridge, 326 p.