

Electron probe microanalysis of minerals: microanalyzer or scanning electron microscope?

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Abstract

The results of electron probe microanalysis of several rock-forming minerals by wavelength-dispersive spectrometry (WDS) and energy-dispersive spectrometry (EDS) are compared, and the metrological characteristics of both methods are studied. The measurements were made with the use of a JXA-8100 (JEOL) microanalyzer with five wavelength-dispersive spectrometers and a MIRA 3 LMU (Tescan) scanning electron microscope equipped with an INCA Energy 450 XMax 80 (Oxford Instruments) microanalysis system. Specimens with olivine, garnet, pyroxene, ilmenite, and Cr-spinel grains were analyzed.

The variation coefficients that characterize the repeatability of a single determination are found to be ~0.5% for WDS and ~0.9% for EDS in the compositional range of the main components ($C > 10\%$). For minor components ($1\% < C < 10\%$), the variation coefficients are 1.4% and 3.0%, respectively, and for impurities ($0.3\% < C < 1\%$), 2.7% and 13%, respectively. For lower contents EDS is almost inapplicable. The ratio of the results obtained by the two methods is reproduced with high precision: For major components, the variation coefficient is 0.56%; for minor components, 1.7%; and even for impurities, it is ~8%. The magnitude of the bias is between 0.2 and 3.2 rel.%, which is acceptable.

The results show that the accuracies of WDS and EDS are similar for measuring major and minor components of rock-forming minerals. Energy-dispersive spectrometry is inferior to wavelength-dispersive spectrometry for impurities and is completely inapplicable for still lower contents. This method is easier to implement, and the results are available soon after switching on the instrument. Wavelength-dispersive spectrometry needs more time for preparation, but it ensures a precise high-efficiency large-scale analysis of samples of similar compositions, even when the element contents are lower than 1%.

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Introduction

Electron probe microanalysis (EPMA) and scanning (raster) electron microscopy (SEM) are the most widespread analytical methods for the electron probe study of minerals. Electron probe microanalysis is meant mainly for the determination of chemical composition, whereas SEM is meant for the imaging of surface with phase or topographic contrast. Electron probes of modern design—microanalyzer in EPMA and scanning electron microscope in SEM—do not show radical differences, but they differ in purpose and, therefore, in instrumentation.

The most important difference in instrumentation is the difference in the devices for recording X-rays. To do this,

X-ray spectrometers of two types are used. In wavelength-dispersive spectrometers (WDS), radiation is decomposed into a spectrum as a consequence of diffraction on the grid of the analyzing crystal and the recording is carried out with the use of proportional gas counters. In fact, a WDS is a monochromator, which separates only one wavelength from the spectrum at the moment, so that the recording of the spectrum within the given interval requires successive change of the angle of incidence of radiation to the crystal. To cover an interval of wavelengths which is wide enough, a set of crystals with different interplanar spacings should be used. An energy-dispersive spectrometer (EDS) is a solid-state semiconductor detector, which records X-rays within the whole energy range simultaneously and with high efficiency. Its detection efficiency is higher by an order of magnitude, which permits analysis at low current and easier study of minerals unstable in the case of electron bombardment. However, WDS have an

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obvious advantage in terms of resolution and the ratio of analytical to background signal. Wavelength-dispersive spectrometers appeared considerably earlier (early 20th century), so that methods for measurement with the use of these spectrometers are better developed. Energy-dispersive spectrometers, in turn, are a product of the second half of the 20th century. They are in the process of permanent improvement, and their full potential is far from known (Friel and Mott, 1998).

Electron probe microanalyzers are now always equipped with several (up to five) WDS, while an EDS is an auxiliary instrument. On the contrary, a scanning electron microscope (SEM) is usually equipped with an EDS, whereas a WDS with replaceable analyzing crystals is sometimes used as a supplement. Note that the installation of WDS makes the equipment considerably more expensive. For example, the price of a microprobe equipped with the maximum possible number of WDS is more than two times that of a SEM with an EDS. Nevertheless, multichannel instruments with WDS are traditionally used in the quantitative EPMA of minerals, which are almost exclusively multicomponent compounds.

Energy-dispersive spectrometers were first applied for the quantitative determination of the composition of rock-forming minerals as early as the 1970s (Dunham and Wilkinson, 1978; Reed and Ware, 1973). Studies in this field were carried out occasionally for a long time. However, there has been a considerable increase in the number of SEM quantitative determinations in recent years, and the method itself got the name “energy-dispersive spectrometry,” or “EDS.” The increase is due to the widespread application of microscopes; the appearance of a new generation of semiconductor detectors with thermoelectric cooling, which allow for high counting rates; and progress in the development of corresponding software. Under these circumstances it is important to compare the metrological characteristics of quantitative determinations carried out by EDS and classical EPMA with WDS, or the WDS method (Çubukçu et al., 2008; Ekimova and Karabtsov, 2008). The aim of this paper is to make such a comparison for the analysis of rock-forming minerals, which is the most widespread kind of analytical determinations in Earth sciences.

Methods

Measurements were taken using a JXA-8100 (JEOL) electron probe microanalyzer and a MIRA 3 LMU (Tescan) SEM. Accelerating voltage was 20 kV in both cases. Samples were prepared by the conventional technique as epoxy blocks with mounted mineral grains. The polished surface of the sample was covered with a conducting carbon coating ~25 nm thick.

The JXA-8100 microanalyzer was equipped with five WDS, one of which was a high-efficiency spectrometer. Radiation was recorded by sealed xenon or argon–methane proportional flow counters. The take-off angle of radiation was equal to 40°. The measurements were taken by a technique almost coinciding with routine WDS EPMA. The analysis lines were the $K\alpha$ lines of the elements under determination,

and the background was measured on both sides of the peak, usually at a distance of ± 2 mm. The signal accumulation time at the peak and on the background was equal to 10 s. Radiation was recorded at the wide window of the amplitude analyzer (from 0.7 to 9.3 V), i.e., almost in an integrated mode. The measured intensities were corrected for the dead time of recording channels and normalized to the current of the probe, whose current value was determined with the use of a Faraday cup before measurement at each “point.” The nominal value of current was 100 nA. Natural minerals and synthetic glasses were used as reference samples, and the set of these samples varied depending on the object of analysis. Corrections for the matrix effect were calculated by the ZAF method from the manufacturer's software of the instrument. In the case of a binary matrix effect (intense absorption combined with the effect of the atomic number), which is usually observed if the sample has an elevated FeO content, the ZAF method is not quite adequate (Korolyuk et al., 2008, 2010), so that it is necessary to recalculate contents using the KARAT software (Lavrent'ev and Usova, 1994) in accordance with the recommendations in (Lavrent'ev and Usova, 1996). The detection limit of components was 0.01–0.02% (3σ criterion).

The MIRA 3 LMU SEM is combined with an INCA Energy 450 XMax-80 (Oxford Instruments) microanalysis system. The width of the $MnK\alpha$ line at the maximum resolution of the detector is 125 eV, and the width of the same line in routine analysis is 127 eV. The take-off angle of radiation is equal to 35°. The beam current was taken to be 1.5 nA; the live acquisition time of spectra, 20 s; and the time of pulse processing with an analog–digital converter, 20 μ s (Process Time 4). Metallic Co was used to control the probe current and the energy shift of the recorded spectrum. In practice, the current drift was no more than 1% for 4–6 h of operation; therefore, the intensity of CoK radiation was not measured more often than once in 3–4 h. The analytical signal was the integrated intensity of the lines of the K -series of the element under determination. The formation of the analytical signal is the manufacturer's know-how, and its details are unknown to the analyst. A single set of reference samples was used which included the simplest compounds and pure metals: quartz SiO_2 (for Si and O), corundum Al_2O_3 (Al), Cr_2O_3 (Cr), blue diopside $MgCaSi_2O_6$ (Mg and Ca), albite $NaAlSi_3O_8$ (Na), orthoclase $KAlSi_3O_8$ (K), and metals (Ti, Mn, Fe, and Ni). Corrections for the matrix effect were calculated by the XPP method from the manufacturer's software in the mode “All elements analyzed.” The result of the analysis is presented as the contents of components, with oxygen content calculated for stoichiometry. The final report was obtained as Excel files using the program designed by S.V. Kanakin (2011). Note that the high stability of the EDS performance made it possible to use the calibration data obtained for all determined elements two years before the measurements described in the present paper.

The study was carried out for samples with the mineral grains selected during the implementation of the program of mineralogical zoning of the Yakutian diamond-bearing province. Each sample contained several hundreds of grains, all of

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