D.C. Lee, A.van Riessen; K.W. Terry*

Ashton Mining Limited	*School of Physics and Geosciences
100 Jersey Street	Western Australian Institute of Technology
Jolimont 6014	Kent Street
Western Australia	Bentley WA 6102

TECHNIQUE

The conventional method of x-ray analysis in the scanning electron microscope (SEM) is to excite the sample with a beam of electrons and to detect emitted x-rays with a lithium drifted silicon (Si (Li)) detector. Such a system has a maximum sensitivity at around 3.5 keV but drops rapidly for higher energy photons.

Improved sensitivity of elements emitting higher energy photons can be achieved by exciting the sample with x-ray radiation. The technique adopted is to direct the electron beam onto a thin metal foil and use the x-rays transmitted through the foil to excite the sample. The consequence of irradiating a sample with an x-ray beam is that one of three mechanisms can take place between the photon and sample. If the sample absorbs a photon with an energy greater than an absorption edge of one of the elements present in the sample, then characteristic photons may be emitted (i.e. x-ray fluorescence). The other two mechanisms that can take place when a sample is irradiated with an x-ray beam are Rayleigh and Compton scattering.

Energy dispersive spectra obtained from the x-ray excited technique consist of characteristic peaks of the sample (fluorescence) superimposed upon a background caused by the combination of Rayleigh and Compton scattering of the primary x-ray beam. The amount of general background can be minimised with the use of a monoenergetic incident x-ray beam. However, in practice there is always some continuum associated with the characteristic line of the incident beam. This undergoes both Rayleigh and Compton scattering and hence gives rise to the general background of the emitted spectrum from the sample. The rest of the background arises from the Rayleigh scattering of the incident monoenergetic x-ray beam, and this beam's Compton scattering which manifests itself as a broader maximum in the background immediately below the Rayleigh peak. In addition there occurs a Compton scattering of detected photons within the lithium drifted silicon detector that results in an increase in background at low energies.

In the design of the thin foil device there are basically four variables that need to be considered, namely, accelerating voltage, foil type, foil thickness and x-ray spot size.

Accelerating Voltage. Excitation of the sample is due to both the characteristic and continuum x-ray photons originating from the foil. The intensity of the primary characteristic lines increases as the 1.67 power of the accelerating voltage of the electron beam while the intensity of the continuum increases linearly. To maximise the x-ray flux impinging on the sample the highest accelerating voltage available should be selected.

Foil Type. For optimum conditions for the x-ray excited technique a foil type should be selected such that its characteristic radiation is slightly more energetic than the critical excitation energy of the element being detected.

Foil Thickness. The fact that the continuum plays an important part in causing secondary fluorescence means that the foil need only be thick enough to prevent electron penetration. Thick foils do extend the very low background region to higher energies but at the expense of primary x-ray flux. Consequently, in order to maximise the counting statistics for reasonable counting time, the thinnest possible foil is desirable.

X-ray Spot Size. The size of the x-ray beam from the foil, impinging on the sample, is determined by collimator length and diameter as well as collimator to sample distance. For the geometry selected (0.6mm diameter collimator, 6mm collimator length and 7.75mm between collimator and sample) an x-ray spot size at the sample of 1.5mm in diameter is obtained. However, the sample is normally tilted towards the x-ray detector so an elliptical spot is formed with a long axis of approximately 2.5mm. The spot size used in this project was found to be satisfactory for most grains. Where grain size was less than the spot size, a correction factor was used on the data collected from the thin foil generated spectra.

Spot size of the x-ray beam also controls minimum detection limits. As spot size is increased, so does the quantity of x-ray flux impinging on the sample, with the

result that minimum detection limits are improved. The restricted size of grains supplied in this project prevented the use of larger spot sizes. <u>Advantages of X-ray Excited XRF</u>. The strength of the thin foil technique stems partly from the ability to select operational conditions which optimise minimum detection limits for a range of elements. Foil type and thickness as well as accelerating potential all contribute to the final sensitivity. Used in conjunction with electron excited results, the thin foil technique considerably expands the capability of the SEM/EDS system for a modest outlay.

A comparison of electron excited and x-ray excited XRF in a SEM has shown that the two methods are complementary. The electron technique is more sensitive to low atomic number elements while the x-ray technique is more sensitive to high atomic number elements. In addition the minimum detection limits have been reduced to better than 20ppm for certain elements using the x-ray excited method.

The x-ray excited technique differs from electron microprobe analysis in that the whole surface of a polished cross-section of a mineral grain is analysed. There is a considerable depth of penetration by the x-rays used to excite the mineral grain and information on trace element content of a relatively large volume of a mineral grain is obtained by this technique. It would be very time consuming and difficult to generate the same information about a single grain by use of an electron microprobe. EXPERIMENTAL DETAILS.

The approach in the project detailed below has been to analyse mineral grains quantitatively for the major and minor elements together with a qualitative assessment of the trace elements. This has been achieved using a scanning electron microscope equipped with an energy dispersive x-ray spectrometer. Results from conventional electron excited XRF were supplemented with those obtained from the x-ray excited XRF method.

Electron Excited XRF. The elemental analyses were carried out using a JEOL JSM 35C scanning electron microscope equipped with a United Scientific lithium drifted silicon detector and associated electronics. The spectra were accumulated in a Tracor Northern TN 1705 multi-channel analyser (MCA). The adopted procedure for elemental analysis was to use 20kV and 5 x 10⁻¹⁰ amps at normal incidence onto a 40 x 40 μ m raster on a polished sample and a detector take-off angle of 35^o. A typical count rate of 5 kcps was obtained. The spectra were collected in the MCA for 50 s live time and were then transferred to a Sirius 1 microcomputer for subsequent processing. The elemental analysis was then computed using the peak integration with background subtraction (PIBS) technique of Ware (1981). The current program provides for an elemental analysis for Na, Mg, Al, Si, P or Zr, Cl, S, K, Ca, Ti, V, Fe, Mn and Zn expressed as oxides and has a sensitivity down to approximately 0.1%.

X-ray Excited XRF. The x-ray excited method adopted was to focus the 39 keV, 1 µA electron beam onto a silver or molybdenum foil of 5 µm thickness which acts as a transmission x-ray target. The resultant collimated primary x-ray beam impinging on the sample consisted of the characteristic peaks together with the continuum that had been self-filtered by the foil. The incident primary x-ray beam caused secondary x-ray fluorescence in the sample so that characteristic x-rays of the elements in the sample were subsequently detected by the Si(Li) detector.

Although better minimum detection levels were achieved compared with electron excited XRF, considerably longer counting times (typically 200s) were required to accumulate sufficient counts. Integrated peak minus background counts from the central seven channels of each peak in the x-ray spectra provided semi-quantitative information regarding the amount of a particular element present in the sample. APPLICATION.

This project with the thin foil device attached to a scanning electron microscope was aimed at finding a practical method of detecting some of the trace elements in mineral grains from kimberlitic sources. A reasonably large number of grains have been analysed in a relatively short time to build up a data base.

A total of 310 grains were selected from kimberlitic and non-kimberlitic rock types: chrome diopside, chromite, garnet, ilmenite, olivine and zircon. The major and minor elemental contents were obtained by using electron excited XRF in the SEM while the x-ray excitation method was used to determine the trace elements.

One set of significant data is that, for the garnets, it can be seen that Cr, Zn and Y are present in higher amounts for the kimberlitic garnets than in the nonkimberlitic samples. The result is of considerable interest as the garnet types chosen for study cannot otherwise be distinguished as either kimberlitic or non-kimberlitic. The reason for the difference in trace element content of almandine garnets from kimberlite and common almandine garnets is not established. It may be a result of late stage metasomatism i.e. diffusion of trace elements from kimberlite magma into mineral grains derived from the earth's crustal zones.

The separation of two samples of eclogitic pyrope into kimberlitic and nonkimberlitic groups is a potentially useful result and worthy of further work to establish whether this would be reliable in exploration.

High trace amounts of Cr, Zr, and Nb in kimberlitic ilmenite distinguish it from the ilmenites in alkali basalts. This is the most useful result of the study and means that some of the picro-ilmenite grains encountered in exploration programmes can be eliminated as of no interest if trace amounts of Nb, Zr, and Cr cannot be detected in them. A large range of ilmenite grains was included in this study and the results are more reliable than for the other mineral types.

Results on the first two groups of olivine grains were not encouraging and no further work was undertaken. Trace element work on zircon grains was also not encouraging and the expected low uranium levels in kimberlitic zircons relative to non-kimberlitic grains could not be confirmed by the x-ray rechnique.

The data has been assessed using the DISCRIMINANT procedure of SPSS. Initially the grains of each mineral type were classified as being from kimberlitic or nonkimberlitic rock sources. The DISCRIMINANT procedure was then run for each mineral type using the subsets of the trace element variables, the oxide variables, and a combination of all the variables. The success rates of predicting the rock source of a grain using the trace element variables are in excess of 90% for the suite of garnet and ilmenite grains. Lower success rates occur for the other grains. Success rates of greater than 90% are obtained for chrome diopsides, garnets and ilmenite grains when the subset of oxide variables are used. When the two sets of variables are combined impressive prediction accuracies of 100%, 98% and 100% are obtained for chrome diopside, garnet and ilmenite grains respectively.

The use of x-ray excitation of individual mineral grains within a SEM has revealed significant differences in elemental content. When this data is combined with major and minor elemental data it has been possible to predict for three mineral types whether the grains come from a kimberlitic or non-kimberlitic rock source. It should be emphasised that only a limited number of mineral grains have been analysed. A larger programme of work is desirable in order to determine whether these differences are maintained for these mineral types from all kimberlitic and non-kimberlitic rock sources.

Reference.

WARE, N.G. 1981. Computer Programs and Calibration with the PIBS Technique for Quantitative Electron Probe Analysis using a Lithium-Drifted Silicon Detector. Computers and Geosciences 7. pp 167-184.