Computer-controlled scanning electron microscopy: A fast and reliable tool for diamond prospecting

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Computer-controlled scanning electron microscopy is introduced as a faster, reliably and cost-reducing alternative to conventional electron microprobe analyses on kimberlite indicator minerals. The method is based on conventional scanning electron microscopy and energy dispersive X-ray spectrometry, but due to extended counting times, optimised settings and computer-controlled particle recognition valid data can be obtained on a low amount of operator and machine time. A comparison of the results between both methods yields that computer-controlled scanning electron microscopy is able to investigate major and minor element concentrations in indicator minerals with almost the same precision as the electron microprobe.

1. Introduction

The elemental compositions of megacrystal and xenocrystal phases within kimberlitic rocks are used as an important diamond exploration tool. Classification schemes have been devised where fields of major and minor element compositions present a defined probability that the phases in question have crystallised under conditions where diamond is stable. For example, the relationships between Cr, Ca and Mn contents of pyrope garnets and the Cr, Ca and Na content of eclogite garnets define such probability fields (Grütter et al., 2004). Other minerals which are routinely used in this way are ilmenites, where Ni, Mg and Cr contents are important (Mitchell, 1995; Wyatt et al., 2004) and diopside where the abundance of Cr has been demonstrated to be pressure dependent (Nimis and Taylor, 2000).

Several analytical techniques have been applied so far to study the properties of these kimberlite indicator minerals (KIM) in order to judge the diamond potential of the hosting kimberlites s.l. Laser ablation-inductively coupled plasma mass spectrometry was utilized on garnets and chromites, which have distinct REE ratios that distinguish diamondiferous from non-diamondiferous source rock (Walting et al., 1995). The mineral grains used in this study are indicator minerals from the Garnet Lake kimberlite body in Western Greenland. Part of the EMP compositional data has previously been published in Hutchison (2005) and Hutchison and Heaman (2008). Garnet Lake is known to be an abundant source of diamonds. A series of hand-picked macrocrysts of ilmenite, pyrope, and olivine, were mounted in an epoxy resin (Fig. 1).

2. Samples and methodology

The mineral grains used in this study are indicator minerals from the Garnet Lake kimberlite body in Western Greenland. Part of the EMP compositional data has previously been published in Hutchison (2005) and Hutchison and Heaman (2008). Garnet Lake is known to be an abundant source of diamonds. A series of hand-picked macrocrysts of ilmenite, pyrope, and olivine, were mounted in an epoxy resin (Fig. 1).
After polishing and carbon-coating, the samples were loaded into the electron microprobe (EMP) and the scanning electron microscope (SEM). EMP analyses were carried out at the University of Copenhagen, Denmark (on a JEOL JXA-8200 Superprobe operated at 15 kV acceleration voltage, 1.5×10⁻⁶ A beam current, 5 µm beam diameter) and the University of Lausanne, Switzerland (using a Cameca SX 50 at 15 kV acceleration voltage, 2.0×10⁻⁸ A beam current).

CCSEM analyses were carried out at the Geological Survey of Denmark and Greenland (GEUS), using a Philips XL40 ESEM, equipped with two EDX detectors; a Pioneer Voyager 2.7 10 mm² window and a Thermo Nanotrace 30 mm² window. The SEM was operated at 17 kV acceleration voltage and 50–70 µA filament current. In BSE contrast mode of the SEM, the grains appear as white and grey minerals in a black matrix, formed by the epoxy (Fig. 1). The grey-level threshold function of the Noran Thermofisher NSS™ CCSEM software is able to separate individual grains from the matrix and to automatically collect spectra to measure their chemical composition (for up to 90 elements simultaneously), as grain-by-grain measurements and as a bulk rock analysis for the whole sample. The software recalculates the data following the Proza (G9Z) data correction and the filtering quantification technique. The resulting data were recalculated with an in-house developed chemical recalculation scheme and mineral classification database at GEUS. Furthermore, the CCSEM software measures the 2D-grain size and grain morphology (e.g. aspect ratio and circularity) for each of the grains. Further details of the applied method are provided by Bernstein et al. (2008) and Keulen et al. (2008).

Apart from point analyses, whole grain-surface compositional scans of individual grains can be made. In this way minor compositional variations within single grains can be taken into account. The software allows the user to define a grid of minerals within which all the grains can be measured automatically. Depending on the settings for the counting intensity (e.g. maximum 50 000 counts/s on both detectors as used in this study) and for the acquisition time per grain (e.g. 5000 counts at maximum full scale as used in this study), a sample of 200 grains can be measured in 1–3 h, with less than half an hour of operator time. The validity of the CCSEM analyses is discussed in Keulen et al. (2008). The error in the precision of the measurements is approximately 1–2% for major elements and 4–8% for minor elements under the indicated conditions. Trace elements (<0.2 wt.%) have relatively high errors (ca. 30%) and can better be assessed with e.g. XRF or EMP measurements.

The CCSEM software stores the images and the pixel coordinates of each grain. Each chemical analysis can therefore be correlated to the specific grain that was measured. This is a useful tool to trace anomalous measurements, rare minerals and elements, or, as in this study, to relate CCSEM measurements to EMP measurements.

3. Results

To test the accuracy of the CCSEM measurements, the data were compared to EMP analyses on the same set of garnet, ilmenite and olivine grains. Table 1 displays representative data for garnet, ilmenite and olivine grains; all data are available as an Electronic supplement to this issue. Note that measurements for NiO2, BaO, Nb2O5, Ce2O3, CuO, P2O5 and SO3 are only shown in the Electronic supplement. Note that the software of the CCSEM automatically recalculates all weight percentages to a total value of 100.0 wt.%, because it is not possible to register the beam current during the EDX measurements. For CCSEM measurements, this value cannot be taken as a measure of the quality of the data.

3.1. Garnet

Fig. 2 shows EMP analyses for the Cr and Ca concentrations in garnets. The reproducibility of the EMP data by the CCSEM is good: the average R²-value for the grains measured with both methods is 0.8 (see Table 2 for details). Fig. 2 was drawn using the classification scheme of Grütter et al. (2004), which concentrates on the minor elements Cr, Ca, Na, and Ti of eclogitic garnets and of pyropes to differentiate eight kinds of garnet. 89% of the garnets plot in the same mineral grain field after classification based on the CCSEM and EMP chemical data. A mismatching of the classification mainly arises close to field boundaries, e.g. for the cluster of G3–G4 garnets in the bottom centre of Fig. 2. The main problems with the Grütter classification are observed for the sub-classification of fields G3, and G4. Here a threshold value of 0.07 wt.% of Na2O divides potentially diamond bearing garnets from other garnets that show a lower likelihood for passing through the diamond window. In the EDX spectrum the peaks for the very light elements Na and Mg display a partial overlap. Trace amounts of Na in grains with abundant Mg are therefore not measured with a reliable precision, even with increased counting times.

3.2. Ilmenite

Wyatt et al. (2004) showed that the ratio between MgO and TiO2 in ilmenite grains can be used as an indicator of a kimberlitic association of these minerals. Ilmenite grains associated with kimberlites plot on the high MgO side of the solid line in Fig. 3. We compared the performance of CCSEM to analyses on the same grains measured with the EMP. All but one of the grains plot within the kimberlite field; thus CCSEM can be used to identify this field correctly in the present case. The CCSEM data show a slightly larger scatter than the EMP data, but have the same average values for TiO2 and MgO. Fig. 4 shows the relation between Cr2O3, MnO and MgO in ilmenite. The minor elements Cr, Mn and Mg can be measured with a good accuracy in ilmenites.

3.3. Olivine

High levels of Cr and Ni in olivine are used as an indication for kimberlitic rocks (Mitchell, 1995). Here, the concentration of Cr2O3 in forsterite grains is shown (Fig. 5). Most of the measured olivine grains plot within the kimberlite field, which lies to the right of Fo88. Cr is only present in very small quantities, but is represented by the CCSEM with a correct average, but a larger scatter compared to EMP measurements.
The relative error in the Cr$_2$O$_3$ measurements is 6%; in the Mg-number 1.2%. The concentration of Cr in olivine is at the same level as Na in the pyropes and eclogitic garnets, but Cr in olivine is much better resolved in the EDX spectrum than Na in pyropes. The reason for this is that the K$_a$-peak of Cr does not overlap with other major or minor elements in olivine, and that elements with an atomic number in the range of Cr are easier to detect by the EDX detector than light elements.

### 4. Discussion

The chosen measurement conditions greatly exceed conventional EDX measurement conditions in terms of the total acquired analytical counts per mineral. These improved measurement conditions were made possible by the application of a second EDX detector, by the automation of the measuring procedure, and by the coupling of the measured chemistry to our mineral database. In this way a much lower error in the precision of the measurements compared to conventional EDX analyses was achieved. The ratio between EMP and CCSEM measurements for garnet and olivine is excellent with values between 0.97 and 1.06 (see Table 2). However, the scatter in the CCSEM data is much larger and therefore a relatively low $R^2$-value between both methods has been obtained. Further differences in the $R^2$-value can be made possible by the application of a second EDX detector.
explained by the normalisation of the CCSEM data to 100% (inherent in the EDX method) versus the summation of the EMP data from 97.8 to 102.9%. The variation in the total amount of measured material, is reflected in the R²-value variation. However, the measurements on the discussed indicator minerals demonstrate a good reproduction of the EMP analyses with the CCSEM and the ability of the CCSEM to put the measured minerals into the right category (Figs. 2–5). We are confident that this validity of the data can also be achieved for other KIM and mantle indicator minerals, such as pyroxene, chromite, phlogopite and apatite.

CCSEM provides a significant cost advantage through reduction in machine time and in particular, man-hours compared to EMP. Only for the measurement of small fractions of Na in pyrope grains is CCSEM machine time and in particular, man-hours compared to EMP. Only for the measurement of small fractions of Na in pyrope grains is CCSEM less suitable compared to the quality of EMP analyses. In this case, CCSEM can still function as a method to investigate the potential of kimberlite samples for further study. With both methods the great majority of the measured KIM presented plotted in the same discriminatory field. CCSEM is able to measure major and minor element concentrations in indicator minerals almost with the same precision as the EMP. As a faster, cheaper, alternative to microprobe measurements on indicator minerals CCSEM is therefore demonstrated to be a valid prospecting tool.

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Appendix A. Supplementary data


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