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

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ABSTRACT

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 eclogitic 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 analysis of KIM is commonly performed by measuring the concentration of approximately ten to fifteen elements using an electron microprobe (EMP) (Meyer, 1968; Gurney and Zweistra, 1995) or proton microprobe (e.g. Griffin and Ryan, 1995). This is a precise method, yet it is rather time-intensive in terms of set-up and analysis acquisition. Therefore, alternative measuring methods have been investigated. Flemming (2007) applied micro-X-Ray Diffraction (μXRD) on KIM to match their unit-cell specific signal to EMP analyses on the same grains in order to provide an alternative to labour-intensive EMP measurements. Her method is based on the different sizes of Mg, Ca, Cr, and Al cations in garnet, which cause different spots in the μXRD spot pattern. Although very promising, this technique is still under development and does not reduce the measuring time per grain.

In this communication, we present CCSEM (Computer-Controlled Scanning Electron Microscopy) as a faster and readily available method to measure the composition of KIM and we compare the results to electron microprobe analyses in order to investigate the quality of the data. CCSEM combines the advantages of energy dispersive X-ray spectrometry (EDX) with those of digital image analysis on back-scattered electron (BSE) micrographs for the automated measurements on hundreds or thousands of single grains. As opposed to the QEMSCAN™ and Mineral Liberation Analyser, MLA™ techniques, two other SEM–EDX analyses systems, we do not concentrate on mineral liberation, mineral phase mapping or the coupling between physical properties and mineralogy of the minerals (Benvie, 2007) in this study, but rather concentrate on the geochemistry of kimberlite indicator minerals.

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).

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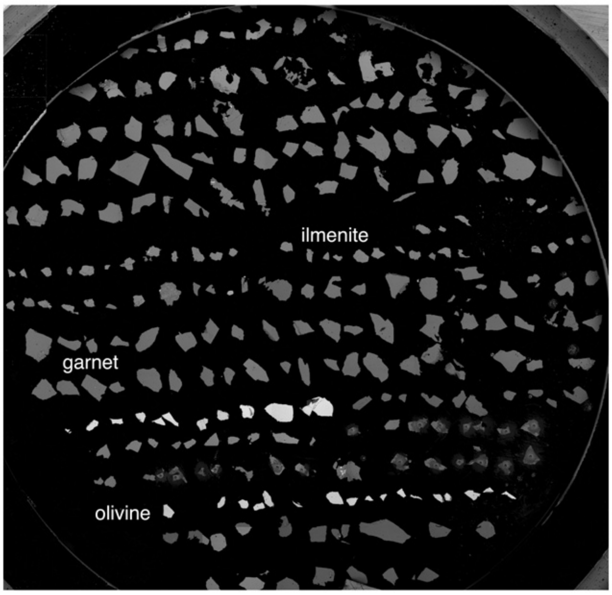

Fig. 1. One of the samples, as seen in back-scattered electrons contrast mode in the SEM. Indicator minerals occur in several shades of grey, the epoxy as a black matrix. A grid of images covering the whole sample area was defined by providing the computer with the coordinates of the sample and by setting the required magnification for the analysis.

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^{-8} 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 mm^2 window and a Thermo Nanotrace 30 mm^2 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 (φρZ) 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 NiO_2, BaO, Nb_2O_5, Ce_2O_3, CuO, P_2O_5 and SO_3 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 R^2-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 Na_2O 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 TiO_2 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 TiO_2 and MgO. Fig. 4 shows the relation between Cr_2O_3, 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 Cr_2O_3 in forsterite grains is shown (Fig. 5). Most of the measured olivine grains plot within the kimberlite field, which lies to the right of Fo_{88}. 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.

Table 1
Representative electron microprobe and computer-controlled scanning electron microscopy data for garnet, ilmenite and olivine grains.

	EMP											CCSEM										
	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	Total	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	Total[a]
Garnet																						
1	0.069	18.434	19.522	41.045	0.000	5.047	0.744	3.611	0.252	11.419	100.143	0.00	17.05	19.44	41.95	0.00	4.69	0.66	3.69	0.31	12.21	100
2	0.154	19.640	21.686	42.096	0.003	3.768	1.014	0.871	0.295	11.983	101.510	0.00	18.21	18.76	42.45	0.01	4.03	1.04	0.83	0.43	13.38	100
3	0.249	10.283	22.262	40.172	0.003	11.507	0.731	0.082	0.271	14.846	100.404	0.00	9.15	19.53	40.73	0.00	12.41	0.57	0.27	0.35	16.46	100
4	0.169	11.793	22.309	40.022	0.000	6.080	0.469	0.092	0.333	19.708	100.975	0.00	19.46	22.66	41.24	0.00	3.48	0.48	0.17	0.35	15.16	100
5	0.010	23.205	18.631	42.204	0.002	3.236	0.183	6.537	0.000	6.215	100.222	0.00	22.01	16.11	43.48	0.00	3.32	0.10	6.53	0.28	7.02	100
6	0.092	19.589	19.724	41.340	0.000	5.152	1.220	2.972	0.221	10.153	100.463	0.00	17.64	19.63	41.90	0.00	4.97	1.00	2.79	0.27	10.39	100
7	0.182	15.506	22.478	41.096	0.004	4.425	0.523	0.111	0.417	16.026	100.765	0.00	14.85	20.82	39.80	0.00	4.59	0.54	0.17	0.44	18.78	100
8	0.065	21.059	19.411	42.221	0.009	5.224	0.145	5.854	0.000	6.578	100.566	0.00	20.41	17.34	43.58	0.00	5.07	0.02	5.86	0.50	6.87	100
9	0.060	19.799	14.168	40.641	0.000	6.577	1.084	10.906	0.000	6.957	100.193	0.00	18.14	13.95	41.86	0.00	6.50	0.99	10.31	0.29	7.57	100
10	0.026	24.011	21.516	43.022	0.007	3.561	0.332	3.414	0.029	4.912	100.829	0.00	19.36	21.04	43.40	0.00	3.86	0.45	3.65	0.37	6.32	100
Ilmenite																						
1	0.016	12.121	0.468	0.021	0.000	0.029	53.789	0.374	0.227	32.553	99.598	0.00	10.77	1.86	0.18	0.00	0.04	53.96	0.46	0.08	32.55	100
2	0.038	12.793	0.560	0.052	0.000	0.014	53.912	0.341	0.225	31.260	99.195	0.00	13.38	2.31	0.23	0.00	0.01	53.14	0.47	0.18	30.05	100
3	0.020	12.158	0.508	0.024	0.000	0.025	54.261	0.349	0.289	32.587	100.219	0.00	10.71	1.13	0.00	0.00	0.01	54.50	0.17	0.24	33.09	100
4	0.017	11.505	0.611	0.092	0.010	0.048	50.530	0.278	0.300	35.392	98.783	0.00	11.19	1.29	0.00	0.00	0.02	52.28	0.39	0.24	34.24	100
5	0.026	12.035	0.521	0.119	0.000	0.029	53.678	0.404	0.235	32.308	99.354	0.00	10.76	0.36	0.19	0.02	0.03	54.67	0.40	0.30	32.99	100
6	0.019	11.341	0.477	0.017	0.000	0.026	52.577	0.391	0.261	33.783	98.891	0.00	10.22	0.50	0.21	0.00	0.08	53.61	0.43	0.15	34.36	100
7	0.000	8.914	0.518	0.008	0.003	0.025	47.703	0.305	0.216	40.101	97.794	0.00	3.37	0.36	0.17	0.03	0.06	48.26	0.36	0.39	46.03	100
8	0.018	10.042	0.339	0.023	0.007	0.018	51.626	0.401	0.252	36.328	99.051	0.00	10.34	0.83	0.19	0.00	0.01	50.72	0.56	0.07	36.55	100
9	0.000	9.540	0.468	0.000	0.000	0.017	49.145	0.823	0.201	37.866	98.059	0.00	9.27	0.82	0.13	0.00	0.09	49.21	0.76	0.38	38.90	100
10	0.033	12.002	0.501	0.036	0.007	0.029	52.625	0.373	0.231	32.206	98.043	0.00	10.67	0.25	0.27	0.00	0.00	54.63	0.37	0.17	32.92	100
Olivine																						
1	0.050	51.340	0.030	41.075	0.000	0.045	0.042	0.066	0.127	7.969	100.745	0.00	50.54	0.00	40.74	0.08	0.00	0.00	0.16	0.00	7.80	100
2	0.008	49.017	0.022	40.533	0.008	0.051	0.046	0.063	0.126	10.417	100.290	0.00	48.45	0.00	43.05	0.00	0.05	0.07	0.05	0.01	7.99	100
3	0.003	49.069	0.036	40.750	0.005	0.044	0.043	0.046	0.107	10.398	100.501	0.00	48.83	0.00	40.11	0.05	0.08	0.02	0.00	0.23	10.40	100
4	0.064	50.935	0.019	41.239	0.005	0.023	0.021	0.052	0.116	7.903	100.377	0.00	51.07	0.04	40.60	0.01	0.01	0.00	0.14	0.19	7.75	100
5	0.025	50.075	0.028	40.866	0.009	0.046	0.027	0.062	0.105	9.392	100.634	0.00	50.51	0.00	39.79	0.00	0.00	0.01	0.20	0.00	8.40	100
6	0.033	47.697	0.026	40.463	0.004	0.039	0.026	0.038	0.148	12.204	100.678	0.00	46.89	0.00	40.06	0.01	0.03	0.10	0.13	0.24	12.14	100
7	0.056	48.851	0.003	41.153	0.000	0.022	0.039	0.044	0.131	11.537	101.837	0.00	48.55	0.00	39.95	0.00	0.00	0.02	0.09	0.14	10.89	100
8	0.025	48.510	0.002	40.865	0.005	0.017	0.063	0.011	0.126	11.469	101.094	0.00	49.72	0.00	40.43	0.00	0.11	0.03	0.19	0.05	8.54	100
9	0.018	50.337	0.004	41.069	0.000	0.023	0.044	0.031	0.163	9.167	100.857	0.00	50.37	0.00	39.96	0.00	0.03	0.06	0.12	0.00	9.14	100
10	0.006	50.224	0.025	41.217	0.001	0.025	0.045	0.023	0.138	9.068	100.770	0.00	50.68	0.00	41.07	0.00	0.00	0.00	0.00	0.05	7.80	100

[a] Samples were additionally measured for P_2O_5, SO_3, NiO, CuO, Nb_2O_5, and Ce_2O_3. Note that the CCSEM software automatically recalculates the totals for the measurements to 100 wt.%.

The relative error in the Cr_2O_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 Kα-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.

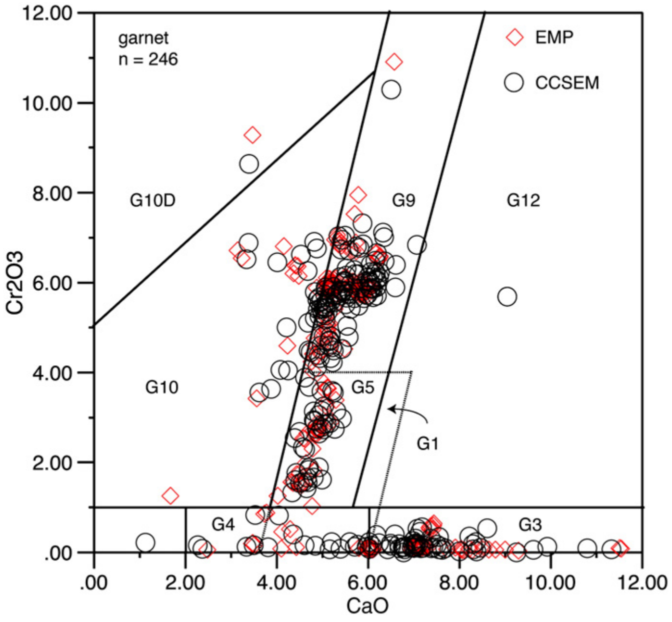

Fig. 2. Comparison between computer-controlled scanning electron microscopy and electron microprobe analyses for CaO and Cr_2O_3 in pyrope and eclogitic garnets. Garnet classification field G1 is defined by the dashed parallelogram; G4 and G5 have solid boxes. The vast majority of the garnets plot in the same garnet classification field, irrespective of the applied analytical technique. (Redrawn after Grütter et al., 2004.)

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

Table 2
Average ratio between CCSEM and EMP measurements and the corresponding R^2 values for major oxides in garnet and olivine.

Oxide	Ratio (CCSEM/EMP)	R^2
MgO	0.98	0.98
Al_2O_3	0.97	0.95
SiO_2	1.00	0.41
FeO	1.06	0.89
CaO	1.06	0.40
Cr_2O_3	1.01	0.98

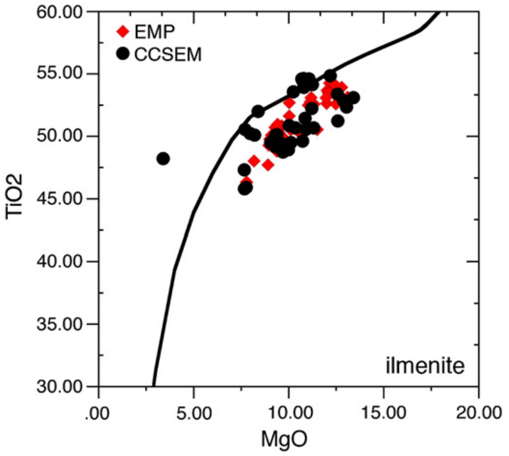

Fig. 3. Evaluation of analyses for TiO_2 and MgO in ilmenite made with computer-controlled scanning electron microscopy and with the electron microprobe. Kimberlitic ilmenite plots at the high Mg-side of the solid line. (Redrawn after Wyatt et al., 2004).

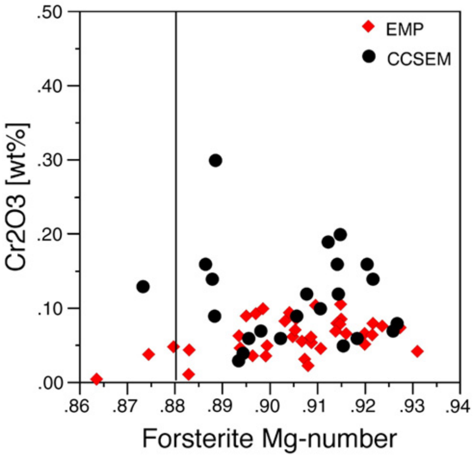

Fig. 5. Computer-controlled scanning electron microscopy and electron microprobe analyses for Cr_2O_3 in forsterite. Even for elements present in low concentrations a similar average concentration between CCSEM and EMP data is obtained.

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 R^2-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 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.

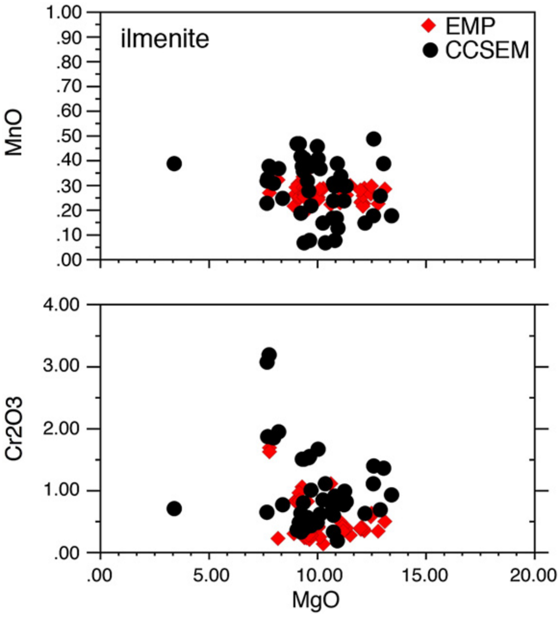

Fig. 4. Comparison between computer-controlled scanning electron microscopy and electron microprobe analyses for Cr_2O_3 and MnO in Mg-rich ilmenite grains.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gexplo.2009.04.001.

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