

Report on analytical and interpretative work performed in chromite grains supplied by Andrew Faragher, RTE, 2003.

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1. Introduction

A total of 83 samples (thin sections) were supplied, with approximately 400 grains selected for WDS electronprobe microanalysis (EPMA) of major and minor elements and laser ablation inductively coupled plasma mass spectroscopy (LA-ICPMS) of trace elements.

In addition to providing the analytical data, an interpretation of the grains was also requested. This was performed using the discriminant analysis technique developed in the late 1990s by Dr Wayne Taylor and his students (Matthew Denny and Mark Richardson) at RSES, to determine the likely provenance of the grains¹. In particular, it was hoped to identify grains likely to have been derived from potentially diamondiferous sources such as kimberlite-sampled magnesian chromite originating from deep (diamond stability field) refractory lithosphere. A document describing the discriminant analysis technique in more detail has also been supplied.

Details of sampling methodologies, geographical locations and geological details pertaining to the selected grains were not provided.

2. Analytical methodology

In all cases, the chromite grains were analysed by EPMA first, followed by LA-ICPMS.

2.1 Electronprobe Microanalysis (EPMA)

EPMA was performed using the RSES' Cameca SX100 4-spectrometer electron microprobe in wave-length dispersive (WDS) mode, using an accelerating voltage of 15kV and beam current of 20nA. The beam was focussed to a diameter of approximately 1 μm . Table 1 lists other details of the calibration and analysis.

2.2 LA-ICPMS

Trace element abundances were determined by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) on an Hewlett Packard Agilent 7500 ICP-MS attached to an Excimer UV Laser ($\lambda=193\text{nm}$) with a custom built sample cell (Eggins, 1998). The following trace elements were measured; Sc, Ti, V, Co, Ni, Zn, Ga, Zr, Nb, Sn, Ba, Hf, and Ta.

The spot size selected was smaller than the dimension of the grain and varied from 70 to 112 μm . The laser pulsed at 10 Hz, delivering 100mJ per pulse. These analytical

¹ A document detailing this approach has also been supplied.

conditions were also used for the calibration and secondary standards employed during melt inclusion runs.

Table 1: EPMA analytical details.

<i>Element</i>	<i>Calibration standard</i>	<i>Spectrometer and peak used</i>	<i>Analytical precision</i>	<i>Estimated detection limit</i>
Zn	sphalerite	LLIF; K _a	2%	100ppm
Ni	Ni metal	LLIF; K _a	2%	100ppm
Cr	Chromium (III) oxide	PET; K _a	<1%	na
Mn	Manganese (II) oxide	PET; K _a	2%	120ppm
Ti	Rutile	LPET; K _a	1%	na
Mg	Periclase	TAP; K _a	<1%	na
Al	Anorthite	TAP; K _a	<1%	na
Fe	Fe metal	LLIF; K _a	<1%	na
V	V metal	LPET; K _a	2%	80ppm

Ablation was conducted under a mixed He+H₂ atmosphere and the ablated material was carried to the plasma in an Ar/He gas stream. The instrument was tuned to optimum sensitivity and to minimise production of interfering oxides species, with ²³²Th¹⁶O/²³²Th routinely ≤0.5%. The analyses were performed in peak hopping mode with a dwell time of 0.05 sec/mass. For each analysis the gas blank was acquired for ≈30 seconds, the laser triggered, and the signal acquired for a further ≈65 seconds.

The analytical protocol essentially followed that of Longerich (1996). The primary calibrating standard was NIST-612 glass and secondary standards BCR2g (Govindaraju, 1994) as well as several chromites (characterised by neutron activation analysis – WR Taylor, *unpublished data*) were routinely analysed as unknowns as a check on data quality control. Batches of analyses of 5-10 “unknowns” (chromite grains and secondary standards) were bracketed by analyses of NIST 612 allowing monitoring of, and correction for instrumental drift.

Data reduction used background corrected count rates and the method established by Longerich (1996). ⁵¹V was measured enabling use of electron microprobe determined V abundances as the internal reference element. Calibration values for NIST-612 used in the data reduction are those of Eggins (2003). A linear drift correction based on the analysis sequence and on the bracketing analyses of NIST 612, was applied to the analyte count rate for each sample. Multiple analyses of secondary standards indicated that analytical reproducibility and accuracy were better than 5% for most reported elements.

3. Results

3.1 Chromite compositions

Based on major element chemistry as determined by EPMA, the chromites were classified into the types shown in Table 2.

Table 2: “Chromite” grains classified on the basis of their major element compositions. A preliminary assessment of their likely source can be made for some types, although full trace element analysis is required for accurate provenance determination. *Magnesian chromite* (MC) and *titanian magnesiochromite* (TMC) are most likely to be diamond indicators.

<i>Chromite type</i>	<i>Explanation</i>	<i>Frequency</i>	<i>Possible sources</i>
TCH	Titanian chromite	10	Metasomatic and crustal layered intrusions
CH	chromite	27	Metasomatic and crustal layered intrusions
ZCH	Zincian chromite	2	
MC	magnesian chromite	221	Diamond indicator or magmatic
TMC	titanian magnesiochromite	68	Metasomatised diamond indicator
TMAC	Titanian magnesian aluminous chromite	17	Metasomatic, shallow mantle and magmatic chromite
FTMC	Ferroan titanian magnesiochromite	6	Oxidised from a variety of different sources
ZTCH	Zincian titanian chromite	2	
MAC	magnesian aluminous chromite	45	Shallow mantle or magmatic
MGT	magnetite	1	magmatic
MCM	Magnesian chrome magnetite	3	Magmatic chromite from kimberlite or lamproite
ZMC	Zincian magnesian chromite	15	
TFMAC	Titanian ferroan magnesian chromite	1	Oxidised mantle metasomatic
AC	Aluminous chromite	1	Crustal
FMAC	Ferroan magnesian aluminous chromite	2	Oxidised chromite
MCAS	Magnesian chromian aluminous spinel	3	Crustal or shallow mantle chromite
OTHER	Not classified	1	

4. Discriminant analysis to determine chromite provenance

The following comments (4.1 to 4.8) refer to columns in the accompanying Excel spreadsheet containing the data and results of the calculations. In particular, the provenance of the grains has been assessed using a variety of approaches, as described below.

4.1 DI Ramsay

This is an assessment of diamond indicator (DI) potential, based on work of Ramsay (1992), using Mg# and Cr# [where $Mg\# = Mg / (Mg + Fe^{2+})$ and $Cr\# = Cr / (Cr + Al + Fe^{3+})$]. DIs have $Cr\# > 0.65$ and Mg# between about 0.3 and 0.8. This technique classified 267 of the analysed grains as diamond indicators and 159 as “other”.

4.2 DI Moore

This is an assessment of DI potential based on Moore (1989) using Al, Cr, Fe, Mn and Mg contents of chromites. This technique classified 67 grains as DI and 359 as “other”.

Note that these two major element based discrimination techniques (4.1 and 4.2) agreed for 52.6% of the grains (224) but disagreed for 47.4% of the grains (202), illustrating the unreliability of techniques based only on major elements.

4.3 DI Major & Minor

This is an assessment of DI potential based on Moore (1989) using Al, Cr, Fe, Mn, Ti, Ni and V and Mg contents of chromites, ie major and minor elements. This technique classified 78 grains as DI and 35 and DI-M (diamond indicator-metasomatised), with the majority of the rest being classified as magmatic, shallow mantle or boninitic.

4.4 DI Cr-V and DI Ni-V

These are assessments of DI potential based on work by Wayne Taylor using Cr or Ni and V contents. Both Cr-V and Ni-V classified 11 grains as DI. 68 were classified as DI using Cr-V and 32 using Ni-V.

4.5 Score

This is a ranking of DI potential combining “DI Major and Minor”, “DI Cr-V”, “DI Ni-V”, Mn-Ni temperature and V content. A score of 6 represents maximum DI potential. Table 3 summarises the results from this suite of grains.

Table 3: Distribution of “scores” based on DI Major and Minor, DI Cr-V and DI Ni-V assessment methods.

<i>Score</i>	<i>Frequency</i>	<i>Score</i>	<i>Frequency</i>
6	27	2	20
5	37	1	79
4	26	0	145
3	90	Total	424

4.6 Trace Score

This is a similar ranking, but includes Ga, V, Nb, Co, Ta and Hf contents, as determined by LA-ICPMS. A score of 10 represents the maximum DI potential. Table 4 summarises the results.

Table 4: Distribution of “trace scores” using major, minor and trace elements.

<i>Score</i>	<i>Frequency</i>	<i>Score</i>	<i>Frequency</i>
10	9	4	37
9	21	3	18
8	10	2	64
7	20	1	19
6	11	0	172
5	31	Total	417

4.7 Trace class

This classification is the result of the full discrimination based on the Taylor method, as described in the accompanying document. It is based on the discrimination factors F1, F2 and F3, which are presented in the last three columns of data table. Table 5 is a summary of the results. **This is considered the most reliable technique for discrimination.**

Table 5: Results of the full discriminant analysis.

<i>Class</i>	<i>Frequency</i>
DI	35
DI_M	51
MANTLE	29
MAGMATIC	208
META_MAG	22
OTHER	21
BONINITIC	47
METAMORPHIC	4
BLANK	9
SUM	426

4.8 F1, F2 and F3

These are the functions, which are used to produce maximum separation of the grains into their various classes, as described in the accompanying document. The key discriminating elements are Al, Co, Cr, Cu, Fe, Ga, Mg, Mn, Nb, Ni, Sc, Ti, V and Zr. The factors F1, F2 and F3 separate grains into the following source rocks or geological settings;

- diamond indicator (DI) (kimberlite or lamproite),
- boninitic,
- diamond indicator/metasomatic (DI-M),
- magmatic,
- shallow mantle and
- metamorphic.

The plots of F2 and F3 against F1 (Figure 1) compare the discriminant analysis of the current suite with the original fields defined by Taylor's work and described in the accompanying document. The results indicate that the discriminant analysis has separated the current chromite suite effectively into the different classes. In particular the diamond related classes (DI and DI_M) are effectively separated from grains of other provenance. This discrimination technique is considered the most reliable as it been tested with several 100 chromites from known sources and was able to discriminate them into their correct sources with about >90% accuracy.

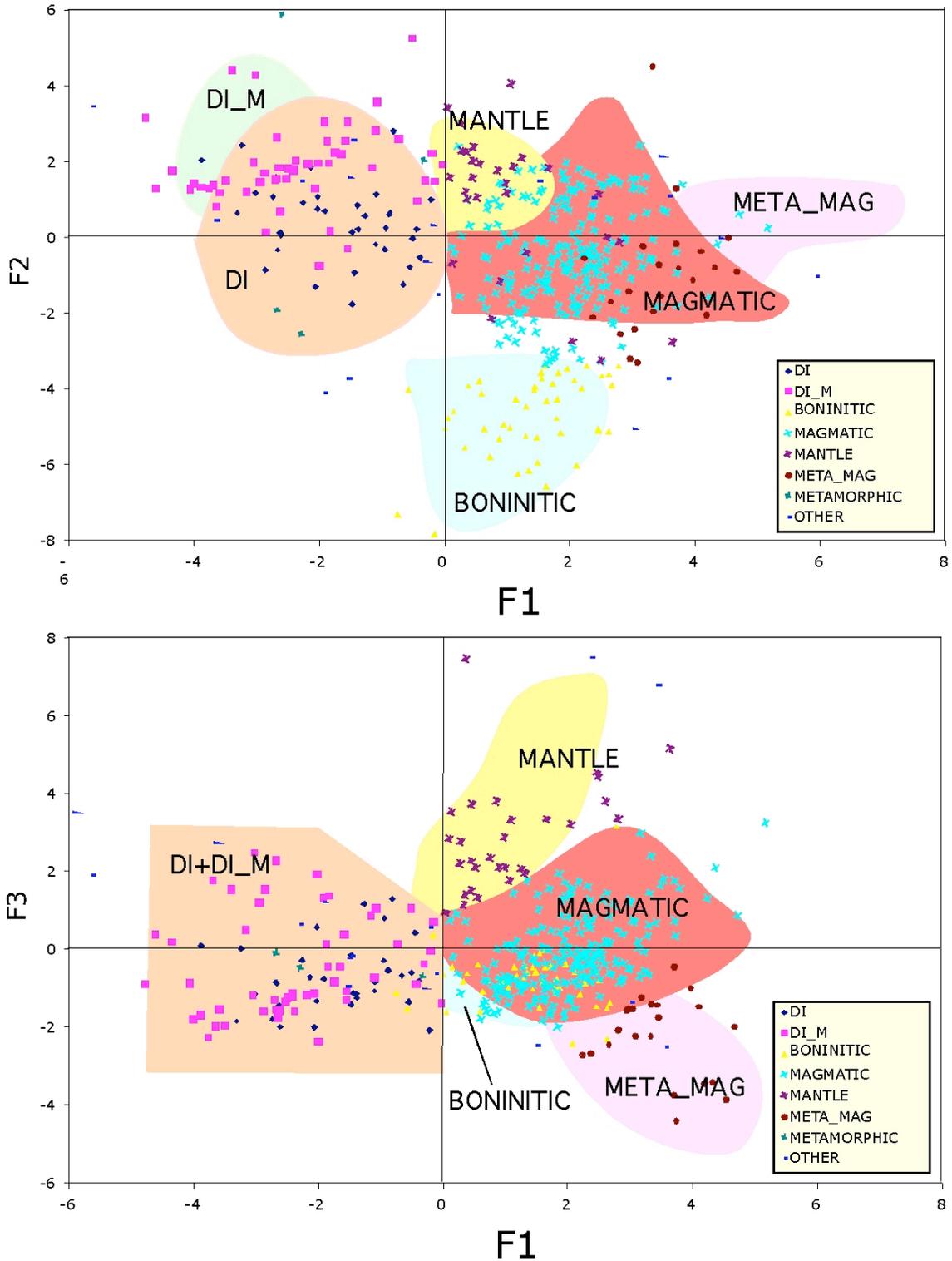


Figure 1: Results of the current chromite suite plotted in F1-F2 and F1-F3 spaces, and compared with approximate fields derived from the original calibration of the technique by Taylor and co-workers.

5. Chromite Equilibration Temperatures

The three columns T(Ni-Zn)^{°C}, T(Ni-Mn)^{°C} and T(Ni-Co)^{°C} contain estimated temperatures of equilibration of the chromites, based on Ni-Zn, Ni-Mn and Ni-Co partitioning between chromite and olivine. The Ni-Co thermometer (Denny 1998) is considered the most reliable, as Ni and Co as determined by LA-ICP-MS should be more accurate than Zn (mass interferences and volatility can compromise Zn analysis by this technique). It is based on exchange of Ni and Co between chromite and olivine under mantle conditions, assuming the olivine's Ni/Co ratio is 21, and a preliminary experimental calibration has been performed by Denny (1998). The other two thermometers have not been experimentally calibrated.

Unless the chromites are demonstrably from a source in which they were in equilibrium with mantle olivine, calculated temperatures should be considered meaningless. It is reasonable to assume that grains classified as DI, DI_M and MANTLE were in equilibrium with mantle olivine, and these probably therefore yield meaningful temperatures. However, other classes of chromite may not have been equilibrated with olivine or, if they were, the olivine was not mantle olivine (eg magmatic) and may not have had Ni/Co close to 21.

The ranges and averages of T[Ni-Co] for these three classes are presented in Table 6. Interestingly, the DI and DI_M classes give almost identical ranges and averages, which are significantly higher than those recorded by the MANTLE chromites. This is consistent with the likely deeper (and therefore hotter) origin of the diamond indicator chromites, compared with those classified as MANTLE, most of which probably derive from the shallower, spinel peridotite facies.

Table 6: Ranges and averages of T[Ni-Co] for chromites classified as DI, DI_M and MANTLE using the full discriminant analysis based on major, minor and trace elements.

	DI	DI_M	MANTLE
T[Ni-Co] _{min} (°C)	953	929	667
T[Ni-Co] _{max} (°C)	1318	1314	1227
T[Ni-Co] _{avge} (°C)	1166	1125	1068

If the temperature range for the DI and DI_M grains is projected in PT space onto a 40mWm⁻² geotherm, almost the entire suite derives from pressures within the diamond stability field. On a 44mWm⁻² geotherm, most of the suite would presumably derive from pressures in the graphite stability field. Without detailed geographical and geological data relating to these samples, it is not possible to make more specific remarks.

6. Chromite oxidation state

Mantle derived chromites record the oxygen fugacity (f_{O_2}) at which they equilibrated in the mantle in their $Fe^{3+}/\Sigma Fe$ value. For the current suite, $Fe^{3+}/\Sigma Fe$ was calculated from the EPMA analyses, assuming perfect stoichiometry. Chromites classified DI or DI_M are plotted on Figure 2 against Cr# (100*Cr/Cr+Al) after Ramsay (1992).

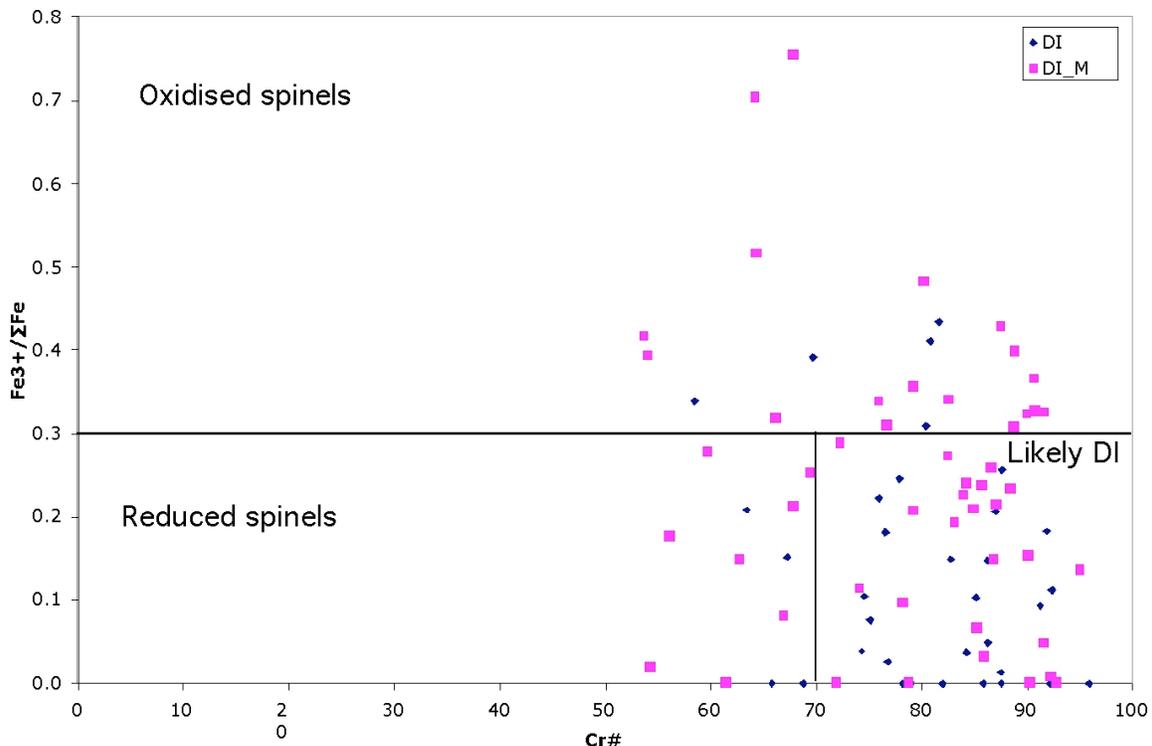


Figure 2: Cr# vs. $Fe^{3+}/\Sigma Fe$ for the current DI and DI_M chromites. Most DI grains tend to be reduced chromites, but there is some indication of oxidation associated with metasomatism in the DI_M. After Ramsay (1992).

Most DI chromites are sufficiently reduced (and sufficiently refractory, i.e. high Cr#) to be associated with diamonds. Similarly, many DI_M (i.e. chromites showing elevated Ti and other HFSE associated with metasomatism in the mantle) are sufficiently reduced to be associated with diamond. Of the more oxidised grains in this suite, however, most are DI_M, consistent with an association between metasomatism and oxidation.

7 Summary

7.1 Over 400 chromite grains were analysed for major and minor elements by EPMA and trace elements by LA-ICPMS, at RSES, ANU.

7.2 The results were subjected to discriminant analysis based on the full data set to ascertain the likely provenance of each grain.

7.3 35 DI and 51 DI_M chromites were identified as a result. The majority of the remaining grains were magmatic (including boninitic), but would have been classified as DI based only on major elements.

7.4 Many of the DI and DI_M grains have equilibration temperatures (assuming cratonic geotherms) consistent with their crystallisation in the diamond stability field. Other olivine-equilibrated chromites (ie MANTLE types) recorded lower temperatures overall, and probably derived from the shallower spinel peridotite facies.

7.5 Many of the DI and DI_M grains are sufficiently reduced to have been in equilibrium with diamond, although there are weak indications of a link between metasomatism and oxidation in some DI_M grains.

7. References

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