

Appendix 1

Technique for the Discrimination of Diamond Indicator Chromites from those of other provenance, based on Major, Minor and Trace Element Analyses - Dr Gregory M. Yacksley

**TECHNIQUE FOR THE DISCRIMINATION OF
DIAMOND INDICATOR CHROMITES FROM THOSE OF
OTHER PROVENANCE, BASED ON MAJOR, MINOR
AND TRACE ELEMENT ANALYSES.**

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1. Introduction

1.1 *Introductory remarks and definition*

The purpose of this paper is to briefly describe the research work undertaken at the Australian National University by Dr Wayne Taylor and students over the last few years, to develop advanced techniques for the discrimination of diamond indicator chromian spinel from chromian spinel derived from other potential provenances. The new techniques utilise the major, minor *and trace element* compositions of spinel grains. The description provided here is a very brief summary, intended to indicate broadly the inadequacy of traditional discrimination methods (normally based on divariant plots of compositional parameters involving only major elements), the type of analytical work undertaken and the nature of the approach used in developing the discrimination technique.

The term diamond indicator (DI) chromian spinel is taken to mean magnesiochromite with compositions consistent with derivation from deep, refractory peridotitic lithosphere, and transported by kimberlite or lamproite magmas to the surface.

The overall approach taken in this study was to analyse a large suite of chromian spinel grains from a range of geological settings, including grains from diamondiferous kimberlites and lamproites. The compositions of these grains were then plotted in compositional spaces traditionally used for discriminating diamond indicators from other grains, in order to assess the accuracy of the traditional techniques. The new data was then subjected to a discriminant analysis to produce new discrimination diagrams based on major, minor *and trace element* compositions. The new discrimination technique was then tested using a second suite of grains from a variety of known geological sources in Australia's Kimberley region.

1.2 *The inadequacy of existing discrimination techniques based on major and minor elements*

Existing techniques for discrimination of diamond indicator chromite have attempted to define areas in various compositional spaces, which are unique to chromian spinel grains transported by kimberlite from deep refractory lithosphere (diamond stability field). Major and/or minor element compositions of spinel from known diamondiferous kimberlite or lamproite sources, or from syngenetic chromite inclusions in diamond, were used to define DI fields in the compositional spaces, and compositions of grains obtained during exploration campaigns were compared to these fields in order to assess their prospectivity.

In order to assess the accuracy of these existing techniques, ANU scientists have examined the most commonly used diagrams using a comprehensive database (supplied by P. Roedder) of chromian spinels compositions from a wide range of different geological sources (including boninite, chromitite, impactite, kimberlite, lamproite, mafic magmas, magmatic, shallow mantle, metamorphic and ultramafic complexes). Three examples are presented here, namely MgO-Cr₂O₃ space (Fig. 1) (Moore et al., 1989),

Mg#-Cr# space (Fig. 2) (where $Cr\# = 100 * Cr / [Cr + Al]$ and $Mg\# = 100 * Mg / [Mg + Fe]$) (Ramsay, 1992) and Ti-Cr# space (Fig. 3) devised by Wayne Taylor (unpublished data).

The MgO-Cr₂O₃ plot (Fig. 1) contains a DI field from 12-17wt% MgO and 58-78 wt% Cr₂O₃, based on compositions of chromite grains included in diamonds. However, when chromites from other sources (as indicated in the key to Figure 1) are also plotted it is clear that this diagram is inadequate as a means of discriminating DI chromian spinel grains. In particular, the diamond inclusion defined DI field overlaps with spinels from the shallow mantle (therefore non-DI), and also with spinel from boninites, chromitites and ultramafic complexes.

The Mg#-Cr# plot (Fig. 2) similarly contains a DI field defined on the basis of chromite inclusions in diamonds. This field fairly well covers many DI chromites derived from kimberlitic and lamproitic magmas, but also overlaps with spinels from chromitites, boninites, ultramafic complexes, and the shallower, non-diamondiferous mantle.

The DI field on the Ti-Cr# plot (Fig. 3) either entirely or completely overlaps the fields of komatiitic and boninitic chromian spinels.

In summary, existing discrimination diagrams are capable of clustering DI spinels in various compositional spaces, but do not remove overlaps of spinels derived from a number of other potential sources.

1.3 Use of trace elements for more advanced discrimination techniques

Because of the demonstrated inadequacy of existing techniques based on major and minor elements to uniquely discriminate DI chromian spinel, a more advanced technique was developed in which trace elements determined by LA-ICPMS were used in conjunction with major and minor elements.

In order to accurately define a diamond indicator (DI) field in a compositional space (eg. Cr# vs Ti or Nb where $Cr\# = Cr / (Cr + Al)$, or Ga/Nb vs Co/V etc), it was first necessary to investigate chromian spinel compositions from as many different spinel types as possible, focusing on those which may overlap with DI types. Therefore, spinels with similar major element compositions to kimberlite-sampled DI chromian spinels were obtained for the study. Grains from the localities and provenances listed in Table 1 were used.

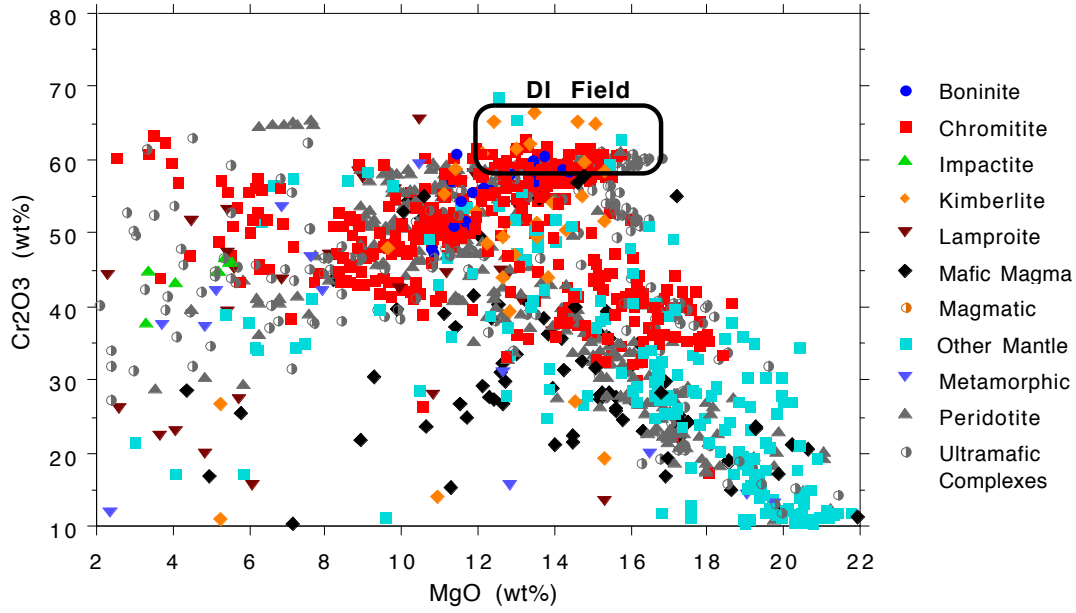


Figure 1: MgO vs. Cr₂O₃ for the database of chromian spinels described in Table 1. The DI field overlaps with fields for chromitites, boninites, ultramafic complexes and other mantle. Also, many spinels from diamondiferous kimberlites plot outside the DI field.

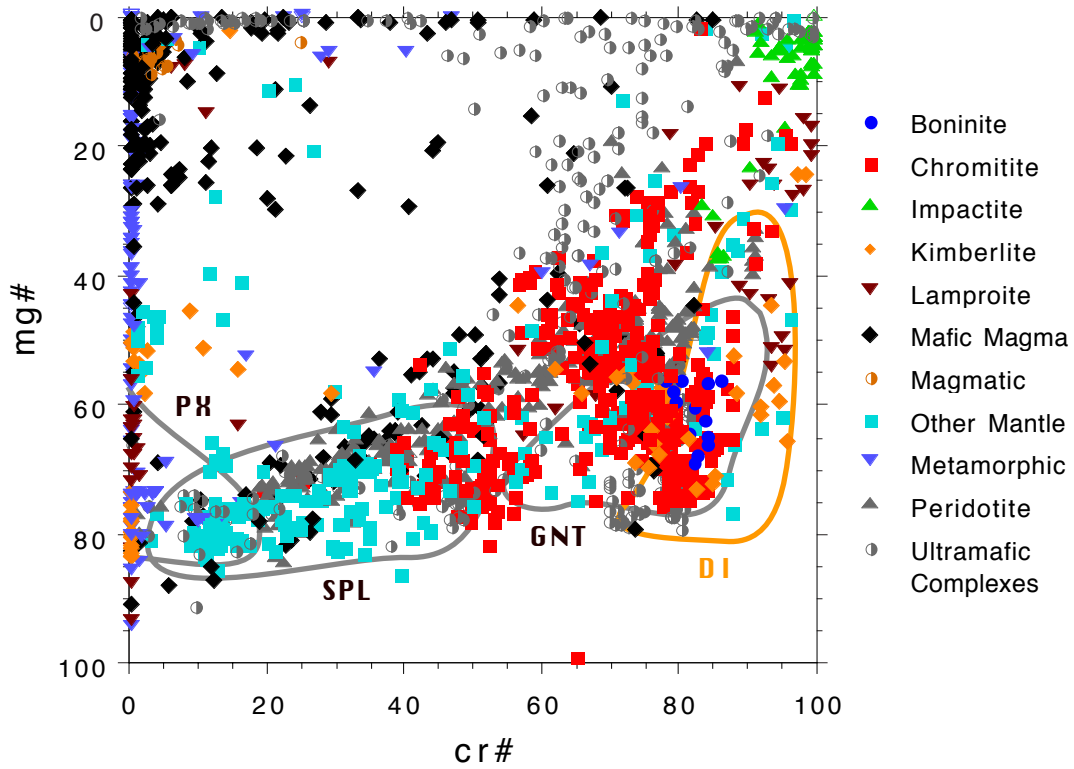


Figure 2: Cr# vs Mg# for the database of chromian spinels described in Table 1. See text for further details.

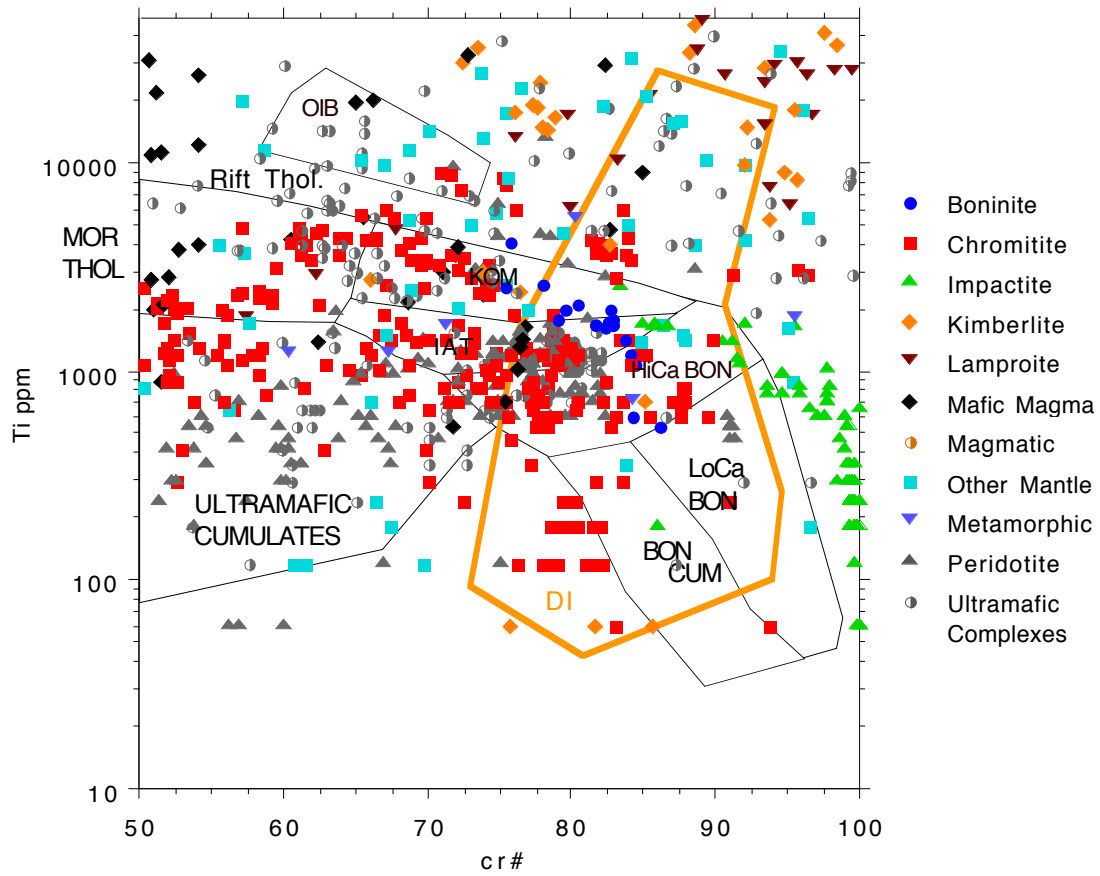


Figure 3: Plot of Cr# vs. Mg# of chromian spinels in Table 1. See text for further explanation.

Table 1: Parental rock types and their localities for chromian spinels analysed in this study.

Parent rock type	Locality	Location
Boninite	Heazelwood	Tasmania
Kimberlite	Jagersfontein	Southern Kaapvaal
Kimberlite	Aries	Central Kimberley Block
Kimberlite	Bulgurri	Northern Kimberley Block
Kimberlite	Bulfontein	Kimberley, Kaapvaal Craton
Kimberlite	Dutoitspan	Kimberley, Kaapvaal Craton
Kimberlite	Frank Smith	Kaapvaal Craton
Kimberlite	Kampfersdam	Kimberley, Kaapvaal Craton
Kimberlite	Leicester	Western Kaapvaal
Kimberlite	Liaoning	Sino-Korean Craton
Kimberlite	Loxton	Kaapvaal Craton
Kimberlite	Premier	Transvaal, Kaapvaal Craton
Kimberlite	Venetia K1	Limpopo Mobile Belt
Kimberlite	Venetia K2	Limpopo Mobile Belt
Komatiite	Cashmere Downs	Central Yilgarn craton
Komatiite	Mt Clifford	Central Yilgarn craton
Lamproite	Walgidee Hills	Western Kimberley Block
Layered intrusion	Bushveldt	Kaapvaal Craton
Layered intrusion	Panton Sills	Eastern Kimberley Block
Meta-kimberlite	Naberru	Northern Yilgarn Craton
Prospect	Ballard	Central Yilgarn Craton
Prospect	Peperill Hill	Central Yilgarn Craton
Prospect	Turkey Well	Central Yilgarn Craton
Meta-shoshonite	Murrin-Murrin	Central Yilgarn Craton
Spinel dunite	Mt Noorat	Victoria
Spinel peridotite	Jugiong	Eastern NSW
Ultramafic complex	Greenhills	Southland, NZ
Ultramafic complex	Trilbar Complex	Narryer
Ultramafic complex	Donqiao	Tibet

Thus, chromites from boninites, diamondiferous kimberlites, komatiites, lamproites, layered intrusions, metamorphosed kimberlite and shoshonite, spinel peridotites and ultramafic complexes were analysed.

An additional suite of chromian spinels from various locations in the Kimberley region of northwestern Australia was obtained and analysed. These samples were of known provenance and their host rocks were of known diamond grade, and included spinels from

- kimberlites from 7 localities in Archean cratonic material or Proterozoic mobile belts, with diamond grades varying from non-diamondiferous up to a maximum of 20 ct/tonne;
- lamproites from Argyle (500 ct/tonne) and Ellendale (1-12 ct/tonne)
- flood basalts (Carson Volcanics) from the central, north and east Kimberley, and
- layered intrusions from the East Kimberley, including Panton Sill, Eastmans Bore and Lamboo.

This data was used to test and refine the new discrimination technique developed on the basis of the grains listed in Table 1.

2. Analytical techniques

2.1 Electronprobe microanalysis for major and trace elements

Chromite major element compositions (Cr, Al, Mg, Fe) were determined by EDS electronprobe microanalysis on the Camebax instrument at RSES, ANU. Minor elements including Ti, Mn, V, Zn, and Ni were measured on the same instrument using the WDS technique. Electronprobe microanalysis (EPMA) is an entirely routine technique in which a finely focussed electron beam is used to excite X-rays from a tiny volume of the sample (a few cubic microns). The X-ray spectrum is measured by spectrometers (WDS) or a detector (EDS) and a multi-element major and minor element analysis of a 1-2 micron spot on the mineral grain is obtained in a few minutes. RSES has recently acquired a new instrument, a 4 spectrometer Cameca SX100, which is capable of automation, thus speeding up analytical output considerably, and *PRISE* has unlimited access to this new instrument.

2.2 LA-ICPMS analysis for trace elements

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.

During LA-ICPMS technique a focussed UV laser beam with a beam diameter typically in the range of a few 10's of μm , is directed onto the polished surface of the grain to be analysed. The laser pulses with a frequency typically in the range 5-10 Hz. This causes a small sample of the grain to be ablated, forming essentially colloidal size particles. A stream of Ar (mixed with H_2) gas is directed across the surface of the ablating sample and carries the ablated particles into a plasma in the mass spectrometer. The plasma vaporises and ionises the material, which is then accelerated through a quadrapole mass spectrometer to a detector, which measures the signal intensity as a function of mass.

The signal intensity of unknown samples (eg. chromites) is compared with the signal intensity of international standard glasses (usually NIST612 or NIST610), referenced to an independently determined element concentration. In the case of chromites, this reference element is normally V, which can be determined precisely by WDS electronprobe microanalysis. This enables calculation of the trace element concentrations in the unknown chromite with excellent precision (usually better than 5% based on replicate measurements of secondary standard chromites) and to detection limits in the low ppm or often ppb range, depending on a range of analytical factors. The system at RSES has particular advantages over many other systems, in particular very rapid and efficient transport of ablated material from sample cell to plasma, and high sensitivity of the detector across the entire mass range.

3 Element correlations

The spinel suites described above were analysed for major and minor elements by EPMA and for traces by LA-ICPMS. The results were then plotted in a number of divariant

element-element plots to assess which compositional parameters produced maximum separation of the DI chromites from chromites from the other sources.

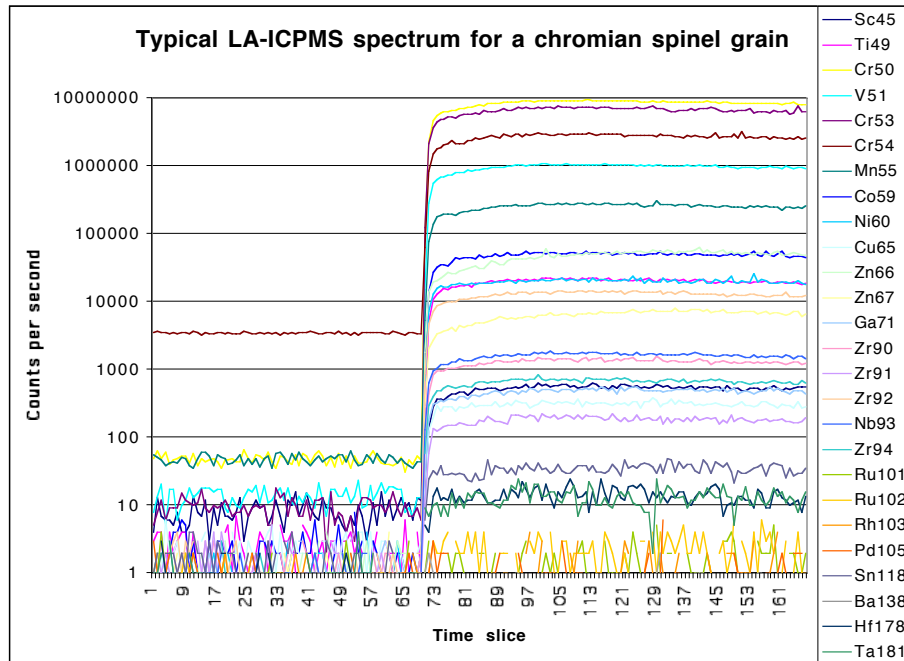


Figure 4: Typical spectrum obtained from LA-ICPMS analysis of a chromian spinel grain. Time slices from 0 to 72 are measurement of background, the laser was triggered at time slice 73, and the signal collected thereafter.

Plots against V and Cr# of the following major, minor and trace elements were examined: Al, Cr, Mg, Fe, Fe₃₊/ΣFe, Co, Ni, Mn, Ti, Zn, Sc, Cu, Ga, Ge, Zr, Nb, Sn, Sn, Hf, Ta and Pb. Figures 5-9 are representative examples, but are by no means comprehensive descriptions of the entire dataset.

Figure 5 shows that Cr and V contents can be used as a rough discriminant diagram for DI chromites. The DI field on the diagram includes both kimberlitic and metakimberlitic chromian spinels, all of which have more refractory (higher Cr) compositions than the “magmatic array” crudely defined by boninites, komatiites, and layered intrusions. This plot can also discriminate lamproitic from kimberlitic spinels. Cr contents of spinels from metamorphosed kimberlites are apparently unaffected by the metamorphic process.

Figure 6 shows that kimberlite sampled chromian spinels exhibit a very wide range of Ti contents from about ≈100 to ≈10000 ppm. A rough magmatic array extends from low Ti and V to high Ti and V and includes (in order of increasing V and Ti abundance) spinels derived from boninites, komatiites and layered intrusions. Whilst many kimberlite DI spinels plot distinctly above or below the magmatic array, many plot within it, and the ability of this compositional space to uniquely resolve DI spinels from others is limited.

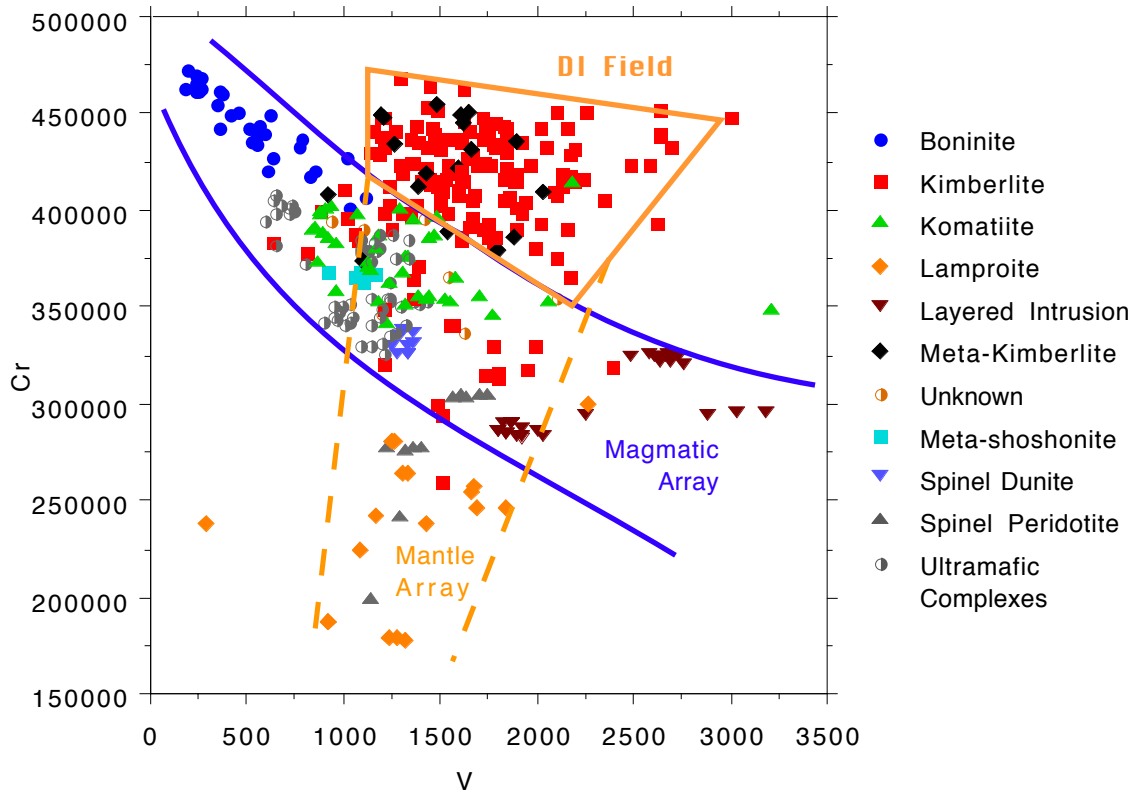


Figure 5: Cr vs V for chromian spinels.

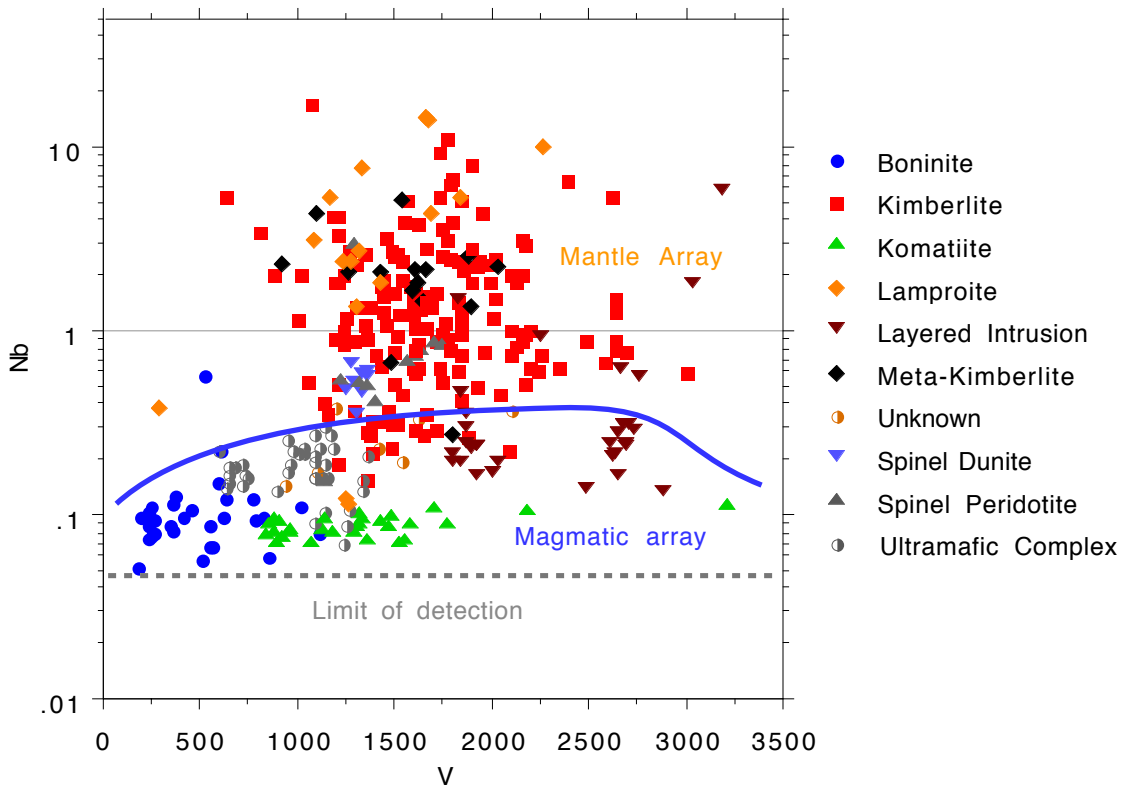


Figure 6: V (ppm) vs Nb (ppm) for chromian spinels. See text for further explanation.

Figure 7 illustrates the importance of the trace element Nb in separating DI spinels from other varieties. Kimberlitic and metakimberlitic spinels contain >0.3 ppm Nb, whereas nearly all other varieties plot below this limit, over a range of V abundances. When coupled with Cr#, Nb is an excellent discriminator of kimberlite derived spinels from other varieties (Fig. 8). Ta behaves in a similar fashion to Nb and when plotted against Cr# provides very good discrimination. Furthermore, a plot of Ga/V-Co/Nb very efficiently resolved kimberlitic and lamproitic spinels from the Kimberley from spinels from flood basalts and magmatic layered intrusions (Fig. 9).

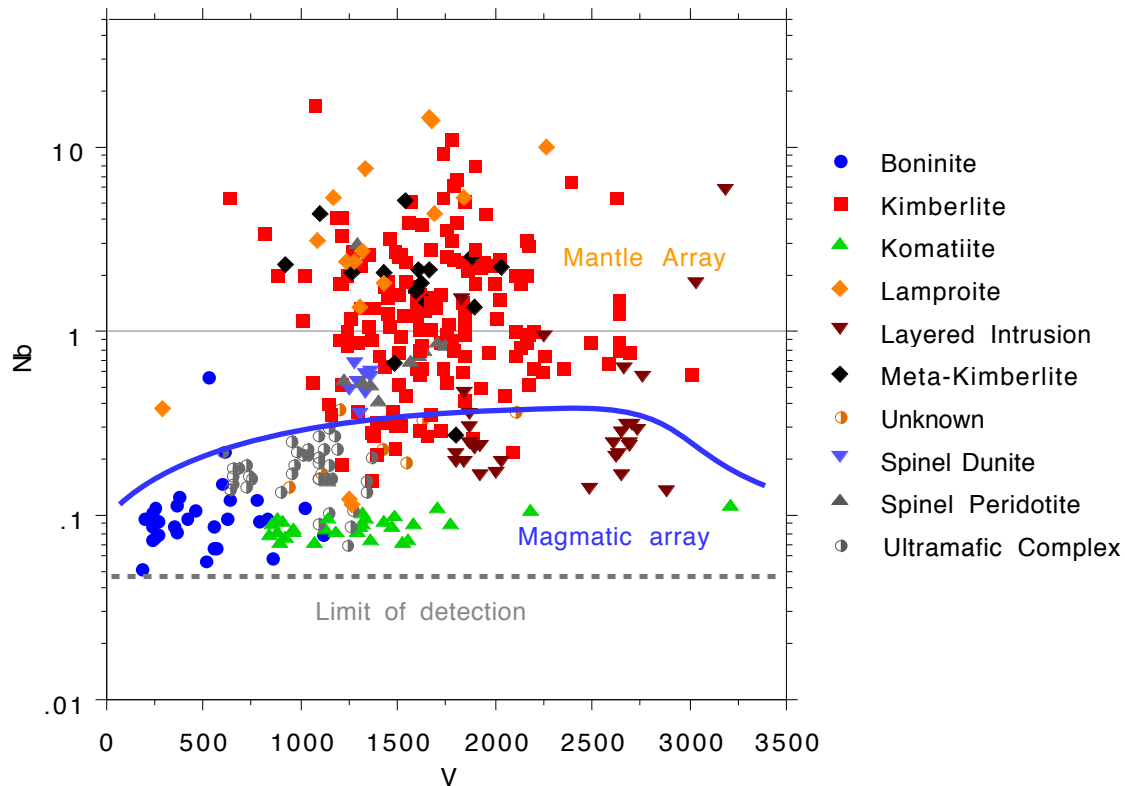


Figure 7: V (ppm) vs Nb (ppm) for chromian spinels. Note the excellent separation of boninitic and kimberlitic (DI) grains.

4. Discriminant analysis and the interpretation of the data

4.1 Discriminant analysis

The compositional data obtained from the chromian spinel suite were subjected to multi-group discriminant analysis (MGDA) (Digby and Kempton, 1987; Mardia et al., 1979) using the program Genstat 5.

MGDA is a statistical method for analysing more than one variable simultaneously, by finding linear combinations of given variables that maximise the between-group and minimise the within-group variation. This results in development of functions of the original variables that can be used to discriminate between the pre-assigned groups.

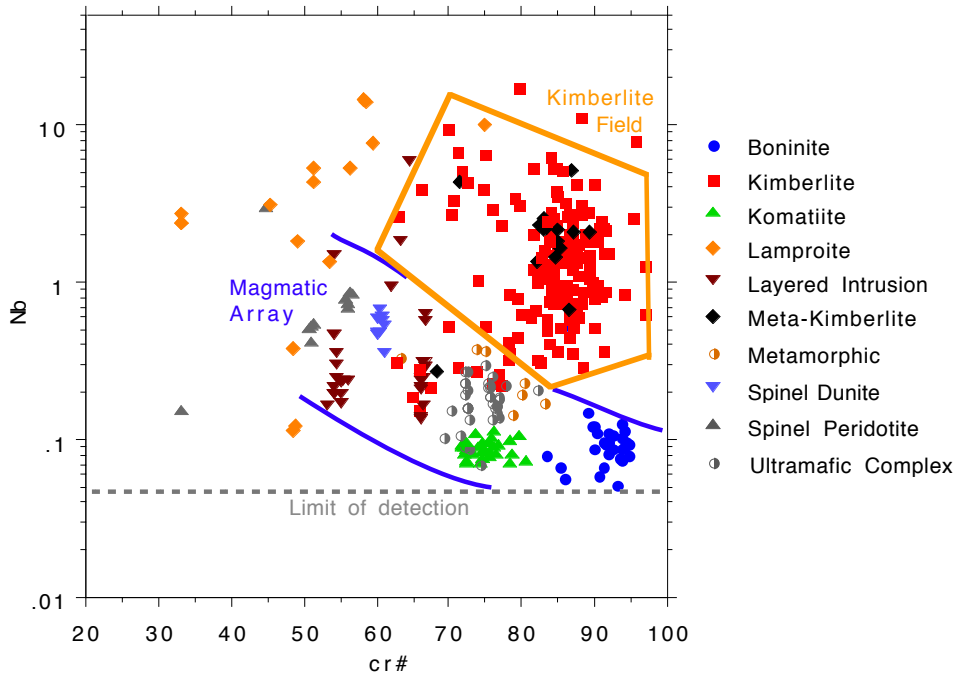


Figure 8a: Cr# ($100 \cdot \text{Cr}/[\text{Cr}+\text{Al}]$) vs Nb (ppm) for the chromian spinels derived from the sources listed in Table 1.

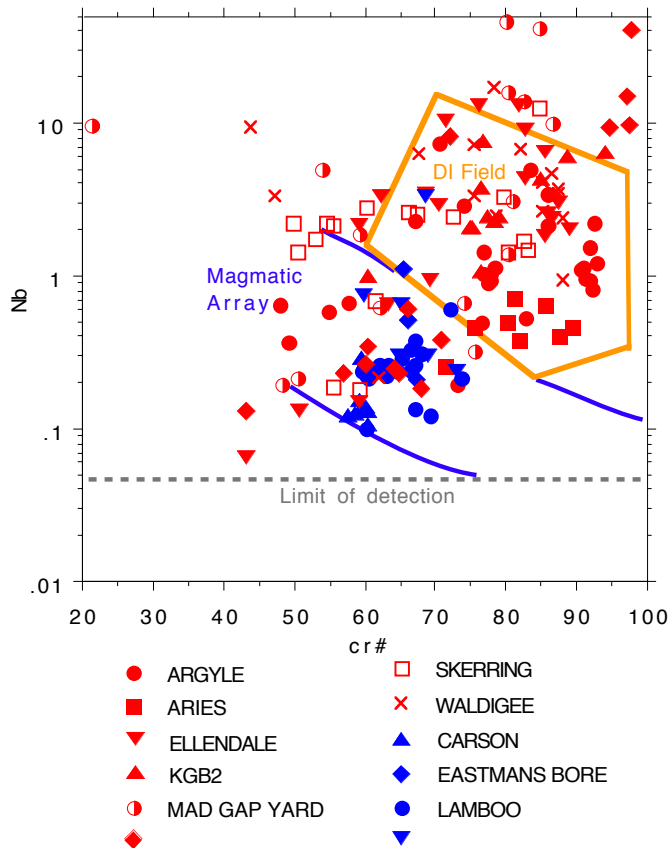


Figure 8b: Cr# vs Nb for spinels from Kimberley region of NW Australia.

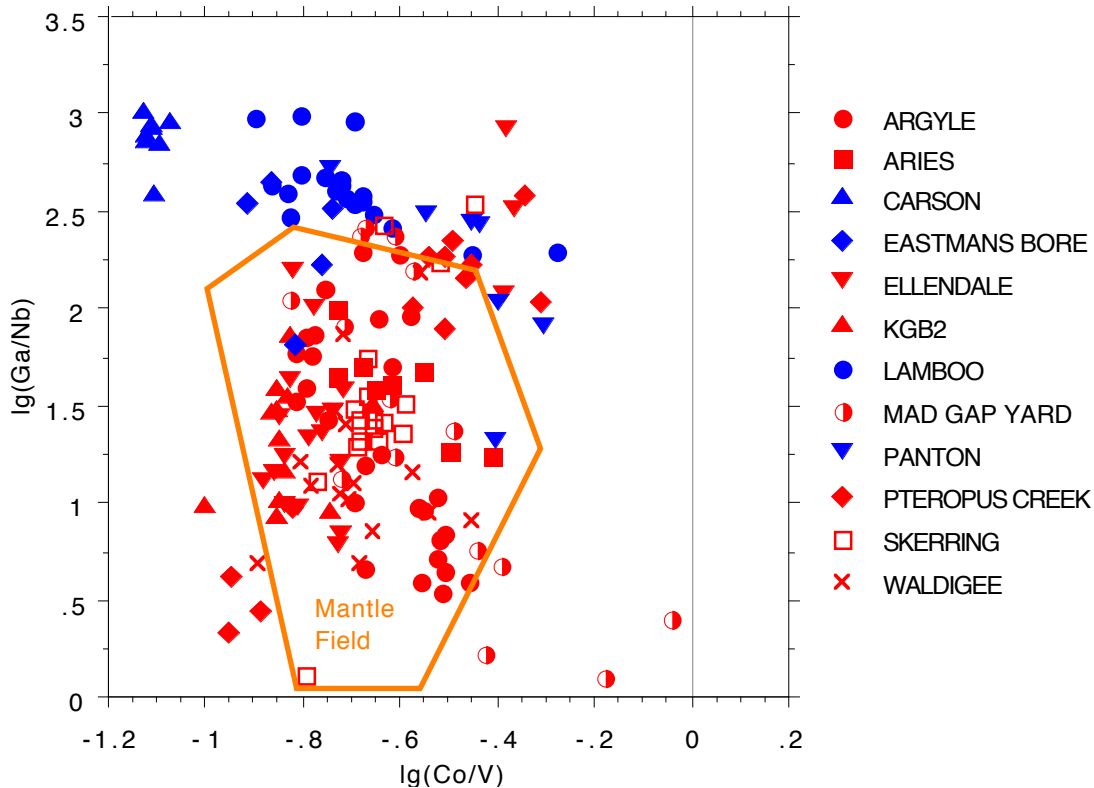


Figure 9: Log Co/V bs Log Ga/Nb for Kimberley chromian spinels.

The pre-assigned groups into which the chromian spinels in this study were placed included *diamond indicator*, *boninitic*, *DI metasomatised*, *metamorphosed magmatic*, *magmatic*, *shallow mantle* and *other*. The functions of the original variables are designated F1, F2 and F3 in Figures 10 and 11, which show the fields for the various groups and data from chromian spinels obtained from the Kimberley region of Australia. The critical elements in these functions were Cr, Fe, Mg, Mn, Ni, Ga, Al, Cu, Sc, V, Co, Ti, Nb and Zr.

Clearly the F1-F2 plots (Fig. 10) shows excellent discrimination of DI chromian spinels from the other categories, and in particular separates the often problematic boninitic spinels very efficiently. The F1-F3 plot (Fig. 11) separates the DI and DI metasomatic field with better than 95% efficiency.

4.2 Data interpretation and presentation

PRISE provides a commercial in confidence service to diamond explorers whereby we will analyse chromian spinel grains by EPMA and LA-ICPMS, and perform the discriminant analysis described above to assess their likely provenance and diamond prospectivity. Data and the results of the discriminant analysis is provided as Excel spreadsheets, which contain additional information, such as results of spinel thermometry (using the Ni-Mn, Ni-Zn and Ni-Co thermometers).

PRISE has provided this service on an ongoing basis to one Australian major diamond explorer and to several junior explorers in Australia and southern Africa.

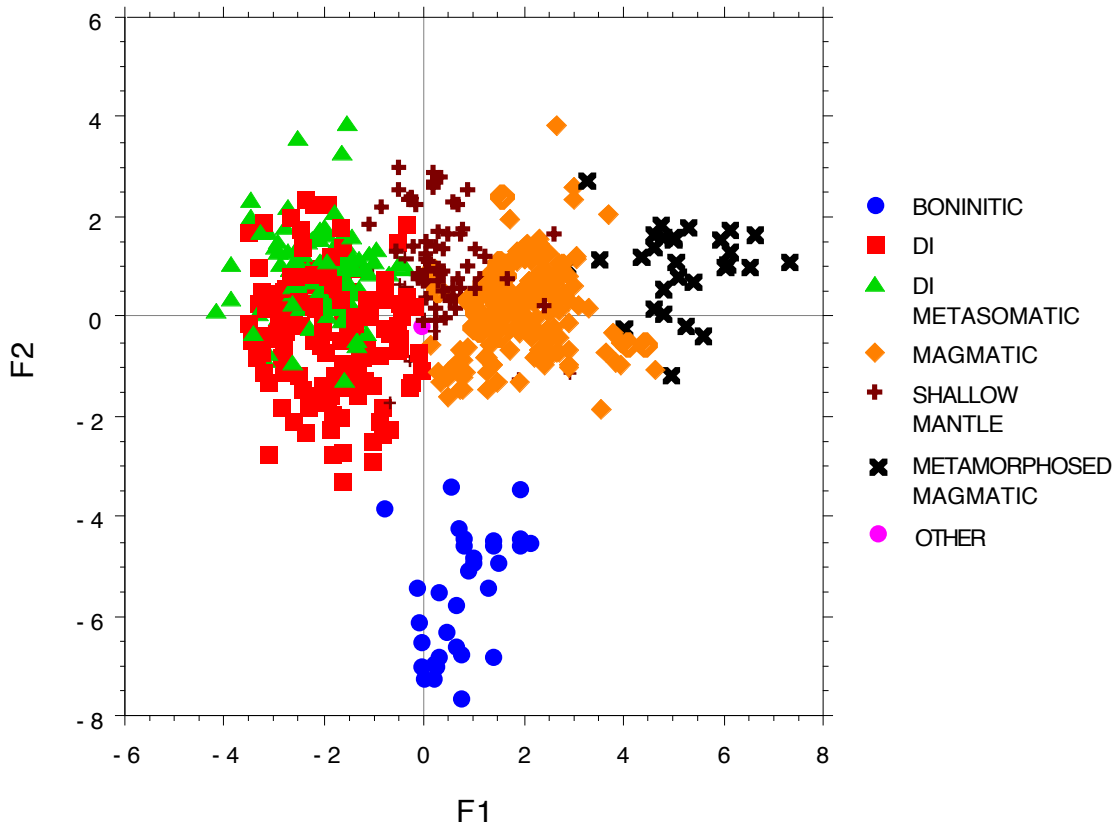


Figure 10a: F1 vs. F2 for chromian spinels, classified into the groups indicated in the key. This data defines the DI field at $-4 < F2 < 0$ and $-4 < F1 < +4$, where F1 and F2 are two of three functions derived from discriminant analysis which give maximum separation of the various spinel groups. Note the clear separation of DI grains from grains from boninites, other magmatic and metamorphic sources and shallow mantle (spinel peridotite field).

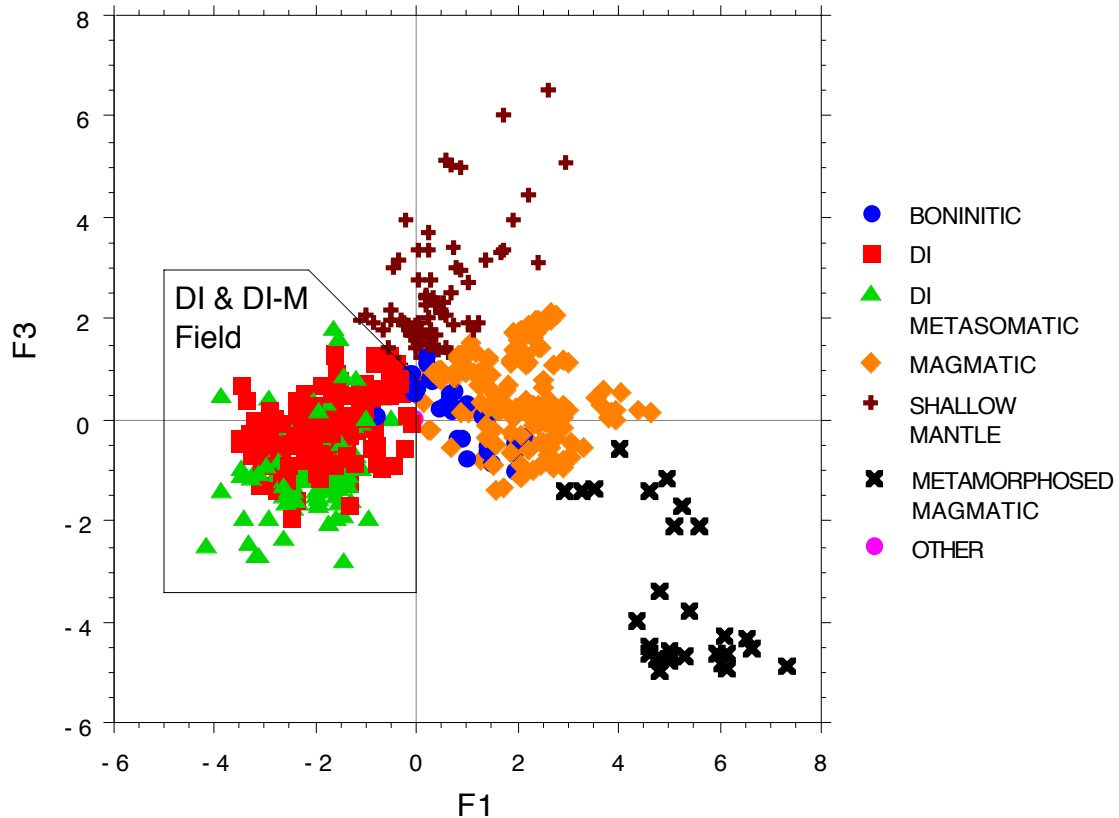


Figure 10b: F1 vs. F3 for chromian spinels, classified into the groups indicated in the key. This data defines the DI field as indicated. Note again the clear separation of DI grains from grains from boninites, other magmatic and metamorphic sources and shallow mantle (spinel peridotite field).

5. Conclusions

In conclusion, the technique described above for assessing prospectivity of chromian spinels obtained from heavy mineral concentrates as a result of diamond exploration represents a significant advance in this field. DI grains can be separated from grains from a variety of different provenances with near 100% accuracy.

6. References

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