

Geochemistry of
single diamond crystals
by Instrumental Neutron Activation Analysis.

by
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Declaration

It is hereby declared that all the analyses, discussion and interpretation contained in this thesis, except where acknowledged in the text, was performed by the author. The work has not been submitted elsewhere for a higher degree.

Signed: A. Damareyusho

Date: 1/2/95

Place: WITS

DEDICATION

This thesis is dedicated to my dearest grandmother,
Boodhanee Budhai,
for being the best
cook, nurse, tailor and teacher
that I know.

*The important thing in science is not so much to obtain new facts as to discover new
ways of thinking of them.*

(In A. Koestler and J.R. Smithie's Beyond Reduction 1968 (London : Hutchinson).

CHALCEDONY OFFERINGS

At Beohari 'neath a peepul tree
The Hindu God Mohadeo is wrought
Upon a rock. Before him have been brought
Offerings of calcite and chalcedony,
Culled from the hills by many a devotee
Who seeing there a shining mineral thought
"With this I will appease his wrath," and sought
For gem-like stones of clear transparency.

Castings from Nature's foundry! - these were made
In cavities of various mould and size
In lavas by solutions that had grown
Wealthy in mineral as they did arise...

FLOWERS FROM FIRE

Before Decay these lavas decomposed,
Disintegrating them to emerald earth,
Before they were in her embrace enclosed,
Great Nature knew not of this streamlet's birth.

Before the mists upon the mountains wept
Their rainbow tears which carved its narrow urn
That as a crystal flood together kept
They might unto the mighty Sea return

Not till lavas, whose live soul was steam,
Had baked as in a kiln the under-clay,
Not till their fire was quenched were they supreme
for blossoms in their myriads seen to-day....

(Kenneth Knight Hallows: The poetry of geology, 1933)

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A complete thesis may be viewed as a contribution of knowledge to the scientific community - but to achieve this one has to travel through a difficult path. During this journey one learns, forgets, remembers, makes and loses friends, thanks and insults God, develops an ulcer, loses ones hair.....and throughout all this, the idea of quitting appears very attractive.

However, like in so many paths in life, dealing with all this are valuable lessons in life. Hence, in the process of starting and finishing a thesis, one is educating and improving one's self - i.e., one is gaining experience and experience builds character. Therefore I'd like to think that my thesis is only a tiny scientific contribution but a huge contribution to building and shaping my character.

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ABSTRACT

Neutron Activation Analysis (NAA) is probably the most powerful technique, available to date, for the analysis of the trace elements in diamond. The carbon matrix of diamond is not activated by neutrons, so there is no interference from the matrix itself. Of the known 62 impurity elements in diamond it is possible to analyze for 55 by neutron activation analysis. In this study the technique of neutron activation analysis has been modified and optimized for the analysis of single, small (0.01-0.5 carat), inclusion-bearing and inclusion-free diamonds.

Instrumental Neutron Activation Analysis (INAA) was used to analyze for up to 40 different elements at the ppb and ppt levels in diamonds from Brazil, South Africa, Colorado and China. Both, peridotitic diamonds (those that contain either purple/red garnet, enstatite, chrome-diopside, olivine, sulphide and chrome-spinel inclusions or combinations of these) and eclogitic diamonds (those that contain either orange garnet, omphacitic-clinopyroxene and sulphide inclusions or combinations of these phases) were analyzed. The data obtained was used to detect and understand the differences between diamonds from the eclogitic and peridotitic parageneses and between diamonds from the different localities.

In this regard, two interelement ratios i.e., Cr/Sc and Au/Ir ratios were found to be useful. Cr/Sc ratios range from <1 to $>10\,000$. The Cr/Sc ratios of eclogitic diamonds are low, usually less than 50, while peridotitic diamonds have Cr/Sc ratios that are always in excess of 100. These are equivalent to the Cr/Sc ratios of basaltic rocks (5-49) and ultramafic rocks (100-400), respectively and is consistent with the behaviour of Cr as a compatible element and Sc as a moderately compatible element during crystallizing/melting of liquids of basaltic composition.

It seems, also, that diamonds from a particular locality or mine have a unique range of Cr/Sc ratios. Furthermore, the identity of the dominant silicate inclusion/s can be deduced from the Cr/Sc ratio of the diamond, since each type of silicate inclusion has a different range of Cr/Sc ratios. Not only is the Cr/Sc ratio distinctive for silicate inclusions in diamonds, it is also quite distinctive for minerals cogenetic with diamond such as orange garnet, red garnet, purple garnet, chrome diopside and orthopyroxene (macrocrysts) which were separated from kimberlites. This confirms that diamond

inclusions are diamond-encased (and thus protected and preserved) xenocrysts found in 'kimberlitic' rocks. Furthermore, there is a positive correlation between Cr and Sc for any one silicate diamond-inclusion type or cogenetic mineral but a negative correlation between Cr and Sc in garnet megacrysts of kimberlites.

Often, diamonds with only visible sulphide inclusions or no visible inclusions can also be identified as belonging to either the peridotitic or eclogitic paragenesis because they may contain detectable quantities of Cr and Sc. The presence of Cr and Sc in these diamonds might be interpreted as a confirmation of the suggestion by Fesq et. al. (1975) of the presence of submicroscopic silicate inclusions in diamond.

Sulphide inclusions may also contain detectable quantities of Au and Ir and the ratio of these two elements can also be used to differentiate between diamonds of the two parageneses. Eclogitic diamonds have a wide range of Au/Ir ratios from low, "mantle" values to high, "crustal" values (1-40). Peridotitic diamonds have low mantle values only (0.01-1).

Carbon isotope ratios of these eclogitic and peridotitic diamonds were also measured. The object here was to compare the carbon isotope ratios of the diamonds to their Cr/Sc and Au/Ir ratios. This comparison revealed that the carbon isotope ratios of diamonds from both parageneses overlap in a narrow range and do not show the clear separations seen with Cr/Sc and Au/Ir ratios. It can be suggested, therefore, on the basis of the suite of 61 diamonds analyzed in this study, that the Cr/Sc and Au/Ir ratios are much more useful tools to distinguish between diamonds of the two parageneses.

TABLE OF CONTENTS

No.	CONTENTS	PAGE
	TITLE	i
	DECLARATION	ii
	DEDICATION	iii-iv
	ACKNOWLEDGEMENTS	v
	ABSTRACT	vii
	TABLE OF CONTENTS	ix
	INTRODUCTION	1
1	ANALYTICAL TECHNIQUES	4
	1.1 Introduction to Neutron Activation Analysis (NAA)	4
	1.2 Irradiation	4
	1.3 Principles of NAA	5
	1.4 Instrumentation	6
	1.5 NAA of diamonds	9
	1.6 Other nuclear techniques used in the geochemical study of diamonds	12
	1.7 Analysis of diamonds by other techniques	12

2	METHODOLOGY	16
	2.1 Diamond selection	16
	2.2 Diamond preparation	16
	2.3 Standardization	17
	2.4 Preparation of quartz vials	19
	2.5 Irradiation	20
	2.6 Post Irradiation Preparation	20
	2.7 Counting	22
	2.8 Short-lived Isotopes	23
3	RESULTS	25
	3.1 Finsch diamonds	26
	3.2 Premier diamonds	28
	3.3 Brazilian diamonds	30
	3.4 George Creek diamonds	31
	3.5 Chinese diamonds	32
4	DISCUSSION	33
	4.1 Cr and Sc in diamonds	33
	4.2 Geochemistry of Cr and Sc in upper mantle rocks and minerals	39
	4.3 Au and Ir in diamonds	43
	4.4 REE in diamonds	46
5	CARBON ISOTOPES	50
	5.1 Methodology	50
	5.2 Results	52
	5.3 Discussion	53
6	CONCLUSIONS	56

7	APPENDIX	59
	7.1 Appendix I: Diamond descriptions	59
	7.2 Appendix II: Standard data and comparisons	64
	7.3 Appendix III: Isotopes for counts 1-4	66
	7.4 Appendix IV: Analytical data	70
	7.5 Appendix V: Carbon isotope data	77
8	REFERENCES	80

LIST OF ILLUSTRATIONS

No.	ILLUSTRATION	PAGE
Photo 1	HPGe, "monster" detector	7
Photo 2	Electronics for gamma-counting	8
Photo 3	The computer used	8
Fig.2.1	Quartz vials.	19
Photo 4	Quartz vials and counting vials.	21
Fig.2.2	Liquids used to clean quartz vials.	21
Fig.4.1	Cr vs Sc in diamonds with silicate inclusions.	34
Fig.4.2	Cr vs Sc in Brazilian and Premier diamonds with sulphide inclusions.	34
Fig.4.3	Cr vs Sc in diamonds with different silicate inclusions.	36
Fig.4.4	Cr vs Sc for heavy minerals separated from South African kimberlites	37
Fig.4.5	Cr/Sc ratio vs Ca/Cr ratio in diamonds.	38
Fig.4.6	Cr vs Al in garnet inclusions in diamond	38
Fig.4.7	Cr vs MgO in diamond inclusions	43
Fig.4.8	Au vs Ir in single diamonds compared to South African kimberlites	44
Fig.4.9	Positive correlation between Au and As in peridotitic, Brazilian diamonds with sulphide inclusions.	45
Fig.4.10	Positive correlation between Ni and Au in peridotitic, Brazilian diamonds with sulphide inclusions.	45
Fig.4.11	Positive correlation between Au/Ir and Fe/Fe+Ni ratios in diamonds with sulphide inclusions.	46
Fig.4.12	REE patterns for diamonds PPG1, FOG1 and FOG2.	47
Fig.4.13	REE patterns for Brazilian and Premier diamonds with sulphide inclusions.	48
Fig.4.14	REE pattern for diamond POM1	48
Fig.4.15	REE patterns for kimberlite contaminated diamonds.	49
Fig.5.1	The carbonate line.	51

Fig.5.2	$\delta^{13}\text{C}$ values for Finsch and Premier eclogitic and peridotitic diamonds analysed in this work.	53
Fig.5.3	$\delta^{13}\text{C}$ values for Finsch and Premier eclogitic and peridotitic diamonds analysed by Deines et al., (1984).	53
Fig.5.4	Cr/Sc ratios versus $\delta^{13}\text{C}$	54
Fig.5.5	Au/Ir ratio versus $\delta^{13}\text{C}$	55

INTRODUCTION

"In many a diamond there is enclosed the clue to its own genesis... Nature, in her infinite variety, has given an individual character to every diamond. No two diamonds are exactly alike."

These are the words of A.N. Wilson in his book *Diamonds: from Birth to Eternity*. His first statement sums up the reason for this and many other research projects being conducted on diamonds and the specks, spots, smears and separate mineral phases (the clues) frequently encountered in them. These imperfections or impurities are elemental and mineral inclusions believed by most geoscientists to be incorporated into the diamond during its genesis in the mantle. Diamond inclusions have been investigated by various, modern analytical techniques (for XRD see Futergendler, 1956; electron microprobes see Meyer and Boyd, 1972; ion microprobe see Hervig et al. 1980a; proton microprobe see Griffen et al. 1988; and neutron activation analysis see Fesq et al. 1975) with the intention of unraveling the clues held so tightly in the strongly bonded carbon atoms.

Over the past three decades this has become a highly specialized branch of geochemistry, as diamonds are not merely beautiful gems, they also have great scientific and industrial value. One of the reasons for their scientific value stems from the fact that they are mantle minerals and thus diamonds can also be viewed as clues to the composition of the mantle. Diamonds and their inclusions provide direct information about the mineralogical and chemical properties of the mantle and processes which have operated therein. They are believed to be xenocrysts (foreign minerals) transported from the mantle to the crust by kimberlites and lamproites (Meyer, 1985 & 1987; Richardson, 1989). Curiously, not all kimberlitic rocks (collective term for kimberlites and lamproites) carry diamonds. Studies have shown that kimberlites or related rocks which have not sampled potential diamond-bearing rock could not possibly contain diamond (Clifford, 1970; Haggerty, 1986, Mitchell, 1986 and others).

Wilson's second statement about the uniqueness of each diamond is also very true, although diamonds do show some broad similarities, and on the basis of these similarities diamonds can be divided into groups and subgroups. For geochemists the most important division is according to paragenesis or inclusion mineralogy. There are two main parageneses in diamonds, that is, diamonds

occur in two main mineral associations or rock-types. Peridotitic diamonds are older (3.2-3.3 Ga; Richardson et al., 1984; Richardson, 1986) and crystallized in ultramafic mantle-rocks such as harzburgites and lherzolites at temperatures which are generally below the subsolidus (Boyd and Gurney, 1986) while eclogitic diamonds are relatively younger (90Ma-1.6Ga; Smith et al., 1991) and crystallized in basaltic mantle-rocks at temperatures that are predominantly above the subsolidus (Boyd and Gurney, 1986).

The most common is the peridotitic paragenesis in which minerals included in diamond are invariably low Ca-chrome pyrope garnet, olivine, enstatite, chrome diopside, Mg-chromite and sulphide (Meyer and Boyd, 1972). The eclogitic paragenesis is dominated by pyrope almandine, omphacitic clinopyroxene and sulphide, although kyanite, rutile and coesite may also occur (Meyer and Boyd, 1972). It is important to note that sulphides are found in both parageneses but to date the differences between sulphides that occur in eclogitic diamonds and those that occur in peridotitic diamonds have not been established (note that the Fe/Fe+Ni ratio used by Haggerty, 1991 to distinguish between sulphide inclusions of the 2 parageneses, does not hold for all the diamonds studied and so does not have a universal application). It is certain, though, that sulphide inclusions are much more abundant in eclogitic diamonds and this off-course has important genetic implications (Haggerty, 1986 and 1994). Besides the mineralogical differences there are also chemical differences between the two parageneses: the major elements in diamonds and their inclusions have been analyzed extensively by electron and proton microprobes. The emphasis in this study is to quantify the trace element differences between the two populations.

Diamonds from different mines and geographical locations also have characteristic mineralogical and geochemical features. For instance, diamonds from a particular mine may have a distinctive carbon isotope range (e.g., Sloan in Colorado: Otter, 1989). Likewise, they may have distinctive chemistries e.g., significant boron in Premier diamonds (Erasmus et al., 1977) and predomination of a particular paragenesis e.g., 90% eclogitic diamonds at Argyle and 99% peridotitic diamonds at Liaoning and Shandong in China (Meyer, 1987). The differences in the diamonds from the different areas has been attributed to the heterogeneity of the mantle (Wilson, 1982; Gurney, 1990). In this project diamonds from Brazil, Colorado, South Africa and China are compared and contrasted and although the sample

size is small the data can also provide information on the variation of mantle chemistry below these geographical locations.

Diamonds do occur in a variety of colours: colourless, yellow, brown, green, blue, black and pink. Colouration in diamonds is taken as evidence that impurities have been incorporated into the diamond structure on an atomic scale (Wilks and Wilks, 1991). Nitrogen for instance gives diamonds a yellow tinge while boron is responsible for a light blue hue (Erasmus et. al., 1977). The other colour categories (except pink) are also studied in this work, to investigate whether they too can be correlated with trace element content (note: only inclusion-free diamonds are suitable for this investigation).

Instrumental neutron activation analysis (INAA) is an ideal technique to study the trace elements in diamonds, since the carbon matrix is "transparent" to neutrons. Matrix effects are thus negligible and allow for extreme sensitivities. Fesq et. al. (1975), in a significant contribution, used neutron activation analysis to study the trace element chemistry of a large suite (1500 stones) of South African diamonds. Their main conclusion was that the major contributor to the impurity of diamonds were the mineral inclusions whether visible or submicroscopic. They referred to the submicroscopic inclusions as "magma droplets". Although their work pioneered this type of study it did have two important shortcomings: firstly, they analyzed their diamonds in packages of about ten stones and secondly, they made no attempt to separate the diamonds into the eclogitic or peridotitic type parageneses. In such a study the composition of diamonds are "averaged out."

Subsequent to the work of Fesq et. al., (1975) there has been vast improvements particularly in the field of detector technology and computers. The improved efficiency and resolution of detectors and advanced computer programs make it possible to analyze minute, single diamond crystals (≥ 0.01 mg) for trace elements at the ppb and ppt levels.

In this project 61 inclusion-bearing and inclusion-free diamonds of both parageneses i.e., eclogitic and peridotitic, have been analyzed by instrumental neutron activation analysis for up to 40 trace elements. The data obtained has been used to distinguish the eclogitic and peridotitic parageneses more comprehensively and to compare the trace element signature of diamonds from different geographical locations and mines. Such a study would help to gain further insight into the chemistry of the upper mantle and the environment of diamond genesis.

1: ANALYTICAL TECHNIQUES.

1.1 INTRODUCTION TO NEUTRON ACTIVATION ANALYSIS (NAA).

Neutron Activation Analysis (NAA) is an analytical technique that involves the irradiation of sample material with neutrons and the subsequent detection of the gamma rays emitted from the activated nuclides of the elements that constitute the sample.

When a rock or mineral sample is irradiated with neutrons the naturally occurring stable isotopes of most of the elements present in the sample are transformed into radioactive or unstable isotopes by neutron capture reactions. The activated nucleus then decays with a characteristic half-life. Most nuclides emit gamma rays at characteristic energies in the process of decay. This gamma radiation can be measured and quantified. The amount of the radioactive nuclide is proportional to the intensity of the characteristic gamma-ray peaks in the gamma spectrum. To measure the intensity of the gamma-ray lines a gamma-ray detector and other associated instrumentation is used. This process is referred to as gamma counting. NAA is a comparative technique and results are quantified by comparison to standard reference material which is irradiated and counted together with the samples of interest.

There are two methods of NAA. One involves the extraction or isolation of a particular element (after irradiation) from a complex spectrum of activities by a wet chemical procedure. This is called radiochemical neutron activation analysis (RNAA). When there is no chemical processing and the isotope in question is counted in the presence of all other induced activity the method is referred to as instrumental neutron activation analysis (INAA).

1.2 IRRADIATION

A neutron source is necessary for NAA. Nuclear reactors are the most popular neutron sources because their high neutron fluxes give the most intense irradiation which is essential for lower detection limits of the required elements. The fission of ^{235}U produces neutrons with energies too high for NAA and they are therefore moderated by water which also serves to cool the reactor. The moderated neutrons can be classified according to their energies into three groups:

a) thermal neutrons (0.001-0.05 eV),

b) epithermal neutrons (0.5-10 KeV) and

c) fast neutrons (>10 KeV).

The neutron flux decreases sharply from thermal to higher neutron energies. Usually thermal neutrons are suitable for most geological materials, however epithermal neutrons are better for certain elements such as As, Br, Rb, Sr, Sb, Ba, Ta and U (Steinnes, 1971; Koeberl, 1991). Interactions between the neutrons and the target nuclei are dependent on the neutron flux. The probability of such an interaction is termed the neutron capture cross-section (σ) and varies from isotope to isotope. The larger the neutron cross-section and the higher the neutron flux the greater the amount of neutron activation that occurs. Elements with isotopes which have large cross sections e.g., Au and Ir are therefore more suitable for analysis by NAA

1.3 PRINCIPLES OF NEUTRON ACTIVATION ANALYSIS.

The activation analysis equation (taken from Hoffman, 1992) for a radioisotope with a half-life of $t_{1/2}$ is : $A = (kNWF\sigma\phi/M)$ (irradiation term) (decay term) where,

A = measured activity of a radionuclide

k = proportionality constant (includes detection efficiency)

N = Avagadro's number (6.023×10^{23} atoms/mole)

W = weight of an element (g)

F = natural fractional isotopic abundance of target isotope

M = atomic weight of an element

σ = nuclear reaction cross section cm^2

ϕ = reactor neutron flux ($\text{n.cm}^{-2}\text{s}^{-1}$)

irradiation term = $[1 - \exp(-\lambda T_i)]$

decay term = $\exp(-\lambda T_D)$

λ = decay constant ($\ln 2/t_{1/2}$) of the radioisotope

T_i = length of irradiation

T_D = length of decay after irradiation

From the equation it can be deduced that NAA sensitivity can be increased by increasing the following:

- a) sample weight,
- b) detection efficiency,
- c) irradiation time,
- d) neutron flux and
- e) counting time.

After irradiation the samples and standards are counted sequentially, under similar conditions i.e. with:

- a) the same detector,
- b) the same sample to detector distance and
- c) identical counting time.

Hence, the activation equation can be simplified as follows:

$W_{sample} = (A_{sample} / A_{standard}) (W_{standard})$, where W is the weight of the element of interest and A is the measured decay-corrected activity.

1.4 INSTRUMENTATION.

The instrumentation for gamma-ray spectrometry consists basically of four main components:

- 1.4.1) a gamma detector, (see photo 1)
- 1.4.2) the electronic signal processing and amplification component, (see photo 2)
- 1.4.3) a multi-channel analyzer for storage of all measured signals and
- 1.4.4) a computer for data evaluation (see photo 3).

1.4.1 The detector used: "monster detector."

The Schonland High Purity Germanium (HPGe) Coaxial Detector System (affectionately called the "monster detector") used in this study, has the following certified specifications and capabilities.

- i) Total Active Volume: 190 cc
- ii) High Voltage Bias: Positive 3500 v

iii) Resolution: 1.77 KeV

iv) Peak-to-compton ratio, ^{60}Co : 72

v) Efficiency: 40%

vi) Maximum count rate allowed: 10 000 counts/s.

Photo 1: Detector in the middle (silver in colour with black, circular sample holder) within a lead cage (blue-grey).



1.4.2/3 Electronic signal processing, amplification and storage.

Voltage pulses from a detector are processed in a preamplifier, a spectroscopy amplifier and an analog-digital converter (ADC). The ADC converts the analog (voltage) signal into a digitized signal which may be stored (as a single event) in a channel of the multi-channel analyzer (MCA). Many gamma-ray interactions with the same energy create many events in the same channel and in this way a gamma peak in the gamma spectrum is produced.

1.4.4 Data reduction.

The computer shown in photo 3 is used to perform data reduction and data evaluation. The Yule computer program (Yule, 1968) is used for gamma peak analysis. Prior to peak areas in the samples

being compared to peak areas in the standards, various corrections have to be made. Peak areas are corrected for:

- a) decay time,
- b) counting time,
- c) irradiation time and
- d) neutron flux (usually thermal).

The concentration of an element (y) is calculated by the equation: $Wt\ of\ element\ y\ in\ sample = (Wt\ of\ element\ y\ in\ standard \times peak\ area\ sample / peak\ area\ standard)$.

Photo 2: The electronics for gamma-ray counting.

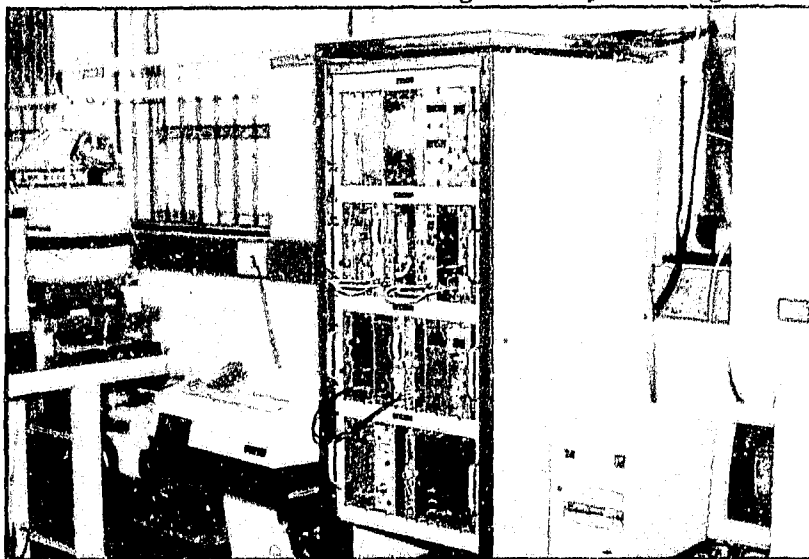
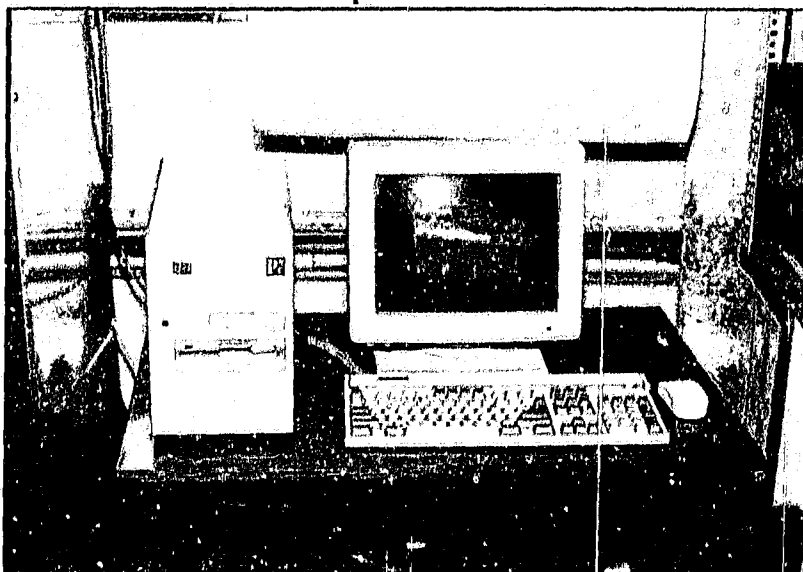


Photo: 3 The computer for data evaluation.



1.5 NEUTRON ACTIVATION ANALYSIS IN DIAMONDS

The technique of neutron activation analysis is very suitable for the analysis of the trace element chemistry of diamonds because the carbon matrix of diamond is not activated by neutrons, so there is no interference from the matrix. Of the known 62 impurity elements found in diamond, it is possible to analyze for a maximum of 55 by NAA (Sellschop, 1987). This includes the use of Fast Neutron Activation Analysis, Instrumental Neutron Activation Analysis (both short-lived and long-lived isotope work) and some wet chemistry. The most useful and simple method is Instrumental Neutron Activation Analysis (INAA) which is the technique used in this project. With the combination of short-lived and long-lived isotope work a maximum of 43 elements can be analyzed by INAA. In this study no quantitative short-lived isotope work was attempted.

Fesq et al., (1975) were the first to use neutron activation analysis on a large suite of diamonds. They analyzed 1500 diamonds from 3 South African mines namely Premier, Finsch and Jagersfontein. At the time when Fesq et al., (1975) did their work, detector technology (detector sensitivity and efficiency for instance) was not good enough to detect trace elements in a single stone. Another limitation was that standards for ultra-trace level analysis of single diamonds had not been developed. Therefore, the diamonds were analyzed in packages of 10-25 stones (to form 1g samples) separated on the basis of source, colour, presence/absence of inclusions, size and quality. In these diamond packages Fesq et al., (1975) determined up to 44 elements by NAA. Since this work there has been vast improvements in both detector technology and computers which resulted in improved detector resolution and the speed of data reduction. In addition standards (see chapter 2) for the analysis of single mineral crystals have been prepared and tested in this work. These developments together with vast improvements in computers and software now allow for the quantitative analysis of single diamond crystals.

1.5.1 Advantages of using NAA in the analysis of diamonds.

- a) The technique is highly sensitive and multielemental. The lower limits of detection approach the theoretical detection limits, chiefly because the carbon matrix of diamond is not activated by neutrons. In diamonds with inclusions there is very low matrix effects from the major

elements such as Si, O, Mg, Al and S because they either have very short half-lives of minutes/seconds or they are not/poorly activated by neutrons.

Table 1.1 lists the lower limit of detection (LLOD) for the various elements that can be analyzed in diamonds by INAA. The lower limits of detection for most elements in diamond are up to 3 orders of magnitude lower than they are in other (geological material) matrices for interference-free conditions. Other factors contributing to the low limits of detection are:

- i) The very long irradiation times used (128 hours).
 - ii) The high neutron fluxes of $2-3 \times 10^{13} \text{ n.cm}^{-2}\text{s}^{-1}$.
 - iii) The very long counting times of up to 24 hours.
 - iv) The high sensitivity and efficiency of the large volume HPGe detector.
- b) Very small, single diamond crystals can be analyzed. Samples as tiny as 0.01 carat or 2 mg have been successfully analyzed.
 - c) The technique is non-destructive. Although diamonds are turned black by the heavy neutron dose they can, nevertheless, be returned to their original colour by annealing them after irradiation.
 - d) The activity produced in diamonds by neutron irradiation is generally very low and hence radioactive diamonds pose no health risks to the researcher.
 - e) There are no depth restrictions since neutrons penetrate the entire diamond.
 - f) Samples are not put into solution prior to analysis.
 - g) Elements can be detected independent of the chemical form in which they exist.

1.5.2 Disadvantages of NAA in diamonds.

- a) Neutrons are electrically neutral, so they seldomly collide with the carbon nuclei in the diamond. Thus a neutron beam irradiates the whole diamond and not just the surface. Consequently, neutrons sample the diamond matrix + inclusion and therefore one can never be certain of the exact source of the impurities. However, this problem can be overcome by analyzing the inclusion and its diamond matrix separately. Furthermore, the technique does not yield information on the distribution and chemical form in which a particular element exists.

- b) If a neutron collides with a nucleus of a carbon atom, it is ejected from its position in the lattice with enough energy to cause damage in the form of interstitials and vacancies. X-ray measurements of the lattice spacing indicates that the damage produced by neutron irradiation causes a slight expansion of the lattice for fluxes of the order of 10^{20} neutrons.cm⁻² (Damask,1958). The X-ray patterns also indicate that damage of this order may eventually reduce the diamond to an amorphous state (Levy and Hammerer, 1955). The colour of the diamond is changed initially to a dark green and finally to an unattractive black colour. With high fluxes (10^{19} neutrons.cm⁻²) density of the diamond can be reduced by 2%.
- c) There are no certified reference standards for the analysis of diamonds.

Table 1.1: Lower limits of detection of various elements in diamond.

ELEMENT	LLOD	ELEMENT	LLOD
Sc	1 ppt	Cu	100 ppb
Cr	0.3 ppb	Zn	200 ppb
La	10 ppt	Ag	400 ppb
Ce	200ppt	Sn	10 ppm
Nd	300 ppb	As	10 ppt
Sm	<1 ppt	Sb	100 ppt
Eu	0.5 ppt	Br	5 ppt
Gd	1 ppb	Ca	50 ppb
Tb	1 ppb	Na	60 ppt
Ho	10 ppt	K	10 ppb
Yb	30 ppt	Ti	10 ppb
Lu	1 ppt	Mn	10 ppt
Au	0.2 ppt	Ga	100 ppt
Ir	20 ppt	Zr	100 ppb
Th	2 ppb	Hf	1 ppt
U	100 ppt	Rb	1 ppb
Ni	100 ppb	Sr	10 ppb
Co	1 ppb	Ba	500 ppt
Fe	200 ppb	Cs	5 ppt
Ta	80 ppt	W	500 ppt

1.6 OTHER NUCLEAR TECHNIQUES USED IN THE GEOCHEMICAL STUDY OF DIAMONDS.

Many other nuclear techniques are used to analyze for elements in diamonds at the trace and ultra-trace levels. The main features, advantages and drawbacks of a few are listed below.

- a) Rutherford Backscattering (RBS) is a multielemental, non-destructive and quantitative technique. However, since it's a charged particle technique it cannot analyze the whole diamond. The volume of the diamond that can be analyzed is totally dependent on the diameter of the beam and the range of the charged particle in a diamond matrix. Furthermore, RBS sensitivity for the light elements is very poor.
- b) Similarly, Proton Induced X-ray Emission (PIXE) which is also multielemental, non-destructive and quantitative can be regarded as a surface or near-surface technique only. In addition, PIXE is insensitive to the light elements (as with NAA).
- c) For the light nuclides, element-specific Charged Particle Activation Analysis (CPAA) is used. Nuclear reactions are chosen for the elements in question. Specific high energy beams are used to induce the required reaction for the analysis of a particular element. Hydrogen, oxygen, boron and nitrogen can be analyzed for in this way.
- d) Mossbauer measurements are used for the analysis of iron in polycrystalline natural diamonds such as carbonado, Stewartite and Framesite. Determination of iron content in single diamond crystals is difficult because of the low concentrations (Bharuthram et al., 1991).

1.7 ANALYSIS OF DIAMONDS BY OTHER TECHNIQUES

1.7a Analysis by vaporization followed by mass spectrometry.

Diamonds are vaporized by heating them in a vacuum. Analyses are then performed with a mass spectrometer. One variation of this technique is to vaporize a diamond by directing a beam of ions on to a small area of the diamond to sputter off the surface atoms. The mass spectrometer is used to measure the ratio of the electron charge on the sputtered ions to their mass. This ratio is then related to a specific element.

This method has been used extensively to measure N contents in inclusion free diamonds (Kaiser and Bond, 1959). Nitrogen is the most abundant substitutional impurity in diamond. Nitrogen contents range from 0-500 ppm (Bibby, 1982) and its mode of aggregation/substitution and concentration has a marked effect on the physical properties of diamond such as colour, crystal shape and conductivity.

Carbon isotope ratios of diamonds i.e., $^{13}\text{C}/^{12}\text{C}$ (see chapter 5) are also measured in this way. Diamonds (C) are vaporized in a vacuum by burning them in oxygen (O_2). The CO_2 gas produced is collected and the ratio of the two isotopes are measured in a mass spectrometer. Since the initial work of Craig (1953) carbon isotopes of diamonds from various sources have been measured by many other workers. The most noteworthy of these are Sobolev et al., (1979), Deines et al., (1984) and Otter et al., (1991).

Another modification is the measurement of radiogenic isotopes in diamond inclusions for the purpose of age dating. The Sm-Nd and Rb-Sr geochronological technique has been used (see Richardson et al., 1984; Richardson, 1989; Smith et al., 1991) for the dating of garnet and pyroxene diamond inclusions. Diamond inclusions are believed to be cogenetic (formed at the same time) with their diamond host. Sm/Nd and Rb/Sr isotopic data (Richardson, 1984) yielded model ages of 3.2-3.3 Ga for a combined sample of peridotitic, low-Ca chrome pyrope garnets hosted by Finsch kimberlite that was erupted at 118 Ma. Eclogitic garnet and clinopyroxene inclusions from Finsch and Kimberly pool yielded proterozoic ages between 990 and 1580 Ma (Richardson, 1986). Smith et al. (1991) found ages of between 1443-2408 Ma for single, large eclogitic suite garnet inclusions from the Finsch Mine.

1.7b Electron probe micro analysis (EPMA)

The electron microprobe has been used widely to analyze inclusions in diamonds (see review by Meyer, 1987). Its use opened up a new and specialized field of geochemistry. It is now a well established technique for in situ non-destructive analyses of the major and trace elements at concentrations generally above 500 ppm. Elements such as P, Cr, Mn, Ca, Ni and Na have been

analyzed at trace levels by Hervig et al., (1980a, b). The detection limits in EPMA are seriously affected by excessive background noise (bremsstrahlung).

By studying the chemistry of the various diamond inclusions, the early electron microprobe workers concluded, that diamond inclusions were of generally, two distinct suites - an ultramafic suite and an eclogitic one (Meyer and Boyd, 1972). This meant that diamonds formed in at least two distinct geochemical environments.

1.7c Proton microprobe (Micro-PIXE)

The proton microprobe, introduced relatively recently (see Griffen et al., 1988 and 1992) is an effective technique for the analysis of small inclusions in diamond, for their trace element content. With this technique detection limits for most elements are in the lower ppm range. The proton beam employed for analysis may vary in diameter or beam spot size. For diamond inclusions a beam spot size of a few microns is sufficient. If the energy of the protons is 20-50 MeV it is possible to look at the L X-rays and K X-rays of medium and heavy elements allowing good resolution. In a valuable contribution Griffen et al., (1988; 1992) analyzed for Mn, Ni, Cu, Zn, Ga, Pb, Rb, Sr, Y, Zr, Nb, Ta, Ba and Mo in eclogitic and peridotitic inclusions in West Australian diamonds by proton microprobe.

The advantage of the proton microprobe is that it is possible (as with the electron microprobe) to determine the distribution of trace elements ("in situ") in a crystal. In comparison to the electron microprobe, the lower detection limits allows one to look at a specific grain and create an elemental-composition map. The technique is generally used to analyze flat polished surfaces.

The disadvantage of the proton microprobe is that analysis is confined to a narrow depth of 50-100 microns from the crystal surface. Bulk composition, therefore, cannot be measured. In addition, certain diamonds (e.g., some from Zaire and Sierra Leone) tend to have elemental zonation, while many exhibit growth strata (Orlov, 1973). One has to be cognizant of the fact that this reflects changes in conditions in the environment of diamond growth. A zonal distribution of inclusions and a decrease

in Fe content in olivines from the central areas to those in the periphery was recorded by Bulanova (1991). Similarly some element/s (S and Fe-Ni-Co-Cu metal solvents?) present in the core of the diamond may be depleted in the first 100 microns of the diamond and it is these elements that are more important for the understanding of the genesis of the diamond for they act as seeds for diamond nucleation.

Hence, to get a more realistic picture of the bulk composition of diamond (or disequilibrium between coexisting phases) by proton microprobe the progressive polishing technique as used by Bulanova (1991) has to be used.

1.7d Ion microprobe

In this technique ion beams are used to sputter off layers of the diamond sample and analysis is then done with the mass spectrometer. The ion microprobe may have better spatial resolution than the proton microprobe (usually $<1\mu$), but there are serious interference and calibration problems.

Hervig. et al., (1980a, b) analyzed for Li, Na, Ca, Sc, Ti and Co, by ion microprobe, in olivine and orthopyroxene inclusions. Shimizu and Richardson (1987) obtained REE, Zn and Ti data from the analysis of purple (G10) garnet inclusions. Their REE patterns for the garnets showed extreme LREE enrichment and they suggested that this enrichment was introduced metasomatically.

2: METHODOLOGY

2.1 DIAMOND SELECTION

A total of 61 inclusion-bearing and inclusion-free diamonds were studied. Although most of the diamonds were colourless, other colour categories e.g., yellow, brown, green and black were also represented. The diamonds analyzed were between 0.01-0.5 carats (with inclusions of up to 600 μ m) and came from the following sources:

- a) Seventeen from the Finsch Mine in the Northern Cape, South Africa.
- b) Twenty from the Premier mine in Northern Transvaal, South Africa.
- c) From Brazil there were nine from the Romario mine, two from the Arenapolis area and one each from the Canastra and Boa Vista regions.
- d) Eight from the George Creek mine in Colorado, United States of America.
- e) Three from the Liaoning and Shandong Provinces in China.

A detailed description of each of the diamonds mentioned above is given in tables 2.1 to 2.11 in Appendix:1. Diamond descriptions were based on colour, inclusion type and morphology.

2.2 PREPARATION OF DIAMONDS FOR ANALYSIS.

Some of the diamonds analyzed in this study were of high quality and purity, hence their total level of impurities (i.e., elements other than carbon) were often quite low (<1ppm). It was therefore essential to restrict any source of contamination for the analytical results obtained to be meaningful. In other words, it is absolutely imperative that the gamma signal counted on the detector came from the body of the diamond and not from any residual surface contamination. Therefore meticulous cleaning of the diamond surface was necessary. Diamonds with large visible cracks had to be avoided because of the obvious contamination problems associated with them. However many of the diamonds did have micro-cracks and these certainly posed problems (discussed in chapter 4). Every diamond had to be cleaned separately to prevent contamination. The following procedure was used before and after neutron irradiation for each diamond:

a) The diamonds were first cleaned with dilute superdecontamine, in an ultrasonic-cleaner for 3 minutes. Any adhering material is dislodged by this process.

b) Diamonds were then rinsed in distilled water.

c) They were then boiled in a concentrated mixture of HNO_3 , HClO_4 and H_2SO_4 for one hour.

This period was found to be necessary to remove kimberlite or other residual contamination from the micro-cracks which can be many microns deep. Although the acids used were of analytical grade, it is still possible that a few ppb's of Br detected in some diamonds could have come from HClO_4 .

d) Distilled water is used to flush out the acid + contamination. This process is repeated several times until there is no visible trace of acid in the water.

f) The diamonds were air-dried and weighed (in grams correct to 5 decimal places).

2.3 STANDARDIZATION

In order to quantify the trace element data in single diamond crystals, it was essential to develop suitable standard reference material with trace element concentrations that are comparable to diamond. Three options were considered:

i) diluting rock standards in a carbon matrix.

ii) using very small masses (few μg) of rock standards or

iii) preparing liquid standards by adding known quantities of trace elements to a suitable liquid.

The last option was difficult in that it required the pipetting of extremely low concentrations of more than 40 elements. Since the first two options involved existing certified standards, it was decided they would be implemented.

2.3.1 Diluting rock standards.

This method involved reducing the concentrations of elements in certified rock standards by "solid dilution." Specpure graphite was used to dilute several rock standards: PTO1, NEM-1, NIM-L, NIM-P and NIM-N (Mintek certified rock standards). Graphite was chosen because as is the case with diamond the carbon matrix is not activated by neutrons. So the activities produced after irradiation are low and comparable to diamond. This enables the researcher to count irradiated diamonds and the

standards after a short cooling period. Various ratios of graphite to rock standards were tried. In this study it was found that a 1:50 mixture of PTO1 to graphite, a 1:50 mixture of NEM-1 to graphite, a 1:90 mixture of NIM-G to graphite and a 1:90 mixture of NIM-L to graphite were the most suitable. The standards were chosen to cover the broad range of elements sought. PTO1 was more suitable for the siderophile and chalcophile elements, NEM-1 for Br, As, W, Sb, and both NIM-G and NIM-L for the other lithophile elements. The concentrations of most elements in the diluted standards were found to be ideal for diamonds with silicate inclusions.

Large volumes of these mixed standards were analyzed both at the Schonland Research Centre, University of the Witwatersrand and at the Institute of Geochemistry, University of Vienna. The interlaboratory comparisons and replica analyses (for PTO1 the most problematic standard in terms of inhomogeneity - see table 2.12 in Appendix:2) provide a measure of the accuracy and precision of the analyses. Note that there are significant differences between the Schonland value and the Vienna value for some of the lithophile elements, viz., Br, Sc, Ba and Eu. The Sc value, because of its importance in the study, was rechecked several times. In most cases (see table 2.13: Appendix:2) the Schonland values were used because of their better reproducibility. However, it is important to note that for the lithophile elements, the NIM-G, NIM-L and NEM-1 standard values provided better calibration curves. In essence the PTO-1 values given, represent the extreme case or 'worst case scenario' for the lithophile elements. PTO-1 was used chiefly for the siderophile elements i.e., Au and Ir, the chalcophile elements and Cr.

Furthermore, note that the absolute concentrations for Cr and Sc in the standards are not of critical importance in this study because deductions (see chapter 4) are made from the ratio of the 2 elements and not from their absolute values.

The basic problem encountered was that of inhomogeneity of the standards which is further compounded for ultra-trace level analyses. This problem was overcome to a certain extent by using standards in triplicate. The concentrations of the various elements in the graphite standards are given in table 2.13 of Appendix:2.

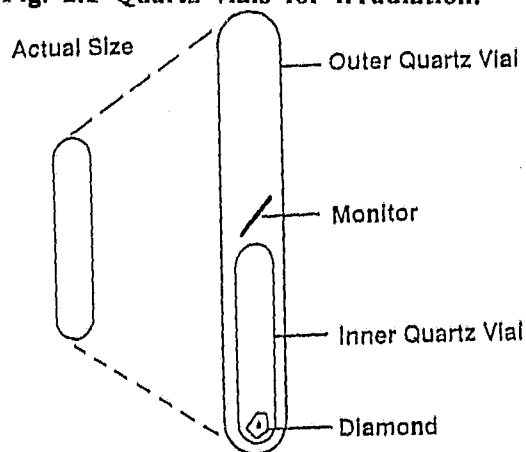
2.3.2 Using microgram masses of rock standards.

The other method of rendering standard reference material comparable to diamond is to reduce the masses proportionately. With this method $\pm 6 \mu\text{g}$ of the rock standards Allende Meteorite and G2 are used. Each standard is prepared in triplicate to reduce inhomogeneity problems. Such small masses are used so that the activities produced after irradiation are low and similar to that produced in irradiated diamonds. Measurements of the masses need to be done with care and must be correct to 5 decimal places because of the very small quantities used. This method was found to be as good as the graphite-diluted standard method but handling such small masses proved to be quite a challenge.

2.4 PREPARATION OF QUARTZ IRRADIATION-VIALS.

High purity quartz vials are prepared for the diamonds and standard reference material. Extreme care is taken in ensuring that the vials are clean before inserting samples in them. Weighed diamonds and standards are heat-sealed in the quartz vials as shown in Fig.2.1. Note that each diamond and standard is encapsulated in the smaller, inner quartz vial. The larger, outside vial serves to protect the inner vials from any contamination that may be picked up in the reactor and also to isolate the sample/standard from the Fe-Ta wire, flux monitor which accompanies each sample. Furthermore, if the outer vials are broken in the reactor, the diamonds remain safe and uncontaminated.

Fig. 2.1 Quartz vials for irradiation.



** Note: Standards are also sealed in a similar manner in the small inner quartz vials.*

2.5 IRRADIATION

Samples were wrapped in aluminium foil (to keep the samples together in case of breakage) and placed in aluminium rabbits for irradiation. The samples were irradiated in the 5 MW capacity, Oak Ridge-type Research Reactor at Pelindaba. Since a high neutron flux and a long irradiation period were needed, the samples were irradiated for 128 hours in the Poolside Facility of the reactor which has a neutron dose of about $2 \times 10^{13} \text{ N.cm}^{-2}/\text{s}$. To fit in with the schedule of the Pelindaba Research Reactor the following procedure was used:

- a) Irradiation for 5 days (this activates the long and short-lived isotopes).
- b) Cooling for 2 days (the reactor is not operational during weekends).
- c) Irradiation again for 32 hours (this relatively short burst is necessary to reactivate the short-lived isotopes after the 2 day cooling period).
- d) Cooling for 15 hours (this includes the necessary cooling period after removal from the reactor and the traveling time back to the laboratory at Schonland Centre).

2.6 POST IRRADIATION PREPARATION.

After cooling for 15 hours the samples are brought back to Schonland Centre and are prepared for counting. The procedure is as follows:

- a) Each aluminium parcel is opened up within a large lead cage and the activity of the parcel and damage or loss (if any) is recorded.
- b) The vials are then cleaned in a succession of liquids i.e., dilute superdecontamine, dilute HCl, water and acetone (see Fig.2.2). This is done to remove radioactivity and other contamination from the outsides of the vials.
- c) The outer vials are then cut open, carefully, with a tungsten carbide-knife and the diamond or standard and monitor are removed. In the case of the diamond-bearing vials - both vials are cut open and the diamond crystal is removed to be boiled later in acid for 30 minutes. A further modification was to cut open the quartz vials (containing the irradiated standards) and put the active standard material in a small polyethylene vial for counting (reweighing is essential since

all the material cannot be transferred). This modification was necessary because irradiated quartz vials contribute certain elements such as Na, Ce, Br and K.

- d) Monitor wires are cleaned in superdecontamine, water and acetone but not in HCl (see Fig.2.2). Each monitor is then inserted in separate high purity, polyethylene counting bottles which have foam inserts to ensure constant counting geometry.
- e) After the irradiated diamonds are cleaned, they are placed in the centre of a small polyethylene vial for counting.

Photo 4: Quartz vials and counting vials.

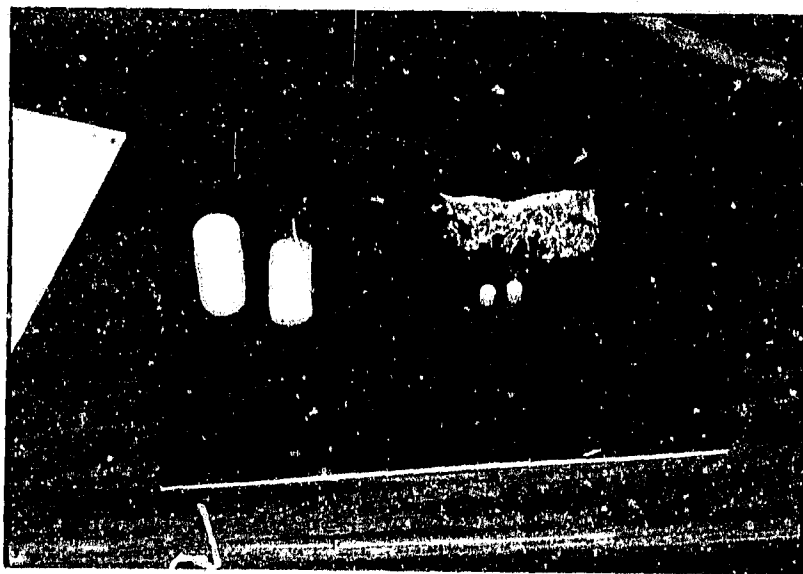


Fig.2.2 Liquids used to clean quartz vials and monitor wires.

Monitor+vial	Vial only	Monitor+vial	Monitor+vial
DILUTE DECON	DILUTE HCL	WATER	ACETONE

2.7 COUNTING

The samples are counted 17 hours, 3 days, 12 days and 30 days after irradiation. This is to ensure the best statistics for the medium and long lived isotopes (see tables 2.14-2.18 in Appendix:3). Diamonds and their accompanying standards are counted at the detector head for maximum efficiency. Relative neutron flux factors are obtained by counting monitors wires about 2 weeks after irradiation.

2.7.1 Count 1

This count is performed at approximately 17 hours to 1.5 days after irradiation. Each sample is counted for 10 000 seconds each. A maximum of 18 isotopes can be processed, from this count (see table 2.14 in Appendix:3). Note that important elements such as Ca, K, Mn and Cu which have short half-lives can decay before or during this count, if the samples are not counted in time (designated as N/A in tables 3.1-3.8 in Appendix:4).

2.7.2 Count 2

Count 2 is usually done 2-5 days after irradiation and each sample is counted for 3 hours each. Twenty one isotopes can be processed from this count. Table 2.15 (of Appendix:3) lists the isotopes for count 2. Only the main peaks are listed in the tables. It is assumed that these peaks are interference-free. However, interferences occur often. In this case alternate peaks are chosen or interference corrections are applied.

2.7.3 Count 3.

Count 3 is performed 10-15 days after irradiation. Depending on the activity of the samples each diamond and standard is counted for 6 or 12 hours. Essentially, only 6 isotopes are processed from this count (see table 2.16 of Appendix:3), but some isotopes from the first and third counts can be included in this count as a check.

2.7.4 Count 4/5

This count is done 30-40 days after irradiation for the long-lived isotopes. The diamonds and the standards are counted for 24 hours each. Most of the 24 isotopes listed in table 2.19 (of Appendix:3) can be counted at a later date in a fourth count to improve counting statistics.

2.7.5 Count 5

This count is not always necessary. It is done 70-100 days after irradiation to improve counting statistics for the long-lived isotopes and sometimes to eliminate interferences from medium-lived isotopes (see table 2.20 of Appendix:3). Samples are counted for a duration of 48 hours each.

2.7.6 Monitor count.

The monitor wires are counted about 2 weeks after irradiation. They need to be counted for 20 minutes each only. Ta-182 peaks are used to measure the neutron flux (see table 2.17 of Appendix:3). The counts for these peaks are ratioed and averaged for each sample to give a flux factor. These flux factors are entered in the computer files that were created for the samples. The spectra are then reprocessed by the computer (the counts for every isotope in each spectrum are divided by the flux factor).

2.8 Short-lived isotope work.

Many significant elements have short-lived radioactive isotopes. These are radioactive isotopes with half-lives of seconds and minutes. Some important short-lived isotopes are given in table 2.18 (of Appendix:3). As a result of the very short half-lives, counting has to take place at the irradiation site. The reactor at Pelindaba has a remote facility for irradiations of such a nature. Only qualitative short-lived isotope work was attempted. Single diamond-crystal analysis for short-lived isotopes is complicated by a number of factors. For short-lived isotopes, irradiations are usually of 10 minute duration and cooling time is one minute. These short irradiations do not produce enough activity in diamonds. There are a few reasons for this. Firstly, because of the carbon matrix, purity and small size of the diamonds. Secondly, most of the short-lived radionuclides do not have large neutron cross-sections. Furthermore, the portable detector used for such experiments is a low energy detector. This means that it is suitable only for those elements which have significant peaks in the energy region between 60 and 400 KeV. The portable detector is also less efficient, less sensitive and has a smaller volume than the monster detector. Consequently, apart from Ti-51 none of the short-lived isotopes can be detected at reasonable counting errors. The only way enough activity can be produced from small, single diamond crystals is by cyclic counting. This involves repeated sequences of irradiation

and counting until enough counts have been accumulated for the isotope to be detectable at acceptable counting statistics. Cyclic counting was not implemented in this study.

3: ANALYTICAL RESULTS FOR SINGLE DIAMOND CRYSTALS.

The geochemistry of 61 diamonds investigated in this study is presented in tables 3.1 to 3.8 in Appendix:4. The concentrations of the elements detected in the diamonds are given in ppb, unless otherwise stated. This means that the concentrations of the elements are given in parts per billion by weight (ppbw) of the diamond matrix + inclusion, hence, the absolute concentration of an element that occurs in an inclusion is diluted by the diamond matrix. The concentrations of the elements in the large inclusions themselves were calculated to be up to 20 000 times higher than that reported for the diamond matrix + inclusion. Consequently, in most cases, conclusions are drawn from ratios rather than absolute abundances. In this study the diamonds range in weight from 0.01-0.5 carats (see tables 2.1-2.11 of Appendix:1) and the inclusions are generally less than 600 microns in size. The size, number and nature of the inclusions are the most important factors affecting the concentration of elements in a diamond.

The data given in the tables includes diamonds of both parageneses, many of which contain inclusions of silicate or sulphide or both. The colour of the different inclusions are distinctive allowing one to make rough estimations of their major element composition as well as reasonably accurate estimation of their paragenesis i.e., either eclogitic or peridotitic. Eclogitic diamonds are characterized by orange garnets which have high Fe, Mn, Na and Ca but low Cr and pale green, omphacitic clinopyroxene which have high Ca and Na but low Cr. Peridotitic diamonds are characterized by purple garnets having high Cr and Mg but low Ca and emerald green chrome diopsides which are characterized by high Cr and Ca. Olivine and enstatite which are distinguished by high Mg and moderate Cr are usually colourless and are peridotitic (Meyer and Boyd, 1972; Hervig et al. 1980; Gurney, 1985; Meyer, 1987; McCandless & Gurney, 1989).

3.0 RESULTS

Analytical results for the diamonds are grouped here, according to region and diamonds with silicate inclusions are handled separately from those with sulphide inclusions. Note that in all the diamonds analyzed, i.e., both peridotitic and eclogitic diamonds, there are positive correlations between the

elements Cr, Fe, Ni, and Co. The concentrations of these elements vary widely but the highest concentrations (except for Fe concentrations) are found in the diamonds with peridotitic, purple garnets. The highest Fe concentrations are found in eclogitic, orange garnet inclusions.

Eclogitic diamonds are characterized by relatively low Cr concentrations of between <1 and 9510 ppb. Their Sc concentrations are similar to those for peridotitic diamonds i.e., between 0.2 to 447ppb. Thus their Cr/Sc concentrations are low and range from <1 to 43. Eclogitic diamonds are relatively enriched in Fe, Na, Mn, Ca, K, HREE, Ga and Au.

The peridotitic diamonds are characterized by higher Cr concentrations of between 71 and 131745 ppb. Sc concentrations in these diamonds are between 0.3 to 377ppb and are within the range for the eclogitic diamonds. This gives these diamonds much higher Cr/Sc ratios of between 174-10773. Peridotitic diamonds are also relatively enriched in Ni, Co, LREE and Ir.

3.1 FINSCH DIAMONDS

3.1.1 FINSCH DIAMONDS WITH SILICATE INCLUSIONS.

The diamonds with orange (eclogitic) garnet inclusions (FOG1&FOG2) have Cr values of 463-1201 ppb and Sc values of 66-132 ppb (see table 3.1 of Appendix:4). Their Cr/Sc ratios are relatively constant i.e., between 7 and 11. The diamond with omphacitic (eclogitic) clinopyroxene inclusions has higher Cr (2929 ppb) while its Sc value (68.7 ppb) is comparable to orange garnets. This gives the diamond a much higher Cr/Sc ratio of 42.6. The diamonds with purple (peridotitic) garnet inclusions (FPG1-FPG5) have the highest Cr values ranging from 22319 to 131745 ppb. Scandium values are also fairly high (67-357 ppb). Their Cr/Sc ratios are greater than 100.

The diamonds with orange garnet inclusions have an order of magnitude more Mn than the purple garnets and it is known that the orange colour of the garnets is caused by Mn^{2+} ions in distorted cubic coordination (Manning, 1967a). There is a positive correlation between Fe and Mn in all garnet inclusions. In two diamonds with purple garnet inclusions (FPG1&FPG5), the chalcophile elements W and As were detected. These elements are rare in diamonds without visible sulphide inclusions.

3.1.2 FINSCH DIAMONDS WITH SULPHIDE INCLUSIONS.

There are positive correlations between the chalcophile elements Fe, Ni, Co, Sb and W in the diamonds containing sulphide inclusions (FS1 & FS2, see table 3.2 of Appendix:4). The Fe/Fe+Ni ratios of both diamonds are similar i.e. 0.92 and 0.91 respectively. Au and Ir were detected in diamond FS2 only. The presence of elements such as Na, Cs, LREE, Th, Ba and Hf which are not expected to be found in sulphide minerals may be taken as evidence for the presence of kimberlite contamination in these diamonds. FS1 has higher Cr, Sc, Ta, Br, Cs and Na concentrations but lower La, Ce and Ba concentrations than FS2.

Submicroscopic silicate inclusions could be the source for Cr and Sc. This enables one to determine their paragenesis. As discussed above, diamonds with Cr/Sc ratios below 50 are eclogitic and those with Cr/Sc ratios above 100 are peridotitic. It follows then that FS1 is probably eclogitic ($Cr/Sc \approx 35.5$) while FS2 may be peridotitic ($Cr/Sc = 190$).

3.1.3 INCLUSION-FREE FINSCH DIAMONDS

Although diamonds FIF1-FIF6 have no visible inclusions they still contain detectable Cr, Sc, Ni, Co, Fe, W, Na and Au (see table 3.2 of Appendix:4). This suggests the possibility of submicroscopic inclusions (Fesq et al., 1975). The presence of detectable Au in FIF1-FIF3 is also noteworthy. The concentrations of Na, Cr, Sc, W, Co and Ni in FIF1-FIF4 are low. There is a marked difference in the concentrations of these elements in diamonds FIF5 & FIF6, when compared to FIF1-FIF4. They have higher Cr, K, Ca, Fe and Ni contents. Diamonds FIF5 and FIF6 are fragments that remained after omphacite and orange garnet inclusions were removed, from large diamonds, for dating of single inclusions (see Smith et al., 1991). Therefore the higher concentrations of the lithophile elements suggests that traces of the large inclusions (that were removed) remain in the diamond. These diamonds still retain their eclogitic character, as their Cr/Sc ratios are below 50. Diamonds FIF1-FIF4 have low Cr and Sc values and should therefore be eclogitic.

FB1, the black Finsch diamond, is characterized by very high La, Ce, Na, Cr and Fe, but moderate concentrations of HREE, Sc, Co, Ni, Au and Ir. The chemistry of "black" diamonds is easily distinguishable from that of other diamonds because of the large number and high concentrations of

elements detected in them. More than 25 elements were detected in this diamond. The black colour is not a body colour and is probably due to the intensity of submicroscopic inclusions and graphite. The presence of Au and Ir suggests that some submicroscopic inclusions may be sulphides. FB1 has a Cr/Sc ratio of 41 (a ratio typical of all diamonds with eclogitic clinopyroxene inclusions discussed thus far) which implies that besides the sulphide inclusions, the diamond is dominated by omphacitic clinopyroxene inclusions. This accounts, also, for the high Na, LREE, and Cr contents.

3.2 PREMIER DIAMONDS

3.2.1 PREMIER DIAMONDS WITH SILICATE INCLUSIONS.

Diamond POM1 (see table 3.3 of Appendix:4) has high Ca, Na, Sc and Fe and moderate concentrations of REE, Cr, Sc, Ni and Co, which is typical of diamonds with omphacitic clinopyroxene inclusions. POM2 has high Na, K, Ni and Fe and moderate concentrations of LREE, Cr, Sc and Co. In this diamond Ca was not analyzed. Diamond POC1 has the highest Ca and Fe of all the diamonds studied. This is consistent with the diamond having orange garnet and omphacitic, clinopyroxene inclusions. The concentrations of Na, K, Cr, Sc, Ni and Co are moderate in comparison to Fe and Ca.

The diamonds with peridotitic pyroxene inclusions (PC1 & PC2) have similar inter-element ratios. They include Co/Ni (~0.08), Ni/Fe (~0.03), Sc/Fe (~0.0001), Ca/Fe (~0.002) and Na/K (~11.5). However, diamond PC2 is characterized by LREE-enrichment, high Ca, Cr, Na and K, moderate Ni and Co but low Sc. This is typical for diamonds with chrome diopside inclusions. PC1 differs in that it has a lower concentration of REE, Na and K. The diamond has a high Cr content but its Sc concentration is low. These features are characteristic of diamonds with enstatite inclusions. Diamond PPG1 has visible purple garnet inclusions and this accounts for its high Cr, Fe and Ni, LREE-enrichment and low Ca. Au and Ir are also present and this together with high Ni leads one to interpret that sulphide inclusion/s may be present in this diamond, as well.

Although the Cr and Sc values vary in diamonds POM1 and POM2, their Cr/Sc ratios are nearly the same (± 40) and are distinctive of diamonds with omphacitic clinopyroxene inclusions. Sample POC1 which has been described as having visible orange garnet inclusions as well as an omphacitic

clinopyroxene inclusion has a Cr/Sc ratio of 7. This indicates that the chemistry of the diamond is dominated by the orange garnet inclusions. The Cr/Sc ratios of PC1 (743) and PC2 (10773) are higher than those of the rest of the diamonds in this study and are typical of diamonds with peridotitic pyroxene inclusions. The extremely high Cr/Sc ratio of PC2 may suggest the presence of chrome spinel inclusions in addition to the chrome diopside inclusion in this diamond. Such extreme Cr/Sc ratios are distinctive of chrome spinels. The ratio rarely exceeds 1000 in chrome diopside. Diamond PPG1 with purple garnet inclusions has a Cr/Sc ratio of 276 which is comparable to other diamonds with purple garnet inclusions, such as the Finsch diamonds (Cr/Sc: 174-410) discussed above.

3.2.3 PREMIER DIAMONDS WITH SULPHIDE INCLUSIONS.

Diamond PS1 (see table 3.4 of Appendix:4) is characterized by high Fe and moderate Co but no detectable Ni. PS2 is distinguished by high Fe, moderate Ni and low Co. PS3 has high Fe, Ni, Co and Cu. PS4 also has high Fe, Ni and Cu. Diamonds PS5 and PS6 contain moderate Fe and Ni but low Co. The ratios of the elements Fe, Ni, Co and Cu indicate that the sulphide inclusions are probably Fe-Ni-Cu sulphides such as monosulphide solid solution ($Mss=FeNi_{(1-x)}S$: probably PS2, PS5 and PS6), pyrrhotite ($Fe_{1-x}S$: probably PS1), cubanite ($FeCu_2S_3$) + Mss (PS3 probably) and pyrrhotite + pentlandite ($FeNi_9S_8$: probably PS4). Au concentrations, detected in diamonds PS1-PS5 are between 0.1 and 0.9 ppb. Ir was also detected in the same diamonds and ranged from 0.024 -0.25 ppb. The most striking feature of the data for these diamonds is the fairly constant Au/Ir ratios which are between 3.6 and 4.3 (see Fig. 4.3). All the diamonds have low concentrations of Na, Cr and Sc. In diamond PS1 moderate amounts of LREE and HREE were detected but moderate amounts of LREE only, were detected in diamonds PS2, PS4, PS5 and PS6. No REE were detected in PS3. A relatively high concentration of Ca was detected in PS5 while the other diamonds have much lower Ca contents.

Diamond PS4 has a Cr/Sc ratio of 35 (once again a value indicative of diamonds with eclogitic clinopyroxene inclusions). This suggests that it probably has submicroscopic, omphacitic clinopyroxene inclusions together with its visible sulphide inclusion. The other diamonds (PS1, PS2

and PS5) have very low Cr/Sc ratios which seem to be typical for eclogitic diamonds with large, visible, sulphide inclusions.

3.2.4 INCLUSION-FREE PREMIER DIAMONDS.

Five brown, inclusion-free diamonds were analyzed for the sole purpose of attempting to correlate trace element chemistry to their brown colour. However, besides some negligible concentrations of Fe and Co, only Na values are worth reporting. Na values are moderate and vary from 3.44 to 87.6 ppb. Whether the Na is responsible for the brown colour cannot be ascertained at this stage.

In the yellow, inclusion-free Premier diamonds only 3 elements are noteworthy of mention i.e., Na, Co and Ni. All three diamonds have only a few ppb of Na. Iridium (0.35 ppb) was detected in diamond PYB and is accompanied by 17 ppb Co and 247 ppb Ni. Diamonds PYS and PCY are quite similar. They have approximately the same Na (2-3ppb), Co (0.5-0.6 ppb) and Ni (24-32 ppb) concentrations.

3.3 BRAZILIAN DIAMONDS

With the exception of D4 and D6 (which have unidentified colourless inclusions) the diamonds from Romaria (see table 3.5 of Appendix:4) have no visible inclusions. They are however, very "messy" diamonds which have spots (possibly due to radiation damage since, U and Th are present in some diamonds) and graphite along planes. The diamonds are rich in lithophile elements especially LREE and Na. This could be due to kimberlite/alluvial contamination because no suitable host minerals were recognized in the diamonds. The presence of Ba, Cs, Hf and Th in some diamonds also support this suggestion. Au was detected in all these Brazilian diamonds and ranges from 0.0004 to 13.5 ppb. The values of 13.5 ppb (D9) and 9 ppb (D7) are the highest detected in the diamonds studied. It is possible that the diamonds could have submicroscopic sulphide inclusions hosting the Au, which is corroborated by the presence of other chalcophile elements i.e., Sb, W and As. Low concentrations of As and Br are common in these diamonds. Cr and Sc were detected in only 3 diamonds from Romaria (D7, D8 and D10) which yield low Cr/Sc ratios indicating that the diamonds are eclogitic.

The Brazilian diamonds with sulphide inclusions (table 3.6 of Appendix:4) have moderate (in A1&B1) to high (in A2&C1) concentrations of Fe and Ni. The Co values are low in all the diamonds. Au values are lower (0.02-0.16 ppb) than those for the Premier diamonds but the Ir concentrations are significantly higher (0.4-5.33 ppb). Au/Ir ratios are low and range from 0.01 to 0.1 (refer to Fig. 4.3). Note that the ratio of 0.01 attained for A2 is the lowest measured in this study. Cu was detected in C1, the diamond with highest Fe, Ni and Co concentrations of the 4 diamonds. As was detected in all 4 diamonds and ranged from 0.13-0.25 ppb. The 4 diamonds have moderate amounts of Na and K and are enriched in LREE. Cr concentrations are also moderate but Sc values are low. The presence of Zr (6470 ppb in C1), Hf (in C1) and Ba (in A2&C1) may be indicative of contamination from the kimberlite/sediment as this is an alluvial diamond. The Zr/Hf ratio is very high and is not kimberlitic. Note that (with the exception of A1 from Arenapolis) there are positive correlations between the elements Fe, Ni, Co, Cr, Au. Diamond A1 does not show these correlations probably because it has a peridotitic olivine inclusion in addition to its large sulphide inclusion. The chemistry of these diamonds with sulphide inclusions is dominated by Fe, Ni, Ca, Ir and As in order of decreasing abundance.

The Cr/Sc ratios of all four diamonds (A1, A2, C1 and B1) are greater than 100 (196-1157) which suggests that they are peridotitic. The olivine inclusion in A1 supports this statement. The essential difference between the Brazilian diamonds with sulphide inclusions and the Premier diamonds with sulphide inclusions, discussed above, is one of paragenesis. The Premier diamonds have Cr/Sc ratios that are less than 50, so they are eclogitic (see Fig. 4.8). The Brazilian diamonds, as mentioned above, have Cr/Sc ratios that are much greater than 100 and are thus peridotitic (see Fig. 4.8).

3.4 DIAMONDS FROM GEORGE CREEK, COLORADO

The data for the George Creek diamonds is given in table 3.7 of Appendix:4. GC1, the dark green almost black diamond, has very high REE, Na, Ba and Fe contents. As with all black diamonds analyzed, the intensity and variety of the impurities is distinctive. There are no visible inclusions in this diamond, therefore impurities are probably the result of the presence of submicroscopic inclusions or tiny inclusions masked by the green-black colour. The diamond has the highest U and

Th detected in these diamonds. The presence of radioactive elements U and Th (which are rare elements in diamonds) could possibly be partly responsible for the dark green colour, through radiation damage. GC2, the honey brown diamond, has moderate Fe, Ni, Co, Cr and Na concentrations. Its brown colour cannot be correlated with any specific element. GC3 which is a messy diamond with altered inclusions and graphite along planes is also rich in REE, Na, Ba and Fe and is similar to GC1, although the concentrations of these elements are lower in GC3. The similarity in the impurities (especially the presence of Ba in both diamonds) evokes the suspicion that the impurities are possibly kimberlite contamination, introduced into the diamond through micro-cracks. GC5, the blue-green, inclusion-free diamond has moderate levels of Na, Cr, Fe, Ni and Co concentrations. GC6 is a gem quality diamond and this is reflected in the almost total absence of impurities. Only low concentrations of Na and Co are present in this diamond. In diamond GC7 (a yellow-green, inclusion-free diamond), moderate amounts of only Fe, Ni and Co were detected. The impurity elements in GC8 (low concentrations of La, Sm, Na and Co) may be due chiefly to the secondary material which was observed in the diamond. GC9 which has an altered (mica) inclusion possesses moderate Fe, Ni and Co concentrations that are very similar to GC7.

Diamonds GC1, GC3 and GC9 have low i.e., eclogitic Cr/Sc ratios. GC5 which may have a sulphide inclusion has a Cr/Sc ratio of 144. This ratio suggests that submicroscopic chrome pyrope inclusions may be present as well and that the diamond is peridotitic.

3.5 CHINESE DIAMONDS

The diamonds from Liaoning CHJ2 and CHJ17 (see table 3.8 of Appendix:4) share some similarities. They have roughly the same amounts of Na, Sc and Fe but they differ in their Co and Ni concentrations. Note also that the diamond with the higher Ni and Co concentrations (CHJ17) has detectable Ir (0.13 ppb), while CHJ2 with lower Co and Ni has detectable Au. Only small concentrations of Na, Co and Sc were detected in diamond CHA36 from Shandong.

4: DISCUSSION OF DATA

The most noteworthy aspects of the data reported in chapter 3, in order of decreasing importance, are the Cr/Sc ratios, Au/Ir ratios and the rare earth element contents of diamonds. These will be discussed further, with the objective of distinguishing between diamonds of the eclogitic and peridotitic parageneses and between diamonds from the different geographic locations.

4.1 CHROME AND SCANDIUM IN DIAMONDS

A Cr versus Sc plot for the diamonds with silicate inclusions is shown in figure 4.1. The Cr/Sc ratios of the two parageneses are clearly different, with the eclogitic diamonds having $\text{Cr/Sc} < 50$ and peridotitic diamonds having $\text{Cr/Sc} > 100$. Moreover, the Cr/Sc ratios distinguish between diamonds on the basis of geographic location, and in all cases there are positive correlations between Cr and Sc in each diamond group.

Much of the variations in Cr and Sc concentrations shown in Fig.4.1 are due to inclusion size and inclusion type: a comparison of Premier diamonds to those from Finsch indicate that the Premier eclogitic diamonds appear to be richer in Cr and Sc than the Finsch eclogitic diamonds, however, the Premier peridotitic diamonds have lower Cr and Sc compared to those from Finsch. The Cr and Sc differences in the eclogitic diamonds are attributed to the fact that the Premier eclogitic diamonds are dominated by omphacitic clinopyroxene inclusions while the Finsch eclogitic diamonds are dominated by orange garnet inclusions. The Finsch peridotitic diamonds investigated in this study are dominated entirely by purple-garnet inclusions. However, the Finsch peridotitic diamond inclusions in general (as reported in the literature) belong to the garnet-harzburgite suite (Nixon et al., 1987, Gurney, 1989) and therefore are dominated by olivine, orthopyroxene, chrome-pyroxene (purple) garnet (in order of decreasing abundance) while clinopyroxene is usually absent. Thus the Finsch peridotitic diamonds investigated in this study were biased towards those with garnet inclusions. These harzburgitic garnet inclusions are usually subcalcic and extremely Cr-rich (Harte et al., 1980). The Premier peridotitic diamonds, on the other hand, are dominated by pyroxene inclusions (including

chrome diopside) which suggests that the host rock for the Premier peridotitic diamonds may have been lherzolite (Gurney, 1989).

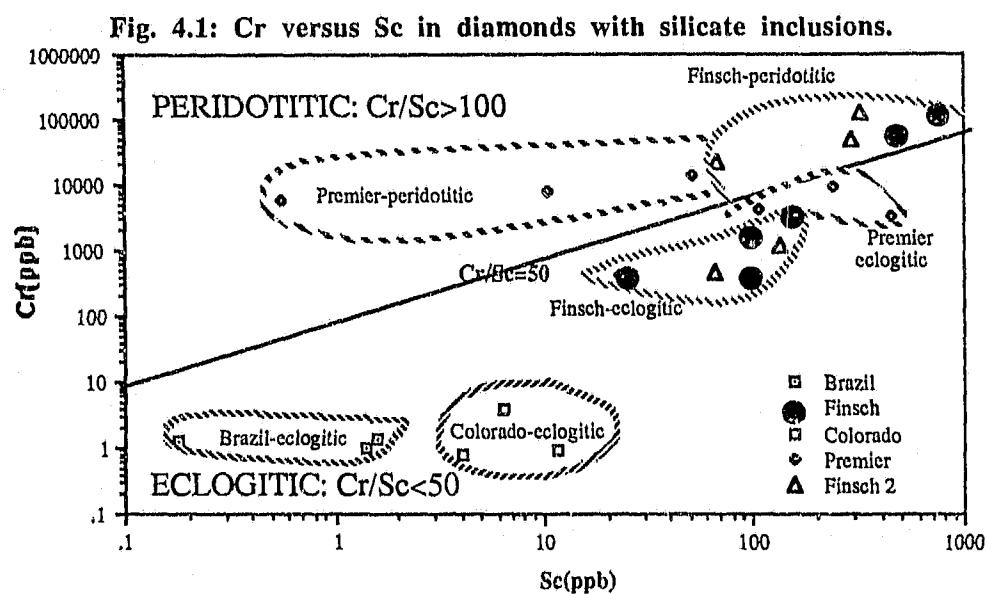
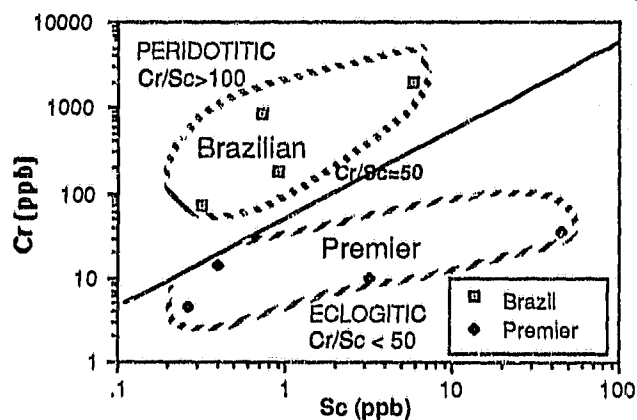


Fig. 4.2: Cr vs Sc in Brazilian and Premier diamonds with sulphide inclusions.



The most exceptional difference between Premier peridotitic diamonds and the Finsch peridotitic diamonds are the Sc concentrations. The Premier peridotitic diamonds have Sc values < 51 , while the Finsch peridotitic diamonds have Sc values between 67-357. This may also have significant

implications for lherzolitic and harzburgitic diamonds in general i.e., when like-minerals are compared the lherzolitic inclusions are Sc-poor in comparison to the harzburgitic inclusions. This is a corollary of the fact that there are positive correlations between Cr and Sc in any one diamond-inclusion type.

However, it is possible that the Cr and Sc differences between diamonds of the two kimberlites may be due to geographic location as well as the mineralogically controlled differences outlined above.

The low concentrations of Cr and Sc in the Brazilian and Colorado diamonds is probably due to the fact that these diamonds have no visible inclusions, thus the Cr and Sc detected in these stones may be due to submicroscopic, eclogitic, silicate inclusions as suggested by Fesq et al., (1975). However, it does appear that the Colorado Diamonds have an order of magnitude more Sc than the Brazilian diamonds, once again indicating the possibility of differences in these elements from one geographic location to the next.

The Cr versus Sc plot (Fig.4.2) for diamonds with sulphide inclusions from Brazil and Premier also show similar differences in the Cr/Sc ratios of the parageneses, to that observed in the silicate inclusions, and there are also positive correlations between Cr and Sc for each diamond group. Figure 4.2 suggests that the Brazilian diamonds are peridotitic (substantiated by the presence of a visible olivine inclusion in A1 and probably B1 as well) and that the Premier diamonds are eclogitic. The occurrence of non-chalcophile elements (Cr and Sc) in sulphide bearing diamonds without visible silicate inclusions are once again interpreted as being due to the presence of submicroscopic silicate inclusions.

4.1.1 Cr and Sc in relation to inclusion-type and its implications.

The differences in the Cr/Sc ratios between diamonds of the eclogitic and peridotitic parageneses is thought to be due to the characteristic Cr and Sc ratios of the different mineral inclusions (see table 4.1 and Fig. 4.3). In figure 4.4 it is demonstrated that the Cr/Sc ratio is also distinctive for silicate minerals cogenetic with diamond such as orange garnet, red garnet, purple garnet, chrome diopside and orthopyroxene which were separated from kimberlites. There are strong similarities between figures 4.3 and 4.4: firstly, there is a positive correlation between Cr and Sc for any one type of cogenetic mineral (which was seen in the diamond inclusions above) and secondly, the relative

positions of the different minerals on the Cr/Sc plot for the cogenetic minerals are similar to those for the diamond inclusions.

Fig. 4.3: Cr vs Sc in diamonds with different silicate inclusions.

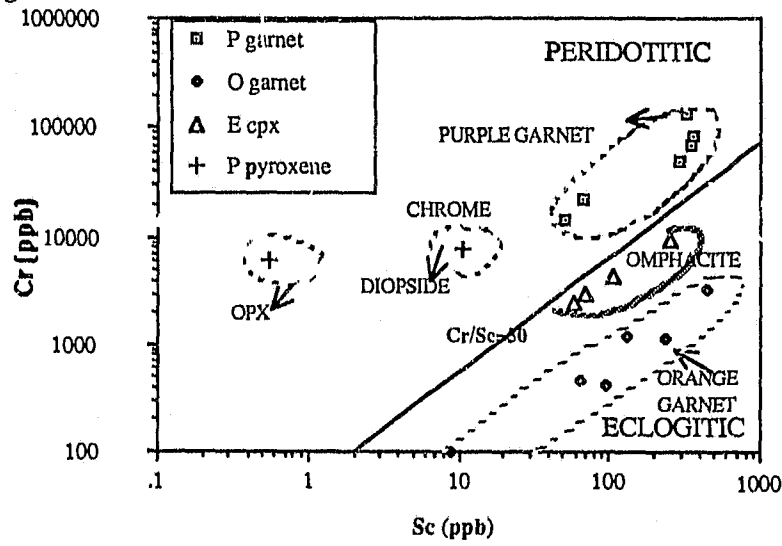
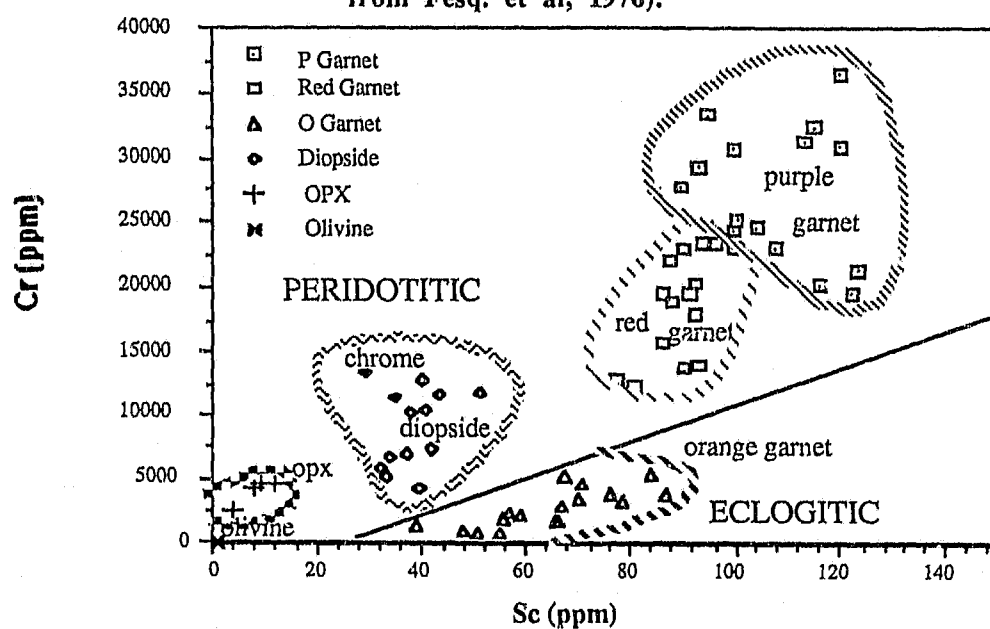


Table 4.1 Cr/Sc ratios in diamond inclusions

PURPLE GARNET	ORANGE GARNET	OMPHACITIC CLINOPYROXENE	PERIDOTITIC PYROXENE
410	9.1	40	743
333	7	38	10773
174	7	28	-
273	10	22	-
231	4	-	-
215	5	-	-
-	6.4	-	-
(174-410)	(4-10)	(22-40)	(743-10773)

Fig.4.4: Cr vs Sc for heavy minerals separated from South African kimberlites (data from Fesq. et al, 1976).



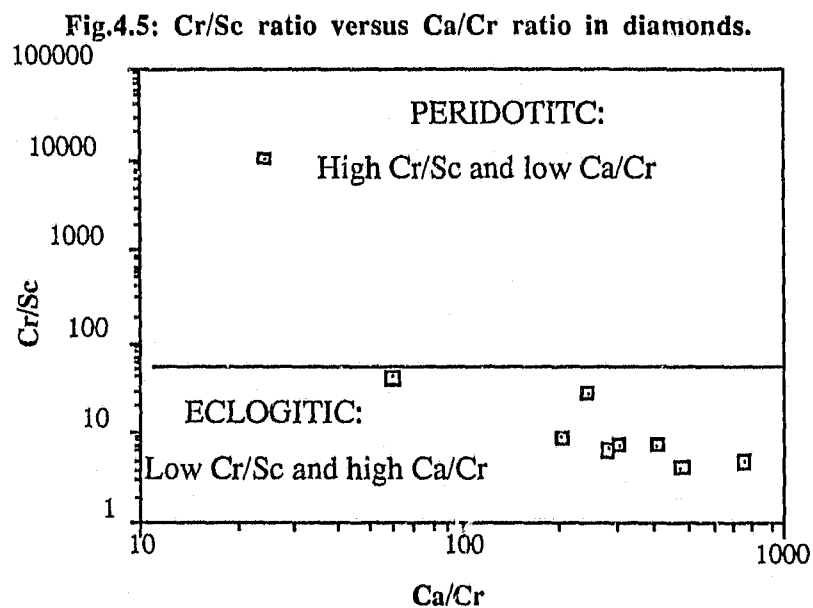
Note the similarity between this plot for kimberlite macrocrysts and that for the diamond inclusions in Fig.4.3

These observations are consistent with the interpretation that diamond inclusions are diamond-encased (and thus protected and preserved) xenocrysts found in 'kimberlitic' rocks, and are similar to their unencapsulated counterparts which end up as macrocrysts in kimberlitic rocks. In contrast to the macrocrysts however, there is a negative correlation between Cr and Sc in megacrystic garnets of kimberlites (Gurney et al., 1973) which could be interpreted to suggest that macrocrysts and megacrysts are genetically unrelated.

4.1.2 Cr/Sc ratios in relation to other inter-element ratios

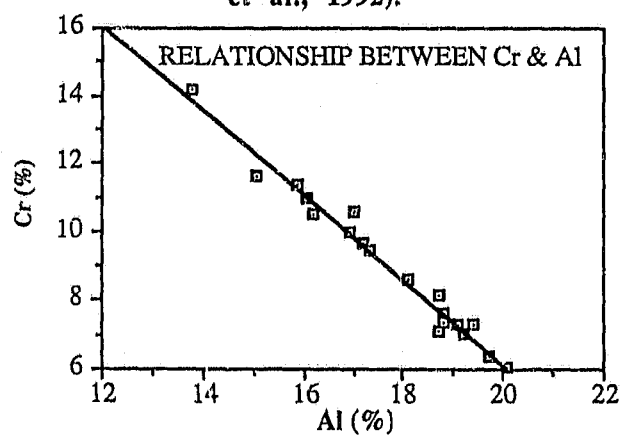
Gurney (1989, 1990) used Ca/Cr ratios to distinguish between eclogitic and peridotitic minerals, especially garnets. Eclogitic garnets have high Ca/Cr ratios whereas low Ca/Cr ratios are typical of peridotitic garnets, classified as G10 garnets by Dawson (1975). Thus the Ca/Cr ratio (or Cr/Ca ratio) is similar in function to the Cr/Sc ratio. In Fig.4.5 Ca/Cr ratios of eclogitic garnets, omphacite and

chrome diopside inclusions are plotted against their Cr/Sc ratios. Peridotitic diamonds have high Cr/Sc ratios and low Ca/Cr ratios, whereas eclogitic diamonds have low Cr/Sc ratios but relatively higher Ca/Cr ratios.



There is a negative correlation between the Cr/Sc ratio and the Ca/Cr ratio in diamond inclusions.

Fig. 4.6: Cr vs Al in garnet inclusions in diamond (electron probe data from Griffen et al., 1992).



Similarly, figure 4.6 shows that there is a negative correlation between Cr and Al in garnet inclusions which suggests that Cr-rich garnets i.e., peridotitic garnets are Al-poor while Cr-poor (eclogitic) garnets are Al-rich. Consequently peridotitic garnets have low Al/Cr ratios whereas eclogitic garnets have higher Al/Cr ratios.

4.2 THE GEOCHEMISTRY OF Cr AND Sc IN UPPER-MANTLE ROCKS AND MINERALS.

It can be deduced from the discussion, in section 4.1 above, that the distribution or partitioning of Cr and Sc between minerals of the peridotitic paragenesis (olivine, orthopyroxene, chrome-pyroxene and chrome-diopside) and those of the eclogitic paragenesis (omphacitic clinopyroxene and pyrope-almandine garnet) are significantly different. These differences reflect differences in the environment of diamond crystallization and hence are genetically controlled.

Diamonds of the peridotitic paragenesis are older (>3.0 Ga: Richardson, 1986) and crystallized in ultramafic mantle rocks such as harzburgites and lherzolites at temperatures that were generally below the subsolidus (Boyd and Gurney, 1986), whereas eclogitic diamonds are relatively younger (90 Ma - 1.6 Ga: Smith et al., 1991) and crystallized in eclogitic mantle rocks, which have a composition that is similar to basalts, at temperatures that were predominantly above the subsolidus (Boyd & Gurney, 1986). The partitioning of trace elements such as Cr and Sc are greatly influenced by factors such as temperature, pressure and composition of the phases involved. These factors clearly differed during the crystallization of diamonds of the two parageneses.

The partitioning of a trace element is defined by its partition coefficient (K_D) = (Conc. in mineral/Conc. in liquid), which is a constant. If $K_D > 1$ for an element, that element is described as being compatible and so will be retained or extracted in the residual or crystallizing solid phases respectively. Whereas, if $K_D \ll 1$ for a particular element, that element is referred to as being incompatible and will be preferentially concentrated in the liquidus phase during melting and crystallization.

Although partition coefficients and trace element modeling have been used extensively in geochemical studies of basaltic rocks (see table 4.2, data from Irving, 1978 and Irving, Frey, 1978 and

Henderson, 1982), very little work has been attempted in rocks of peridotitic composition. The average partition coefficients of Cr and Sc, for liquids of basaltic composition (table 4.2) may be used for the eclogitic minerals but are found to be erroneously low for the Cr-rich end members of clinopyroxene (chrome diopside) and garnet (Cr-pyrope garnet). Therefore the maximum values for Cr are used for these minerals. Considering that there is a positive correlation between Cr and Sc in each mineral type, the maximum values for Sc are used for these minerals as well. In this study the K_D for Cr in chrome diopside and Cr-pyrope garnet have been extrapolated from figure 4.7 (see table 4.2). Table 4.2 shows that K_D for Cr is usually greater than unity (up to 20) so Cr behaves as a compatible element, in the mineral phases given, whereas K_D for Sc ranges from < 1 in olivine to 8 in garnet and so Sc behaves as only a moderately compatible element in olivine but a compatible element in the rest of the mineral phases given.

In the evolution of a magmatic liquid, more than one mineral phase is involved, therefore the partitioning is described by the bulk distribution coefficient (D) which is calculated from the weight proportions of each mineral. For example, the bulk distribution (partition) coefficient of Cr and Sc ($D_{Cr/Sc}$) for a hypothetical garnet peridotite consisting of 50% olivine, 25% orthopyroxene, 15% garnet and 10% chrome-diopside will be as follows:

$$\begin{aligned} D_{Cr} &= 0.5 \times 3.0 + 0.25 \times 10 + 0.15 \times 20 + 0.1 \times 20 & D_{Sc} &= 0.5 \times 0.2 + 0.25 \times 1.2 + 0.15 \times 3.0 + 0.1 \times 5.0 \\ &= 1.5 + 2.5 + 3 + 2 & &= 0.1 + 0.3 + 0.45 + 0.5 \\ &= 9 & &= 1.35 \end{aligned}$$

$$\text{so } D_{Cr/Sc} = 6.7$$

Similarly the bulk distribution coefficient of Cr and Sc for a hypothetical eclogite consisting of 50% omphacitic clinopyroxene and 50% pyrope-almandine garnet will be as follows:

$$\begin{aligned} D_{Cr} &= 0.5 \times 8 + 0.5 \times 2 & D_{Sc} &= 0.5 \times 3 + 0.5 \times 5 \\ &= 4 + 1 & &= 1.5 + 2.5 \\ &= 5 & &= 4 \end{aligned}$$

$$D_{Cr/Sc} = 1.25$$

The bulk distribution coefficient for Cr in this garnet peridotite is about 7 times more than it is for Sc. On the other hand, the bulk distribution coefficient for Cr in the eclogite is only 1.25 times greater than it is for Sc. Hence, the bulk distribution coefficients explain the mineralogically-controlled reasons for the Cr/Sc ratios of peridotitic rocks being higher than they are for basaltic rocks (see table 4.3). However, they do not account for the magnitude of the difference between the 2 parageneses. The very high Cr/Sc ratios of some upper mantle peridotites point to a secondary enrichment process or melt extraction episode/s (which predated peridotitic, diamond genesis). An enrichment process would require the addition of Cr such as through metasomatism. Melt extraction episode/s would involve the preferential removal of Sc and the subsequent enrichment of Cr in the residue. Liang & Elthon (1990) suggest that the abundance of Cr in upper-mantle peridotites is indicative of the extraction (prior to 3.0 Ga) of picrite to komatiite liquids from the Earth's upper mantle. This follows from Boyd and Gurney (1982) who proposed that diamond-bearing harzburgites (of the Kaapvaal Craton) may be the residues from the formation of komatiite lavas.

As mentioned above, the partitioning of Cr and Sc are significantly influenced by the composition of the solid and liquid phases. The MgO content of the phases, in particular, plays an important role in the structure of the phases and thus affects the partitioning of these elements. Figure 4.7 is a plot of Cr against MgO for silicate diamond-inclusions analyzed by electron microprobe (Moore & Gurney, 1988; Otter & Gurney, 1988). Note that the trend for the peridotitic suite differs from that for the eclogitic suite. The plot for the peridotitic minerals suggests a crystallization trend (see arrow in Fig.4.7): Cr increases and MgO decreases with the crystallization of olivine, orthopyroxene, chrome-pyropene garnet and chrome-diopside (in that order). A maximum in Cr concentration is found between 20 -25% MgO and occurs in the Cr-pyropene garnets.

In the eclogitic field Cr increases as MgO increases. The eclogitic suite therefore, suggests a melting trend and the order is omphacitic clinopyroxene and then pyropene-almandine garnet. The basaltic nature of the eclogitic suite is emphasized by the fact that the eclogitic minerals plot between 10-20% MgO.

Table 4.2 Partition coefficients for Cr and Sc used in this study.

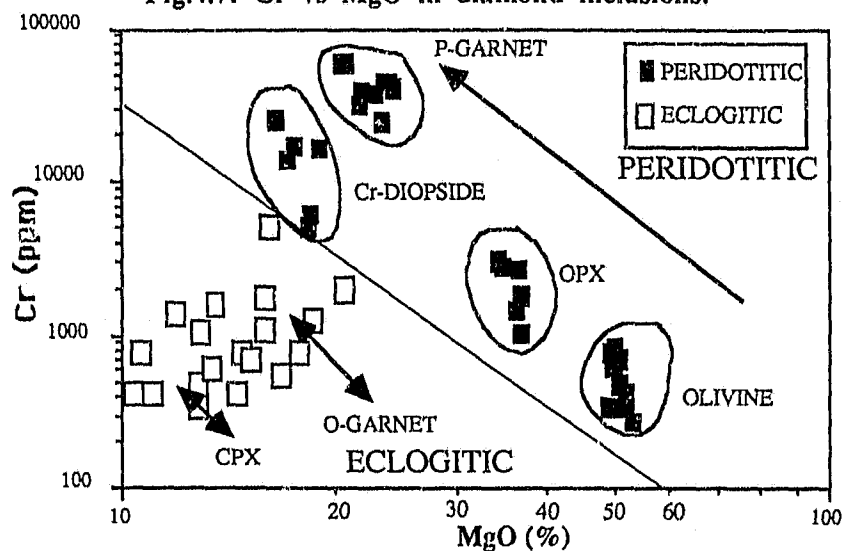
ELEMENT	MINERAL	KD	AVERAGE KD
Cr	olivine	1.1-3.1	2.1
	orthopyroxene	10	10
	clinopyroxene	4.7-20	8.4
	garnet	0.06-20*(extrapolated)	4
Sc	olivine	0.14-0.22	0.17
	orthopyroxene	1.2	1.2
	clinopyroxene	1.7-3.2	2.7
	garnet	2.6-7.4	5.0

Table 4.3 Average Cr/Sc ratios in various rocks (*data from Bergman, 1987).

ROCK/INCLUSION	Cr (ppm)	Sc (ppm)	Cr/Sc
Barren lamproites*	520	17	30
Diamondiferous lamproites*	1010	19	53
Diamondiferous kimberlites*	1400	12	117
Barren kimberlites*	1000	21	48
Primitive mantle*	3000	11	273
Basalts*	250	25	10
Peridotites	2900	11	263
C1 chondrite	3200	9	356

Observe, also, that this plot is quite similar, in function, to the plot of Cr against Sc (Fig.4.4) for heavy minerals separated from South African kimberlites (xenocrysts - cogenetic with diamond). That is both plots separate the eclogitic minerals from the peridotitic minerals.

Fig.4.7: Cr vs MgO in diamond inclusions.



4.3 Au AND Ir IN DIAMONDS

Au and Ir are usually detected in diamonds with visible sulphide inclusions. Their detection in diamonds without visible sulphide inclusions (e.g., FB1) may indicate the presence of sub-microscopic sulphide inclusions, which is sometimes corroborated by the detection of other chalcophile elements such as Fe, Ni, Co, As and Cu.

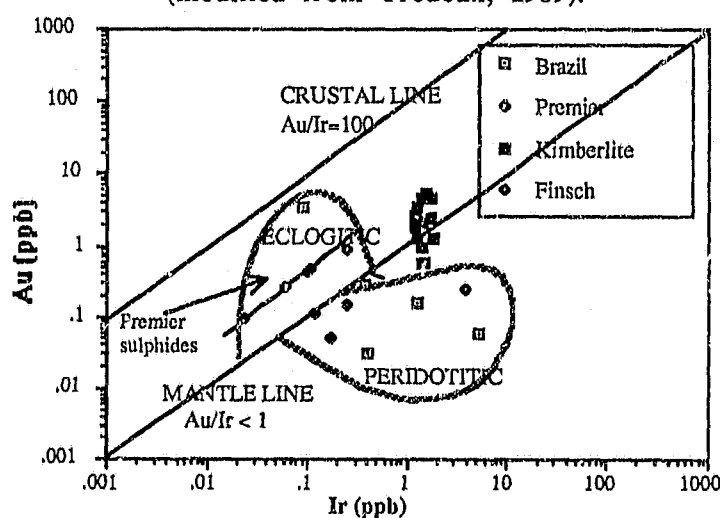
The eclogitic diamonds, analyzed in this study, are characterized by relatively high Au/Ir ratios, whereas the peridotitic diamonds have relatively low Au/Ir ratios (see Fig.4.8). The eclogitic diamonds have a wide range of Au/Ir ratios from 1-40, while peridotitic diamonds have Au/Ir ratios that are ≤ 1 . The eclogitic diamonds plot in the field between the crustal and mantle line of Tredoux (1989) and are equivalent to the Au/Ir ratios of basalts. The peridotitic diamonds plot below the mantle line and the Au/Ir ratios of these diamonds are equivalent to those of most peridotites.

The Au/Ir ratios in the Premier eclogitic diamonds are relatively constant i.e., between 3.4 and 3.6, which could be indicative of a relatively homogenous environment with regard to Au and Ir. It is noteworthy that the diamonds with low Au/Ir ratios are also characterized by high Cr/Sc ratios. Furthermore, there are positive correlations between Au and As (Fig.4.9) and Au and Ni (Fig.4.10)

in the peridotitic diamonds with sulphide inclusions, but these relationships were not observed in the eclogitic diamonds with sulphide inclusions.

Au/Ir ratios are thus similar in function to the Fe/Fe+Ni ratios of Haggerty (1991) who pointed out that eclogitic diamonds with sulphide inclusions have the highest Fe/Fe+Ni ratios of between 0.88-0.99, while peridotitic diamonds with sulphide inclusions have moderate Fe/Fe+Ni ratios of 0.55 to 0.65. This holds, in general, for the diamonds analyzed in this study, except where the sulphide inclusions are accompanied by large silicate inclusions as well. Nevertheless, there is a broad positive correlation between the Au/Ir ratios and the Fe/Fe+Ni ratios of the diamonds analysed.

Fig.4.8: Au Vs Ir in single diamonds compared to South African kimberlites
(modified from Tredoux, 1989).



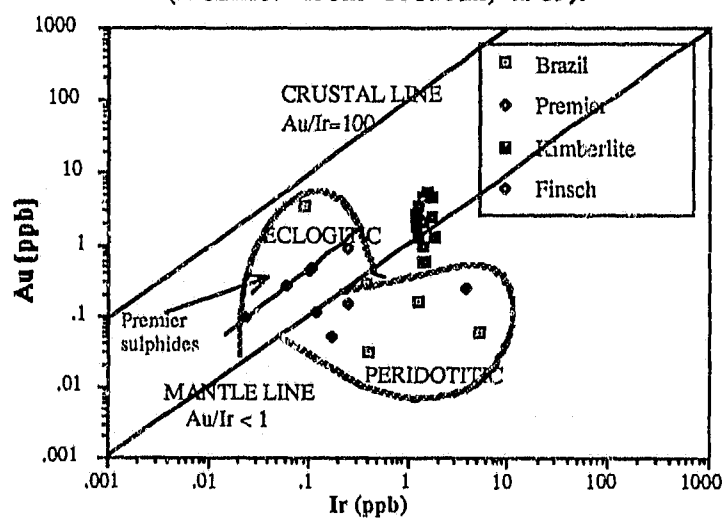
Note also, the very low limits of detection for both Au and Ir.

Kimberlite data from McDonald (1993).

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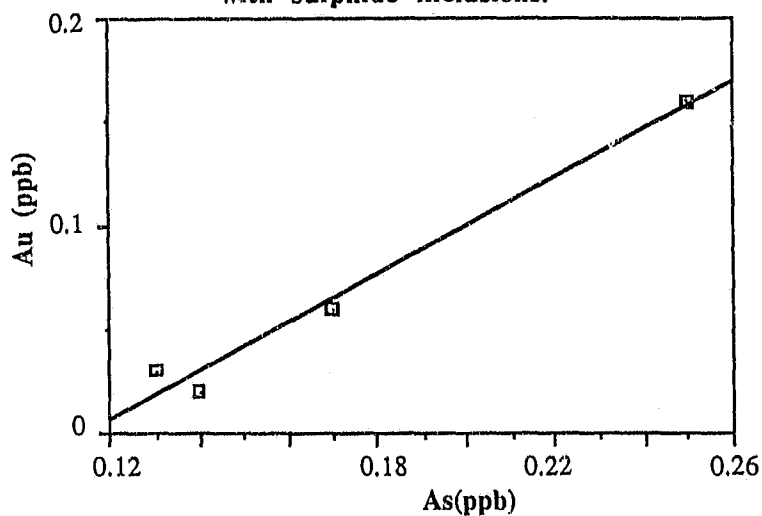
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(modified from Tredoux, 1989).



Note also, the very low limits of detection for both Au and Ir.

Kimberlite data from McDonald (1993).

Fig.4.9: Positive correlations between Au and As in peridotitic, Brazilian diamonds with sulphide inclusions.



This relationship is not seen in the Premier eclogitic diamonds with sulphide inclusions.

Fig.4.10: Positive correlation between Ni and Au in peridotitic, Brazilian diamonds with sulphide inclusions.

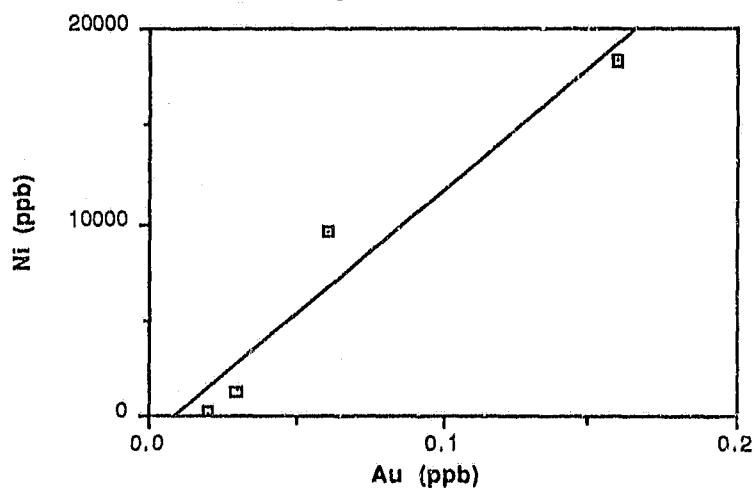
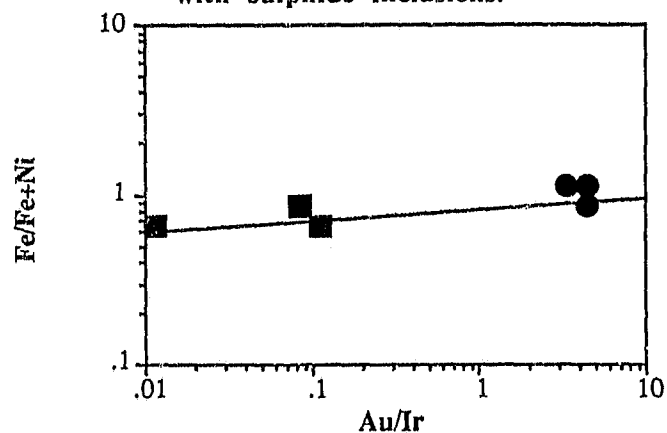


Fig. 4.11 Positive correlation between Au/Ir ratios and Fe/Fe+Ni ratios in diamonds with sulphide inclusions.



4.3 RARE EARTH ELEMENTS IN DIAMONDS.

The rare earth element (REE) data in these diamonds are difficult to interpret because of the varied and unusual (chondrite normalized) REE patterns that are observed. Nevertheless, the REE patterns of diamonds can be divided into 4 broad groups.

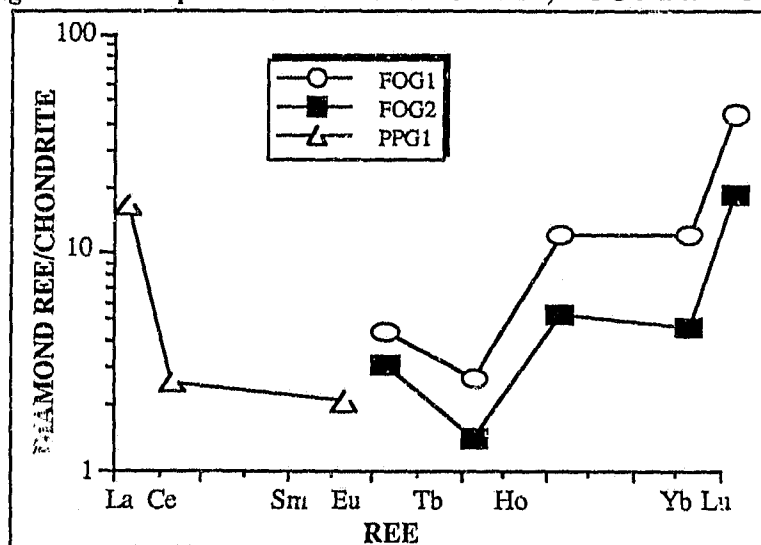
4.3.1 LREE-enriched patterns.

The LREE-enriched patterns are characteristic of diamonds with either purple garnet (Fig.4.12), chrome diopside or omphacitic clinopyroxene inclusions (e.g., FPG1-FPG5, PPG1: see Fig.4.12, FOM1, PC1 and PC2). These observations are consistent with those of Shimizu and Richardson, (1987). The LREE-enriched pattern of the Brazilian peridotitic diamonds with sulphide inclusions (see Fig.4.13) can be interpreted to indicate the presence of submicroscopic purple garnet or submicroscopic peridotitic, pyroxene inclusions.

4.3.2 HREE-enriched patterns.

HREE-enriched patterns are characteristic of diamonds with orange garnet inclusions (e.g., FOG1 and FOG2). The HREE enriched pattern is therefore a good indicator of the eclogitic paragenesis and of the influence of pyrope-almandine garnet. The Premier diamond with a sulphide inclusion (see Fig.4.13) shows HREE-enrichment and this is interpreted to indicate submicroscopic orange garnet inclusions.

Fig.4.12: REE patterns for diamonds PPG1, FOG1 and FOG2.



4.3.3 Sub-horizontal pattern.

This is found in the eclogitic diamond POM1, where the REE content is the sum of the contributions of the visible and submicroscopic orange garnet and omphacitic, clinopyroxene inclusions (see Fig.4.14). This pattern is relatively flat.

4.3.4 LREE-enriched subparallel patterns.

Some LREE-enriched diamonds display subparallel patterns with higher than usual concentrations of REE and these can be explained in terms of variable amounts of kimberlite contamination superimposed on the contribution from the diamond itself. Kimberlite contamination can be introduced into the diamonds through micro-cracks, and it seems that the cleaning procedure cannot remove this contamination, entirely. However, such kimberlite contamination (especially REE) may also have its advantages, since it leaves a fingerprint of the kimberlite. Thus, diamonds from different kimberlite-sources can be differentiated on this basis. Figure 4.15 shows that diamonds (with different inclusion mineralogies) from different localities (e.g., Romaria, Finsch and George Creek) have distinctive LREE-enriched subparallel patterns.

Fig.4.13: REE patterns for Brazilian diamonds and a Premier diamond with sulphide inclusions.

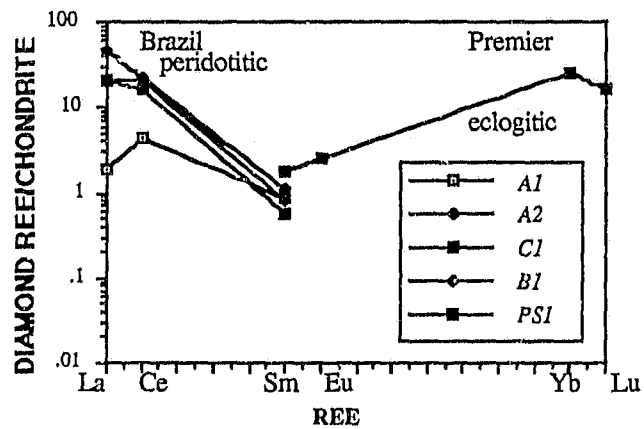
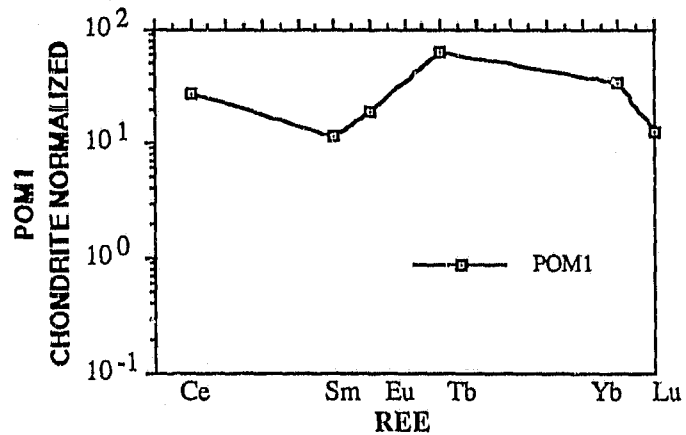
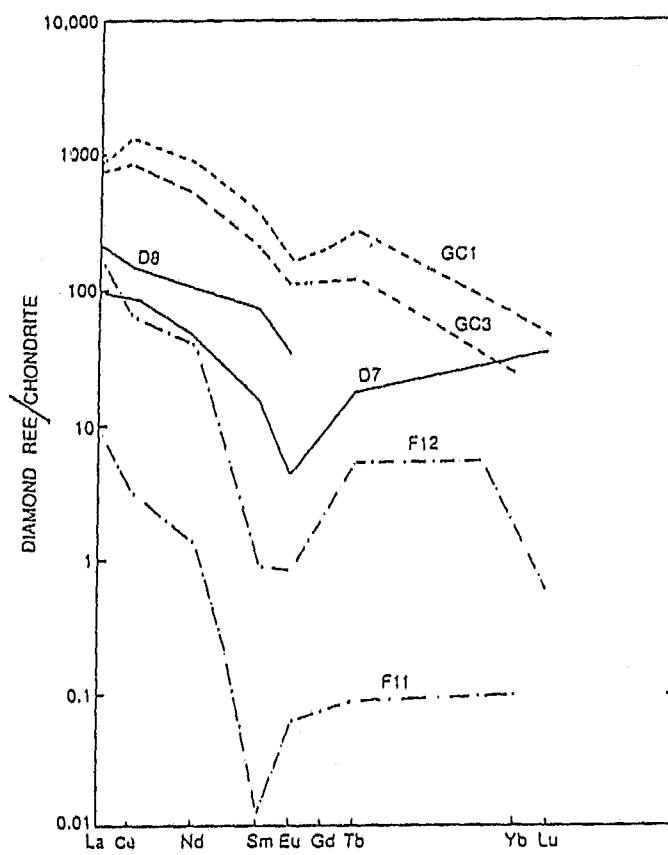


Fig.4.14: REE pattern for diamond POM1



This diamond shows enrichment in both LREE and HREE, and this is responsible for the relative flattening of the chondrite normalized pattern.

Fig.4.15: REE patterns for kimberlite-contaminated diamonds.



5: CARBON ISOTOPE RATIOS

In this work carbon isotope analysis of 33 inclusion-bearing and inclusion-free diamonds (which were previously analyzed by INAA) was carried out. The analyses were performed using the carbonate line (see Fig.5.1) at the University of Cape Town. The main objective of this work was to compare the carbon isotope ratios, of the diamonds, to their geochemistry, in particular their relationship to the Cr/Sc and Au/Ir ratios. The data is also compared to carbon isotope data from the literature.

5.1 METHODOLOGY

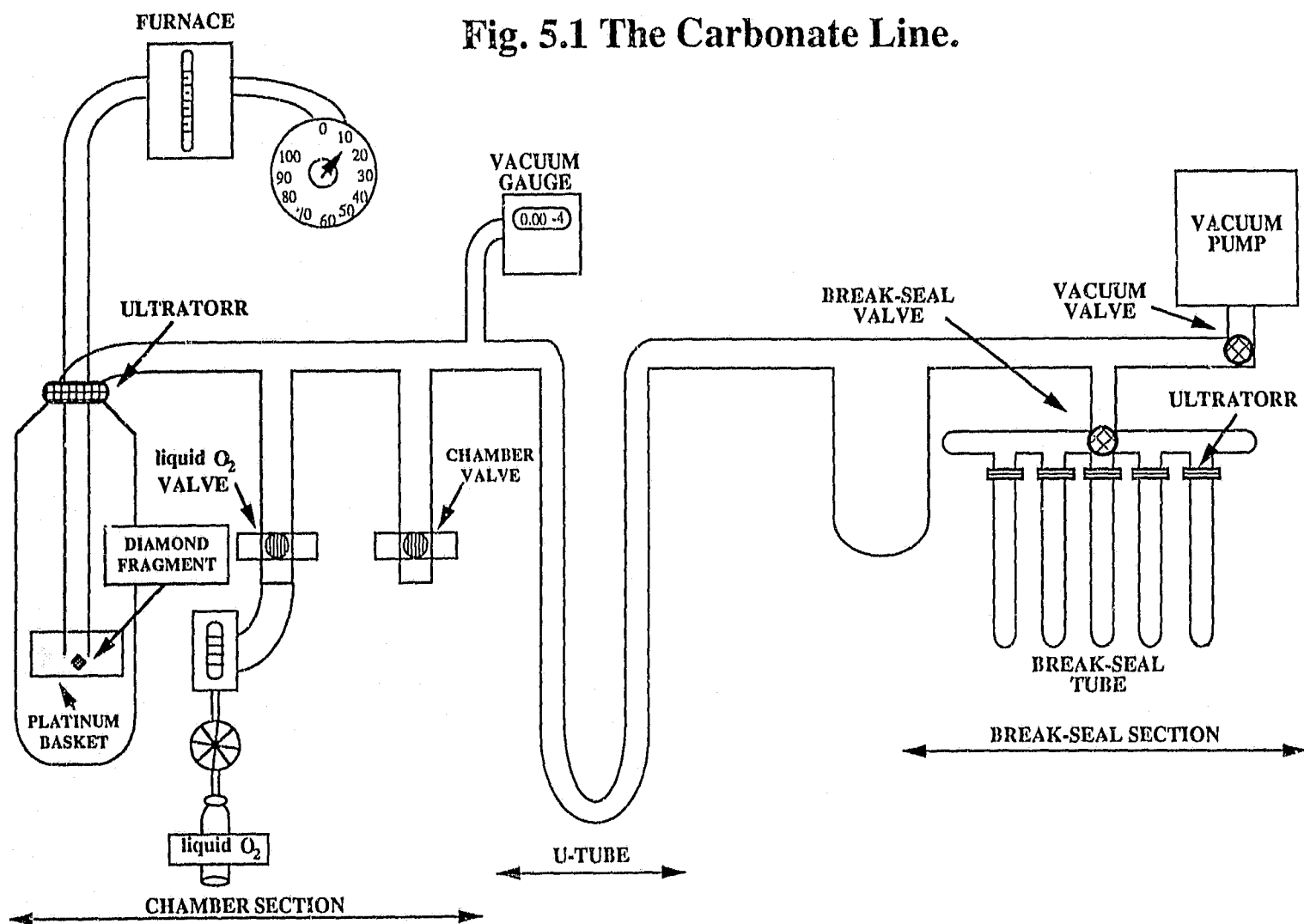
5.1.1 Diamond preparation/selection.

The diamonds were analyzed according to the technique described by Kirkley (1992, pers.comm.). The diamonds were first described with strong emphasis being placed on the surface features. Particular attention was paid to resorption morphology, presence or absence of ribbing, pits, laminae and striations (see Robinson, 1979), in order to facilitate the recognition of the external and internal fragments of each diamond. The diamonds were then broken in a steel pestle and mortar. Great care was taken to avoid contamination by cleaning the pestle and mortar (with alcohol and then water) after each sample. One external and one internal fragment (0.1-0.2 mg) of each diamond was selected for analysis. Recognition of the external and internal fragments was based on the presence or absence of the surface features mentioned above. Each fragment selected was then weighed.

5.1.2 CO₂ collection

Each diamond fragment is placed in the platinum basket (located in the chamber section: see Fig.5.1) and then burnt in oxygen. The diamond (C) in the presence of O₂ forms CO₂. This CO₂ yield, which is measured by the vacuum gauge, is then recorded. The CO₂ is then transferred from the chamber section to the end of a break-seal tube (see Fig.5.1) by using liquid-nitrogen traps (alternate liquid-nitrogen freezing and artificial heating is used to transfer the gas along the chamber). Once the CO₂ is frozen at the bottom of the break-seal tube, the tube is heat-sealed.

Fig. 5.1 The Carbonate Line.



5.1.3 Standardization.

Four NBS graphite standards were also burnt and their CO₂ collected in this manner. This is done to check on the efficiency of the extraction procedure.

5.1.4 Analysis by mass spectrometer.

The JEOL Mass Spectrometer was used to measure the ratio of "CO₂-mass 45"/"CO₂-mass 44" which is the ratio of $[(^{13}\text{C} + 0^{16}, 0^{16})/(^{12}\text{C} + 0^{16}, 0^{16})]$ in each sample of CO₂ extracted. Basically, this involves breaking the break-seal tube and releasing the CO₂ into the system. The sample gas is compared to a reference gas.

5.1.5 Calculating $\delta^{13}\text{C}$ values.

The raw values for "mass 45" and "mass 44" obtained from the mass spectrometer are then converted into $\delta^{13}\text{C}$ by the following formula: $\delta^{13}\text{C sample} = [(R \text{ sample} - R \text{ standard})/R \text{ standard}] \times 1000$ where $R = ^{13}\text{C}/^{12}\text{C}$. Therefore δ is the difference in isotopic ratio between a sample and a standard, expressed in parts per thousand or permil (‰). The $\delta^{13}\text{C}$ values are reported relative to the PDB standard (belemnite from the Peedee Formation).

5.2 RESULTS

The data obtained for the 33 diamonds analyzed, is given in tables 5.1-5.6 (in Appendix:5) and plotted on a bar graph (see Fig.5.2). Values for both the external fragment (ext) and internal fragment (int) are given. The $\delta^{13}\text{C}$ values range from -1.8 to -16.4 ‰. With the exception of GC3 (-16.4 ‰) the values are well within the range for the majority of diamonds worldwide (Kirkley, 1991). In some diamonds (e.g., D2, D3 and POC1) there are noteworthy differences between the values for the external and internal fragments.

The George Creek diamond yielded the lightest carbon isotope ratio (-16.4 ‰) of all the diamonds analyzed (see table 5.1). This may be significant in that some other North American diamonds e.g., Sloan (see Otter et al., 1991) are also reported to have high negative values. The data for the Finsch and Premier diamonds compares reasonably well with the data of Deines et al., 1984 (see Fig.5.2-5.3)

Fig.5.2: $\delta^{13}\text{C}$ values for Finsch and Premier eclogitic and peridotitic diamonds analysed in this work.

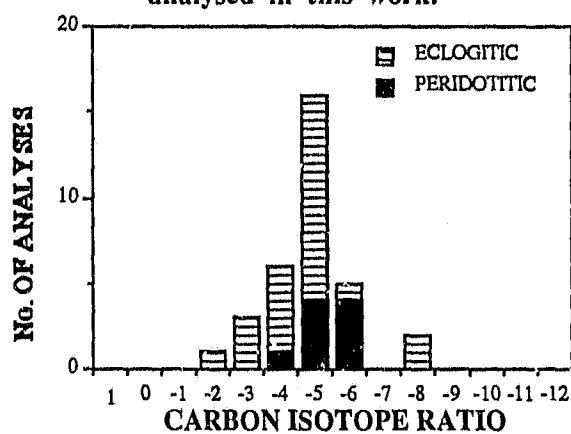
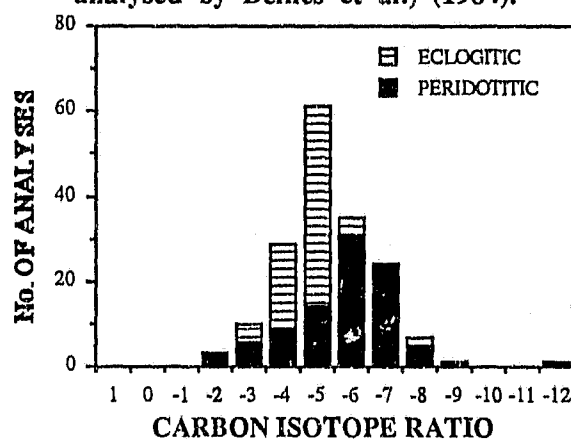


Fig.5.3: $\delta^{13}\text{C}$ values for Finsch and Premier eclogitic and peridotitic diamonds analysed by Deines et al., (1984).



5.3 DISCUSSION OF DATA

The carbon isotope compositions of more than 1000 diamonds from Roberts Victor (Deines et al., 1987), Finsch and Premier (Deines et al., 1984), Star (Hill, 1989), Sloan (Otter, 1989), New South Wales (Sobolev, 1984) and Argyle and Ellendale (Jaques et al., 1989) have been determined in the past decade. These analyses revealed that most peridotitic diamonds have $\delta^{13}\text{C}$ values between -10

and -1 permil (‰) with a sharp peak in the distribution at -5 permil, while eclogitic diamonds have $\delta^{13}\text{C}$ values between -34 and +3 permil and a small peak at -5 permil. Furthermore, it is apparent that carbon isotopic compositions of diamonds from different localities are in general quite unique (Kirkley et al., 1991; Otter et al., 1991).

The $\delta^{13}\text{C}$ values of the diamonds measured in this study do not show any correlation with paragenesis. The $\delta^{13}\text{C}$ ratios of the diamonds were plotted against their Cr/Sc ratios (see Fig. 5.4) and although Cr/Sc ratios clearly separate the two parageneses, this is not achieved with the $\delta^{13}\text{C}$ data. Although there may be a broad correlation between the Cr/Sc ratios and $\delta^{13}\text{C}$ values (as suggested by the correlation between these ratios and inclusion type) it is proposed that this is not observed in this study because of the limited data set. It is suggested further, that the limitations of the $\delta^{13}\text{C}$ values as a discriminant tool when dealing with a limited number of samples is probably due to inhomogeneities of $\delta^{13}\text{C}$ within the diamond and in the mantle itself, whereas the correlation of Cr/Sc with inclusion type is based on more sound geochemical principles of chemical equilibrium and partitioning of elements between phases.

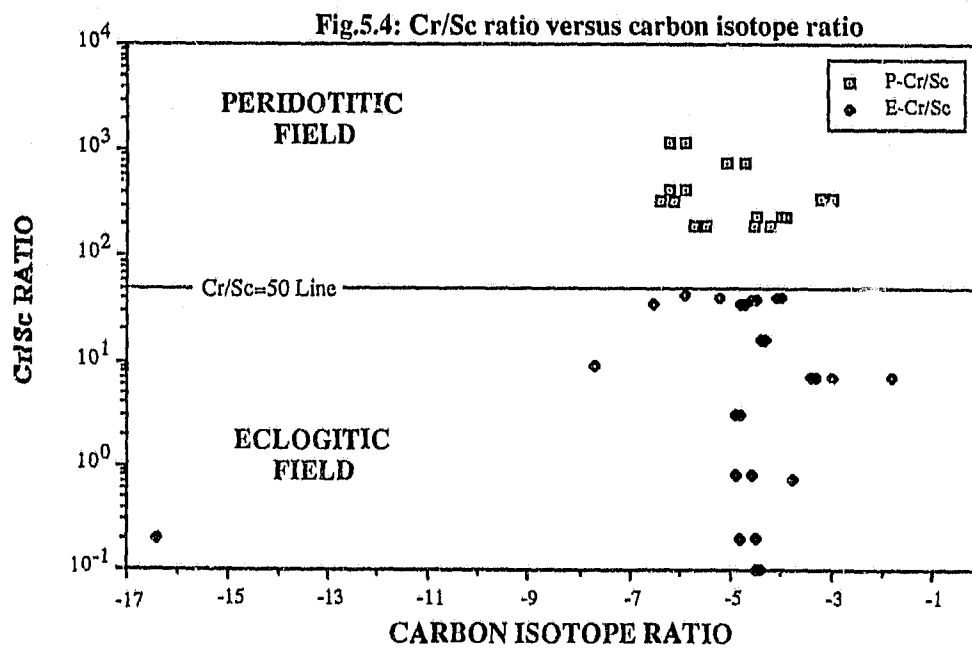
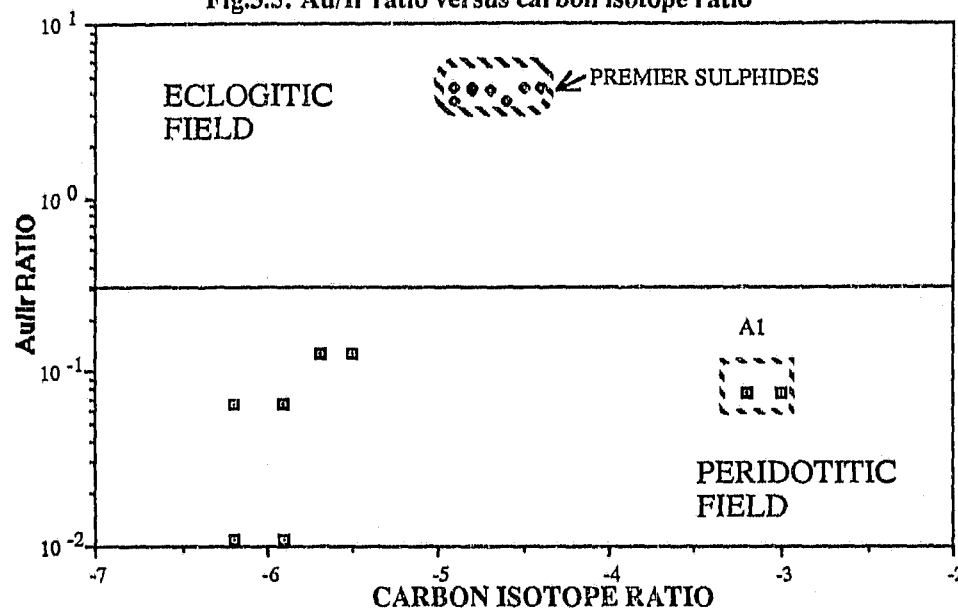


Fig.5.5: Au/Ir ratio versus carbon isotope ratio



Similarly a plot of Au/Ir ratios versus $\delta^{13}\text{C}$ (see Fig.5.5) shows that although there may be a broad correlation between the Au/Ir ratios and $\delta^{13}\text{C}$ (with the exception of sample A1 which is anomalous; see chapter 3) only the Au/Ir ratios separate the 2 parageneses clearly. Nevertheless, note the fairly constant Au/Ir ratios and $\delta^{13}\text{C}$ values for the Premier diamonds with sulphides inclusions which are all eclogitic.

6: CONCLUSIONS

The most significant conclusions reached in this study (in the order in which they were attained in the body of the thesis) are listed below.

- 6.1) For standardization of single diamonds the graphite-diluted standard mixtures (1 part rock standard to 50/90 parts graphite), of 1:50 PTO-1, 1:50 NEM-1, 1:90 NIM-G and 1:90 NIM-L were the most suitable.
- 6.2) Long irradiation periods of 128 hours at a neutron dose of $2 \times 10^{13} \text{N.cm}^{-2}/\text{s}$, in an Oak-Ridge-type nuclear reactor, were necessary for the analysis of single diamonds.
- 6.3) For short-lived isotope analysis, cyclic counting at the site of irradiation, is obligatory.
- 6.4) More than 40 elements can be detected at the ppb and sub-ppb levels, in single diamonds, by INAA.
- 6.5) The most important factors affecting the concentration of elements in diamond are the size, number and nature of the mineral inclusions.
- 6.6) There are positive correlations between the elements Cr, Fe, Ni and Co in all diamonds.
- 6.7) Eclogitic diamonds are characterized by low Cr/Sc ratios of between <1 and 50. They are enriched in Fe, Mn, Na, Ca, K, HREE, Ga and Au relative to the peridotitic diamonds.
- 6.8) Peridotitic diamonds are characterized by much higher Cr/Sc ratios, i.e., >100 . Peridotitic diamonds are also enriched in Ni, Co, LREE and Ir relative to the eclogitic diamonds.
- 6.9) In diamonds with no visible inclusions or only visible sulphide inclusions, the presence of Cr and Sc may be taken as evidence for the presence of submicroscopic silicate inclusions in diamond, as suggested earlier by Fesq et al., (1975). Therefore these diamonds can also be distinguished as either eclogitic or peridotitic using the Cr/Sc ratio.
- 6.10) The brown and yellow body-colouration in diamonds cannot be correlated to any of the element/s analysed. However, the dark-green to black colouration is often due to the intensity of submicroscopic inclusions and sometimes graphite as well.
- 6.11) The Cr/Sc ratio can be used, in this data set, to distinguish between diamonds from different geographical locations/mines (Finsch, Premier, George Creek and Romaria).

- 6.12) There are positive correlations between Cr and Sc for any one type of silicate diamond inclusion or cogenetic mineral (kimberlite macrocrysts). In contrast, there is a negative correlation between Cr and Sc in garnet megacrysts of kimberlites (Gurney, 1973).
- 6.13) Lherzolitic diamonds are poorer in Cr and Sc relative to the garnet-harzburgitic diamonds.
- 6.14) The difference in the Cr/Sc ratios between diamonds of the eclogitic and peridotitic paragenesis is thought to be due to the characteristic Cr/Sc ratios of the different mineral inclusions in diamond.
- 6.15) There is an inverse relationship between the Cr/Sc and the Ca/Cr ratios of diamonds with silicate inclusions.
- 6.16) There is an inverse relationship between Cr and Al in garnet inclusions of diamonds.
- 6.17) Cr and Sc behave as compatible elements. Nevertheless, the bulk distribution coefficient for Cr in a typical peridotite is about 7 times more than it is for Sc. On the other hand, the bulk distribution coefficient for Cr in a typical eclogite is only 1.25 times greater than it is for Sc. This explains why the Cr/Sc ratios of peridotitic diamonds are higher than those of eclogitic diamonds but it does not account for the magnitude of the difference between the 2 parageneses. The incongruously high Cr/Sc ratios of upper mantle peridotites points to a further enrichment process or episode/s of melt extraction.
- 6.18) It is possible that melt extraction such as through the formation of komatiitic lavas (Boyd and Gurney, 1982) may have left behind a relatively Cr-enriched upper mantle.
- 6.19) The Cr/Sc ratios of peridotitic diamonds are equivalent to those of most ultramafic rocks worldwide. The Cr/Sc ratios of eclogitic diamonds are equivalent to those of most basaltic rocks worldwide. Furthermore, diamondiferous kimberlitic rocks (kimberlites and lamproites), in general, have significantly higher Cr/Sc ratios than barren kimberlitic rocks.
- 6.20) Eclogitic diamonds have a wide range of Au/Ir ratios from 1-40, while peridotitic diamonds have Au/Ir ratios that are ≤ 1 .
- 6.21) The Premier diamonds with sulphide inclusions (which are eclogitic) have remarkably constant Au/Ir ratios of between 3.6 and 4.3.

- 6.22) Eclogitic diamonds have Au/Ir ratios that are equivalent to those of most basaltic rocks.
Peridotitic diamonds have Au/Ir ratios that are equivalent to most ultramafic rocks.
- 6.23) There is a broad positive correlation between the Au/Ir and Fe/Fe+Ni ratios in diamonds with sulphide inclusions.
- 6.24) All peridotitic diamonds are LREE-enriched (see also Shimizu & Richardson, 1987).
- 6.25) HREE-enriched (chondrite-normalized) patterns are typical of diamonds with eclogitic, orange garnet inclusions.
- 6.26) Sub-horizontal (chondrite-normalized) REE patterns are typical of eclogitic diamonds with omphacitic clinopyroxene and orange garnet inclusions.
- 6.27) Kimberlite contaminated diamonds yield (chondrite-normalized) REE patterns that are subparallel and distinctive of that particular kimberlite source.
- 6.28) There is no apparent relationship between the Cr/Sc and $\delta^{13}\text{C}$ ratios of the diamonds analysed.
- 6.29) There seems to be a broad positive correlation between the Au/Ir and $\delta^{13}\text{C}$ ratios of the diamonds analysed.

7: APPENDIX

7.1 APPENDIX 1: DIAMOND DESCRIPTIONS

Table 2.1: Description of Finsch diamonds with silicate inclusions.

Sample	Wt(g)	Description
FOG1	0.08187	Colourless dodecahedron with orange garnet inclusions.
FOG2	0.09350	Colourless, irregular, twinned diamond with orange garnet inclusions.
FPG1	0.12239	Tetrahexahedroid with purple garnet inclusions. Surfaces are not smooth - etch features are present.
FPG2	0.11145	Colourless, perfect octahedron. It has a purple garnet inclusion.
FPG3	0.07325	Colourless, rounded octahedron with trigons. Has a purple garnet inclusion.
FPG4	0.02635	Nearly colourless, rounded dodecahedron with peridotitic garnet and olivine inclusions.
FPG5	0.02922	Brown, rounded dodecahedron with five peridotitic garnet inclusions. White/grey contaminating material in surface depressions.
FOC1	0.03288	Yellow, rounded dodecahedron with subordinate octahedral faces, containing four eclogitic, clinopyroxenes and many small orange-garnet inclusions.
FOM1	0.02954	Light brown, rounded dodecahedron with subordinate octahedral faces, containing four eclogitic clinopyroxene inclusions.

Table 2.2: Description of Finsch diamonds with sulphide inclusions.

Sample	Wt(g)	Description
FS1	0.03257	Fairly deep yellow, rounded dodecahedron containing a large sulphide inclusion. There is whitish, contaminating material in surface depressions.
FS2	0.02693	Deep brown, rounded dodecahedron with a large sulphide inclusion. White contaminating material in surface depressions.

Table 2.3: Description of inclusion-free Finsch diamonds.

Sample	Wt(g)	Description
FIF1	0.03437	Deep yellow, rounded dodecahedron without inclusions.
FIF2	0.03693	Pinkish brown octahedron with subordinate, rounded dodecahedral faces, without inclusions.
FIF3	0.03121	Colourless, inclusion-free dodecahedron.

Table 2.3 continued

FIF4	0.02075	Colourless fragment.
FIF5	0.1224	Colourless fragment with a grey spot near the surface.
FIF6	0.04025	Colourless fragment.
FB1	0.03455	Black cube partly modified to a rounded dodecahedron. White contaminating material in surface depressions.

Note that diamonds FIF4-FIF6 are actually fragments, of diamonds from which large eclogitic silicate inclusions were removed for age-dating of single inclusions by Smith et al., (1991). They were analyzed to see whether the inclusion-free fragments still retained their eclogitic signature (discussed further in chapter 3)

Table 2.4: Description of Premier diamonds with silicate inclusions.

Sample	Wt(g)	Description
POM1	0.08382	Colourless, rounded octahedron with two greenish-black (omphacite) inclusions. Small orange garnet inclusions are also present.
POC1	0.07321	Colourless octahedron with one blackish-green inclusion and small orange-brown inclusions.
PC1	0.06027	Colourless, planar octahedron with slightly frosted surface. Has a green clinopyroxene (chrome diopside?) inclusion.
PPG1	0.09544	Colourless, frosty, rounded dodecahedron with 2 purple garnet inclusions.
POM2	0.09884	Dirty brown, frosty and pitted tetrahexahedroid with a broken edge. Has a green clinopyroxene inclusion.
PC2	0.06994	Colourless, rounded dodecahedron with broken edges. There are 2 green "wings" which may be clinopyroxene.

Table 2.5: Description of Premier diamonds with sulphide inclusions.

Sample	Wt(g)	Description
PS1	0.05506	Rounded dodecahedron - orangy-brown in colour. Has one big, sulphide inclusion.
PS2	0.04152	This is a cube with trigon development. It has one sulphide inclusion.
PS3	0.04824	The diamond has one large and one small black sulphide inclusion.
PS4	0.04479	Colourless octahedron with trigons and 4 sulphide inclusions
PS5	0.06392	Colourless, rounded dodecahedron with a black sulphide (?) inclusion.
PS6	0.04333	Colourless, rounded dodecahedron with one large, sulphide (?) inclusion.

Table 2.6: Description of brown, inclusion free Premier diamonds.

Sample	Wt(g)	Description
B1	0.04573	Brown, inclusion-free octahedron with one side broken off.
B2	0.05585	Brown, inclusion-free, rounded dodecahedron.
B3	0.03170	Brown, inclusion-free, irregular stone.
B4	0.06439	Brown, inclusion-free, rounded dodecahedron.
B5	0.04210	Brown, inclusion-free octahedron with one edge broken off.

Table 2.7: Description of yellow, inclusion-free Premier diamonds.

Sample	Wt(g)	Description
Y1	0.07145	Deep yellow, inclusion-free, rounded dodecahedron.
Y2	0.05343	Lighter yellow, inclusion-free, rounded dodecahedron.
Y3	0.04962	Rounded dodecahedron with a yellow tint.

Table 2.8: Description of Brazilian diamonds with sulphide inclusions.

Sample	Wt(g)	Description
A1*	0.02855	Yellow octahedron, slightly resorbed and twinned. Brown and green diffusive spots on the surface. Peridotitic garnet, sulphide and olivine inclusions are present.
A2*	0.03128	Highly resorbed. Has a sulphide inclusion. Also has a crack or hole.
B1*	0.02674	Highly resorbed, and on one surface highly frosted. Has a sulphide and probably an olivine inclusion as well.
C1*	0.03567	Highly resorbed and frosted. Big sulphide and other small "wing" inclusions.

The four diamonds (A1, A2, C1 and B1), also from Brazil, were bought at Arenapolis, Canastra and Boa Vista. Once again these are alluvial diamonds and their source is unknown. The diamonds have black sulphide and/or graphite inclusions.

Table 2.9: Description of diamonds from Romaria, Brazil.*

Sample	Wt(g)	Description
D2	0.00644	Colourless, irregular dodecahedron with no visible inclusions.
D3	0.01248	Colourless octahedron with a slightly stepped surface. One face has an embayment.

Table 2.9 continued.

Sample	Wt(g)	Description
D4	0.02466	Elongated, colourless dodecahedron with slightly frosted faces and one large colourless inclusion (300 μm).
D5	0.01806	Greenish octahedron with 6 flat faces and enclosing a smaller dodecahedron inside. No visible inclusions.
D6	0.00919	Clear deformed dodecahedron with one small interior cleavage giving a black film appearance. Possibly one very tiny colourless inclusion.
D7	0.01552	Off-coloured octahedron that has been partly broken. One orange spot near the surface.

** This batch of Brazilian diamonds are from the mine at Romaria, Western Minas Gerais, which is working an upper Cretaceous conglomerate. The source of the diamonds and the conglomerate is unknown.*

Table 2.10: Description of diamonds from George Creek, Colorado.

Sample	Wt(g)	Description
GC1	0.0042	Dark-green to almost black, partially rounded octahedron. No visible inclusions.
GC2	0.0045	Gold to honey brown octahedron with etch-pitting. One corner is broken off. Colour is a body colour.
GC3	0.0043	Colourless fragment which may have been part of a twinned octahedron. There are inclusions but these appear altered. Possibly a light green clinopyroxene (or opx) inclusion with uncertain bright red specks probably on a fracture plane (haematite?). Graphite on fractures. This is a bit of a messy diamond.
GC5	0.0026	Green fragments. The bluish-green tinge looks to be a surface coating. No inclusions. Originally part of a rounded dodecahedron.
GC6	0.0023	Clean, unresorbed octahedron. Two corners are broken off. There are no inclusions This is a gem.
GC7	0.0035	Yellow (deep) to yellow-green dodecahedron. No inclusions except for some internal graphite on a plane near one surface.

Table 2.10 continued

GC8	0.0042	Colourless fragment, broken with one end badly pitted. Some white material in surface crack (secondary?).
GC9	0.0045	Yellow (weak tint) fragment, with strongly pitted external surfaces and smooth cleaved surface. Two inclusions, one tiny, and the other ~ 100µm which could possibly be altered mica.

Table 2.11: Description of Chinese diamonds.

Sample	Wt(g)	Description
CH1	0.00799	Dirty-brown, irregular crystal that looks like a grain of sand. May have an inclusion.
CH2	0.00949	Inclusion-free, frosty octahedron.
CH3	0.00225	Colourless, inclusion-free, rounded dodecahedron.

7.2 APPENDIX:2: STANDARD DATA AND COMPARISONS

Table 2.12: A comparison of the data (in ppb) for the graphite standard PTO1 analyzed at the University of Vienna and Schonland Research Centre.

Element	Vienna mean	Schonland mean	n	Std. Dev.
La	60	86	8	30
Na ppm	100	96	8	12
Br	120	68	8	12
As	70	53	8	8.8
Au	14	8	8	3.5
U	-	5	11	4
Nd	100	110	2	1.4
Ba ppm	6	12	7	11
Lu	5	2	-	3
Yb	20	28	5	13
Ce	110	177	4	44
Cr ppm	108	130	9	23
Eu	35	112	4	9.6
Co ppm	2.3	2.9	8	1.4
Fe%	0.17	0.11	7	0.05
Ta	17	18	8	1.4
Sc	460	803	8	11
Ni ppm	55	72	8	17
Tb	20	13	4	8.1
Cs	50	43	6	8.8
Hf	20	25	4	13
Ir	-	1.5	2	6
W	40	43	7	23
Th	15	20	7	3.4

Table 2.13: Concentrations of the various elements in the graphite standards (in ppm unless otherwise stated).

ELEMENT	NEM 1:50	PTO1 1:50	NIM-G 1:90	NIM-L 1:90
La	0.15	0.1	1.26	2.12
Na%	0.003	0.01	0.027	0.059
Br	0.1	0.1	0.16	0.11
As	0.02	0.07	0.13	0.03
Sm	0.05	0.012	0.16	0.0450
Au	0.0005	0.014	0.0002	0.0003
U	0.07	0.005	0.16	0.16
Th	0.29	0.02	0.56	0.51
W	0.05	0.05	0.13	0.05
Ba	15	20	2.5	4
Sb	0.1	0.11	0.012	0.006
Eu	0.005	0.003	0.002	0.01
Co	0.15	3.4	0.015	2
Fe%	0.006	0.18	0.016	0.072
Ta	0.04	0.02	0.041	0.21
Lu	0.0058	0.005	0.021	0.0047
Yb	0.044	0.04	0.15	0.045
Tb	0.014	0.016	0.037	0.04
Nd	0.3	0.1	0.96	0.39
Sc	0.16	0.7	0.0048	0.0022
Ni	3	60	1	2
Cs	0.05	0.04	0.056	0.058
Hf	0.129	0.02	0.137	2.39
Cr	10	130	0.27	0.1
Ir	0.0009	0.0014	0.001	0.0006
Zn	0.5	3.2	0.8	3.4
Se	0.1	0.09	0.06	0.25
Rb	0.12	0.8	3.92	2.08
Ga	0.3	2.1	3	2.4

Table 2.13 continued

ELEMENT	NEM 1:50	PTO1 1:50	NIM-G 1:90	NIM-L 1:90
Sr	5	5	3	35
Zr	5	10	5	102
Ag	0.05	0.04	0.025	0.011
Gd	0.2	-	0.2	0.22
Tm	0.05	-	0.03	-
Ho	-	0.017	-	-
Ti	92.6	-	-	-
Ca%	0.15	0.11	-	-
K%	-	-	0.065	0.065
Mn	-	-	3.7	110
Cu	-	-	-	0.3
Sn	-	-	0.1	-
Dy	-	-	0.35	-
Mo	-	-	0.1	-

7.3 APPENDIX:3: ISOTOPES FOR COUNT 1-4

Table 2.14: Isotopes for count 1A

Isotope	Energy/Peak (KeV)	Half life
Pr-142	1575.5	19.20H
K-42	1524.7	12.42H
Ni-65	1481.7	2.54H
Na-24	1368	15.00H
Cu-64	1345.5	12.75H
Mn-56	846.8	2.58H
Eu-152M	841.4	9.30H
Ga-72	630.1	14.10H
Zn-69M	438.6	13.90H
Te-127	418	9.4H
Gd-159	363.5	18.00H
Ir-194	328.4	17.40H
Er-171	308.2	7.52H

Table 2.14 continued

Isotope	Energy/Peak (KeV)	Half life
Re-188	155	16.75H
Dy-165	94.7	2.3H
Pd-109*	88	13.50H
Ho-166	80.6	26.80
Pt-197*	77.3	18.00H

Table 2.15: Isotopes for count 1B

Isotope	Energy/Peak (KeV)	Half-life
La-140	1596	40.22H
K-42	1524.7	12.42H
Na-24	1368.4	15.00H
Sc-48(Ti)	983.5	1.83D
W-187	685.7	23.90H
Sb-122	564	2.80D
As-76	559.2	26.50H
Br-82	554.3	35.40H
Cd-115	527.7	53.50H
Au-198	411.8	2.70D
Yb-175	396.1	4.21D
Ce-143	293.2	33.40H
Pm-149(Nd)	285.8	53.10H
U-(Np-239)	277.5	2.38D
Au-199	158	3.2 D
Ca-47	160/1297	4.53D
Sc-47(Ca)	160	3.39D
Re-186	137	3.75D
Hg-197	134	23.90H
Sm-153	103.2	47.00H

Table 2.16: Isotopes for count 2

Isotope	Energy/Peak (KeV)	
Rb-86	1076.6	18.66D
Sn-125	1067	9.40D
Ba-131	496.3	12.00D
Au-198	411.8	2.7D
Lu-177	208	6.72D
Os-191	129.4	14.6D
Nd-147	91/531	11.06D

Table 2.17: Ta isotopes for flux monitoring.

Isotope	Energy/Peak (KeV)	Half-life
Ta-182	1231	115.00D
	1221.3	
	1189	

Table 2.18 Important short-lived isotopes.

Isotope	Half-life (min)	Energy/Peak (KeV)
Mg-27	9.5	170.7
Al-28	2.3	1779
V-52	3.8	1434
Ti-51	5.8	320
Cu-66	5.1	1039.2

Table 2.19: Isotopes for count 3

Isotope	Energy/Peak (KeV)	Half-life
Sb-124**	1691/603	60D
Eu-152**	1408/124	12.00Y
Co-60**	1332.4	5.26Y
Ta-182**	1221/67.8	115.00D
Fe-59	1099/1291	45.00D
Rb-86	1076.6	18.66D
Sc-46**	889.4	83.90D
Tb-160	879.3	72.10D
Ni(Co-58)**	810.8	71.30
Cs-134**	795.8/605	2.90Y
Zr-95**	756.9	65.50D
Ag-110M**	657.6	253D
Ru-103	610/497	36.90D
Sr-85**	514	64.00D
Hf-181	482	42.50D
Cr-51	320	27.80D
Ir-192**	316.5/468	74D
Th(Pa-233)	311.8	27D
Hg-203	279.2	46.80D
Ce-141	145.4	32.53D
Os-191	129.4	14.6D
Gd-153**	97.4/103.2	242D
Yb-169	63.5/198	32D

** indicates that the isotope can be counted later to improve counting statistics.

Table 2.20: Isotopes for count 4

Isotope	Energy/Peak (KeV)	Half-life
Zn-65	1115.5	244D
Se-75	264.7	120D
Co-57(Ni)	122	270D
Gd-153	97.4/103.2	242D
Tm-170	84.3	128.6D

7.4 APPENDIX:4: ANALYTICAL DATA

Table 3.1 Data for Finsch diamonds with silicate inclusions (in ppbw).

Element	FOG1	FOG2	FPG1	FPG2	FPG3	FPG4	FPG5	FOM1	FOC1
La	-	0.79	11.6	0.72	0.73	-	0.32	0.33	186
Ce	-	-	1062	-	-	-	279	148	-
Sm	4.26	3.74	5.12	1.25	0.48	0.02	0.009	0.009	-
Eu	0.29	0.2	-	-	-	-	-	-	-
Tb	0.11	0.06	-	-	-	-	-	-	-
Ho	0.79	0.35	-	-	-	-	-	-	0.07
Yb	2.2	0.87	-	0.85	-	-	-	-	-
Lu	1.28	0.55	-	0.78	-	-	-	-	-
Ca	243864	142295	-	-	-	-	-	-	-
Na	6442	3329	433	112	996	7.62	519	142477	701
K	12900	3041	6813	418	638	N/A	N/A	N/A	N/A
Cr	1201	463	131745	22319	50489	82817	68676	2929	399
Sc	132	65.9	321	67	291		350	68.7	36.3
Ga	45.3	25.2	-	18.7	-	-	-	-	-
As	-	-		-	-	-	2.08	-	-
Mn (counts)	4.4 E9	2.4 E9	5.5 E8	1.8 E8	8.3 E8	N/A	N/A	-	-
Fe	623000	354667	109233	30947	134300	131179	6882	18410	172838
Ni	812	1900	14057	991	1460	5600	569	3508	567
Co	243	165	434	61.8	177	257	82.5	225	69.0
Cu *	-	1.30 E5	2.2 E4	-	-	-	-	-	-
Au	-	0.15	0.25	-	-	-	-	-	-
Ir	-	-	3.8	0.12	0.21	-	-	0.14	-
W	-	-	3.7	-	-	-	2.11	-	-
RATIOS									
Cr/Sc	9.1	7.0	410	333	174	232	196	42.6	11
Mn/Fe	0.07	0.07	0.05	0.06	0.06	-	-	-	-
Ca/Cr	203	307	-	-	-	-	-	-	-
Au/Ir	-	-	0.066	-	-	-	-	-	-

Table 3.2 Data for Finsch diamonds with sulphide inclusions and inclusion free
Finsch diamonds (in ppbw).

Element	FS1	FS2	FIF1	FIF2	FIF3	FIF4	FIF5	FIF6	FB1
La	0.72	2.8	-	-	-	-	-	-	183
Ce	88.8	123	-	-	-	-	-	-	2795
Nd	-	-	-	-	-	-	-	-	24.5
Sm	0.01	0.002	-	-	-	-	-	-	0.17
Eu	0.007	0.004	-	-	-	-	-	-	0.06
Tb	-	-	-	-	-	-	-	-	0.27
Yb	0.03	-	-	-	-	-	-	-	1.12
U	-	-	-	-	-	-	-	-	0.04
Th	2.54	4.18	-	-	-	-	-	-	128
Na	1024	175	8.32	14.9	3.86	4.6	906	0.69	19245
Cr	370	117	15.3	10.2	-	-	50	32	2394
	10.4	0.61	-	0.4	0.71	-	1.76	5	58.5
K	-	-	-	-	-	-	41634	-	N/A
Ca	-	-	-	-	-	-	12190	9000	N/A
Mn (counts)	-	-	-	-	-	-	4.3 E7	-	N/A
Ba	-	143	-	-	-	-	-	-	1212
Cs	2.27	1.53	-	-	-	-	-	-	17.1
Br	8.9	3.17	2.8	-	-	-	-	-	359
Hf	0.03	-	-	-	-	-	-	-	0.15
W	21.5	4.42	3.82	1.45	-	-	-	-	16.1
As	-	0.07	-	0.18	-	-	-	-	5.10
Sb	0.14	0.06	-	-	-	-	-	-	0.34
Ta	1.56	0.71	-	-	-	-	0.39	0.61	3.20
Fe	12253	4642	-	-	-	213	8352	19035	83450
Ni	751	438	4844	-	-	620	687	3299	2585
Co	17	6.43	4.88	-	1.5	-	-	43.4	59.4
Au	-	0.06	9.8	0.9	0.03	-	-	-	0.12
Ir	-	0.15	-	-	-	-	-	-	0.12
RATIOS									
Cr/Sc	35.5	192	-	25.5	-	-	28	6.4	41

Table 3.3 Data for Premier diamonds with silicate inclusions (in ppbw).

Elements	POM1	POM2	POC1	PC1	PC2	PPG1
La	-	3.94	1.98	-	-	4.64
Ce	22.7	-	-	232	29	1.87
Sm	2.21	0.97	2.26	-	0.69	0.36
Eu	1.35	-	0.85	-	0.37	-
Tb	2.99	-	-	-	-	-
Yb	6.94	-	7.5	-	-	-
Lu	0.41	-	0.78	0.57	-	0.6
Ca	253020	N/A	1292282	N/A	145537	-
Na	69338	8079	13695	1528	25272	1084
K	-	3146	2043	133	2141	4785
Cr	4258	9510	3182	7874	5925	14075
Sc	106	251	447	10.6	0.55	51
Hf	4.91	-	-	-	-	-
As	-	1.02	-	-	-	-
Fe	350437	68284	604372	108470	308415	118470
Ni	3108	17270	1644	3551	6269	38025
Co	425	1003	667	253	557	974
Au	-	-	-	-	-	0.15
Ir	-	-	-	-	-	0.2
RATIOS						
Cr/Sc	40	38	7	743	10773	276
Ca/Cr	60	-	406	-	25	-
Co/Fe	0.001	0.01	0.001	0.002	0.002	0.01

Table 3.4 Data for Premier diamonds with sulphide inclusions (in ppbw).

Elements	PS1	PS2	PS3	PS4	PS5	PS6
La	-	-	-	0.42	30.6	1.64
Ce	-	-	-	-	66.6	9.22
Sm	0.33	0.13	-	-	0.18	0.16
Eu	0.18	0.09	-	-	-	0.11
Yb	5.26	-	-	-	-	-
Lu	0.54	-	-	-	-	-
Na	1020	3835	46	414	34.5	148
Cr	35.9	9.74	-	14	-	4.38
Sc	45.4	3.22	-	0.4	0.17	0.27
Rb	-	110	-	-	-	-
Ca	85.1	59.5	50.8	-	43981	-
K	-	25.2	-	-	701	923
As	-	-	-	-	0.48	-
Th	-	-	-	-	19.8	-
Fe	82378	12510	57171	83824		1092
Ni	-	310	14777	24698	200	109
Co	98.9	19.1	561	-	7.30	4.17
Cu	-	-	2997	4265	-	-
Au	0.9	0.44	0.47	0.1	0.26	-
Ir	0.25	0.1	0.11	0.024	0.06	-
RATIOS						
Cr/Sc	0.81	3	-	35	<1	16
Au/Ir	3.6	4.4	4.3	4.3	4.2	-
Fe/Fe+Ni	1.0	0.98	0.79	0.77	0.77	0.91

Fig.3.5 Data for diamonds from Romaria, Brazil (in ppbw).

Elements	D2	D3	D4	D5	D6	D7	D8	D9	D10
La	456	110	-	14.4	-	103	231	5.06	1.83
Ce	-	-	-	-	-	367	595	-	-
Sm	52	3.7	-	0.89	-	5.21	22.8	-	0.22
Eu	-	-	-	-	-	0.2	1.43	-	-
Tb	12.3	-	-	-	-	-	-	-	-
Yb	-	-	-	-	-	21.6	-	-	-
U	5.39	-	-	-	-	-	-	-	-
Th	21	105	-	-	-	7.72	-	15.3	-
Na	3722	-	4165	387	-	13.8	223	130	107
Ba	2767	4020	-	-	-	-	-	-	-
Cs	-	-	-	-	-	1.62	-	-	-
Cr	-	-	6.87	-	-	1.36	1.04	-	1.26
Sc	-	-	-	-	-	1.58	1.4	0.72	0.18
Br	3	7.03	0.58	0.46	-	8.28	6.49	3.39	-
Hf	-	-	-	-	-	1.53	-	-	-
W	-	7.4	-	-	-	1.72	0.21	-	-
As	4	12.2	0.8	-	1.08	1.68	-	-	-
Sb	-	-	-	-	-	1.79	-	-	-
Ta	4.19	-	-	-	-	3.32	-	5.59	-
Fe	-	-	43600	-	-	4200	12500	-	9800
Ni	715	-	3537	-	6577	4724	-	10039	-
Co	-	-	180	-	171	4.24	71.9	-	110
Au	0.04	0.04	0.002	0.06	0.0004	9	0.55	13.5	0.69
Ir	-	-	-	-	-	-	-	-	0.17
Cr/Sc	-	-	-	-	-	0.86	0.75	-	7

Table 3.6 Data for Brazilian diamonds with sulphide inclusions (in ppbw).

Elements	A1	A2	C1	B1
La	0.6	6.57	6.66	14.8
Ce	3.49	16.6	13	18
Sm	0.17	0.16	0.11	0.21
Na	90	164	95.8	68.9
Ba	-	1134	697	-
K	446	4595	3665	4111
Cr	2009	845	178	74
Sc	5.86	0.73	0.91	0.32
Hf	-	-	6.54	-
Zr	-	-	6470	-
Br	-	-	30	-
As	0.13	0.17	0.25	0.14
Th	-	-	-	0.94
Fe	5331	17047	22500	5543
Ni	1351	9514	18346	280
Co	19	160	202	11
Cu *	-	-	4600	-
Au	0.03	0.06	0.16	0.02
Ir	0.4	5.33	1.27	-
RATIOS				
Cr/Sc	343	1157	196	231
Au/Ir	0.075	0.011	0.126	-
Fe/Fe+Ni	0.8	0.64	0.55	0.95
Zr/Hf	-	-	989	-

* indicates that the value given is in counts because the element was not detected in the standards used and is included merely for comparison to the Premier diamonds with sulphide inclusions (see table 3.4).

Table 3.7: Data for diamonds from George Creek, Colorado (in ppbw).

Elements	GC1	GC2	GC3	GC5	GC6	GC7	GC8	GC9
La	972	1.82	825	-	-	-	7.3	33.5
Ce	5521	-	3511	-	-	-	-	401
Nd	54.1	-	30.6	-	-	-	-	-
Sm	99.4	-	73.1	-	-	-	0.24	6.7
Eu	7.45	-	4.72	-	-	-	-	1.18
Tb	27	-	19.3	-	-	-	-	-
Yb	88.1	-	-	-	-	-	-	-
U	33.3	-	-	-	-	-	-	-
Th	156	-	21.9	-	-	-	-	-
Na	3375	102	5639	2639	-	-	395	2347
Ba	2040	-	8007	-	-	-	-	-
Cr	0.94	53.7	0.81	70.5	-	-	-	-
Sc	11.7	-	4.08	0.49	-	-	-	6.34
Br	19.9	-	-	-	8.09	-	-	-
Hf	0.49	-	0.31	-	-	-	-	-
As	2.47	-	-	-	-	-	-	-
Ta	8.04	-	-	-	-	-	-	-
Fe	33900	5269	23500	8722	-	15236	-	14800
Ni	4216	4886	1246	1411	-	4750	-	4112
Co	252	248	47.4	33.1	14.6	112	10.7	179
Au	-	-	0.27	0.03	-	-	-	0.05
Ir	0.11	-	-	-	-	-	-	-
Cr/Sc	0.08	-	0.20	144				0.60

Table 3.8 Data for inclusion-free Chinese diamonds.

Element	CHJ2	CHJ17	CHA36
Na	4.64	5.55	3.4
Sc	0.5	0.26	1.28
Fe	1530	2973	-
Co	1.95	487	10.1
Ni	87	455	-
Au	0.03	-	-
Ir	-	0.13	-
RATIOS			
Co/Ni	0.02	1.07	
Fe/Ni	17.6	6.5	

7.5 APPENDIX:5: δC^{13} VALUES FOR THE 33 DIAMONDS ANALYSED

(SEE CHAPTER:5)

Table 5.1: δC^{13} values for the Chinese Diamond and the George Creek diamond.

Diamond	$\delta C^{13}(‰)$	Std. Deviation.	Type
CH2-ext.	-3.3	0.14	U
CH2-int.	-3.6	0.14	U
CH2-int.	-3.6	0.14	U
GC3	-16.4	0.12	E

The TYPE column indicates a peridotitic (P), eclogitic (E) or unknown (U) paragenesis.

Table 5.2 δC^{13} values for the Brazilian diamonds.

Brazilian diamonds.	$\delta C^{13}(‰)$	Std. Deviation	Type
A1-ext.	-3.2	0.14	P
A1-int.	-3	0.14	P
A2-ext.	-6.2	0.14	P
A2-int.	-5.9	0.14	P
B1-ext.	-3.9	0.14	P
B1-int.	-4	0.14	P
C1-ext.	-5.5	0.14	P
C1-int.	-5.7	0.14	P
D2-ext.	-5.3	0.14	U
D2-int.	-6.3	0.14	U
D3-ext.	-5.2	0.14	U
D3-int.	-4.1	0.14	U
D5-ext.	-5.2	0.14	U
D5-int.	-5.5	0.14	U
D6	-5.2	0.14	U
D8	-3.74	0.10	E

Table 5.3: δC^{13} values for the Premier diamonds with sulphide inclusions.

Premier diamond	$\delta C^{13}(‰)$	Std. Deviation.	Type
PS1-ext.	-4.9	0.14	E
PS1-int.	-4.6	0.14	E
PS2-ext.	-4.9	0.14	E
PS2-int.	-4.8	0.14	E
PS3-ext.	-4.4	0.14	E
PS3-int.	-4.5	0.14	E
PS4-ext.	-4.8	0.14	E
PS4-int.	-4.7	0.14	E
PS5-ext.	-4.8	0.14	E
PS5-int.	-4.5	0.14	E
PS6-ext.	-4.3	0.14	E
PS6-int.	-4.4	0.14	E

Table 5.4 δC^{13} values for Premier diamonds with silicate inclusions.

Premier diamond	$\delta C^{13}(‰)$	Std. Deviation.	Type
POM1-ext.	-4.0	0.14	E
POM1-int.	-4.1	0.14	E
POC1-ext.	-3	0.14	E
POC1-int.	-1.8	0.14	E
PC1-ext.	-4.7	0.14	P
PC1-int.	-5.1	0.14	P
POM2-ext.	-4.5	0.14	E
POM2-int.	-4.6	0.14	E

Table 5.5: δC^{13} values for the Finsch diamonds without visible silicate inclusions.

Finsch diamond	$\delta C^{13}(‰)$	Std. Deviation.	Type
FIF1	-4.14	0.1	U
FS1	-6.51	0.1	E
FS2	-4.55	0.1	P
FB1	-5.20	0.1	E

Table 5.6: δC^{13} values for the Finsch diamonds with silicate inclusions.

Finsch diamond.	$\delta C^{13}(‰)$	Std. Deviation	Type
FOG1-ext.	-7.7	0.14	E
FOG1-int.	-7.7	0.14	E
FOG2-ext.	-3.3	0.14	E
FOG2-int.	-3.4	0.14	E
FPG1-ext.	-5.9	0.14	P
FPG1-int.	-6.2	0.14	P
FPG2-ext.	-6.1	0.14	P
FPG2-int.	-6.4	0.14	P
FPG4	-4.51	0.11	P
FPG5	-4.20	0.11	P
	-5.90	0.11	E

The TYPE column indicates a peridotitic (P), eclogitic (E) or unknown (U) paragenesis.

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