



Research article

Diamond fingerprinting for source discrimination using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and Fourier transform infrared spectrometry (FTIR)

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ABSTRACT

The Kimberley Process Certification Scheme (KPCS) was established in 2000 as a means of controlling the flow of conflict diamonds, mostly, from the African continent. In 2013, the KPCS imposed an embargo on diamonds from the Central African Republic (CAR). Since then the embargo has been lifted in certain prefectures of the country, however, smuggling is suspected from non-compliant areas.

Three parcels of diamonds suspected to have mining origins in the CAR, were analysed. These diamonds were investigated for their morphological and chemical characteristics, to establish a diamond fingerprint and to determine if these diamonds had the same fingerprint as previously analysed diamonds from CAR or the Democratic Republic of the Congo (DRC). The analyses of these diamonds were included in the already established diamond database of rough diamonds from the African continent.

The morphological characteristics identified included the mass (ct), colour, surface coatings, dominant, secondary and tertiary form, shape, breakage, inclusions, abrasion and surface features that are specific to octahedral, dodecahedral and cubic shapes. The morphological characteristics determined from the diamonds revealed that morphology alone cannot be used as a discriminatory method for diamond fingerprinting.

Fourier transform infrared spectroscopy (FTIR) identified the nitrogen concentration and aggregation state of that N. This allowed for the typing of the diamonds as Type I (containing N) and Type II (containing no measurable N). The concentration of N in the three parcels is less than 600 ppm. Further classification of Type I diamonds was performed according to the N aggregation state as single, double or four-fold. The vast majority of diamonds show a combination of nitrogen aggregation states while few were classified as Type II. Fourier transform IR showed no discernible trends between the current study and the established database.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used as a means of determining the trace element concentrations of ⁶⁹Ga, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ²³²Th and ²³⁸U. Laser ablation ICP-MS determined that not all elements produce statistically viable data, however, the data could still be used to discern trace element differences and trends among the parcels. In the current set of diamonds, laser ablation ICP-MS data for parcels A and B showed an excellent agreement with each other as well as those from diamonds previously analysed from CAR. None of the three parcels showed any similarity to data from Bria River or the DRC. It is concluded that the diamonds from parcels A and B are very likely to have mining origins in the same area in the CAR, whereas parcel C is distinct and of possible mixed origin.

1. Introduction

Conflict minerals are those that are mined illegally and traded for profit to fund violence and armed conflict, predominantly on the African continent. Conflict minerals include coltan, cassiterite, wolframite, gold

and diamonds. Illicit trading comes at the expense of the legitimate governments and people of countries where conflict diamonds are sourced.

Currently, diamonds from the Central African Republic (CAR) are the only ones that are considered to have uncertain origins (M. van

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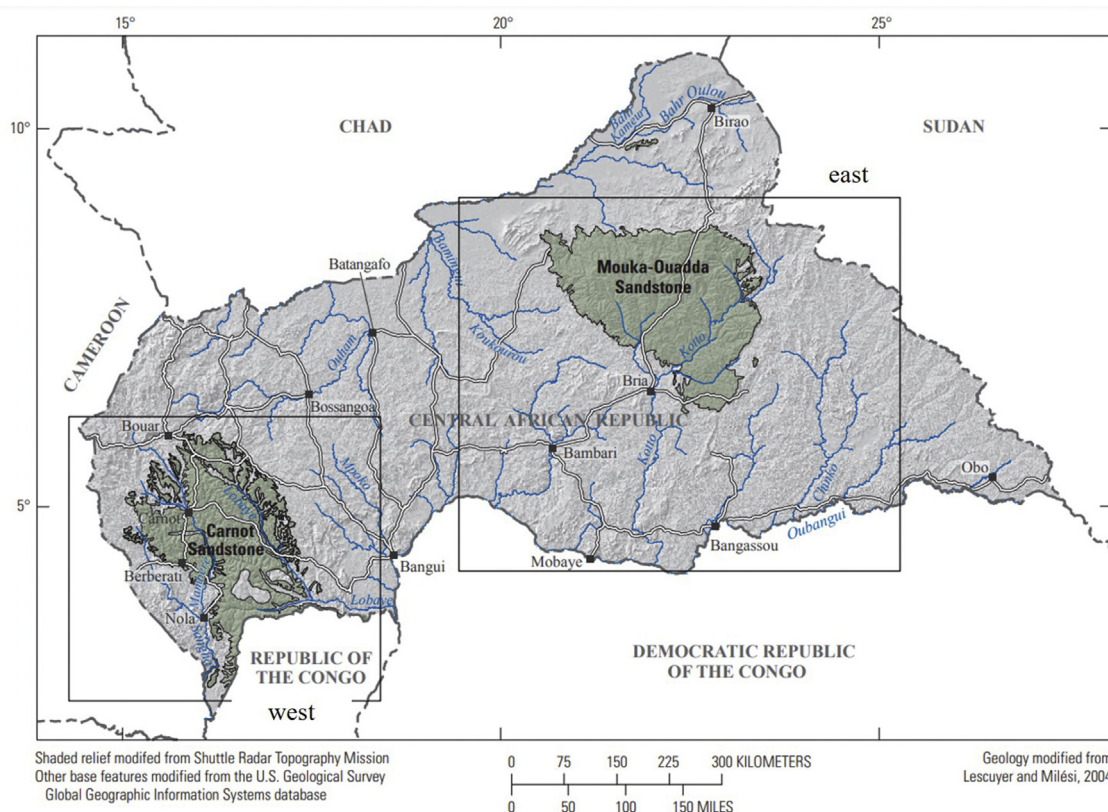


Figure 1. Locality map of the Central African Republic indicating the two diamondiferous areas of the country loosely referred to as “west” and “east” (Chirico et al., 2010).

Table 1. Diamond parcels previously analysed in the Mintek-SADPMR diamond provenance laboratory including geographical information. Parcel names in italics refer to parcels under discussion, noting that the DRC is discussed as the four parcels together.

Parcel Examined	Locality	Origin
<i>Longatshimo</i>	Southern Democratic Republic of the Congo	Alluvial
<i>Kanowa</i>		Alluvial
<i>Tshikapa</i>		Alluvial
<i>DRC1*</i>		Alluvial
Birim River	Ghana	Alluvial
<i>Bria River</i>	Central African Republic	Alluvial
Finsch	South Africa	Kimberlite
Helam		Kimberlite
Marsfontein		Kimberlite
Cullinan		Kimberlite
Welverdiend		Alluvial
Jagerfontein		Kimberlite
Williamson	Tanzania	Kimberlite
Orapa	Botswana	Kimberlite
<i>CAR E</i>	Central African Republic	Alluvial
<i>CAR W</i>		Alluvial
<i>Parcel A</i>	Central African Republic?	Alluvial
<i>Parcel B</i>		Alluvial
<i>Parcel C</i>		Alluvial
Total		

* The exact location of the DRC1 sample is unknown, however it has been confirmed to have the same signature of the other parcels from DRC.

Bockstael, personal communication). Alluvial diamond deposits in the CAR have been located from two diamondiferous areas based on their location within the country. These are roughly referred to as “west” and “east” as indicated in Figure 1. These areas are associated with the Carnot Sandstone in the Kadéi-Mambéré-Sangha region in the west of the country and the Mouka-Ouadda Sandstone in the Haute-Kotto region in the east of the country (Chirico et al., 2010). Diamonds are derived from a thick succession of flat-lying Mesozoic sandstones and conglomerates, which, in the wetter western region, are concentrated in stream and river valleys, and in the dryer eastern region are more dispersed in colluvial deposits resulting in skarp retreat (Janse and Sheahan, 1995). Diamond indicator minerals have not been found in these diamond producing areas, suggesting that the source of the diamonds is elsewhere. This has been suggested as the Congo Craton to the south of the CAR.

The Kimberley Process Certification Scheme (KPCS) was established in 2000 when diamond-producing countries met to discuss ways to stop the flow of conflict diamonds. In addition, these member states wanted to ensure that conflict diamonds did not fund rebel groups on the African continent. The KPCS was established to frame a set of rules for controlling rough diamond production and trade (www.kimberleyprocess.com). Under the auspices of the KPCS, Mintek, in South Africa, established a diamond provenance laboratory in conjunction with the South African Diamond and Precious Metals Regulator (SADPMR) in 2008. This laboratory was established to collate physical and chemical characteristics of diamonds sourced from the African continent into a database. This would allow for the analysis of diamonds from unknown and/or dubious localities to be analysed and matched to an area already within the database.

In 2013, the KPCS imposed an embargo on diamonds from the CAR (Gridneff, 2015), owing to a violent coup and civil unrest (Idriss, 2014), in which various factions appear to have benefited from the country’s diamonds. Oakford (2015) notes that armed groups earn as much as

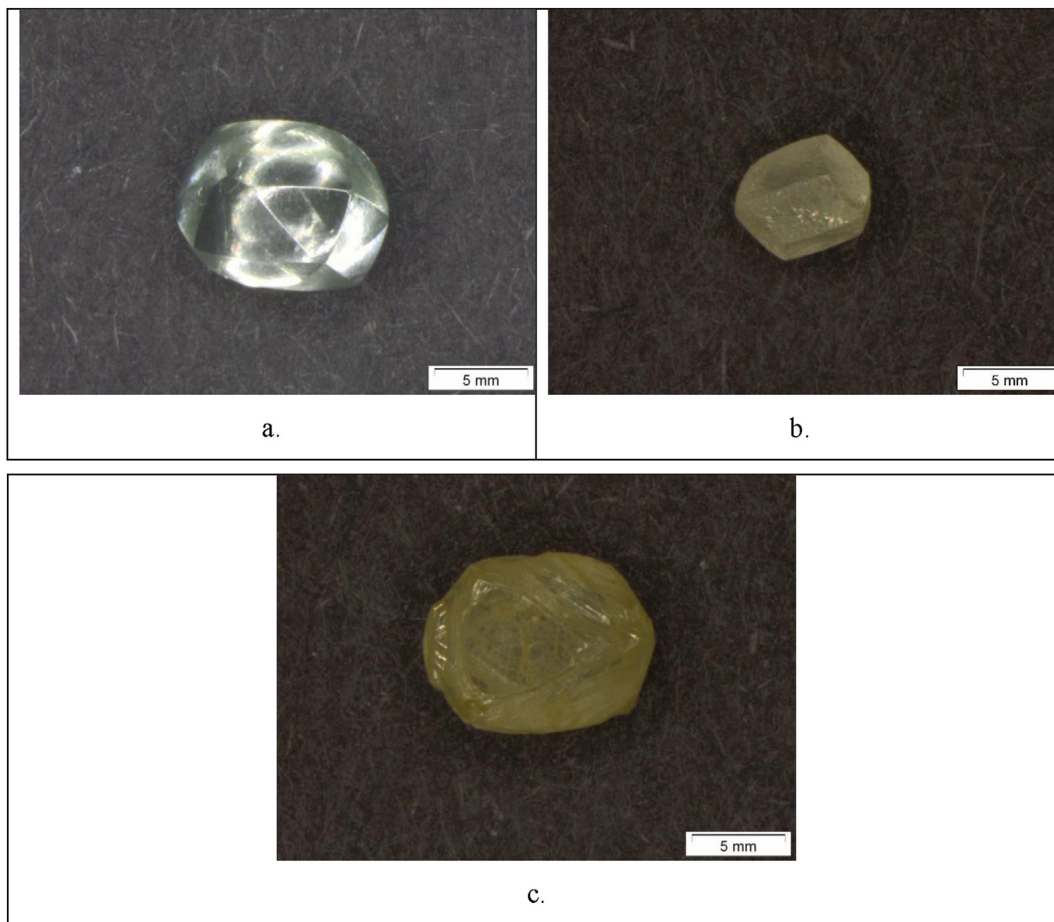


Figure 2. (a) White dodecahedral diamond from parcel A; (b) white, frosted dodecahedral diamond from parcel C and (c) yellow dodecahedral diamond from parcel B indicating terraces, brown spots and cracks.

US\$5.8 million annually from the mining and sale of diamonds and illegal taxation in that country. Additionally, despite the embargo, an estimated 140 000 carats of diamonds, worth US\$24 million, have been smuggled out of that country (Idriss, 2014). In continued efforts between the CAR government and the KPCS, the embargo on the CAR was lifted.

However, this was only partial to the western mining area as the eastern mining zones are still under rebel control. The prefectures of Boda, Carnot, Nola, Berberati and Gadzi have to date been declared compliant (Arief and Husted, 2016; Graff, 2016) and only diamonds from these areas may be released into the legitimate trade.

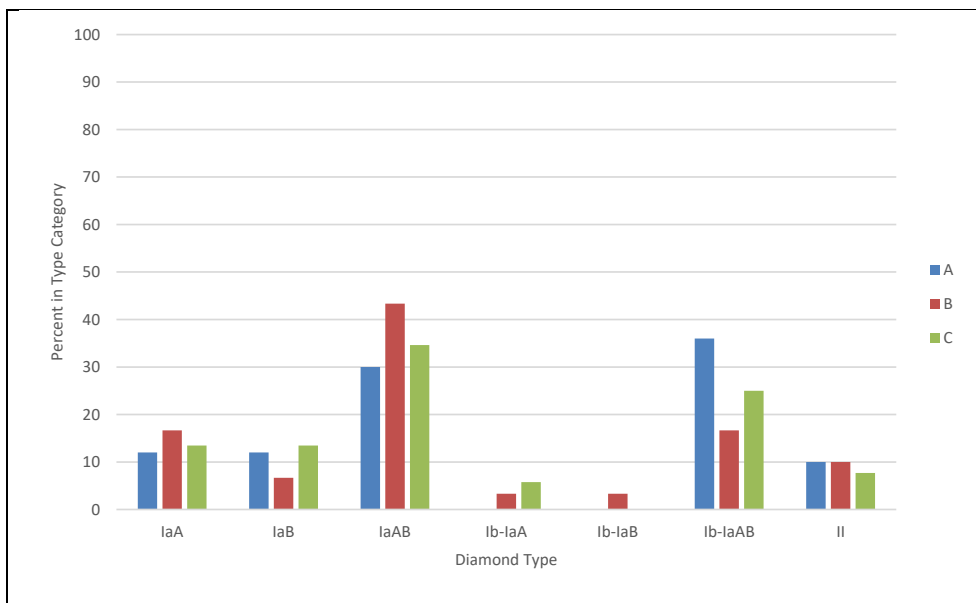


Figure 3. Percentage of diamonds in each Type category.

Table 2. Mean, 1 sigma error, median, mean MDL, number of outliers and %>MDL for parcel A. Italicised text indicates statistically insignificant data.

Elemental Isotope	Mean (ppm)	1 σ error (ppm)	Median (ppm)	Mean MDL (ppm)	% Outliers	%>MDL
⁶⁹ Ga	1.06	0.270	0.165	0.241	17	41
⁸⁸ Sr	33.2	5.05	0.666	0.155	17	76
⁸⁹ Y	2.92	0.778	0.113	0.0698	16	66
⁹⁰ Zr	12.3	1.89	0.273	0.0880	19	73
⁹³ Nb	1.18	0.210	0.0580	0.0509	15	46
¹³³ Cs	0.205	0.172	0.139	0.320	7	11
¹³⁷ Ba	33.1	5.05	1.24	0.437	21	66
¹³⁹ La	70.9	10.9	1.51	0.0509	19	78
¹⁴⁰ Ce	10.6	15.0	2.0650	0.0502	15	81
¹⁴¹ Pr	8.02	1.25	0.207	0.0457	16	71
¹⁴⁶ Nd	22.3	3.86	0.845	0.192	18	75
¹⁴⁷ Sm	3.17	0.665	0.192	0.253	13	49
¹⁵³ Eu	0.493	0.116	0.0668	0.0951	17	44
¹⁵⁷ Gd	1.81	0.506	0.299	0.515	14	41
¹⁵⁹ Tb	0.219	0.0572	0.0343	0.0503	14	47
¹⁶³ Dy	1.02	0.220	0.128	0.165	15	47
¹⁶⁵ Ho	0.162	0.0426	0.0314	0.0476	15	42
¹⁶⁶ Er	0.463	0.139	0.0758	0.126	12	44
¹⁶⁹ Tm	0.0846	0.0343	0.0255	0.0528	11	30
¹⁷² Yb	0.554	0.171	0.132	0.207	13	39
¹⁷⁵ Lu	0.0919	0.0413	0.0262	0.0633	11	19
¹⁷⁸ Hf	0.532	0.177	0.0915	0.135	13	44
¹⁸¹ Ta	0.107	0.0468	0.0382	0.0734	12	33
²³² Th	9.14	3.12	0.175	0.0373	17	75
²³⁸ U	0.310	0.0979	0.0518	0.0817	18	37

Table 3. Mean, 1 sigma error, median, mean MDL, number of outliers and %>MDL for parcel B. Italicised text indicates statistically insignificant data.

Elemental Isotope	Conc. (ppm)	1 σ error (ppm)	Median (ppm)	Mean MDL (ppm)	% Outliers	%>MDL
⁶⁹ Ga	0.890	0.228	0.136	0.242	18	33
⁸⁸ Sr	32.3	4.26	0.221	0.154	18	59
⁸⁹ Y	2.47	0.349	0.114	0.0676	18	63
⁹⁰ Zr	4.12	0.528	0.305	0.0948	17	73
⁹³ Nb	0.972	0.220	0.0240	0.0544	16	40
¹³³ Cs	0.142	0.129	0.105	0.237	2	13
¹³⁷ Ba	26.3	4.81	0.580	0.401	17	64
¹³⁹ La	99.3	17.8	0.345	0.0546	16	81
¹⁴⁰ Ce	94.5	14.5	0.763	0.0548	18	80
¹⁴¹ Pr	11.3	1.51	0.140	0.0479	18	67
¹⁴⁶ Nd	35.1	4.81	0.536	0.187	19	63
¹⁴⁷ Sm	4.14	0.821	0.196	0.243	18	46
¹⁵³ Eu	0.753	0.195	0.0615	0.0947	13	38
¹⁵⁷ Gd	2.38	0.685	0.314	0.486	17	34
¹⁵⁹ Tb	0.264	0.0551	0.0301	0.0511	13	33
¹⁶³ Dy	1.13	0.233	0.120	0.166	17	44
¹⁶⁵ Ho	0.161	0.0452	0.0334	0.0477	11	34
¹⁶⁶ Er	0.394	0.0964	0.0805	0.126	12	32
¹⁶⁹ Tm	0.0737	0.0320	0.0317	0.0539	12	30
¹⁷² Yb	0.315	0.129	0.120	0.213	8	20
¹⁷⁵ Lu	0.0602	0.0314	0.0292	0.0607	10	24
¹⁷⁸ Hf	0.294	0.0895	0.0748	0.128	13	37
¹⁸¹ Ta	0.119	0.0567	0.0372	0.0726	8	21
²³² Th	2.26	0.610	0.166	0.0436	14	79
²³⁸ U	0.178	0.0680	0.0532	0.0958	13	32

Table 4. Mean, 1 sigma error, median, mean MDL, number of outliers and %>MDL for parcel C. Italicised text indicates statistically insignificant data.

Elemental Isotope	Mean (ppm)	1 σ error (ppm)	Median (ppm)	Mean MDL (ppm)	% Outliers	%>MDL
⁶⁹ Ga	0.436	0.312	0.233	0.528	19	24
⁸⁸ Sr	2.10	0.698	0.236	0.331	15	40
⁸⁹ Y	1.96	0.676	0.0950	0.143	13	33
⁹⁰ Zr	5.26	1.29	0.197	0.200	13	53
⁹³ Nb	0.740	0.258	0.0347	0.116	8	28
¹³³ Cs	0.307	0.273	0.191	0.477	13	10
¹³⁷ Ba	4.59	1.66	0.625	0.904	19	40
¹³⁹ La	6.24	2.00	0.0900	0.107	22	49
¹⁴⁰ Ce	10.1	3.26	0.123	0.105	19	56
¹⁴¹ Pr	1.10	0.373	0.0800	0.0988	15	47
¹⁴⁶ Nd	3.52	1.22	0.288	0.363	12	47
¹⁴⁷ Sm	0.876	0.428	0.269	0.489	7	29
¹⁵³ Eu	0.213	0.131	0.0983	0.194	10	25
¹⁵⁷ Gd	1.05	0.691	0.459	0.974	11	23
¹⁵⁹ Tb	0.154	0.0919	0.0610	0.106	10	35
¹⁶³ Dy	0.615	0.305	0.191	0.335	11	30
¹⁶⁵ Ho	0.147	0.0818	0.0510	0.0998	9	29
¹⁶⁶ Er	0.387	0.224	0.132	0.256	11	24
¹⁶⁹ Tm	0.104	0.0709	0.0550	0.113	10	21
¹⁷² Yb	0.515	0.300	0.220	0.411	9	25
¹⁷⁵ Lu	0.116	0.0842	0.0559	0.125	11	22
¹⁷⁸ Hf	0.423	0.223	0.160	0.248	8	34
¹⁸¹ Ta	0.124	0.100	0.0670	0.157	15	15
²³² Th	0.414	0.224	0.0577	0.0829	19	39
²³⁸ U	0.166	0.114	0.0937	0.188	15	19

In this study, a sample of three parcels were examined. The purpose of this investigation was to determine if these diamonds were also from CAR by comparing them to previously-analysed parcels from that country as well as other countries in the database, specifically the Democratic Republic of the Congo (DRC), as the CAR and DRC share a border.

2. Previous studies

Coney et al. (2012), describe diamond discrimination studies from a physical and chemical perspective from as early as 1975, when Harris

et al. (1975) tried to discriminate diamonds from various mines in central and west Africa. They further note that studies of impurities have taken place since the same time when Fesq et al. (1973) and Erasmus et al. (1977) used Instrumental Neutron Activation Analysis (INAA) to measure major, minor and trace element impurities in diamonds. Erasmus et al. (1977) discussed chemical content application for source discrimination, and found that some source discrimination was possible. Stemming from this, the application of laser ablation inductively-coupled mass spectrometry (LA-ICP-MS) to detect and measure a suite of trace elements in diamonds was published by Watling et al. (1995). This was further

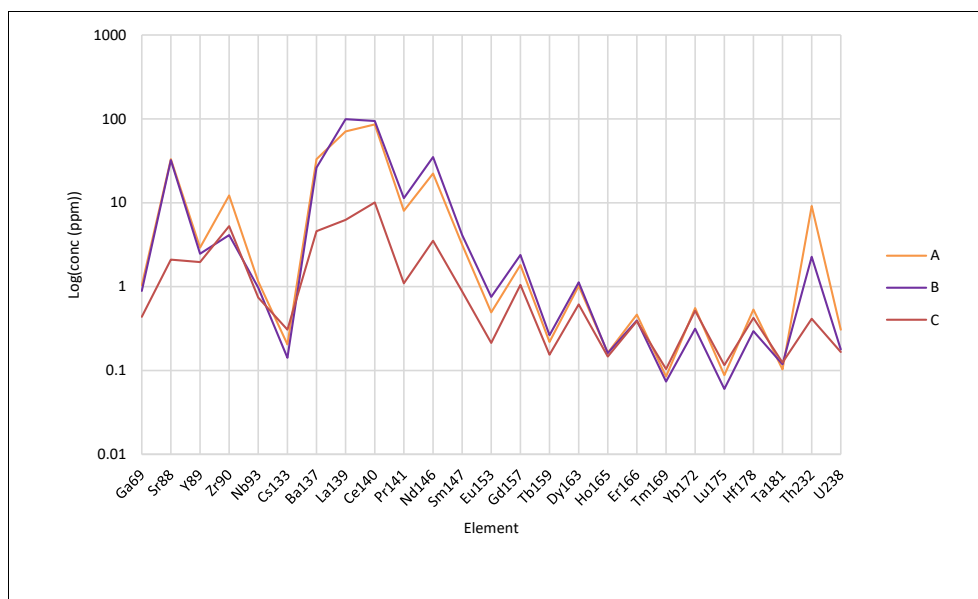


Figure 4. Log concentration of average trace elements per parcel.

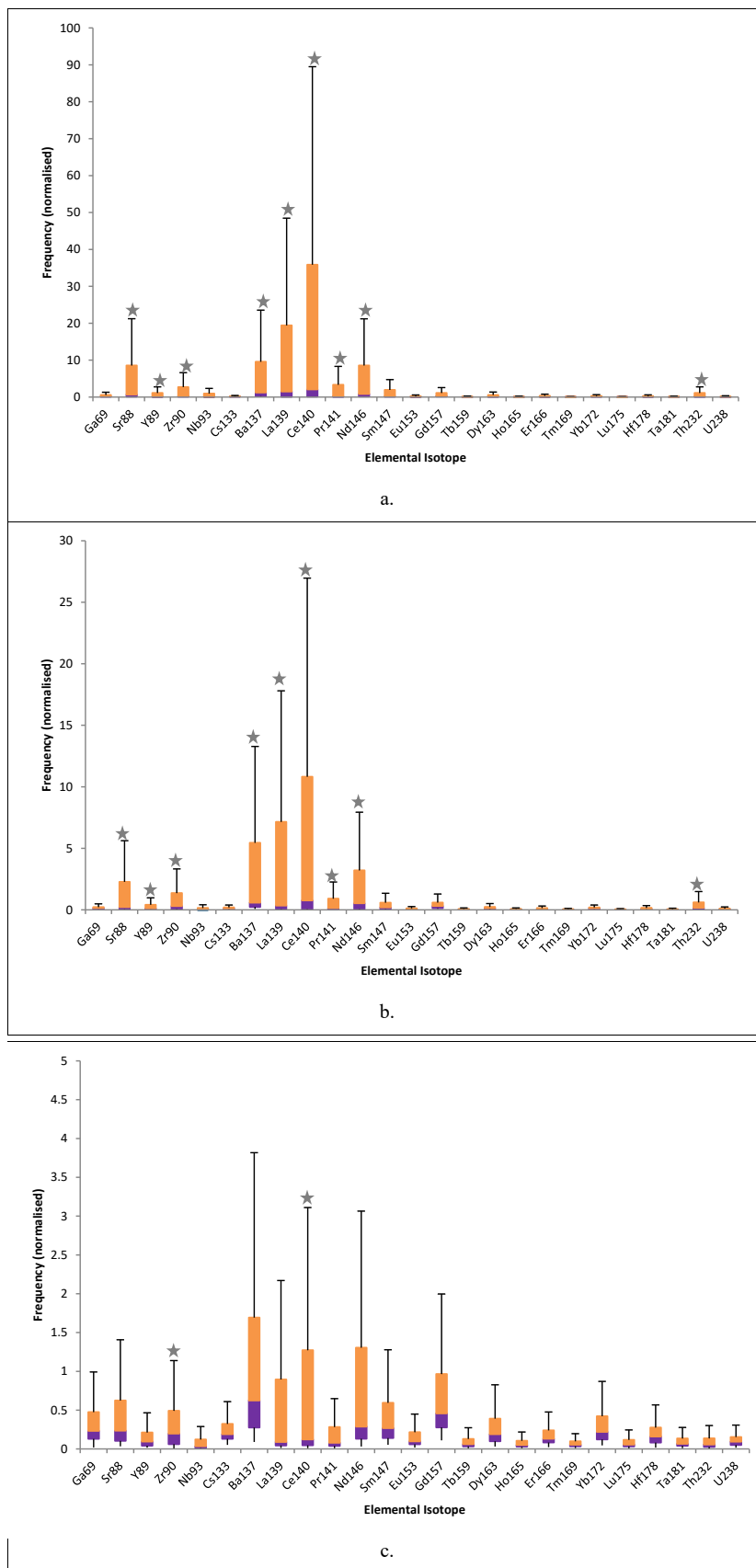


Figure 5. Box and whisker plot of the elemental concentrations obtained in diamonds from (a) parcel A, (b) parcel B and (c) parcel C. Stars indicate elements that returned a concentration above MDL in more than 50 % of diamonds, not including outliers.

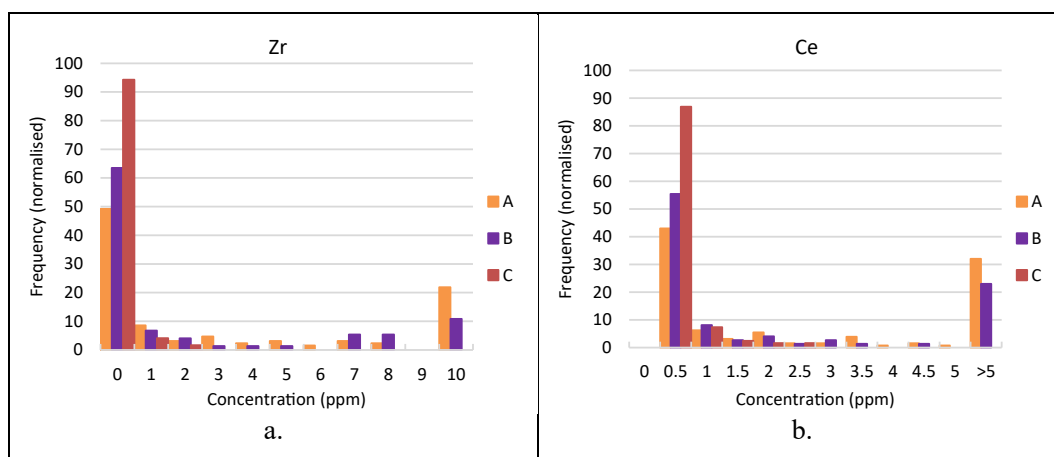


Figure 6. Normalised frequency histogram of the concentrations of (a) Zr and (b) Ce in the three parcels.

refined by Resano et al. (2003) who also concluded that discrimination may be possible. Rege et al. (2005) were responsible for the development of standards for LA-ICP-MS analysis to ensure that matrix-matched analytical protocols were implemented, while McNeill et al. (2009) adapted the methodology to ensure the lowest detection limits possible (Coney et al., 2012). Dalpé et al. (2010) reported specifically on statistically robust forensic diamond discrimination. The conclusion from that study was that discrimination is possible, however, large enough data sets need to be produced and utilised to ensure convincing discrimination.

Since its inception, 1087 diamonds have been examined for their fingerprints in the Mintek-SADPMR diamond provenance laboratory (Table 1). Physical characteristics are described, Fourier Transform Infrared spectrometry (FTIR) is used to establish nitrogen concentration and aggregation, and (LA-ICP-MS) is applied to measure trace element concentration. Diamonds have been analysed from South Africa, southern Democratic Republic of the Congo (DRC), CAR, Ghana, Tanzania and Botswana. The results of the above studies provide inputs for the discrimination database from each country. Those of the DRC and CAR will be discussed as these will be compared to the diamonds from the present study.

General characteristics of diamonds from the DRC (Longatshimo, Kanowa, Tshikapa and DRC1), Bria River, CAR E and CAR W from the diamond provenance database are summarised as follows. Diamonds from the DRC display three colours: colourless, brown and yellow, with colourless stones being predominant. The dodecahedral form is the dominant shape over octahedral. The diamonds contain inclusions of graphite, sulfides, and other coloured mineral inclusions. The physical features of diamonds from Bria River and CAR E and W indicate a predominance of brown colours with a few exhibiting green irradiation spots. The dominant shape is dodecahedral and a variety of inclusions were identified in these diamonds.

The FTIR results of diamonds from Bria River, CAR E and CAR W indicate no distinct relationship between the percentage of aggregation and total concentration of N. Further, the concentration of N measured varied from below detection limit to ~570 ppm in the CAR parcels. The FTIR trends revealed from diamonds from DRC indicate that those diamonds contained up to 4000 ppm N and the degree of aggregation is generally less than 80 %.

The trace element distributions of diamonds from CAR E and CAR W, Bria River and DRC show distinct trends. That of DRC is the least enriched in terms of trace elements. The trend of Bria River is also less enriched for the lightest and heaviest trace elements but in the same range for the mid-mass elements. Finally, the parcels of CAR shows two distinct trends – one in the same range as others from Bria River and one that shows a depletion in trace elements.

3. Methodology

Diamond fingerprinting is a three-stage process that identifies the physical and chemical characteristics of these minerals. All diamonds that are brought for fingerprinting undergo the same processes. Equipment utilized is housed in a clean, dust-free, temperature- and humidity-controlled environment.

The purpose of this investigation was to determine if a set of diamonds displayed the same fingerprint as previously analysed parcels from the CAR as it believed that the CAR was the origin of these diamonds.

3.1. Morphological observation

Morphological classification took place using an Olympus SZX16 stereomicroscope under cold light and various magnifications, connected to an Olympus UC300 digital camera and desktop computer. The analysis Olympus imaging software package was used for capturing photographs of individual diamonds and surface features of interest. Morphological characteristics including colour, shape, surface coatings, defects, breakage, inclusions and breakage were identified and collated in an Excel spreadsheet.

3.2. Fourier Transform Infrared spectrometry (FTIR)

A Varian 640-IR FTIR and 610-IR microscope were employed to determine concentrations and aggregation states of N of each diamond. The FTIR was operated at a resolution of 4 cm^{-1} over a spectral range of $4000\text{ to }700\text{ cm}^{-1}$. Each diamond was attached to the edge of a glass slide using Prestik to allow for transmitted light analysis with no substrate interference. The diamonds were analysed once each whereby each analysis undertook 50 scans on background and 50 scans per diamond. The detection limit for nitrogen is 20 ppm (Kaminsky and Khachatryan, 2001).

Following analysis of all diamonds, the results were baselined in the Resolutions Pro software programme and then processed for the N concentrations and aggregation states using an in-house deconvolution programme developed by the Measurement and Control Division at Mintek, specifically for the Varian 640-IR, based on software provided by Dr David Fisher (DTC Research Centre, Maidenhead). The deconvolution software normalises the spectrum for thickness, removes the two-photon energy tail and decomposes the resultant spectrum into various nitrogen curves (Coney et al., 2012). Absorption coefficients for the IaA and the IaB forms are from (Boyd et al. 1994, 1995; Coney et al., 2012). The thickness absorbance factor is calculated at 1992

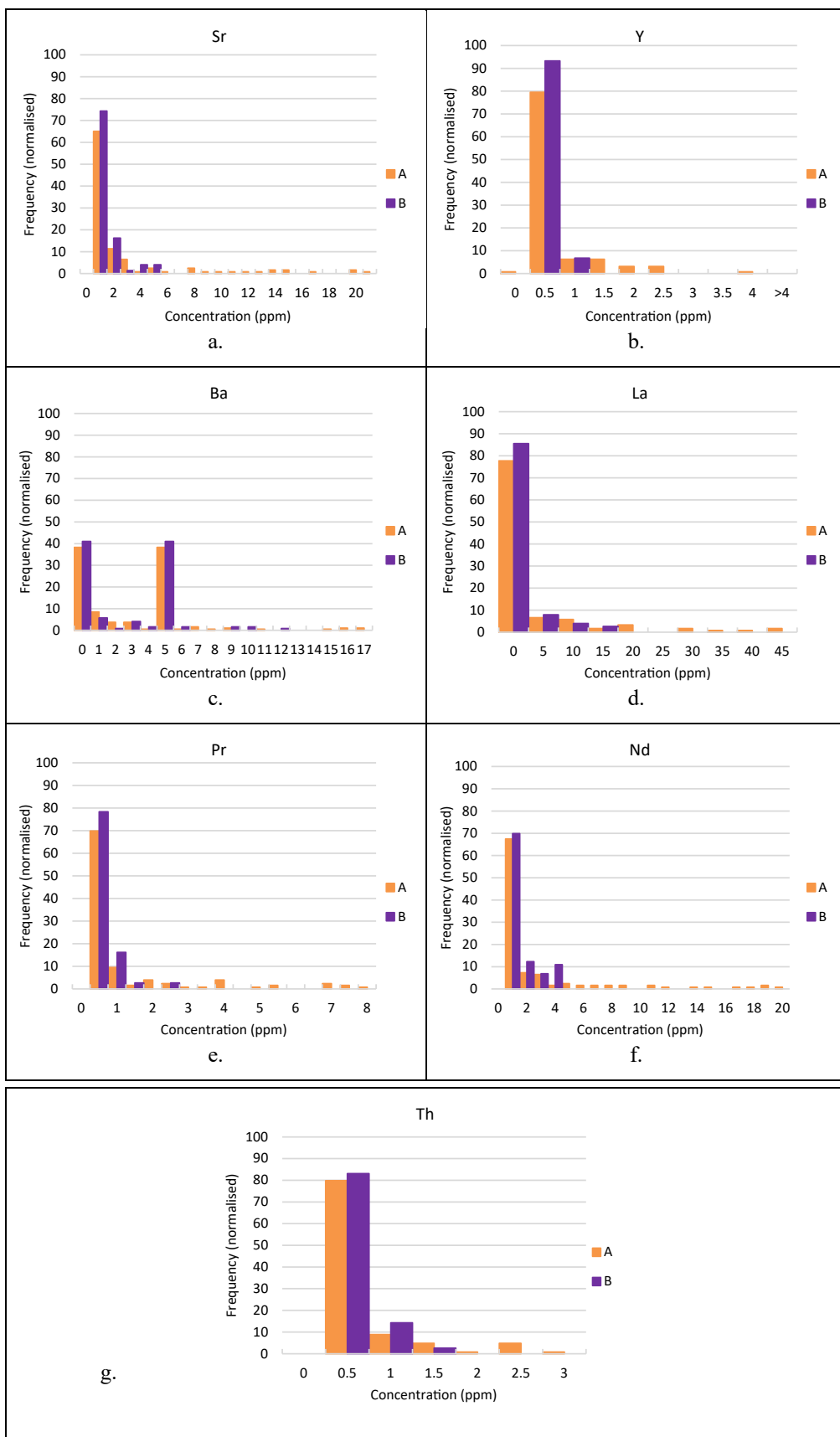


Figure 7. Normalised frequency histogram of the concentrations of (a) Sr, (b) Y, (c), Ba, (d), La, (e) Pr, (f) Nd and (g) Th in parcels A and B.

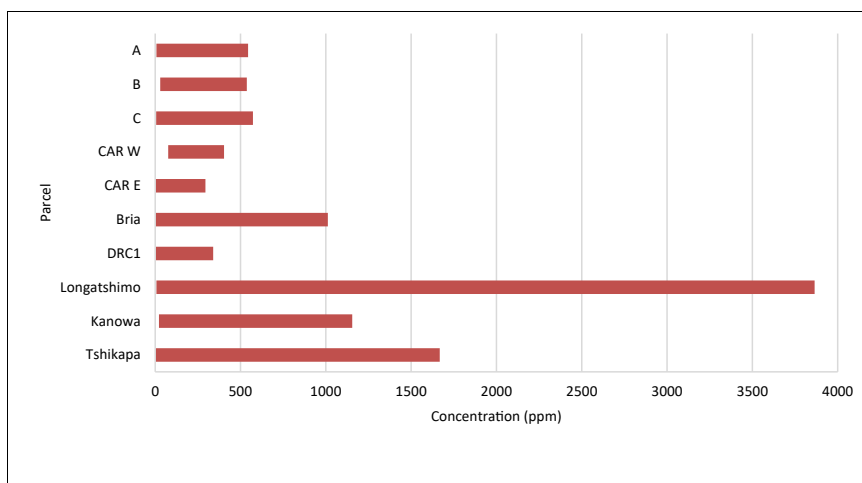


Figure 8. Total concentration range of nitrogen (ppm) in diamonds from parcels A, B and C compared to those previously analysed from CAR, Bria River and the DRC.

cm^{-1} while hydrogen peak areas, platelet peak areas and position were determined directly from the spectra (Coney et al., 2012).

3.3. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

The Diamond Provenance Laboratory houses a New Wave Research 193 nm ArF Excimer LA system coupled to a Thermo Element XR ICP-MS. Tube connections between the laser and the ICP-MS make use of Tygon tubing from Saint-Gobaine and these were changed in between each parcel analysis to mitigate contamination effects. Three spots were ablated per diamond with a spot size of 100 μm at 8 mJ laser energy and 10 Hz repetition rate. A platinum sampler and skimmer cone were utilised in the ICP-MS. Cooling, auxiliary, sample and carrier gases flowed at 16, 0.8, 0.95 and 0.5 L/min, respectively. Backgrounds were monitored to ensure maximum stability of the instrument before tuning on the first reference material (RM; in this case, the National Institute of Standards (NIST) 614 glass standard, utilizing the values of Pearce et al., 1997) and subsequent ablation of the diamonds.

Prior to ablation, all diamonds were cleaned in individual Savilex containers according to the method described by Rege et al. (2005). Following this, the diamonds were only handled with gloves, disposable tweezers and/or lint-free wipes.

Two external standards were used during the analyses: the calibration material (CM) was a synthetic carbon vapour deposited (CVD) diamond purchased from Element Six Technologies and the second RM was a doped multi-element cellulose pellet developed by Rege et al. (2005). The CVD was further utilised to determine gas blanks. The NIST614 glass standard was used as the quality control (QC) RM to determine the repeatability/accuracy of the LA-ICP-MS sequence and to monitor instrument drift. The ^{13}C isotope was used as the internal standard for data reduction.

Instrument warm-up, ablation and washout times were kept to 40, 90 and 60 s, respectively. This was the method employed by Coney et al. (2012) and used for consistency with analyses. The ^{13}C , ^{69}Ga , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{133}Cs , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{232}Th and ^{238}U isotopes were selected as those of interest. These were identified by Coney et al. (2012), Rege et al. (2005; 2010), Weiss et al. (2008) and McNeill et al. (2009) as being present in significant proportions.

Analysis took place using the bracketing technique whereby five diamonds were “bracketed” by the RM, QC and CM. Following the method of Coney et al. (2012):

- Data reduction took place offline using the GLITTER software package to realise the initial concentration (ppm), 1 sigma errors (1σ) and minimum detection limit (MDL) values for each elemental isotope in each spot analysis.

$\text{MDL} = 2.3\sqrt{(2B)}$ and B is the total counts in the background interval selected in GLITTER (Longerich et al., 1996). The MDL data, at the 99% confidence level, were determined by Poisson counting statistics.

- Data were examined in Excel and using the QI Macros add in.
- Where initial concentrations were determined to be below the MDL of each spot analysis, a fraction of the MDL (in this case MDL/2) was used as the initial concentration in calculating average concentrations, as per the method of the Analytical Methods Committee (2001) and Winderbaum et al. (2012).
- Blank values determined by ~ 100 analyses on the CVD were subtracted from the initial concentration to account for elemental interferences on ^{69}Ga , ^{90}Zr , ^{93}Nb , ^{175}Lu , ^{181}Ta , ^{232}Th and ^{238}U . This produced the final concentration (per spot analysis) used for statistical analysis.
- The MDL of each spot analysis was subtracted from the final concentration of each spot analysis to determine how many final concentration values were above the MDL. Only if more than 50% of all spot analyses for a given element in a parcel were above MDL, was the elemental concentration considered to be statistically significant for that parcel.

4. Results

4.1. Morphology

The morphological results are purely descriptive in nature as these do not form a definitive comparison when assessing parcels from various regions. When considering the diamonds from all three parcels, the diamonds are predominantly white in colour (42.4%; Figure 2a). There are also a fair number of yellow diamonds noted at 28% while brown and green diamonds comprise 15% each. The primary form determined is dodecahedral, which was noted in 79% of the diamonds (Figure 2a). The remaining 21% comprises octahedral

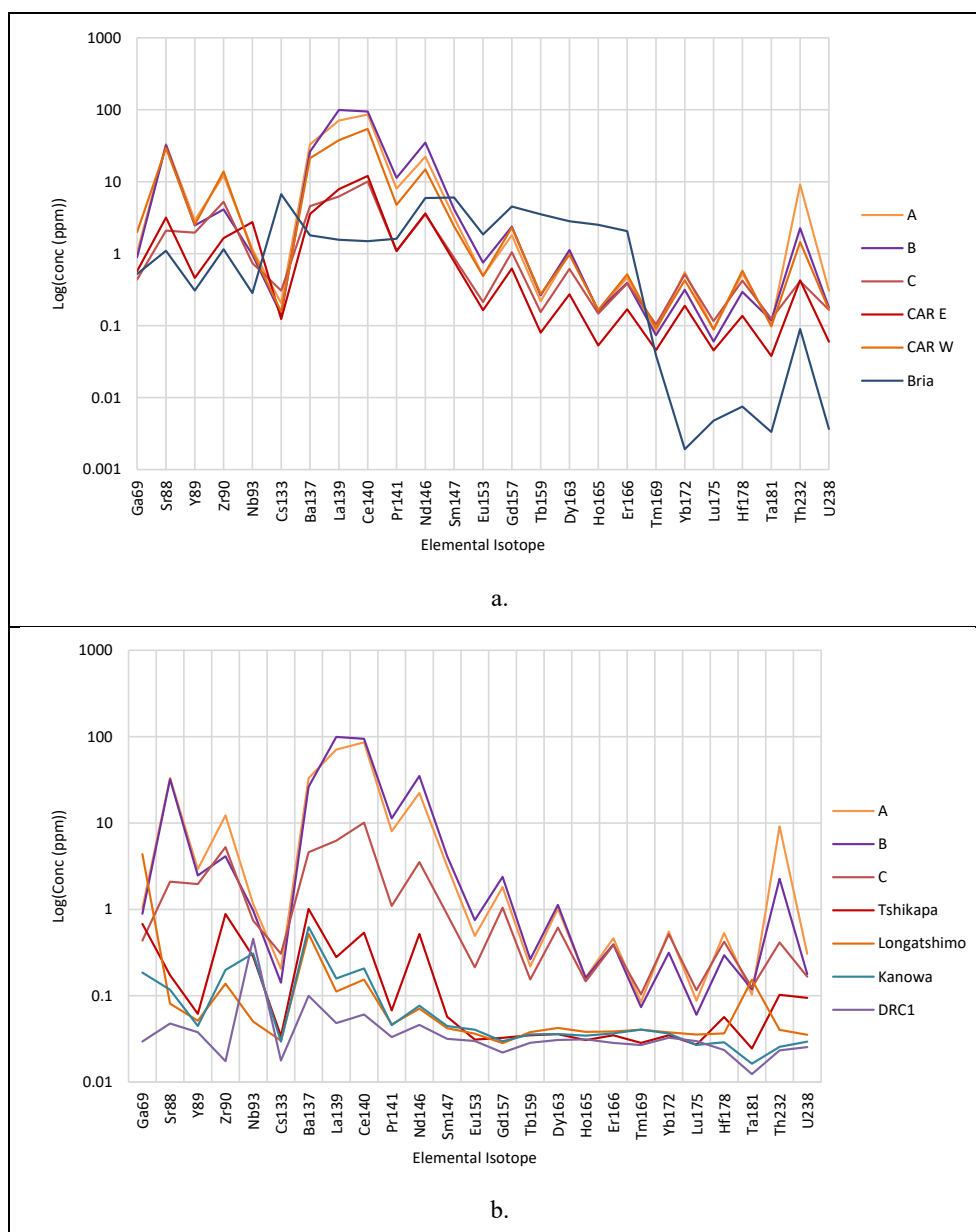


Figure 9. Average concentrations (ppm) of the trace elements in diamonds from (a) parcels A, B and C compared to that analysed from the Central African Republic (CAR E and CAR W) and Bria River and (b) Democratic Republic of the Congo (Tshikapa, Longatshimo, Kanowa and DRC1).

and agglomerate-shaped diamonds. Sand particles, frosting (Figure 2b) and coloured spots (green, brown and black) are very common across the parcel however, inclusions are not – between 65 and 77 % of the diamonds were noted to contain no inclusions. Where present, inclusions range from singular or mixed and are black, colourless, brown and orange. Despite the diamonds having alluvial origins, 50 % of the entire parcel contains no surface abrasion – the remaining 50 % reveal abrasion on lines, points and faces. The most common surface features of the diamonds are terraces (Figure 2c), deformation lines, hillocks and trigons. A multitude of surface features were identified, however, these do not allow any discrimination between parcels.

4.2. Nitrogen concentration and aggregation states

Most diamonds show absorption in the mid-infrared range (IR) due to substitutional impurities (Anon, n.d.). Nitrogen is incorporated in the

diamond lattice as single (Type Ia), double (Type IaA) or double-double atoms (Type IaB) (aggregation state) substituting for carbon during diamond growth resulting in an effect on a diamond's appearance. Nitrogen may also be unaggregated resulting in Type Ib. The majority of diamonds with N in their crystal lattice reveal combinations of aggregation states, for example Type IaAB. Fourier transform IR is responsible for determining whether or not diamonds contain N, the aggregation state of the N as well as the concentration of N. A diamond that contains no detectable N is classified as Type II.

The maximum concentration of N determined from the three parcels is between 544 and 572 ppm, while the minimum is 5.4ppm (Figure 3a). Close inspection of the full data set shows that the concentration of N in six diamonds across the parcels is less than 20 ppm (detection limit of FTIR, Kaminsky and Khachatryan, 2001).

The percentage of diamonds in each Type category have been highlighted in Figure 3. The image indicates that in each sub-parcel, the majority of stones are Type IaAB and Ib-IaAB, i.e. that they have a mixed

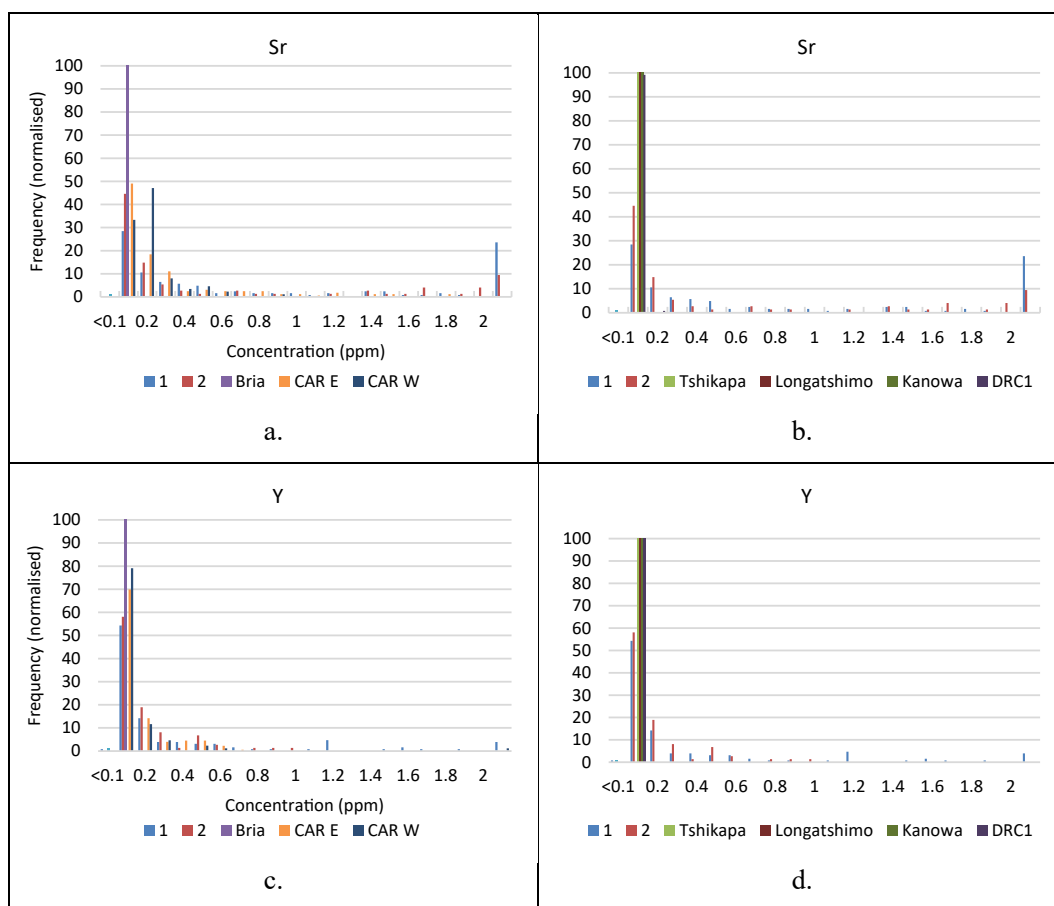


Figure 10. Normalised frequency histograms of the concentration of (a) Sr comparing parcels A and B to Bria River, CAR E and CAR W; (b) Sr comparing parcels A and B to Tshikapa, Longatshimo, Kanowa and DRC1; (c) Y comparing parcels A and B to Bria River, CAR E and CAR W; and (d) Y comparing parcels A and B to Tshikapa, Longatshimo, Kanowa and DRC1.

N aggregation state. Further, less than 20% of stones from each parcel report to the Type IaA and IaB categories and have either double or double-double aggregation states. No diamonds comprise N in the Type Ia category as singly aggregated N. At most 10% of diamonds from each parcel are classified as Type II and very few comprised aggregated and unaggregated N and report to the Type Ib-IaA and Ib-AaB categories.

4.3. Trace element trends

Trace element data (as the average for each parcel) of diamonds analysed are presented in Table 2, Table 3, Table 4 and Figure 4. All concentration and 1σ error values and MDL are shown to a maximum of three significant figures depending on the uncertainty and percentages are shown as whole numbers. The statistical analysis of each element's data set is represented by the percentage $>$ MDL. Values that are greater than 50 % for each element are considered statistically significant. Values less than 50 % are reported in italics. The mean, 1σ error, median and mean MDL were calculated inclusive of outliers. Outliers were determined as any value greater than 1.5 times the interquartile range (middle 50 % of data), subtracted from Q1 and added to Q3 – the 25th and 75th percentiles respectively in the data set. These values were not used in box and whisker plots or histograms.

The average concentration of trace elements in each parcel, including values that report to $<$ MDL (i.e. MDL/2) in more than 50 % of cases, is shown in the spider diagram of Figure 4. The diagram indicates a clear relationship between parcels A and B in that they follow the same trend and display very similar elemental average concentrations. Zirconium, Th, and to a lesser extent Hf, have a greater enrichment in parcel A, while

La, Nd, Eu, Gd and Tb are slightly more enriched in parcel B. It is also evident from the graph that the general trend of parcel C shows a lower concentration of the lighter trace elements (Ga, Sr, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy) and an equal or slight enrichment in the heavier trace elements (Ho to U), except for Th, which is depleted, in comparison to parcels A and B.

Box and whisker plots of the concentrations per element analysed per parcel, with outliers removed, are shown in Figure 5. Those parcels that returned concentration value greater than the MDL in more than 50 % of cases are indicated by the star above each box and whisker. Outliers are not indicated on the plots, however, the number of outliers for each parcel are reported in Table 2, Table 3 and Table 4.

Zirconium and Ce are common among the three parcels displaying statistically significant concentrations. These elements are further compared in the normalised frequency histograms of Figure 6a and b. The distribution curves of each element show a positively skewed distribution for all three parcels, however, the distribution tends to bimodality at the higher concentrations for parcels A and B. The distribution of each elemental concentration is narrower for parcel C – the concentration distribution of Zr in parcel C is between -0.5 and 1.5 ppm, whereas for parcels A and B, the distribution is up to 5 ppm. The concentration of Ce in parcel C is maintained between 0 and 2.5 ppm, while for parcels A and B, the concentration reaches up to 90 ppm.

Normalised frequency histograms for Sr, Y, Ba, La, Pr, Nd and Th are shown in Figure 7 for parcels A and B. These elements were plotted as they show statistically significant concentrations, which were not evident in parcel C. Again, outliers are excluded from the plots. The histograms plotted show that the data has a positively skewed distribution for both

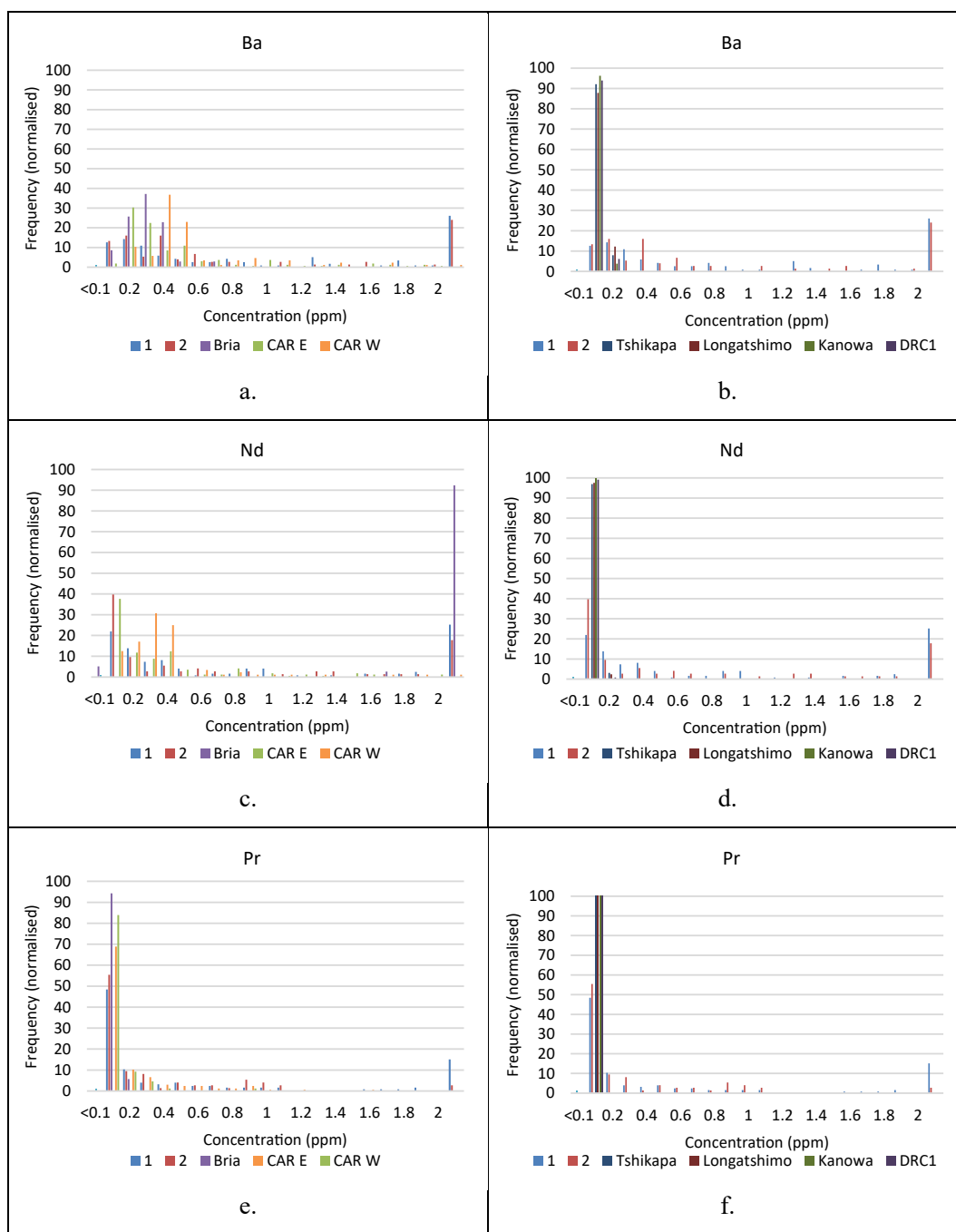


Figure 11. Normalised frequency histograms of the concentration of (a) Ba comparing parcels A and B to Bria River, CAR E and CAR W; (b) Ba comparing parcels A and B to Tshikapa, Longatshimo, Kanowa and DRC1; (c) La comparing parcels A and B to Bria River, CAR E and CAR W; (d) La comparing parcels A and B to Tshikapa, Longatshimo, Kanowa and DRC1; (e) Pr comparing parcels A and B to Bria River, CAR E and CAR W and (f) Pr comparing parcels A and B to Tshikapa, Longatshimo, Kanowa and DRC1.

parcels. The majority of the data also plots in a very narrow concentration range for each element.

5. Discussion

The over-arching purpose of creating a fingerprint database is to discriminate the source of conflict diamonds using physical and chemical information. As such, around 1000 gem-quality diamonds from six African countries have been examined to determine their fingerprints as a baseline for those from “unknown” or dubious origins. The aim of this piece of work was to compare a parcel with suspected origins in the CAR to those previously analysed from that country and to further compare

the data to those from countries such as the DRC. In other words – are we at the point that this technique works to discriminate diamonds on a regional basis?

It is evident from the morphological and N data that discrimination within the entire parcel is inconclusive. The physical properties of the examined diamonds were too indistinct in nature. Further, the distribution of N is likely inhomogenous throughout any diamond due to zoning and growth sectors, as noted by [Whitehead \(2005\)](#) in a set of Cullinan diamonds examined and others by [Sitnikova and Shatsky \(2009\)](#). As such, the concentration of N from any one point in a stone would be different from that at another point.

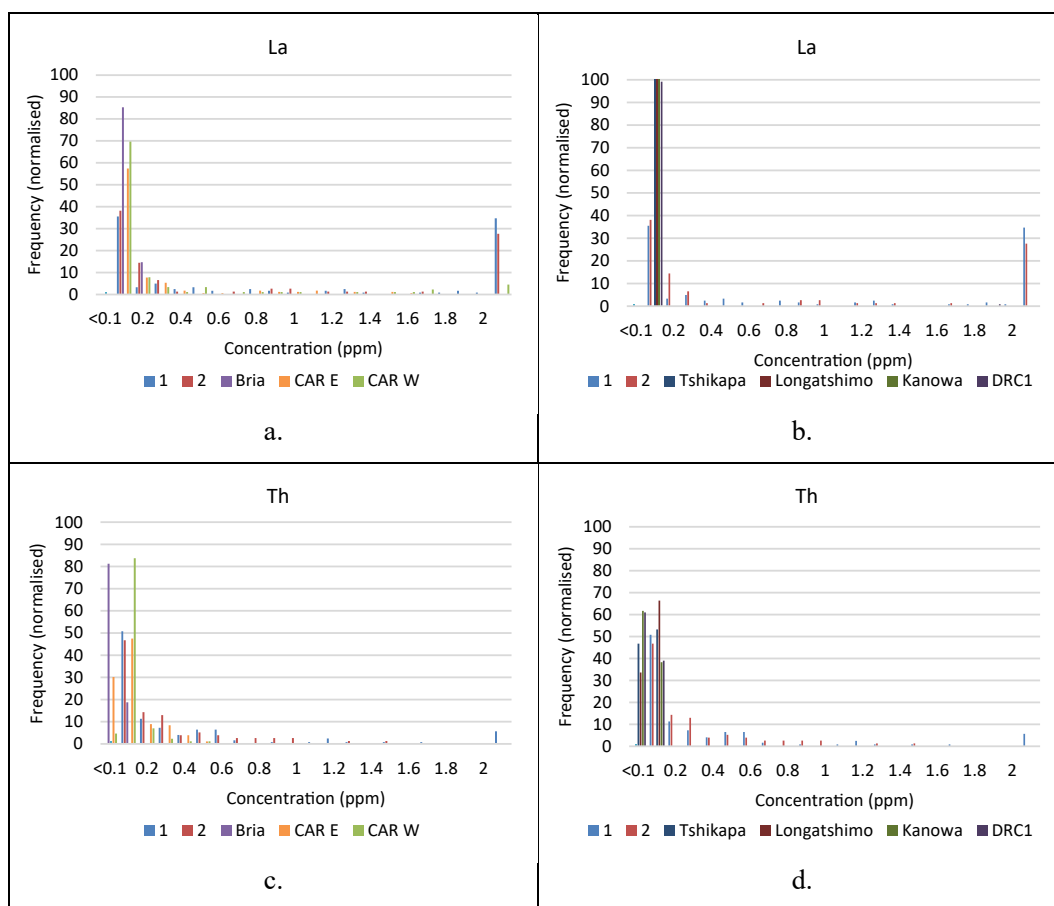


Figure 12. Normalised frequency histograms of the concentration of (a) Nd comparing parcels A and B to Bria River, CAR E and CAR W; (b) Nd comparing parcels A and B to Tshikapa, Longatshimo, Kanowa and DRC1; (c) Th comparing parcels A and B to Bria River, CAR E and CAR W; and (d) Th comparing parcels A and B to Tshikapa, Longatshimo, Kanowa and DRC1.

A comparison of the total concentration of N in the diamonds from the parcels to those from previously analysed parcels from CAR and the DRC is shown in Figure 8. The parcel from the CAR consisted of diamonds sourced from the western and eastern mining zones (CAR W and CAR E). A small parcel of diamonds from the Bria River area (western CAR) is also shown. The data from the DRC represents diamonds from the southern portions of that country – Longatshimo, Kanowa, Tshikapa and DRC1.

Overall, the N concentration ranges of the three parcels in question, CAR W, CAR E and Bria River are small and account for low concentrations – Bria River displayed the highest concentration of N at just over 1000 ppm. The concentration range of N in diamonds from the DRC is much greater than those from CAR; Longatshimo achieved a maximum of 3858 ppm – over 6 times greater than any value obtained for parcels A, B or C.

As with the morphological observations, FTIR data are inconclusive in discriminating sources, however, it can be argued that parcels A, B and C have similar ranges of N concentration to that of other parcels analysed from the CAR, but also similar to that achieved from the diamonds from the DRC1 parcel.

Comparison of the current trace element data set to that of the diamonds described previously from CAR E and W, Bria River and the DRC (Tshikapa, Longatshimo, Kanowa and DRC1) is shown in the discrimination diagrams of Figure 9a and b. The graph of Figure 9a indicates a similarity in the trace element trend between parcel A and B with that of CAR W. The concentrations of Sr to Cs, and Eu to Ta are near identical for

these parcels. The concentration trend of parcel C is similar to CAR E in the light trace elements (from Ga to Eu, except for Y, Zr and Nb). From Gd to U (except Th) it becomes similar in trend and concentration to that of CAR W. This may indicate that parcel C was a mixed parcel of diamonds from both CAR E and CAR W. Figure 9a further indicates that neither of the trends of parcels A, B or C are the same as that achieved from Bria River, indicating that none are likely related to Bria River diamonds.

Comparison of trace element trends of parcels A, B and C with those from the DRC diamonds indicates that the diamonds from Tshikapa, Longatshimo, Kanowa and DRC1 are depleted in trace elements and follow very different trends to those from this study (Figure 9b).

The normalised frequency distributions of the statistically significant elements Sr, Y, Ba, La, Pr, Nd and Th, for parcels A and B, are shown in Figure 10, Figure 11 and Figure 12 as a comparison of the current data set to those obtained from CAR, Bria River and DRC, respectively.

These histograms indicate positively skewed data for all sets of elements and all samples, except Ba from Bria, which displays a normal bell curve and Nd, also from Bria, which indicates a negatively skewed distribution. In comparison to CAR E, CAR W and Bria, the data set from the current study, has a wider distribution of concentrations, except for Ba and Nd, whose concentrations span the same range as parcels A and B. Parcels A and B also display a tendency towards bimodality, particularly parcel A.

The data from the current study has a wider distribution of concentrations, compared with many elements from the DRC parcels that report

100 % frequency in one or two concentration classes (for e.g. Sr and La from Tshikapa, Longatshimo, Kanowa and DRC1). Concentrations of significant trace elements are less than 0.4 ppm.

6. Conclusions

The purpose of the current investigation was to determine a fingerprint of a set of parcels that were suspected to have origins in the CAR. In addition, these needed to be compared to diamonds previously analysed from CAR and the DRC.

Morphology and FTIR are supplementary sources of information to LA-ICP-MS trace element analysis. While a large amount of features were identified in the three parcels, morphological data do not present a firm fingerprint to the parcels.

Fourier transform IR determined the total concentration of N. It is seen that the total concentrations between the three parcels differ only slightly with parcel B having the smallest range in total N concentration and parcel C having the largest range. In comparison to total N concentration of the diamonds within the database, only those from CAR E, CAR W and DRC1 have similar total N concentrations to those in the current study. The total concentration of N ranges for Longatshimo, Tshikapa and Kanowa are much larger. Unfortunately, no meaningful conclusions can be drawn from the data nor can any be drawn by comparison to the database.

Laser ablation ICP-MS appears to be the most robust technique used in the fingerprinting process and produces unique data from one parcel to the next, i.e. trace element concentrations offer higher sensitivity levels for comparison of diamond populations.

Trace element trends showed that parcels A and B are very similar and also reveal identical concentrations of certain elements. The trend of parcel C reveals a general depletion in trace elements, in comparison. The trend of parcels A and B were near-identical to that of CAR W suggesting that these two parcels are from the same source. The trend of parcel C indicates a trend with similarities to both CAR W and CAR E, suggesting that the parcel is of mixed origin. Comparison of the current parcels to those previously analysed from Bria River and the DRC indicated dissimilar source areas.

Descriptive statistics of significant trace elements highlighted that parcels A and B shared common trace elements, while parcel C only shared two common trace elements with parcels A and B. This further highlighted the distinctness of parcel C to A and B. Comparison of these trace elements to CAR E, CAR W and DRC parcels, indicated that for parcels A and B a wide range of concentrations was apparent, similar to CAR W for all elements except Sr and Th. The data from CAR E revealed a wide distribution for some elements but a narrow distribution for others. The data from Bria River and those of the DRC displayed a narrow distribution, further highlighting the disparity between parcels A and B from Bria and DRC.

For the fingerprinting method, diamonds need to be considered on a parcel-by-parcel basis, while the size of that parcel is also important. In order to produce data with statistical confidence, parcels of >50 diamonds are recommended, however smaller parcels have produced discernible trends when observed on a parcel-by-parcel basis. Additionally, a comprehensive database of diamond data is required to provide good comparison against. With these in place, diamond source discrimination shows potential for success.

Declarations

Author contribution statement

S. Brill: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

N. Lilimu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

D. Chetty: Analyzed and interpreted the data; Wrote the paper.

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Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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