TRACE ELEMENT ANALYSIS OF DIAMOND BY LAM ICPMS: STANDARDISATION, RESULTS AND DIRECTIONS

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Introduction

The trace element patterns of natural diamonds can provide new information on the environment and processes of diamond crystallization in Earth's mantle, and may have the potential to identify diamonds from specific sources, for forensic purposes. Most of the trace elements in diamonds probably reside in microinclusions, rather than in specific lattice sites. Fibrous or cloudy stones therefore typically have relatively high trace element contents, whereas gem-quality diamonds have detectable levels of far fewer elements. The characterization of diamonds therefore will require extremely sensitive multi-element analysis, by techniques that cause as little damage as possible to the diamond. The natural variation in absolute abundances and trace-element patterns among stones analysed thus far means that any chance of "fingerprinting" diamonds will require statistical analysis of multi-element data on large sample sets. Such a treatment will require quantitative, rather than qualitative data, especially if more than one laboratory is to be involved. The most promising technique appears to be laser-ablation (LAM-) ICPMS, which drills a hole 50-200 microns across and ca 15 microns deep.

Standardisation

Quantitative LAM-ICPMS analysis requires an internal standard, which for diamond can only be carbon, and a homogeneous external standard containing well-characterised abundances of a wide range of trace elements, and carbon as a major element. There are several problems with existing carbon-based standards, such as natural coals and carbonates; these contain relatively few certified elements at useful levels, and most are heterogeneous at the 100-micron scale. GEMOC therefore has developed two approaches to standardization. One uses trace-element doped oils as the primary standard; these are enclosed in glass capillaries and ablated through a hole in the glass. The other uses a cellulose pulp, doped with trace elements at a nominal 20 ppm, homogenized, dried and prepared as a pressed pellet. Once one or more elements have been determined in a given diamond, these also can be used as internal standards and other concentrations derived by comparison with well-known silicate standards such as the NIST glasses. Cross-analysis of the cellulose standard using the SRM NIST612 glass as the external standard, and Sr as the internal standard, shows good precision (1σ typically 1-2%) and accuracy (vs a solution analysis of the cellulose standard) for most elements (Table 1). It also demonstrates that despite elaborate homogenization procedures, several elements (Si, K, Ca, Cr, Fe, Zn, Ba, W) still show significant lateral heterogeneity in the cellulose pellets (typically 15-50%, up to 600% for Ba). We find that the cellulose standard gives slightly better external precision (reproducibility of results), and lower carbon backgrounds, than the oil standard, and is simpler to use.

Analytical techniques

Ablations are carried out in He, which is mixed with Ar before entering the ICPMS torch. Tests with three different lasers (266 and 213 nm Nd:YAG, 193 nm excimer) have shown that the 266nm wavelength gives the best overall intensities and peak/background. Analyses are carried out on an Agilent 7500s ICPMS, tuned to optimize sensitivity across the mass range from Li to U. Data reduction is done using the in-house GLITTER software, which displays each run in a way that highlights spikes, inclusions and other heterogeneities, and allows selection of the most stable part of the signal for integration. A typical run will include two analyses of the cellulose standard, one analysis of the NIST612 glass, one analysis of a "standard" diamond (JWA115; see below), ten unknown diamonds (2 spots each), and two further analyses of the cellulose standard to correct for any instrumental drift.

The technique as currently applied can collect data for 50 elements, with detection limits ranging from 1-15 ppm for some light elements (Na, Si, S) to 2-10 ppb for many heavy elements (Sr, Zr, Nb, Ba, most REE). In typical fibrous diamonds 25-40 of these elements are above detection, including the light REE (La, Ce, Pr) and some

heavy REE (Yb, Lu); this list drops to 10-15 elements in gem-quality stones. To increase mean counting times, a "short list" of 33 elements has been adopted for routine use.

 "Standard" diamonds
Analyses of the cellulose standard must be done at lower laser energies than analyses of diamonds, because of the different ablation characteristics of the two materials. It has therefore been critical to test the accuracy of the technique by analysis of known diamonds. We have used two fibrous diamonds (JWA115, JWA 110) from Jwaneng, previously analysed by INAA (Schrauder et al., 1994, 1996) and PIXE (Griffin et al., 1993). These stones are heterogeneous in composition because of the nonuniform distribution of microinclusions (fluid, melt, mineral), and concentrations of individual elements can range by factors of 3-10 from spot to spot (Tables 2, 3).

Despite the heterogeneity of these stones, the mean values determined by INAA, PIXE and ICPMS on JWA115 agree within one standard deviation for 23 of 28 elements (Table 2). The lower Ni values derived by ICPMS agree better with the PIXE values (Table 3), and the agreement is good for JWA110 (not shown). Similarly, the ICPMS value for Cr is higher than the INAA and PIXE values for JWA115, but agrees for JWA110. In these cases the discrepancies may simply reflect the heterogeneity of the diamond and/or the standard (Table 1). The ICPMS values for Si are higher than the INAA value for both JWA115 and JWA110; however, the wide variability in values suggests that no artefact is involved; the INAA values may be in error. P and As values are clearly too high, and relatively constant from point to point; they probably reflect an unidentified artefact. We conclude that the technique produces accurate and precise data for most elements, and that the heterogeneity of natural diamonds is a major limiting factor on the reproducibility of the results.

The same analyses have been processed using the SRM NIST612 glass as the external standard, and Sr, derived from the cellulose calibration, as the internal standard. The results show excellent agreement with those derived from the cellulose calibration. This agreement indicates that the matrix effects are much less significant than commonly supposed.

Results to date
Fibrous diamonds from several localities show striking overall similarities in trace-element patterns, and some significant differences (Fig. 1). These diamonds are enriched in incompatible elements such as the REE, Rb, Sr, Ba, Th and Nb, reflecting the nature of the melts and fluids trapped in their inclusions. Most localities show lower HREE and higher LREE than Jwaneng; some show negative Y anomalies. There are large ranges in Al, Mg, Zr and Ti, relative to adjacent elements, among the localities. The broad similarity of these patterns to those of kimberlites and (especially) carbonatites has been noted previously (Davies et al. 2000; Rege et al. 2003).

Averaged data for diamonds of different parageneses are shown in Fig. 2. The "superdeep" paragenesis consists of diamonds with lower-mantle inclusions from the Slave Craton kimberlites and Juina (Brazil) alluvial deposits. The "subduction" paragenesis includes diamonds from the alluvial deposits of eastern Australia, which contain rodingite-related mineral inclusions; these are strikingly similar in trace-element pattern to Argyle diamonds. All non-fibrous diamonds are strongly depleted in LREE, LILE and HFSE relative to fibrous diamonds. While most eclogitic, peridotitic and subduction-related diamonds show strong negative Y anomalies, these are absent to very small in most fibrous diamonds and superdeep diamonds (and thus are unlikely to be analytical artifacts). Superdeep and subduction diamonds tend to have very low Sr and Ba contents. The superdeep diamonds from Slave and Juina have markedly different patterns, especially in the REE and HFSE.

Analyses carried out to date on single localities show some consistent differences between diamonds of different parageneses. Similarly, averaged patterns for diamonds of the same parageneses from different localities show clear differences in the ratios of particular elements. These variations can provide the basis for the development of statistical discriminants (fingerprints") for stones from individual localities. However, the range of variability seen within individual localities indicates that a very large body of quantitative analytical work remains to be done before the technique can be credibly applied to forensic analysis. In the meantime, these data offer the potential for new insights into the processes of diamond formation.

Table 1. Cellulose standard analysed as an unknown with SRN NIST612 glass as the external standard, and Sr as the internal standard.

| ELEMENT	Cellulose Solution ICPMS results (ppm)	LAM-ICPMS (ppm)			
		MEAN N=317	1σ	MIN ppm	MAX ppm
Na	216	183	11.9	137	225
Mg	232	224	12.5	179	269
Al	22.6	20.7	2.0	16.5	30.7
Si	61.3	100	12.4	75.9	165
P	21.5	18.0	4.4	11.7	27.9
K	102	102	7.4	81.8	125
Ca	1052	933	55.2	771	1151
Ti	20.9	21.0	1.1	17.4	25.9
V	20.4	16.6	1.0	14.0	20.5
Cr	209	184	11.2	153	227
Mn	20.5	17.4	0.9	14.6	21.4
Fe	116	95.0	8.0	67.0	115
Co	20.9	16.8	1.0	14.0	21.2
Ni	20.5	18.9	1.1	15.6	23.7
Cu	20.3	15.0	1.0	12.6	18.8
Zn	18.6	13.8	2.4	8.6	20.4
Ga	20.9	15.6	0.9	12.9	19.8
As	19.9	19.0	1.7	14.4	25.7
Rb	20.1	17.3	1.0	14.5	21.7
Sr	19.9	20.0	1.0	16.1	25.0
Y	21.0	25.0	1.6	21.0	31.0
Zr	20.0	21.8	1.4	18.1	27.3
Nb	22.3	19.6	1.5	15.8	27.0
Mo	20.5	17.2	1.1	14.6	21.2
Cs	19.8	16.9	1.0	14.3	20.8
Ba	19.3	15.3	9.1	10.9	105
La	19.9	17.4	1.0	14.6	21.6
Ce	19.4	19.2	1.1	16.3	23.9
Pr	20.5	18.8	1.0	15.9	23.3
Nd	20.1	17.3	1.0	14.7	21.6
Sm	19.2	17.6	1.1	14.8	21.9
Eu	20.2	17.8	0.9	15.1	22.1
Gd	20.5	19.7	1.2	16.7	24.6
Dy	20.1	20.9	1.3	17.6	26.2
Ho	20.3	21.0	1.4	17.8	26.5
Er	20.5	21.0	1.3	17.3	25.9
Yb	19.0	21.8	1.4	18.2	27.3
Lu	19.1	20.6	1.4	17.5	26.0
Hf	19.1	20.5	1.3	16.9	25.4
Ta	19.5	19.6	1.5	16.0	25.6
W	24.6	17.1	1.6	14.3	29.9
Pb	18.9	16.6	1.5	13.3	25.0
Th	19.9	20.9	1.4	17.3	25.8
U	19.9	19.1	1.2	16.2	23.7
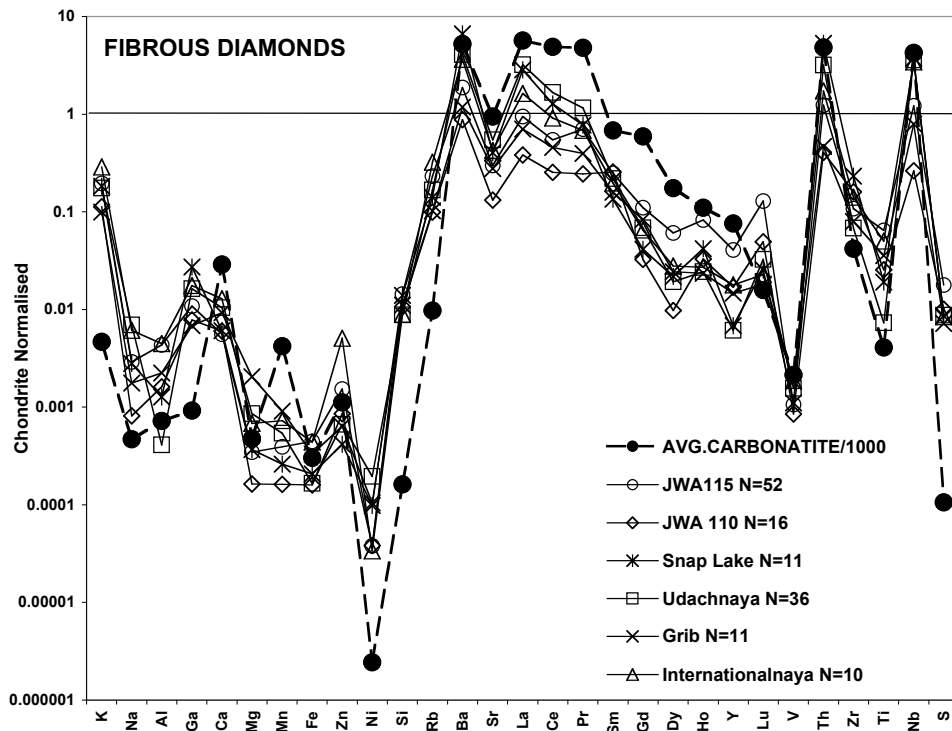
Fig. 1: Chondrite-normalised trace-element data for fibrous diamonds, derived using the cellulose calibration technique. Data from Zedgenizov and Rege (in prep.).(average carbonatite after Woolley and Kempe,1989)
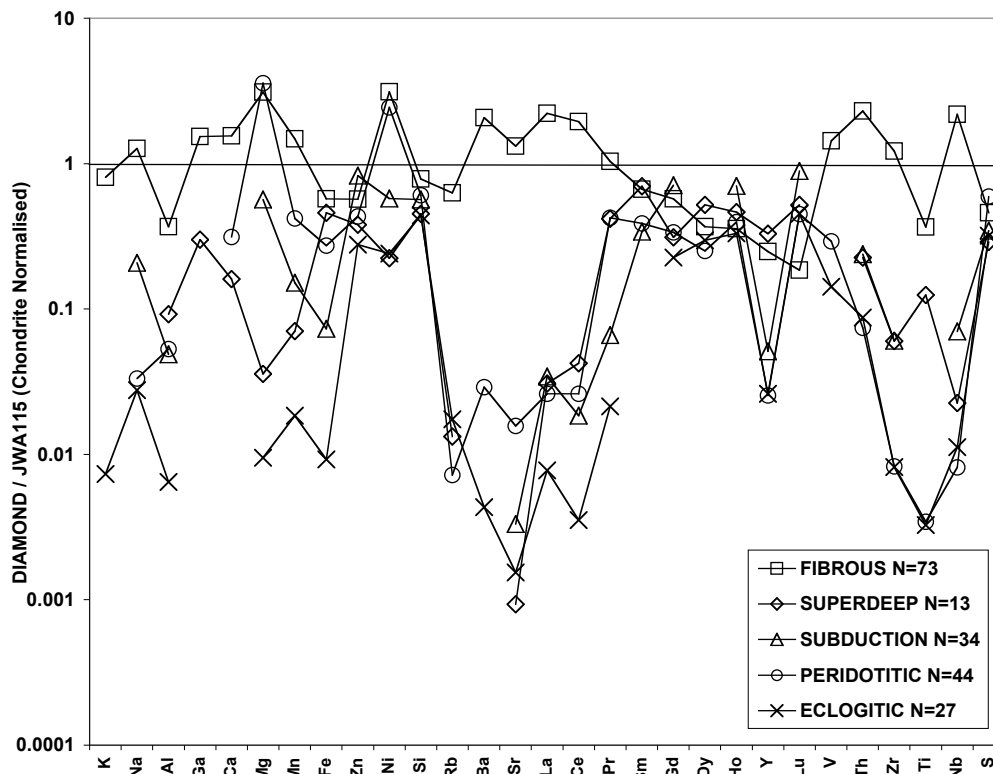

Fig. 2: Averaged trace-element data for diamonds of different parageneses worldwide, illustrating the range of variation in absolute abundances and element ratios.

Table 2. Analysis of JWA115: comparison of INAA and LAM-ICPMS (cellulose standard) results

| | JWA 115 | | | | | | | |
| | | INAA (Schrauder et al., 1996; 1994) | | | LAM-ICPMS | | |
Element	MAX ppm	MIN ppm	Mean N=2	Mean N=52	1 s	MAX ppm	MIN ppm	Mean DL
Na	21.4	11.7	16.5	18.1	7.15	33.9	6.14	1.51
Mg	33.8	18.2	26.0	35.4	8.50	60.5	17.1	0.42
Al	35.7	19.3	27.5	39.5	9.54	62.0	19.4	0.17
Si	299	161	230	1427	702	3971	746	15.5
P	5.01	2.70	3.85	38.3	16.0	65.4	12.8	3.89
Cl	15.3	8.2	11.8	37.2	13.5	66.5	17.6	5.16
K	128	69.0	98.5	111	25.2	188	58.5	0.49
Ti	35.1	18.9	27.0	30.2	8.17	62.7	15.4	0.29
Cr	0.24	0.23	0.24	2.30	1.82	6.5	0.79	0.34
Fe	88.4	49.9	69.1	84.8	20.4	143	41.4	2.64
Ni	1.32	1.12	1.22	0.42	0.10	0.84	0.28	0.051
Zn	0.19	0.18	0.19	0.60	0.52	2.34	< DL	0.12
As	0.004	0.002	0.003	0.90	0.32	1.7	< DL	0.35
Br	0.027	0.013	0.020	0.061	0.043	0.16	< DL	0.011
Rb	0.59	0.40	0.50	0.56	0.13	0.96	0.27	0.020
Sr	2.40	1.95	2.18	2.23	0.48	3.71	1.16	0.003
Zr	0.50	0.42	0.46	0.44	0.12	0.955	0.21	0.004
Cs	0.091	0.035	0.063	0.014	0.037	0.235	< DL	0.006
Ba	3.71	1.90	2.81	4.56	1.21	8.00	2.33	0.007
La	0.24	0.13	0.19	0.24	0.059	0.39	0.12	0.004
Ce	0.41	0.22	0.32	0.35	0.090	0.611	0.16	0.003
Sm	0.029	0.016	0.023	0.037	0.030	0.125	< DL	0.012
Eu	0.01	0.007	0.009	0.007	0.010	0.049	< DL	0.002
Gd	0.020	0.010	0.015	0.025	0.023	0.097	< DL	0.010
Yb	0.005	0.003	0.004	0.010	0.019	0.092	< DL	0.003
Hf	0.015	0.008	0.011	0.008	0.010	0.031	< DL	0.005
Th	0.036	0.018	0.027	0.039	0.017	0.094	< DL	0.005
U	0.010	0.010	0.010	0.008	0.011	0.069	< DL	0.003

Table 3. Analysis of JWA115: comparison of PIXE and LAM-ICPMS (cellulose standard) results

| | JWA 115 | | | | | | | | |
| | Proton Microprobe (Griffin et al., 1993) | | | | LAM-ICPMS | | | | |
Element	MAX ppm	MIN ppm	Mean N=9	1 σ	Mean N=52	1 σ	MAX ppm	MIN ppm	Mean
Ca	38	20	28	6	52	17	92	22	20
Ti	46	21	31	8	30	8	63	15	0.29
Cr	0.3	0.04	0.2	0.1	2.3	1.8	6.5	0.79	0.34
Fe	147	71	104	28	85	20	143	41	2.6
Ni	1.1	0.4	0.9	0.3	0.42	0.10	0.84	0.28	0.05
Cu	0.9	< DL	0.4	0.3	0.25	0.12	0.57	< DL	0.10
Zn	2.9	0.7	1.7	0.8	0.60	0.52	2.3	< DL	0.12
Br	0.3	< DL	0.1	0.1	0.06	0.04	0.16	< DL	0.01
Sr	3.9	1.9	2.8	0.6	2.2	0.5	3.7	1.2	0.003
Zr	2.0	0.2	0.9	0.5	0.44	0.12	0.96	0.21	0.004