SYSTEMATIC STUDIES OF NITROGEN IN DIAMONDS

FROM KNOWN SOURCES

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INTRODUCTION

Nitrogen is a major impurity in natural diamond with, occasionally, as much as 0.5at.% being present (Burgermeister 1979). In the one-phonon region of the spectrum, between 7μm (wavenumber 1417cm^{-1}) and 10μm (wavenumber 1000cm^{-1}), infrared spectroscopy most definitively identifies this element and a classification scheme is well established (Robertson *et al*. 1934). Two main types are recognised; Type I (nitrogen containing) and Type II (no detectable nitrogen). Type I diamonds are further sub-divided according to whether the nitrogen is single substitutional (Type Ib diamonds), or whether the nitrogen is aggregated within the carbon lattice (Type Ia diamonds). Nitrogen aggregation occurs principally in either the A-form (a nitrogen pair) or the B-form (a more complicated arrangement, but probably four nitrogen atoms and a vacancy). In addition, Type Ia diamonds may contain a so-called platelet peak and have N3 centres (triangles of nitrogen). With Type II diamonds the vast majority are subdivided into Type IIa but the rare Type IIb diamonds, which electrically conduct, have considerable importance as heat sinks (see Bibby 1982).

The amount of nitrogen within Type Ia diamonds can be determined by decomposing the infrared spectra (Davies 1981, Evans and Qi 1982). Both methods involve the absorption peak at 7.8μm (1282cm^{-1}) which is related to the <u>total</u> nitrogen present. With careful preparation, errors in nitrogen values range from ±7% for pure Type IaA diamonds to ±25% for pure Type IaB. As the majority of Type Ia diamonds have mixtures of both A- and B-centre nitrogen, but generally with Type IaA dominant, an average error of between 12 to 15% in the nitrogen value is likely. A measure of which centre is dominant is obtained from the ratio of the principal A- and B-peaks, the ratio for pure Type IaA being approximately 2.0 and for pure Type IaB being approximately 0.36.

The work reported here is an investigation into the prevalence, amount and aggregation state of nitrogen in representative inclusion-bearing diamonds from seven kimberlites in southern Africa and one lamproite from western Australia with the objective of determining inter-relationships.

RESULTS

Some general relationships are recorded in Table 1. Of the two diamond parageneses, 'eclogitic' diamonds are more commonly Type I, with the exception of Roberts Victor. With respect to Type II diamonds, they are: a) commonest in the 'peridotitic' paragenesis with the exception of Jagersfontein, b) rare in sulphide-bearing diamonds except at Jagersfontein. Nitrogen levels in 'peridotitic' diamonds (DeBeers Pool excepted) show a marked positive skewness with the vast majority having <300ppm. This skewness is independant of which inclusion paragenesis is dominant. A positive skewness, but with a much longer tail (up to 1700ppm) is also present among the 'eclogitic' diamonds at Koffiefontein, Jagersfontein, Roberts Victor and Argyle but not at the remaining mines, where the distribution is even over the same ppm values. With nitrogen in sulphide-bearing diamonds Jagersfontein and Argyle show positive skewness, but for the other mines nitrogen ranges evenly up to a maximum of 2100ppm.

In terms of the nitrogen aggregation states, no distinctions are apparent between the three recognised assemblages in the presently-available data set. Overall, diamonds from DeBeers Pool and Roberts Victor are the most dominantly Type IaA and

TABLE 1
Inclusion-bearing diamonds: P = peridotitic; E = eclogitic; S = sulphide
Diamond sizes range from 1.09mm (-2+1) to 2.46mm (-9+7)

| SOURCE		Diamond Size	Approx. % inclusion abundance	Number studied	TYPE I	TYPE II	% of diamond with <300ppm N_2
Premier	P	-6+5	40	36	28	8 (22%)	83
	E	-6+5	60	131	129	2 (2%)	24
Finsch	P	-6+5	97	80	57	23 (29%)	88
	E	-6+5	3	12	12	– –	20
Koffiefontein	P	-6+5	31	38	28	10 (26%)	80
	E	-6+5	2	22	21	1 (4%)	77
	S	-6+5	66	62	60	2 (3%)	33
Jagersfontein	P	-5+3		22	18	4 (18%)	86
	E	to	No data	16	11	5 (31%)	75
	S	-2+1		23	16	7 (30%)	61
Roberts Victor	P	-6+5	78	62	48	14 (23%)	84
	E	-6+5	12	14	4	10 (71%)	79
	S	-6+5	10	20	19	1 (5%)	40
DeBeers Pool	P	-6+5	88	58	56	2 (3%)	24
Orapa	P	-6+5	20	22	20	2 (9%)	54
	E	to	65	33	33	– –	25
	S	-9+7	15	19	19	– –	16
Argyle	P	-6+5	11	11	10	1 (9%)	64
	E	to	76	76	76	– –	83
	S	-9+7	13	14	14	– –	71
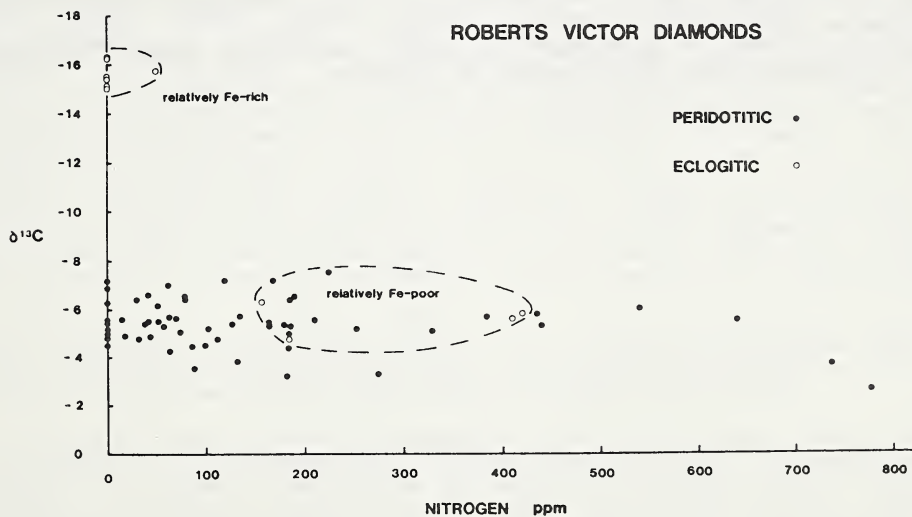
Fig. 1
Nitrogen concentration versus δ^{13}C for inclusion-bearing diamonds Roberts Victor

Argyle the most dominantly Type IaB. For the remaining mines, nitrogen aggregations are broadly spread between Type IaA and Type IaB. The relationship between Type IaB diamonds and relatively low nitrogen levels can be clearly demonstrated at Argyle (see Table 1 and data in Harris and Collins 1985). Plots of ratios of principal absorption peaks also indicate that the path of nitrogen aggregation in diamond, as proposed by Brozel *et al.* (1978), is incorrect for the step from A- to B-centres.

Figure 1 is an example of how the nitrogen signatures from the mines studied can further help define the growth environment of diamond. The 'eclogitic' diamonds at Roberts Victor can be separated into two distinct sub-populations and, furthermore, the chemistry of the inclusions associated with these sub-populations indicate that one environment is more Fe-rich. The figure also illustrates the general lack of correlation between $\delta^{13}C$ and nitrogen concentration for the predominant 'peridotitic' diamond paragenesis.

CONCLUSION

From the data reported here, no distinctions between different diamond sources on the basis of nitrogen characteristics are apparent. So far, no single relationship correlates amount and/or aggregation state of nitrogen to diamond paragenesis. Combining nitrogen with $\delta^{13}C$ values from the same diamonds allows sub-populations within a particular paragenesis to be recognised. The role of nitrogen in mantle processes associated with diamond is, therefore, complex and a full elucidation of this element will require integrated studies of both carbon and nitrogen isotopes as well as work into phase systems such as C-H-N-O.

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