Available online at www.sciencedirect.com

SCIENCE DIRECT®

Lithos 77 (2004) 359–373

LITHOS

www.elsevier.com/locate/lithos

Constraining diamond metasomatic growth using C- and N-stable isotopes: examples from Namibia

Pierre Cartigny[a,*], Thomas Stachel[b,c], Jeff. W. Harris[d], Marc Javoy[a]

[a] IPGP et Universite Paris 7, Laboratoire de Géochimie des Isotopes Stables, Institut de Physique du Globe, UMR CNRS 7047, 4 Place Jussieu, T54-64 E1, 75251 Paris cedex 05, France
[b] Department of Earth and Atmospheric Science, University of Alberta, Edmonton, AB, Canada T6G 2E3
[c] Institut für Mineralogie, Universität Frankfurt, Senckenberganlage 28, 60054 Frankfurt, Germany
[d] Division of Earth Sciences, University of Glasgow, Gregory Building, Glasgow G12 8QQ, Scotland, UK

Received 21 June 2003; accepted 25 January 2004
Available online 24 May 2004

Abstract

The present paper provides C- and N-stable isotope characteristics, N-contents and N-aggregation states for alluvial diamonds of known paragenesis from placers along the Namibian coast. The sample set includes diamonds with typical peridotitic and eclogitic inclusions and the recently reported "undetermined" suite of Leost et al. [Contrib. Mineral. Petrol. 145 (2003) 15] which resulted from infiltration of high temperature, carbonate-rich melts. δ^{13}C-values range from -20.3‰ to -0.5‰ ($n=48$) for peridotitic diamonds and from -38.5‰ to -1.6‰ ($n=45$) for eclogitic diamonds. Diamonds belonging to the "undetermined" suite span a narrower range in δ^{13}C from -8.5‰ to -2.7‰ ($n=13$). When compared with previous studies, diamonds from Namibia are characterised by unusually low proportions of N-free (i.e. Type II) peridotitic and eclogitic diamonds (3% and 2%, respectively) and an unprecedented high proportion of N-rich diamonds (15% and 73%, respectively, have N-contents >600 ppm). δ^{15}N-values for diamonds of the peridotitic, eclogitic and "undetermined" suites range from -10‰ to $+13$‰ without correlations with either N-content or δ^{13}C. The similarity in N-isotopic composition and the N-rich character of diamonds belonging to the eclogitic, peridotitic and "undetermined" suites is striking and suggests a close genetic relationship. We propose that a large part of the diamonds mined in Namibia formed during metasomatic events of similar style that introduced carbon and nitrogen into a range of different host lithologies.

Keywords: Diamond; Placer deposit; Namibia; Nitrogen; Stable isotopes; Metasomatism

1. Introduction

Increasing evidence suggests that *some* eclogite nodules are recycled oceanic crust (e.g. Jagoutz et al., 1984; Jacob et al., 1994; Barth et al., 2000, 2002) of Archean age (see Shirey et al., 2002 for review). Inferring that diamonds in these rocks actually represent carbon subducted together with the oceanic crust critically depends on the question if the carbon was already present during subduction or was brought after incorporation of the eclogite hosts into the cratonic lithosphere. This assumption may not be true,

---

* Corresponding author. Tel.: +33-1-44-27-60-88; fax: +33-1-44-27-28-30.

E-mail address: cartigny@ipgp.jussieu.fr (P. Cartigny).

0024-4937/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.lithos.2004.03.024

as mounting evidence documents diamond growth during metasomatic episodes introducing carbon into eclogites *after* their formation and incorporation into the cratonic lithosphere.

Evidence for de-coupling of the formation of diamonds from their eclogite hosts comes from several independent studies including 3D X-Ray tomography of eclogite xenoliths (Schulze et al., 1996; Keller et al., 1999), trace element analysis of inclusions in diamonds (e.g. Taylor et al., 1996), fluid(s) trapped during diamond growth (e.g. Izraeli et al., 2001 and references therein) and the presence of metasomatized inclusions within diamonds (Loest et al., 2003, see below). A number of these studies demonstrated that CO_2-rich (carbonatitic) melts/fluids are involved in the crystallization of diamonds.

Although *some* eclogitic and peridotitic diamonds apparently are related to metasomatism, it is not clear whether *all* diamonds from the mantle share this origin. In addition, the spectrum of possible CHO fluids for diamond precipitation is not limited to (hydrous) carbonatites but may extend also to more reduced methane–water mixtures. The significant metasomatic enrichment evident from the trace element patterns of inclusions in diamonds (e.g. Shimizu and Richardson, 1987; Griffin et al., 1992; for review see Stachel et al., 2004) bringing elements such as Rb, Sr, Sm and Nd may have implications for the interpretation of diamond formation ages. Up to now, mass balances for the metasomatic input into eclogites and/or peridotites leading to diamond growth remain however to be established.

In this context of metasomatic versus non-metasomatic diamond formation, diamonds from the placer deposits along the Namibia coast may provide important clues. A detailed study of the mineral inclusion content of these diamonds not only led to the identification of typical peridotitic (Harris et al., 2004) and eclogitic (Stachel et al., 2004) inclusions, but also to the recognition of an "undetermined" suite (Loest et al., 2003).

The "undetermined" suite of inclusions (in 13 diamonds) is characterised by (1) unusual textural features such as lamellar exsolution of orthopyroxene from clinopyroxene, (2) in part low Mg-values and high K, Ba, Sr, and (3) the presence of additional unusual inclusions such as $MgCO_3$, $CaCO_3$, a Ti-rich phase (lindsleyite?), phlogopite and coesite. The chemistry of this inclusion suite points towards diamond formation during infiltration of a CO_2 (carbonate)-rich fluid/melt with an unusually high fluid/rock ratio leading to an olivine-free mineral association. To completely eliminate olivine via carbonation reactions requires that the source for the "undetermined" suite was locally "flooded by the CO_2 (carbonate)-rich fluid/melt" (Loest et al., 2003, p. 23). The paragenesis of the pre-metasomatic host rocks can still be recognized using chemical criteria (Mg-number, Ni and Cr contents of the inclusions) and comprises both former peridotites and eclogites.

This unique combination of diamonds from typical peridotitic and eclogitic sources with the unusual "undetermined" suite offers an opportunity to examine possible links between these different diamond groups. The present work provides the C- and N-stable isotope characteristics, N-contents and N-aggregation levels for diamonds from all three growth environments.

2. Samples and analytical techniques

All 106 diamonds from Namibia analysed by us were previously studied for their syngenetic mineral inclusion content (Loest et al., 2003: "undetermined" suite; Harris et al. (2004: peridotitic suite; Stachel et al., 2004: eclogitic suite). On the basis of the inclusion studies, our sample set contains 49 peridotitic, 43 eclogitic, one websteritic and 13 diamonds from the "undetermined" suite. From the broken fragments left after inclusion release, two diamond chips were chosen, weighing between 0.15 and 2.30 mg. The first diamond chip was combusted for $\delta^{13}C$ analysis. After sample combustion in an O_2 atmosphere (see Boyd et al., 1995a) and quantification (to check for total combustion), $\delta^{13}C$-values were determined from the resulting CO_2 gas using a conventional dual-inlet mass spectrometer. The results are expressed in the conventional delta-notation, where $\delta^{13}C=(^{13}C/^{12}C_{sample}/^{13}C/^{12}C_{PDB}-1)\times 1000$. The second diamond chip was analysed by micro-Fourier transform infrared (FTIR) spectroscopy to determine both nitrogen content (N_{FTIR}) and nitrogen aggregation state. Because of limited sample material, this second step could only be carried out for 88 of the 106 diamonds. Nitrogen contents and aggregation states were calculated from FTIR spectra applying the absorption coefficients for nitrogen A- and B-centres determined by Boyd et al. (1994a, 1995b). Nitrogen aggregation states are expressed as the relative proportion of the B-defect of the total nitrogen content (%B). Errors in nitrogen content (N_{FTIR}) and aggregation state are estimated to be better than 20% and 5%, respectively.

Fifty-five diamonds from the set of 106 have so far been analysed for $\delta^{15}N$, total nitrogen content (N_{comb}) and $\delta^{13}C$ (as a second analysis) by bulk combustion (BC). These analyses follow the experimental procedure given by Boyd et al. (1995a) with accuracies of 0.5‰, 5% and 0.1‰ (all 2σ) for $\delta^{15}N$, N-contents and $\delta^{13}C$, respectively. The 55 samples analysed using BC include 12 (out of 13) diamonds from the "undetermined" suite, 17 peridotitic and 26 eclogitic diamonds. Peridotitic and eclogitic diamonds were chosen to cover the full range in $\delta^{13}C$ and of N-contents (e.g. Nam-27 with $\delta^{13}C$ as low as − 38.5‰ or Nam-43 with a N-contents as high as 1900 ppm) or for containing inclusions displaying negative (Nam-5 and Nam-74) or positive (Nam-59 and Nam-89) Eu-anomalies.

3. Results

Columns 3 to 6 in Tables 1–4 report the weight (mg), $\delta^{13}C$, N_{FTIR} and nitrogen aggregation states (%B) determined on the 106 diamonds of the eclogitic, peridotitic, and "undetermined" suite and those of unknown paragenesis from the Namibian placer deposits. Columns 7 to 10 of Tables 1–3 show the weights, $\delta^{13}C$, $\delta^{15}N$ and N_{Comb} for the 55 diamonds referred to earlier.

As illustrated in Fig. 1, the Namibian diamonds cover an unusually large range of $\delta^{13}C$-values. Eclogitic diamonds vary from − 38.5‰ to − 1.6‰, thereby extending the known range for diamonds from worldwide sources to lower (isotopically lighter) values. Two of the four eclogitic diamonds containing inclusions with Eu anomalies in their REE_N patterns have mantle-like $\delta^{13}C$-values of − 5 ± 1‰ (Nam-59 and 89). Nam-5 and Nam-74, containing a garnet inclusion with a negative Eu-anomaly have very light carbon isotopic compositions (< − 24.7‰). Peridotitic diamonds range from − 20.3‰ to − 0.5‰ with the one very light value occurring in a zoned sample (Nam-62, ranging from − 20.3‰ to − 4.8‰; Table 2). For the undetermined suite, a narrower distribution in $\delta^{13}C$ between − 8.5‰ and − 2.7‰ is observed and the six diamonds of unknown paragenesis (no inclusions recovered) range from − 21.1‰ to − 2.6‰ (Table 4).

Column 5 in Tables 1–3 lists the nitrogen contents (based on FTIR analyses) in Namibian diamonds which range from 0 to 1860 ppm for the eclogitic suite, 0 to 1090 ppm for the peridotitic suite and 0 to 875 ppm for the "undetermined" suite. Compared to diamonds from worldwide sources (e.g. Harris and Spear, 1986; Deines et al., 1999 and references therein), our Namibian samples are characterised by a low proportion of Type II (i.e. N-free) diamonds in both the peridotitic (3%) and eclogitic (2%) suites and a high proportion of N-rich diamonds (>600 ppm, see Fig. 2). Nitrogen aggregation states (%B, Fig. 3 and Tables 1–4) vary from IaA (poorly aggregated; N-pairs) to IaB (highly aggregated; clusters of four N-atoms surrounding a vacancy) diamonds, with no clear relation to either paragenesis or N-content (Fig. 3).

Of the 55 diamonds in the second analytical set, the 17 peridotitic diamonds (Table 2) have $\delta^{15}N$-values ranging from − 9.8‰ up to + 12.4‰. No correlations between $\delta^{15}N$ and $\delta^{13}C$ (− 6.7‰ to − 0.5‰; Fig. 4A) or N-content (40 to 800 ppm, BC; Fig. 4B) are observed. However, it is important to note that the two peridotitic diamonds with the highest N-content (Nam-16 and 36, >700 ppm) have positive $\delta^{15}N$-values (+ 12.4‰ and + 3.7 ‰, respectively). This relationship contrasts with results for the central part of the Kaapvaal (Kimberley Pool) where peridotitic diamonds with the highest N-contents show negative $\delta^{15}N$-values (Cartigny et al., 2004).

The 26 eclogitic diamonds have $\delta^{15}N$-values from − 8.5‰ up to + 14.8‰. The large spread in nitrogen isotopic composition is not related to variations in $\delta^{13}C$: for a range in carbon isotopic composition of − 5.0 ± 1.5‰ (Table 1; Fig. 4A) an associated spread in $\delta^{15}N$ of − 8.5‰ to + 14.8‰ is observed. No correlation between nitrogen isotopic composition and content is observed but again, high N-contents

Table 1
δ^{13}C, δ^{15}N, N contents (determined by infrared spectroscopy and/or bulk combustion) and percentage of the B species in eclogitic diamonds from Namibia

Sample	Paragenesis	Weight (mg)	δ^{13}C (‰)	N FTIR (ppm)	%B	Weight (mg)	δ^{13}C (‰)	δ^{15}N (‰)	N Comb. (ppm)
Nam-005	E	0.7528	−24.70	265	54.7	1.8834	−26.63	+11.8	188
Nam-011	E	0.3567	−3.55	1198	20.5	1.7834	−4.42	+1.2	1254
Nam-013	E	1.3320	−4.77	428	66.2				
Nam-014	E	0.5609	−6.50	919	6.7				
Nam-019	E	0.8154	−2.35	867	22.8				
Nam-020	E	0.4077	−5.94	1285	21.4	1.3601	−5.10	−8.5	1044
Nam-021	E	1.6516	−5.21	617	35.8				
Nam-022	E	0.8766	−6.02	1194	21.9	2.1614	−5.97	+1.4	1367
Nam-026	E	0.7040	−4.64	680	15.3				
Nam-027	E	0.5134	−38.54	0	–	2.2640	−38.59	−3.8	9
		0.5644	−38.52			2.2336	−38.65	−2.2	16
Nam-034	E	2.2037	−4.76	1483	39.9	1.5379	−4.91	−6.7	1361
Nam-035	E	0.4886	−5.57	764	78.6	1.3446	−5.37	+3.3	745
Nam-038	E	1.0909	−3.42	1437	29.4	1.7211	−3.58	+7.2	1140
Nam-041	E	0.4500	−7.94	1003	76.1	0.1326	−6.89	−0.2	1270
Nam-042	E	0.3450	−5.76	1134	18.8				
Nam-043	E	1.0766	−16.93	1859	70.3	2.6501	−16.68	+7.2	2116
Nam-044	E	1.0806	−19.97	106	41.8	2.8455	−21.35	+14.8	92
Nam-047	E	1.3689	−5.00	46	49.6				
Nam-053	E	0.4507	−7.14	998	77.0				
Nam-056	E	0.7318	−29.33	35	70.6	1.9358	−29.26	+6.7	55
Nam-059	E	0.7390	−5.29	753	24.0				
Nam-063	E		−6.36						
Nam-068	E	2.3939	−4.11	614	17.6				
Nam-074	E	0.7964	−25.68	327	90.6	0.9238	−27.09	+3.5	255
Nam-078	E	0.3076	−5.81	1008	11.6	0.2348	−5.94	−4.8	883
Nam-079	E	0.3717	−8.08	863	30.6				
Nam-080	E	0.6379	−6.30	1262	27.6				
Nam-080-Bis	E	0.7157	−1.63	957	68.0				
Nam-081	E	0.3326	−6.17	1574	34.1	0.2847	−6.66	−2.7	1704
Nam-086	E	0.3241	−6.21	844	15.8	0.3275	−5.69	−1.5	797
Nam-089	E	0.7095	−4.05	812	50.8	0.5137	−4.23	−1.4	805
Nam-095	E	0.6319	−5.96	725	59.4				
Nam-096	E	0.1737	−3.71	1332	23.1	0.2042	−3.74	−7.5	1410
Nam-097	E	0.3464	−5.84	834	83.9				
Nam-098	E	0.7609	−5.93	277	40.7	1.2413	−5.61	+3.1	515
Nam-102	E	0.3673	−28.70	711	90.1	0.5398	−28.70	+0.3	1178
Nam-114	E	0.5386	−26.93	35	80.9	1.2173	−26.93	+4.0	28
Nam-202	E	1.0498	−5.76	546	66.0				
Nam-203	E	0.9623	−3.91	946	21.9	1.3088	−3.46	−1.4	1005
Nam-205-Bis	E	0.7389	−4.18	57	21.4				
Nam-207	E	0.6795	−6.33	1032	23.7				
Nam-208	E	1.0626	−5.70	653	75.5	1.6902	−5.54	−6.8	637
Nam-212	E (W)	0.3459	−4.53	128	100.0	1.5296	−4.66	+11.6	34
Nam-216	E	0.5140	−4.44	1308	28.9	0.6010	−5.90	−0.5	1483
Nam-218	E	0.6134	−4.66	1070	30.7	1.6456	−5.14	−1.3	1204

Note that sample numbers with the extension-B refer to separate samples and not just analytical duplicates.

are associated with positive δ^{15}N-values. Eclogitic diamonds with δ^{13}C-values between −16‰ and −10‰ also show positive δ^{15}N-values, the lowest δ^{13}C-value (i.e. −38.5‰, Nam-27, Table 1), however, is associated with a negative δ^{15}N-value of about −3‰ (Fig. 4A).

Table 2
$\delta^{13}C$, $\delta^{15}N$, N contents (determined by infrared spectroscopy and/or bulk combustion) and percentage of the B species in peridotitic diamonds from Namibia

Sample	Paragenesis	Weight (mg)	$\delta^{13}C$ (‰)	N FTIR (ppm)	%B	Weight (mg)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	N Comb. (ppm)
Nam-016	P	0.6466	−5.83	484	97.5	0.9254	−5.47	+12.4	722
Nam-018	P	0.9052	−3.95	128	3.6				
Nam-024	L	0.9080	−4.59	1093	49.0				
Nam-028	P	1.9980	−7.79	144	48.8				
Nam-029	P	0.7811	−4.17	117	24.0	1.6620	−4.89	−1.3	147
Nam-030	P	0.2722	−7.19						
Nam-031	P	0.7675	−4.95						
Nam-033	P	0.3952	−6.26	0	–				
Nam-036	P	0.5450	−5.02	889	32.3	0.9028	−5.16	+3.7	806
Nam-037	L	0.6634	−5.05	614	43.5				
Nam-040	P	0.6493	−3.57	487	39.9	0.4754	−4.20	−6.8	434
Nam-046	P	0.7010	−7.43	176	97.0	2.3291	−6.71	+10.2	215
Nam-050	P	0.8665	−4.66	163	94.6				
Nam-051-Bis	P	0.7126	−3.98	308	11.1	2.0913	−4.26	−6.2	350
Nam-052	P	0.1205	−6.57						
Nam-054	P	0.4635	−5.69			0.7677	−5.66	−3.2	52
Nam-055	P	2.1756	−5.64						
Nam-061	P	1.0213	−7.24	484	53.1				
Nam-062	P	0.6039	−20.26	557	73.0	1.3945	−4.84	−5.4	536
Nam-064	P	0.2285	−4.47						
Nam-065	P	0.5407	−4.99						
Nam-070	P	0.1048	−7.28						
Nam-071	P	0.6964	−5.44	165	40.5				
Nam-072	P	0.5058	−5.61						
Nam-073	P	0.4808	−5.28	224	31.5	0.5935	−3.69	−1.0	200
Nam-075	P	0.5995	−5.47						
Nam-077	P	0.3331	−0.53	386	20.4	0.4267	−0.53	−9.3	473
Nam-082	P	0.1244	−7.81						
Nam-087	P	0.2739	−5.59						
Nam-092	P	0.4250	−7.77						
Nam-093	P	0.4476	−5.15	102	79.6				
Nam-094	P	0.5431	−5.19	174	50.2	0.7637	−5.35	+2.4	278
Nam-101	P	0.4034	−5.93	279	10.4	1.3116	−5.98	+5.9	232
Nam-103	P	0.9748	−0.42	343	54.6				
Nam-104	P	0.2997	−5.59	151	34.8	1.2284	−5.49	+11.0	143
Nam-105	P	0.3842	−5.92	151	34.8				
Nam-108	P	0.3957	−1.52	573	72.3				
Nam-109	P	0.3898	−7.03	51	56.3	1.2008	−5.97	+1.3	40
Nam-110	P	0.7013	−4.26	13	15.7				
Nam-111	P	0.7777	−6.00	58	66.9				
Nam-112	P	0.5889	−5.10	147	98.6				
Nam-113	P	0.6909	−4.46	363	16.2	1.3656	−4.57	+1.1	351
Nam-115	P	0.5114	−4.82						
Nam-116	P	1.3464	−3.64	161	34.6				
Nam-118	P	0.4481	−5.95	25	9.1				
Nam-210-Bis	P	0.9653	−4.60			0.6907	−4.52	−9.8	475
Nam-214	P	0.4670	−4.83	669	0.0	0.9254	−5.04	−4.9	475
Nam-215	P	0.7363	−4.66	345	27.8				

Table 3
δ^{13}C, δ^{15}N, N contents (determined by infrared spectroscopy and/or bulk combustion) and percentage of the B species in diamonds from Namibia belonging to the “undetermined” suite of Loest et al. (2003)

Sample	Paragenesis	Weight (mg)	δ^{13}C (‰)	N FTIR (ppm)	%B	Weight (mg)	δ^{13}C (‰)	δ^{15}N (‰)	N Comb. (ppm)
Nam-217	Und. (l)	1.7878	−6.75	357	99.1	0.6552	−6.90	+1.8	1572
Nam-210	Und. (l)	0.4968	−5.79	247	15.8	1.1491	−6.33	+3.1	16
Nam-211	Und. (l)	0.4963	−3.99	383	63.5	1.2575	−4.55	−8.3	432
Nam-217-Bis	Und. (l)	0.4056	−4.89	13	57.0	0.9654	−5.30	n.d.	15
Nam-083	Und. (l)	0.8318	−3.76	0					
Nam-100	Und. (l)	0.3095	−2.69	490	51.6	0.4289	−2.57	−6.4	492
Nam-060	Und. (w)	0.4750	−6.23	383	77.0	0.6563	−6.00	+13.2	417
Nam-088	Und. (w)	0.6483	−5.04			0.8017	−5.39		1
Nam-204	Und. (w)	0.7449	−5.93	810	14.6	1.1783	−5.60	−2.8	670
Nam-205	Und. (w)	0.7853	−8.48			1.6404	−8.90	n.d.	4
Nam-206	Und. (w)	0.4215	−7.30	9	0.0	2.3383	−9.51	+4.1	91
Nam-208-Bis	Und. (w)	0.7199	−4.40	875	33.7	1.4022	−4.53	−1.7	807
Nam-209	Und. (w)	0.3804	−4.43	686	20.7	1.9794	−3.85	−2.1	719

δ^{15}N could be determined for only 9 of the 13 samples from the “undetermined” suite (range of −8.3‰ to +13.2‰), the remaining four samples were too low in N-content. Again, co-variations with δ^{13}C (from −9.5‰ to −2.6‰) or N-contents (from 0 to 1600 ppm) are not observed. A division of the “undetermined” suite according to inclusion chemistry (lherzolitic or websteritic affinity, see Table 3) is not reflected in the isotopic composition and nitrogen concentration of the host diamonds.

A comparison of δ^{13}C-values measured on two different fragments of the same diamonds (Fig. 5A and columns 4 and 8 in Tables 1–3) reveals isotopic homogeneity better than 2‰ for all but one sample (Nam-62, Table 2). The observed internal δ^{13}C-variation of 15‰ in this sample is unusual but not unprecedented (cf. Deines et al., 1991 and Cartigny et al., 2004 for similar zonation in diamonds from Jagersfontein and Kimberley Pool, respectively). N-contents measured on the same fragment by combustion and by FTIR compare well (Fig. 5B), with only one sample (Nam-217, see Table 3) being strongly heterogeneous.

Table 4
δ^{13}C, N contents (determined infrared spectroscopy) and percentage of the B species in diamonds of unknown paragenesis (no inclusions recovered)

Sample	Paragenesis	Weight (mg)	δ^{13}C (‰)	N FTIR (ppm)	%B
Nam-009	Unk.	0.6221	−2.55	440	8.4
Nam-025	Unk.	1.0767	−5.35	813	27.4
Nam-057	Unk.	0.4837	−6.01	547	20.5
Nam-058	Unk.	0.4083	−5.75	1127	46.8
Nam-117	Unk.	0.9812	−5.35		
Nam-204-Bis	Unk.	0.7867	−21.08	228	34.4

4. Discussion

4.1. Nitrogen thermometry and inclusions-based geothermobarometry

It is now well accepted that the different nitrogen-bearing defects in diamond are linked by a diffusion process following second-order kinetics (Chrenko et al., 1977; Evans and Qi, 1982), with the percentage of the B-species depending upon the initial nitrogen concentration and the time-integrated thermal history of the diamond. Evans and Harris (1989) noticed that the activation energy for nitrogen in the A-centre to diffuse and form B-defects is very high and hence, the nitrogen aggregation state depends chiefly on nitrogen content and temperature and very little on time. This relationship is illustrated in Fig. 3 by the small difference between two sets of isopleths calculated for mantle residence times of 3 and 1 Ga, respectively. For a typical nitrogen content, this corresponds to a difference of less than 25 °C in residence temperature (see also Evans and Harris, 1989; Taylor et al., 1990; Navon, 1999). Nitrogen aggregation, therefore, is a good geothermometer.

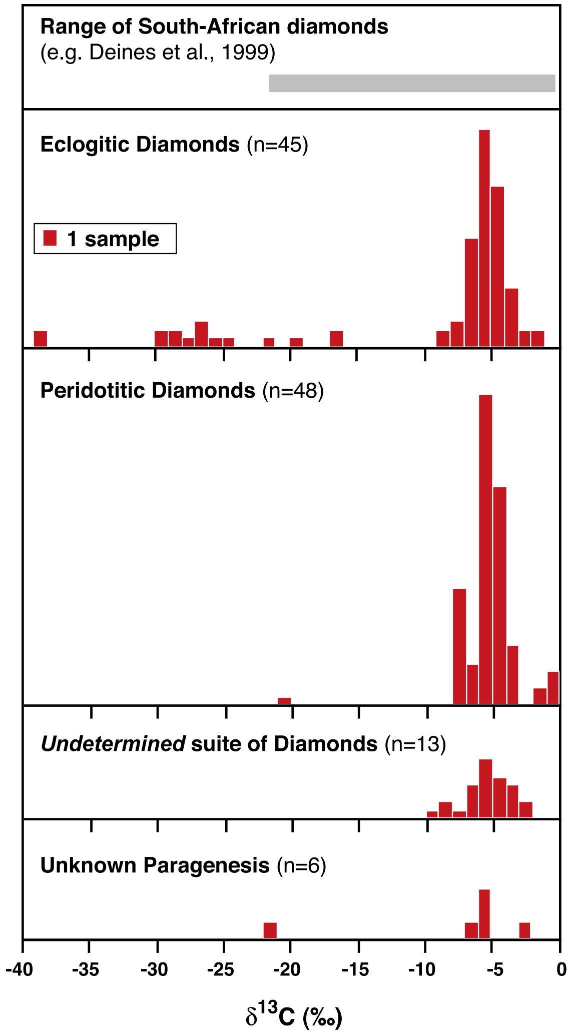

Fig. 1. δ^{13}C distributions of Namibian diamonds based on column 4 in Tables 1–4. Note that eclogitic diamonds extend the known range in δ^{13}C to a new minimum value of −38.5‰ and thereby clearly exceed the δ^{13}C range for known southern Africa diamond sources.

A comparison of temperatures derived from nitrogen aggregation and from exchange equilibria between silicate inclusions can provide further insights into the conditions during diamond formation and during mantle residence. In the case of Namibia, equilibration temperatures between 960 and 1300 °C were obtained for 31 inclusion bearing diamonds (Loest et al., 2003; Harris et al., 2004) of which only 23 were nitrogen-bearing. Table 5 compares the results of inclusion and nitrogen based temperature estimates, for the latter assuming mantle residence times of 1 ($T_{1\mathrm{Ga}}$) and 3 Ga ($T_{3\mathrm{Ga}}$). Nitrogen aggregation confines temperatures to a narrow interval ($T_{1\ \mathrm{Ga}}$: 1106–1272 °C). The extremely poor agreement between the two datasets is also illustrated in Fig. 6. Plastic deformation, heating, and possibly also the presence of other impurities within the diamond structure may enhance nitrogen aggregation (see Taylor et al., 1990; Navon, 1999) thereby causing differences between nitrogen and inclusion thermometry. However, these processes should lead to consistently higher temperatures derived from nitrogen aggregation and not to the scatter observed in Fig. 6. The large temperature range for the inclusions (340 °C) may also result from chemical disequilibrium between some non-touching inclusion pairs but poor agreement with estimates based on nitrogen aggregation is also evident where temperatures were derived from touching inclusions.

Based on inclusion thermometry and the presence of opx exsolutions from originally homogenous high-T clinopyroxenes, Loest et al. (2003) concluded that diamonds of the “undetermined” suite formed at high temperatures of about 1300–1500 °C before cooling to more usual lithospheric temperatures (1100–1300 °C). In view of generally lower equilibration temperatures for peridotitic and eclogitic inclusions (960 to 1300 °C; Harris et al. 2003 and our data), it may be expected that diamonds of the “undetermined” suite display higher nitrogen aggregation states (and consequently higher nitrogen temperatures). However, Fig. 3 shows that nitrogen aggregation and residence temperature for the “undetermined” suite of diamonds is not different from the rest of the dataset.

The only way to reconcile nitrogen aggregation states with the mineral equilibration temperatures is to assume diamond formation during short-lived thermal perturbations. Precipitation of diamonds may have occurred during infiltration of high-temperature melts (probably up to 1500 °C in the case of the “undetermined” suite) into colder subcontinental lithosphere (1100–1300 °C). In this scenario, the non-touching inclusions and the re-combined cpx–opx intergrowths of the “undetermined” suite (Loest et al., 2003) record the temperature of diamond formation, whereas N-aggregation reflects a time averaged thermal histo-

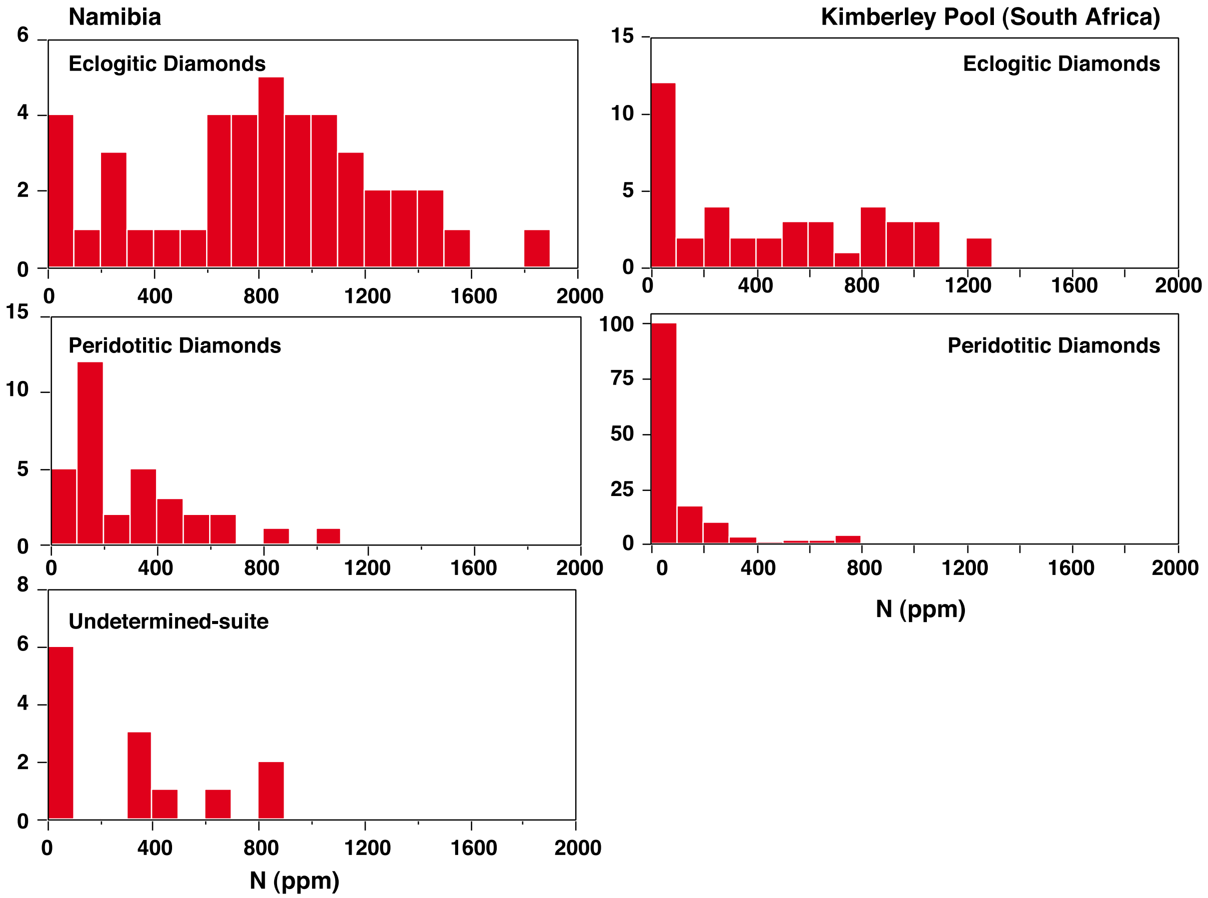

Fig. 2. Histograms comparing the N-contents (ppm, i.e. µg/g) in diamonds from Namibia and from the Kimberley Pool, South Africa (Cartigny et al., 2001a) as a typical example of diamond populations elsewhere.

ry. This implies that cooling and readjustment to a local geotherm occurred fairly rapidly after diamond formation, otherwise the rather narrow range in residence temperatures (1106–1272 °C) for diamonds of the "undetermined", the peridotitic and the eclogitic suite should not exist.

4.2. Are the eclogitic, peridotitic and undetermined diamond suites related?

The headwaters of the combined Orange and Vaal rivers cover a large portion of southern Africa. Assuming that the diamonds from the Namibian placer deposits are indeed derived from the hinterland of South Africa (e.g. Meyer 1991), it seems unlikely that the suite of diamonds studied here should be derived from a single kimberlitic source. However, our $\delta^{13}C-\delta^{15}N-N$ data appear to suggest the opposite, i.e. that most, if not all, the Namibian diamonds studied were derived from a common source. Our Namibian samples are set apart from diamonds derived from worldwide sources by their overall N-rich character. Previous studies on total nitrogen contents in diamonds ($n \sim 3000$)–mostly derived from the Kaapvaal (e.g. Deines et al., 1987, 1989, 1991) but also from the Sino-Korean Craton (Cartigny et al., 1997), the Slave (unpublished data) and West Africa (Stachel and Harris, 1997)–have shown nitrogen arrays similar to the distribution for Kimberley Pool diamonds (Cartigny

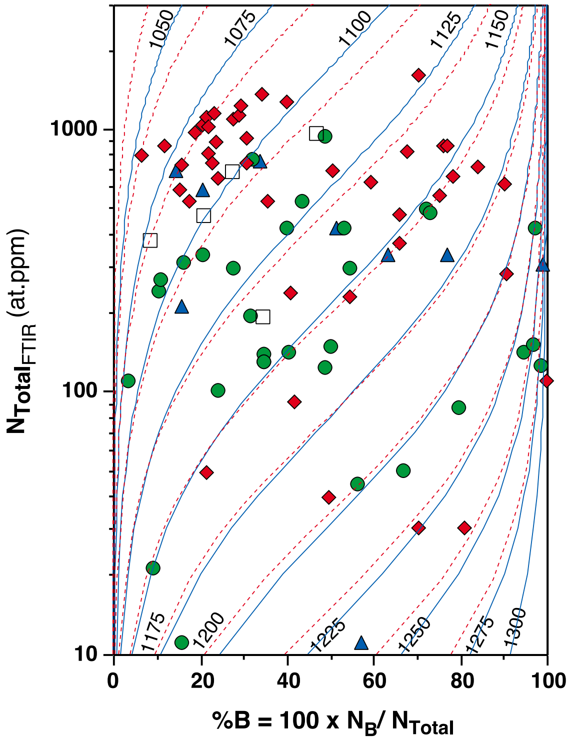

Fig. 3. Relationships of nitrogen aggregation state with total nitrogen content (determined by FTIR). Diamond shaped symbols denote eclogitic samples, circles indicate peridotitic diamonds, triangles represent the "undetermined" suite and open squares are diamonds of unknown paragenesis. Time integrated isopleths (temperature in °C) are constructed for mantle residence times of 3 Ga (solid lines) and 1 Ga (dashed lines).

et al., 2001a) presented in Fig. 2. Worldwide data also typically indicate a significant proportion of Type II diamonds (20% to 80% in some cases, see Harris and Spear, 1986; Deines et al., 1987, 1989, 1991). In contrast, our Namibian sample set contains relatively few Type II diamonds and reveals an unusually high proportion of eclogitic and peridotitic diamonds (there are no worldwide reference data for the undetermined suite) with high N-contents (Fig. 2). For example, ~ 70% of eclogitic diamonds from Namibia have N-contents higher than 600 ppm, compared to only ~ 40% at Kimberley Pool (Cartigny et al., 2001a). The overall N-rich character of Namibian diamonds is unlikely to result from random mixing of sources with characteristics like Kimberley Pool, but rather suggests that most of our samples share a common source and origin. This proposed uniqueness of the primary source for Namibian diamonds is supported by three additional observations:

(a) On a worldwide basis, a relationship of decreasing maximum nitrogen content with decreasing $\delta^{13}C$ has been identified (Stachel and Harris, 1997; Cartigny et. al., 2000a,b) and the corresponding "limit sector" is depicted in Fig. 7. Four eclogitic diamonds from Namibia fall on the "forbidden", nitrogen-rich side of the limit sector. Thus N-rich diamonds from Namibia are not restricted to mantle-like $\delta^{13}C$-values $(\sim -5 \pm 3‰)$ but may also show strongly negative (i.e. $\delta^{13}C < -10‰$) isotopic compositions.
(b) Worldwide data indicate a decrease in maximum nitrogen content with increasing $\delta^{15}N$ (solid line in Fig. 4B) and again, five diamonds (eclogitic, peridotitic and "undetermined" suite) from Namibia plot outside the worldwide array, being too nitrogen-rich for their high $\delta^{15}N$.
(c) With the exception of eight eclogitic diamonds with low $\delta^{13}C$, the overlap of the eclogitic, peridotitic and "undetermined" suites in $\delta^{13}C$–$\delta^{15}N$–N space (Fig 4) is striking. For samples with mantle-like $\delta^{13}C$ (grey horizontal band in Fig. 4B), all three suites of Namibian diamonds extend the previously known $\delta^{15}N$-range towards more positive values.

The observation that Namibian diamonds share certain unique characteristics irrespective of their inclusion paragenesis (peridotitic, eclogitic and "undetermined" suites) suggests a commonality in growth mechanism that is independent of source rock composition. We propose that the common characteristic of overall high nitrogen contents implies a similar metasomatic origin for all Namibian diamonds. Differences in crystallization temperature (e.g. a hot origin for the "undetermined" suite) and in the buffering capacity of the source for CO_2 (facilitating isotopic fractionation for eclogitic sources, Cartigny et al. 1998a,b) introduced some diversity among diamonds of different paragenesis without completely masking the common characteristics of the metasomatic event(s).

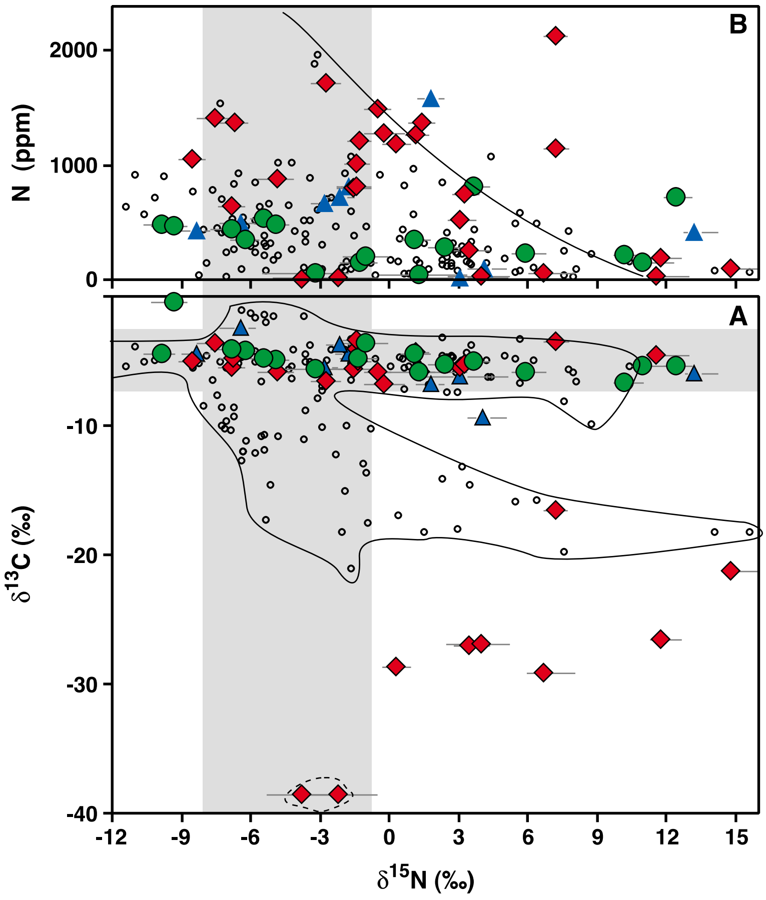

Fig. 4. (A, bottom) δ^{15}N versus N-content for diamonds from Namibia. The decrease in maximum N-content with increasing δ^{15}N identified in previous studies on samples from worldwide sources in indicated by a solid black line. (B, top) δ^{13}C versus δ^{15}N for diamonds from Namibia (same symbols as Fig. 3). Small open circles correspond to published analyses of peridotitic and eclogitic diamonds worldwide (Cartigny et al., 1998a,b; 1999 and references therein), their compositional variation is outlined as a solid black line. The two analyses for Nam-027 are enclosed by a dashed line. The ranges for "mantle-like" δ^{13}C and δ^{15}N are indicated as grey fields in A and B.

4.3. Origin and formation of diamonds from Namibia

A number of isotopic tracers have been employed to establish a link between eclogitic diamonds and subducted oceanic crust (see Navon, 1999 for review), involving, e.g. the oxygen isotopic composition of eclogite xenoliths (Jagoutz et al., 1984; Jacob et al., 1994; Barth et al., 2002), and eclogitic silicate inclusions in diamonds (Lowry et al., 1999; Schulze et al., 2003) or the sulfur isotopic signature of sulfide inclusions in diamonds (Chaussidon et al. 1987; Rudnick et al., 1993; Farquhar et al., 2002). These studies have produced strong evidence that diamond formation in subducted source rocks does indeed occur. However, the oxygen and sulfur isotopic data cannot be used to constrain the source of the carbon from which the diamonds formed as its origin may well be de-coupled from that of the host rocks.

Consequently, the role of isotopically heterogeneous, subducted carbon in the formation of eclogitic diamonds is still subject of considerable debate. Direct formation of eclogitic diamonds from metasedimentary carbon may explain the low δ^{13}C character observed for many of these diamonds. However, considering that about 80% of subducted carbon is inorganic with $\delta^{13}C \approx 0$‰ (see Cartigny et al., 1998a,b, such a process should lead to a large amount of eclogitic diamonds with positive δ^{13}C-

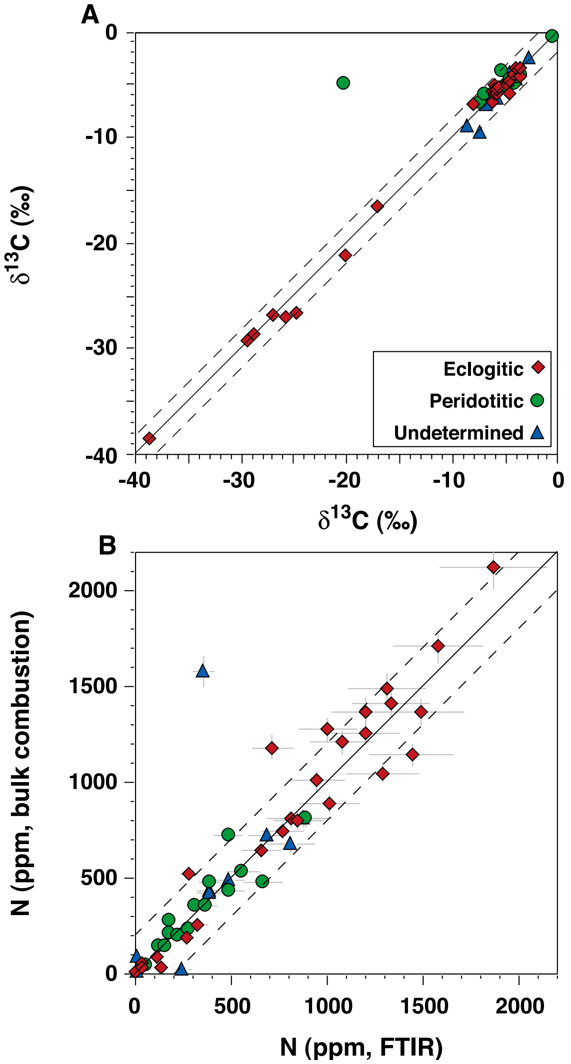

Fig. 5. (A, top) Comparison of δ^{13}C-values measured on two cleavage chips from the same diamond. Dashed lines indicate variations of 2‰. (B, bottom) N-contents as determined by FTIR and by bulk combustion using the same diamond fragment. Dashed lines indicate a difference of 200 ppm. Most samples show heterogeneity smaller than 2‰ and 200 ppm in δ^{13}C and N-contents, respectively.

values. In the present paper and in numerous previous studies, positive δ^{13}C-values were shown to be very scarce. Positive δ^{13}C-values would also be expected if eclogitic diamonds resulted from mixing of mantle-derived and recycled metasedimentary carbon (e.g. Kirkley et al., 1991; Navon, 1999).

A variation of the above mixing model is the selective combination of recycled carbon significantly depleted in ^{13}C (e.g. < -25‰, typical for organic matter) and mantle-derived carbon with a δ^{13}C of around -5‰ (e.g. Navon, 1999). Such a mixing process could occur during injection of mantle-derived carbon into eclogite containing recycled metasedimentary carbon. However, δ^{13}C–δ^{15}N relationships displayed by eclogitic diamonds from Jwaneng and Orapa are inconsistent with such a mixing model (Cartigny et al., 1998b, 1999). In particular, a mixing model would require that the recycled end-member is low in nitrogen (Cartigny et al. 2001a), contrasting with the nitrogen-rich character of indisputably subduction-related diamonds such as the metamorphic diamonds from the Kokchetav massif (see Sobolev and Schatsky, 1990; De Corte et al., 1998; Cartigny et al. 2001b). In addition, mixing of mantle-like carbon into a metasedimentary source should lead to strong zonation within eclogitic diamonds from cores with low δ^{13}C (typical of recycled organic carbon) to rims with δ^{13}C-values around -5‰ (reflecting the composition of the injected primitive carbon). As shown, e.g. in Fig. 5, heterogeneity of diamonds in δ^{13}C is usually restricted to a few per mil. More complex models involving the dissolution of preexisting diamonds are not supported by data on fibrous diamonds (see Boyd et al., 1994a,b). Homogenisation after diamond crystallisation through isotopic diffusion (Harte et al., 1999) also is not supported by new experimental data (Koga et al., 2003).

A subduction origin of diamond carbon can be further tested using N-isotopes. Nitrogen is not only the main impurity in diamond (Kaiser and Bond, 1959) but also has the advantage that its isotopic composition (δ^{15}N) varies strongly from mantle material (mostly negative) to metasediments (strictly positive) (see Cartigny et al., 1998a and references therein). In this framework, available data have revealed strong similarity between eclogitic and peridotitic diamonds with both displaying largely negative δ^{15}N-values (Cartigny et al., 1998a,b, 1999). This observation implies a strong contribution of mantle-derived carbon for both diamond suites. Accordingly, differences in the δ^{13}C-distribution of eclogitic and peridotitic diamonds are in general more readily explained by variations in source min-

Table 5
Temperature estimates based on exchange equilibria between co-existing silicate inclusions and nitrogen aggregation characteristics for 23 Type I diamonds from Namibia

Sample	Paragenesis	Temperature	[Method]	N FTIR (ppm)	%B	$T_{1\ \mathrm{Ga}}$	$T_{3\ \mathrm{Ga}}$
Nam-034	E	1236	[Krogh]	1483	39.9	1125	1099
Nam-038	E	1080	[Krogh]	1437	29.4	1115	1089
Nam-086	E	1165	[Krogh]	844	15.8	1109	1083
Nam-089	E	1207	[Krogh]	812	50.8	1151	1124
Nam-114	E	961	[O'Neill]	35	80.9	1115	1090
Nam-203	E	1193	[Krogh]	946	21.9	1123	1097
Nam-218	E	1304	[Krogh]	1070	30.7	1275	1243
Nam-016	P	1079	[O'Neill]	484	97.5	1123	1097
Nam-029	P	1141	[Harley]	117	24.0	1170	1142
Nam-046	P	982	[O'Neill]	176	97.0	1177	1149
Nam-051-Bis	P	1092	[BKN]	308	11.1	1230	1200
Nam-071	P	1063	[O'Neill]	165	40.5	1214	1185
Nam-094	P	1209	[O'Neill]	174	50.2	1263	1231
Nam-101	P	1206	[O'Neill]	279	10.4	1287	1255
Nam-104	P	1212	[Harley]	151	34.8	1181	1153
Nam-109	P	1041	[Harley]	51	56.3	1190	1161
Nam-110	P	1138	[Harley]	13	15.7	1123	1098
Nam-113	P	1041	[O'Neill]	363	16.2	1129	1103
Nam-210	Underterm (L)	1185	[BKN]	247	15.8	1138	1112
Nam-211	Underterm (L)	1101	[BKN]	383	63.5	1183	1155
Nam-217-Bis	Underterm (L)	1222	[BKN]	13	57.0	1269	1238
Nam-208-Bis	Undeterm. (W)	1269	[BKN]	875	33.7	1132	1105
Nam-209	Undeterm. (W)	1297	[BKN]	686	20.7	1121	1095

$T_{1\ \mathrm{Ga}}$ and $T_{3\ \mathrm{Ga}}$ are temperatures estimated based on mantle residence times of 1 and 3 Ga, respectively. For the calculations, an activation energy of 7.0 eV and an Arrhenius constant of 2.94×10^5 atomic ppm^{-1} s^{-1} for the IaA to IaB transition (Cooper, 1990; Taylor et al., 1990) was used.

eralogy (causing large differences in the buffering capacity for CO_2) than by different carbon sources (Cartigny et al., 1998b).

Interpreting the isotopic characteristics and nitrogen concentrations of Namibian diamonds in the context of this discussion reveals a complex picture that fits neither a pure mantle origin nor a subduction model. About half the diamonds have negative δ^{15}N-values in support of mantle-derived nitrogen and carbon. In such a scenario, lower δ^{13}C and/or positive δ^{15}N-values could result from stable-isotope fractionation of mantle-derived metasomatic fluids with initial δ^{13}C and δ^{15}N of about -5‰. However, such a fractionation model is not feasible in light of the high nitrogen concentrations of some diamonds with "evolved" compositions. For example, in a fractionation model, the eight eclogitic diamonds with δ^{13}C-values < -10‰ should define a trend of decreasing nitrogen content with decreasing δ^{13}C (Cartigny et al., 2001a). In contrast to other locations (e.g. Orapa and Jwaneng), this is not the case for Namibian diamonds where two eclogitic samples with strongly negative δ^{13}C have nitrogen contents >1000 ppm. Similar observations apply to the nitrogen isotopic composition, where some peridotitic and eclogitic diamonds from Namibia with δ^{13}C ≈ -5‰ display high N-contents and positive δ^{15}N-values. Again this is inconsistent with a fractionation model that predicts that positive δ^{15}N should be associated with low N-contents.

Thus, the model derived from eclogitic and peridotitic diamonds from Orapa, Jwaneng and Kimberley Pool (Cartigny et al., 2001a and references therein), stating that variations in C- and N-isotopic composition resulted from fractionation in the mantle, cannot be extended to the present dataset. Diamonds from Namibia (eclogitic, peridotitic and "undetermined" suite) with positive δ^{15}N and simultaneously high N-content may either reflect

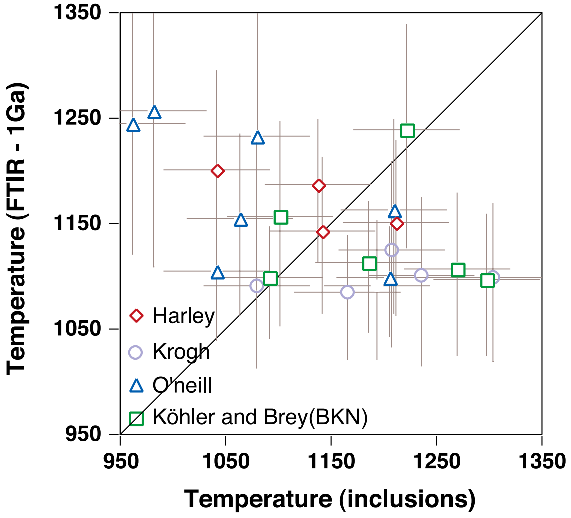

Fig. 6. Comparison of temperatures deduced from nitrogen characteristics assuming a mantle residence time of 1 Ga with results of conventional inclusion thermometry (results of Loest et al., 2003; Harris et al., 2004). The following mineral exchange equilibria were used: Harley = grt – opx; Krogh = grt – cpx; O'Neill = grt – olivine; BKN = cpx – opx.

formation from subduction-related metasomatic fluids/melts, as envisaged for the metamorphic diamonds from the Kokchetav massif (Cartigny et al., 2001a,b) or resulted from complex fractionation (from methane-rich fluids?) or mixing processes which have not been previously recognized.

5. Conclusions

Compared with diamonds from worldwide sources, alluvial diamonds from Namibia are distinctive because of their unusually high N-contents and in part uncommon C and N isotopic compositions. High N contents are not restricted to a single inclusion paragenesis but occur among samples of the eclogitic, peridotitic and "undetermined" suite (the latter related to high-temperature metasomatism). This overall similarity of all parageneses is unlikely to be a coincidence, but suggests a genetic relationship. Consequently, we suggest that most if not all diamonds from Namibia formed during a common metasomatic process that introduced both carbon and nitrogen into the various source rocks.

Negative δ^{15}N-values imply that at least half the diamonds (eclogitic, peridotitic and "undetermined" suite) crystallised from mantle-derived fluids. Whether diamonds with high N-contents together with positive δ^{15}N-values (in some cases associated with δ^{13}C below -10‰) are related to the same fluid source is uncertain. The observation that diamonds with such anomalous compositions are not restricted to the eclogitic suite is not in support of a formation directly from subducted carbon. More likely, this second group documents an additional fluid source which may be a subducting slab.

In any case, the close similarity of diamonds formed in a large variety of source rocks clearly supports precipitation from external carbon sources.

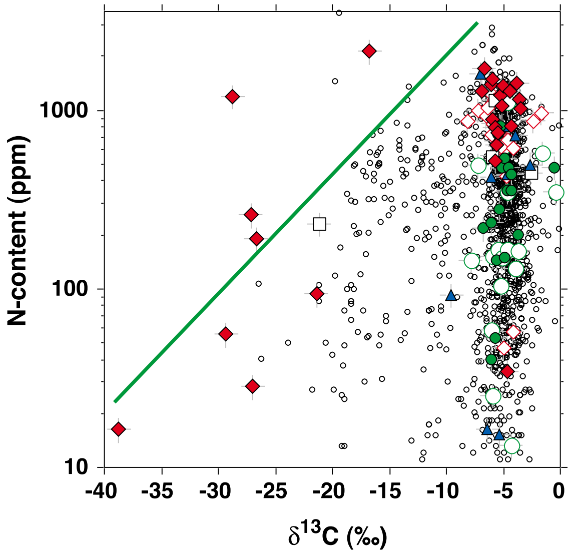

Fig. 7. N-content versus δ^{13}C for eclogitic (diamonds), peridotitic (circles) and undetermined-paragenesis diamonds (triangles) from Namibia. Filled symbols correspond to δ^{13}C–N data obtained by combustion on a single diamond fragment. Open symbols indicate that the N-content was measured by FTIR using a different fragment than the one analysed for δ^{13}C. Diamond from worldwide sources (open circles) and the proposed limit sector of Cartigny et al. 2001a, solid line) are shown for comparison. From the distribution of the data, it is apparent that diamonds from Namibia are characterised by unusually high N-contents (see also Fig. 2 and Fig. 4A).

Acknowledgements

Funding by the German Research Foundation (DFG) and the French INSUE-CNRS is gratefully acknowledged. DeBeers Consolidated Mines Limited is thanked for kindly providing the specimens used in this study. This manuscript benefited from constructive reviews by Peter Deines and Elad Izraeli. IPGP contribution 1960.

References

Barth, M., Rudnick, R.L., Horn, H., McDonough, W.F., Spicuzza, M.J., Valley, J.W., Haggerty, S.E., 2000. Geochemistry of xenolithic eclogites from West Africa: Part I. A link between low MgO eclogites and archean crust formation. Geochim. Cosmochim. Acta 65, 1499–1527.

Barth, M., Rudnick, R.L., Horn, H., McDonough, W.F., Spicuzza, M.J., Valley, J.W., Haggerty, S.E., 2002. Geochemistry of xenolithic eclogites from West Africa: Part 2. Origins of the high MgO eclogites. Geochim. Cosmochim. Acta 66, 4325–4345.

Boyd, S.R., Kiflawi, I., Woods, G.S., 1994a. The relationship between infrared absorption and the A defect concentration in diamond. Philos. Mag., B 69, 1149–1153.

Boyd, S.R., Pineau, F., Javoy, M., 1994b. Modelling the growth of natural diamonds. Chem. Geol. 116, 29–42.

Boyd, S.R., Réjou-Michel, A., Javoy, M., 1995a. Improved techniques for the extraction, purification and quantification of nanomole quantities of nitrogen gas: the nitrogen content of a diamond. Meas. Sci. Technol. 6, 297–305.

Boyd, S.R., Kiflawi, I., Woods, G.S., 1995b. Infrared absorption by the B nitrogen aggregate in diamond. Philos. Mag., B 72, 351–361.

Cartigny, P., Boyd, S.R., Harris, J.W., Javoy, M., 1997. Nitrogen isotopes in peridotitic diamonds from Fuxian, China: the mantle signature. Terra Nova 9, 175–179.

Cartigny, P., Harris, J.W., Javoy, M., 1998. Formation of eclogitic diamonds at Jwaneng: no room for a recycled component. Science 280, 1421–1423.

Cartigny, P., Harris, J.W., Philips, D., Girard, M., Javoy, M., 1998. Subduction-related diamonds?—The evidence for a mantle derived origin from coupled δ^{13}C–δ^{15}N determinations. Chem. Geol. 147, 147–159.

Cartigny, P., Harris, J.W., Javoy, M., 1999. Eclogitic, peridotitic and metamorphic diamonds and the problems of carbon recycling: the case of Orapa (Botswana). In: Gurney, J.J., Gurney, J.L., Pascoe, M.D., Richardson, S.H. (Eds.), Proceedings of the 7th International Kimberlite Conference, vol. 1. Red Roof Design, Cape Town, pp. 117–124.

Cartigny, P., Harris, J.W., Javoy, M., 2001a. Diamond genesis, mantle fractionations and mantle nitrogen content: a study of δ^{13}C–N concentrations in diamonds. Earth Planet. Sci. Lett. 185, 85–98.

Cartigny, P., et al., 2001b. The origin and formation of metamorphic microdiamonds from the Kokchetav massif, Kazakhstan: a nitrogen and carbon isotopic study. Chem. Geol. 176, 267–283.

Cartigny, P., Harris, J.W., Girard, M., Javoy, M., 2004. Eclogitic and peridotitic diamonds from Kimberley Pool kimberlites (South Africa): C- and N stable isotope evidence for a main mantle-derived source. Geochim. Cosmochim. Acta.

Chaussidon, M., Albarède, F., Sheppard, S.M.F., 1987. Sulfur isotope heterogeneity in the mantle from ion microprobe measurements of sulphide inclusions in diamonds. Nature 330, 242–244.

Chrenko, R.M., Tuft, R.E., Strong, H.M., 1977. Transformation of the state of nitrogen in diamond. Nature 270, 141–144.

Cooper, G.I., 1990. Infrared microspectroscopy of diamond in relation to mantle processes. PhD thesis, University of London, p. 262.

De Corte, K., Cartigny, P., Shatsky, V.S., Sobolev, N.V., Javoy, M., 1998. First evidence of fluid inclusions in metamorphic microdiamonds from the Kokchetav massif, Northern Kazakhstan. Geochim. Cosmochim. Acta 62, 3765–3773.

Deines, P., Harris, J.W., Gurney, J.J., 1987. Carbon isotopic composition, nitrogen content and inclusion composition of diamonds from the Roberts Victor kimberlite, South Africa: evidence for a ^{13}C depletion in the mantle. Geochim. Cosmochim. Acta 51, 1227–1243.

Deines, P., Harris, J.W., Spear, P.M., Gurney, J.J., 1989. Nitrogen and ^{13}C content of Finsch and Premier diamonds and their implications. Geochim. Cosmochim. Acta 53, 1367–1378.

Deines, P., Harris, J.W., Gurney, J.J., 1991. The carbon isotopic composition and nitrogen content of lithospheric and asthenospheric diamonds from the Jagersfontein and Koffiefontein Kimberlite, South Africa. Geochim. Cosmochim. Acta 55, 2615–2625.

Deines, P., Viljoen, K.S., Harris, J.W., 1999. Implications of the carbon isotope and mineral inclusion record for the formation of diamonds in the mantle underlying a mobile belt; Venetia, South Africa. Geochim. Cosmochim. Acta 65, 813–838.

Evans, T., Harris, J.W., 1989. Nitrogen aggregation, inclusion equilibration temperatures and the age of diamonds. In: Ross, J. (Ed.), Kimberlites and Related Rocks—Their Mantle/Crust Setting, Diamonds and Diamond Exploration. Spec. Publ.-Geol. Soc., vol. 14. Blackwell, Oxford, UK, pp. 1001–1006.

Evans, T., Qi, Z., 1982. The kinetics of the aggregation of nitrogen atoms in diamond. Phil. Trans. R. Soc. Lond., A 381, 159–178.

Farquhar, J., Wing, B.A., McKeegan, K.D., Harris, J.W., Cartigny, P., Thiemens, M.H., 2002. Mass-independent sulfur of inclusions in diamond and sulfur recycling on early Earth. Science 298, 2369–2371.

Griffin, W.L., Gurney, J.J., Ryan, C.G., 1992. Variations in trapping temperatures and tarce elements in peridotite-suite inclusions from African diamonds: evidence for two inclusion suites, and implications for lithosphere stratigraphy. Contrib. Mineral. Petrol. 110, 1–15.

Harris, J.W., Spear, P.M., 1986. Systematic studies of nitrogen in diamonds from known sources. Ext. Abstracts, 4th Int. Kimberlite Conf. Spec. Publ.- Geol. Soc. Aust., vol. 16. Perth, Oxford, UK, pp. 398–400.

Harris, J.W., Stachel, T., Loest, I., Brey, G.P., 2004. Peridotitic diamonds from Namibia: constraints on the composition and evolution of their mantle source 77, 209–223 this issue.

Harte, B., Fitzsimons, I.C.W., Harris, J.W., Otter, M.L., 1999. Carbon isotope ratios and nitrogen abundances in relation to cathodoluminescence characteristics for some diamonds from the Kaapvaal Province, S. Africa. Min. Mag. 63, 829–856.

Izraeli, E.S., Harris, J.W., Navon, O., 2001. Brine inclusions in diamonds: a new upper mantle fluid. Earth Planet. Sci. Lett. 187, 323–332.

Jacob, D., Jagoutz, E., Lowry, D., Mattey, D., Kudrajavtseva, G., 1994. Diamondiferous eclogites from Siberia: remnants of Archean oceanic crust. Geochim. Cosmochim. Acta 58, 5191–5207.

Jagoutz, E., Dawson, J.B., Hoernes, S., Spettel, B., Wänke, H., 1984. Anorthositic oceanic crust in the Archean Earth. 15th Lunar Planet. Sci. Conf., J. of Geophys. Res., Suppl., 395–396.

Kaiser, W., Bond, L., 1959. Nitrogen, a major impurity in common type I diamond. Phys. Rev. 115, 857–863.

Keller, R.A., Taylor, L.A., Snyder, G.A., Sobolev, V.N., Carlson, W.D., Bezborodov, S.M., Sobolev, N.V., 1999. Detailed pull-apart of a diamondiferous eclogite xenolith: implications for mantle processes during diamond genesis. In: Gurney, J.J., Gurney, J.L., Pascoe, M.D., Richardson, S.H. (Eds.), Proceedings of the 7th International Kimberlite Conference, vol. 1. Red Roof Design, Cape Town, pp. 397–402.

Kirkley, M.B., Gurney, J.J., Otter, M.L., Hill, S.J., Daniels, L.R., 1991. The application of C isotope measurement to the identification of the sources of C in diamonds: a review. Appl. Geochem. 6, 447–494.

Koga, K.T., Van Orman, J.A., Walter, M.J., 2003. Diffusive relaxation of carbon and nitrogen isotope heterogeneity in diamond: a new thermochronometer. Phys. Earth Planet. Inter. 139, 35–43.

Loest, I., Stachel, T., Brey, G.P., Harris, J.W., Ryabchikov, I.D., 2003. Diamond formation and source carbonation: mineral associations in diamonds from Namibia. Contrib. Mineral. Petrol. 145, 15–24.

Lowry, D., Mattey, D.P., Harris, J.W., 1999. Oxygen isotope composition of syngenetic inclusions in diamond from the Finsch Mine, RSA. Geochim. Cosmochim. Acta 63, 1825–1836.

Meyer, H.O.A., 1991. Marine diamonds of southern Africa. Diam. Int., 49–58.

Navon, O., 1999. Diamond formation in the Earth's mantle. In: Gurney, J.J., Gurney, J.L., Pascoe, M.D., Richardson, S.H. (Eds.), Proceedings of the 7th International Kimberlite Conference, vol. 2. Red Roof Design, Cape Town, pp. 584–604.

Rudnick, R.L., Eldridge, C.S., Bulanova, G.P., 1993. Diamond growth history from in situ measurement of Pb and S isotopic compositions of sulfide inclusions. Geology 21, 13–16.

Schulze, D.J., Wiese, D., Steude, J., 1996. Abundance and distribution of diamonds in eclogite revealed by volume visualization of CT X-Ray scans. J. Geol. 104, 109–113.

Schulze, D.J., Harte, B., Valley, J.W., Brenan, J.M., Channer, D.M.R., 2003. Extreme crustal oxygen isotope signatures preserved in coesite in diamond. Nature 423, 68–70.

Shimizu, N., Richardson, S.H., 1987. Trace element abundance patterns of garnet inclusions in peridotite-suite diamonds. Geochim. Cosmochim. Acta 51, 755–758.

Shirey, S.B., Harris, J.W., Richardson, S.H., Fouch, M.J., James, D.E., Cartigny, P., Deines, P., Viljoen, K.S., 2002. Diamond Genesis, seismic Structure, and evolution of the Kaapvaal–Zimbabwe Craton. Science 297, 1683–1686.

Sobolev, N.V., Schatsky, V.S., 1990. Diamond inclusions in garnet from metamorphic rocks: a new environment for diamond formation. Nature 343, 742–745.

Stachel, T., Harris, J.W., 1997. Syngenetic inclusions in diamond from the Birim field (Ghana)—a deep peridotitic profile with a history of depletion and re-enrichment. Contrib. Mineral. Petrol. 127, 336–352.

Stachel, T., Aulbach, S., Brey, G.P., Harris, J.W., Loest, I., Tappert, R., Viljoen, K.S., 2004. The Trace Element Composition of Silicate Inclusions in Diamonds: A Review, 77, 1–19 (this issue).

Taylor, W.R., Jaques, A.L., Ridd, M., 1990. Nitrogen-defect aggregation characteristics of some Australian diamonds: time–temperature constraints on the source regions of pipe and alluvial diamonds. Am. Mineral. 75, 1290–1310.

Taylor, L.A., Snyder, G.A., Crozaz, G., Sobolev, V.N., Yemimova, E.S.., Sobolev, N.V.., 1996. Eclogitic inclusions in diamonds: evidence of complex mantle processes over time. Earth Planet. Sci. Lett. 142, 535–551.