Diamond origin and genesis: A C and N stable isotope study on diamonds from a single eclogitic xenolith (Kaalvallei, South Africa)

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ABSTRACT

In order to study the geochemistry of diamonds formed during similar growth conditions in a very localised environment in the mantle, we carried out a detailed study of the variation in $\delta^{15}N$, $\delta^{13}C$, N content, and N aggregation state of 35 diamonds in a single eclogite xenolith from the Kaalvallei kimberlite in South Africa. Diamond nitrogen contents determined by infrared spectroscopy range from 239 ppm to 1272 ppm, and are positively correlated with nitrogen aggregation states which vary from 11.5% to 43.7% of IaB defects. Modelling of these parameters using second order reaction kinetics suggests that the diamonds likely represent a single population which has been resident in the mantle at temperatures of 1090 °C to 1190 °C. $\delta^{13}C$ values of the diamonds analysed range from -6.0‰ to -4.2‰, while $\delta^{15}N$ values vary from -8.9‰ to -4.1‰, with no correlation between $\delta^{13}C$ and $\delta^{15}N$. These values account for 5% and 15%, respectively, of the worldwide isotopic range for diamonds. The limited variability of C and N isotopic compositions for the diamonds analysed are compatible with a model of metasomatic diamond formation from a single, homogeneous fluid, and this is also supported by the infrared data. Although the absence of any clear correlation between $\delta^{15}N$, $\delta^{13}C$ and diamond N content precludes the accurate identification of the fluid species involved in diamond growth, the lack of correlation may indicate the involvement of a carbonate- or CO_2-type fluid.

The observed range in negative $\delta^{15}N$ values for all the diamonds analysed are within the limits of the so-called mantle range ($\delta^{15}N_{mantle} = -5 \pm 2$‰) which is consistent with a mantle origin for these diamonds. Negative $\delta^{15}N$ is inconsistent with diamond formation from recycled (crustal) material which is enriched in ^{15}N (i.e. positive $\delta^{15}N$).

In contrast, positive europium and strontium anomalies in silicate minerals of the host xenolith, as well as oxygen isotopic data which deviate from the mantle range, are consistent with a protolith consisting of recycled oceanic crust. It is therefore concluded that our data supports a model of metasomatic diamond crystallisation from a mantle-carbon source.

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1. Introduction

The high strength and inert nature of diamond makes it an ideal substance on which to study the interior of the earth from e.g. the base of the lithosphere (150–250 km) to the transition zone, and also in to the lower mantle (>660 km; Stachel et al., 2000a,b). Thus, diamond and its impurities can provide insight into aspects of mantle mineralogy as well as the origin of the lithosphere and its evolution. (Deines et al., this issue; Kaminsky et al., this issue; Batumike et al., this issue; Sobolev et al., this issue). Based on the mineralogy and major element chemistry of inclusions in diamonds, it is by now well established that diamond crystallises primarily in two differing lithologies, namely peridotite and eclogite (Sobolev, 1977; Stachel and Harris, 2008; references therein). Over the last 30 years, these studies have also helped constrain our understanding of e.g. the temporal evolution of the lithospheric mantle (Shirey et al., 2002). Such studies, however, face a series of difficulties. Diamonds are usually recovered as mixed populations from the host kimberlite, and may represent a variety of high-pressure host rocks (as attested by e.g. the variability in the Cr and Ca content of peridotitic garnets occurring as inclusions in diamonds), derived from distinct temperature regimes in the mantle, which may correspond to varying diamond mantle residence times. The presence of such mixed populations might explain why typically only weak correlations between e.g. $\delta^{13}C$ and diamond N contents are observed.

In order to constrain models of diamond genesis more accurately it is necessary to focus on diamond populations characterised by similar growth conditions e.g. those from diamond-bearing eclogite and peridotite xenoliths (see for instance Thomassot et al., 2007). Eclogite represents a comparatively minor component of the earth's mantle

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(Schulze et al., 1996), yet may account for a significant proportion of the xenolith and diamond population at many kimberlites worldwide. Diamond-bearing eclogite also tends to predominate amongst diamondiferous xenoliths (Gurney, 1989). This over-abundance of diamond in eclogite was explained by Luth (1993) as being a consequence of two combined effects: (1) the relatively more reduced nature of eclogite compared to peridotite (O'Neill et al., 1993) would result in enhanced stability of diamond in eclogite (Luth, 1993), and (2) olivine-bearing mantle xenoliths such as peridotites are probably more easily altered and disaggregated relative to eclogite (Luth, 1993).

Diamond-bearing eclogites are unusually abundant at some of the kimberlites in South Africa e.g. the Kaalvallei kimberlite. Eclogites at the locality have also been well-studied (Viljoen, 2005). The current investigation therefore focuses on 35 diamonds extracted from a single eclogite (sample K8/109) from Kaalvallei, and serves to complement an earlier study on diamonds from a diamondiferous peridotite recovered at the Premier diamond mine (Thomassot et al., 2007). It also aims to provide insights into the other major high-pressure diamond host, namely eclogite. Observed relationships between carbon and nitrogen isotopic composition, and diamond growth, place constraints on (a) the origin of eclogitic diamonds and their relationship with their eclogitic host, (b) diamond genesis in relation to metasomatic processes, and (c) the implications thereof for models of diamond growth in the subcratonic lithosphere.

2. Xenoliths and diamonds at Kaalvallei

The Kaalvallei kimberlite is located in the Free State region of South Africa, on the farm Kaalvallei12, approximately 7.5 km from the town of Welkom along the Welkom–Virginia road (Fig. 1 in Viljoen, 1994; Viljoen, 2005). It occurs on the Kaapvaal craton, and intrudes shales and sandstones of the Ecca Group. The occurrence comprises of a roughly circular main pipe with surface area of 2 ha, and a satellite intrusion located 300 m west of the main pipe (Stiefenhofer, 1989). Monticellite-bearing kimberlite varieties predominate and the main pipe is classified petrographically and isotopically as a Group I kimberlite (Smith, 1983; Skinner, 1989), with an Rb–Sr mica age of 85 ± 1 Ma (Viljoen, 1994).

The diamond-bearing xenolith under consideration, K8/109, was previously described by Viljoen (2005). It is bimineralic, comprising mainly of clinopyroxene (70%) and garnet (30%), with trace diamond (<1%). Based on texture, it is a Group I eclogite (i.e. coarse rocks with large rounded garnets, set in a matrix of coarse clinopyroxene; MacGregor and Carter, 1970). As is typical for Group I eclogite xenoliths (including many diamond-bearing eclogites), elevated Na_2O in garnet as well as K_2O in clinopyroxene is observed (McCandless and Gurney, 1989; Viljoen, 2005). Garnet in the xenolith is comparatively Fe-rich (15.32 wt.% FeO), contains substantial TiO_2 (0.44 wt.%) but has low Cr_2O_3 (0.20 wt.%; Viljoen, 2005). The occurrence of diamond in a Group I eclogite from Kaalvallei is consistent with the view that these represent a major high-pressure source rock for diamond (Robinson et al., 1984; McCandless and Gurney, 1989).

Most of the diamonds in Kaalvallei eclogite xenolith K8/109 are colourless with unresorbed octahedral shapes, and with weights ranging from 0.12 to 1.65 mg (0.0006 to 0.0082 carats). The occurrence of small, unresorbed octahedral diamonds in the xenolith is also typical of diamonds from other eclogites at Kaalvallei (Kiviets, 2000), as well as for eclogites from other localities worldwide e.g. the Orapa kimberlite in Botswana (Robinson et al., 1984). No inclusions were encountered in any of the diamonds examined.

3. Analytical techniques

Diamonds were analysed by micro-Fourier transform infrared (FTIR) spectroscopy using a Nicolet Magna-IR 550 to determine both nitrogen content (N_{FTIR}) and nitrogen aggregation state. Spectrum acquisition was accomplished over a spectral range of 650 cm^{-1} to 4000 cm^{-1}, with 300 scans collected at a resolution of 4 cm^{-1}. Nitrogen spectra were deconvoluted utilising a least squares approach, and nitrogen contents and aggregation states determined using an absorption coefficient of 16.5 at ppm cm^{-1} for A defects (Boyd et al., 1994a) and 79.4 at ppm cm^{-1} for B defects (Boyd et al., 1995a). Accuracies are better than 10% for nitrogen content and better than $\pm 3\%$ for nitrogen aggregation state.

Mass-spectrometer-based analysis of diamonds for nitrogen content, $\delta^{15}N$ and $\delta^{13}C$ followed the experimental procedure of Boyd et al. (1995b) with accuracies of 0.5‰ and 0.1‰ (2σ) for $\delta^{15}N$ and $\delta^{13}C$, as well as 5% for total nitrogen measurements. Each diamond was combusted in a pure oxygen atmosphere at a temperature of 1100 °C, and nitrogen was then separated from carbon dioxide using a mixture of CaO and Cu, with nitrogen oxides reduced to N_2 (Boyd et al., 1994b). CO_2 generated was analysed for carbon isotopic composition with a dual-inlet gas source mass spectrometer. Nitrogen concentrations in the gas produced by burning the diamond were measured with a
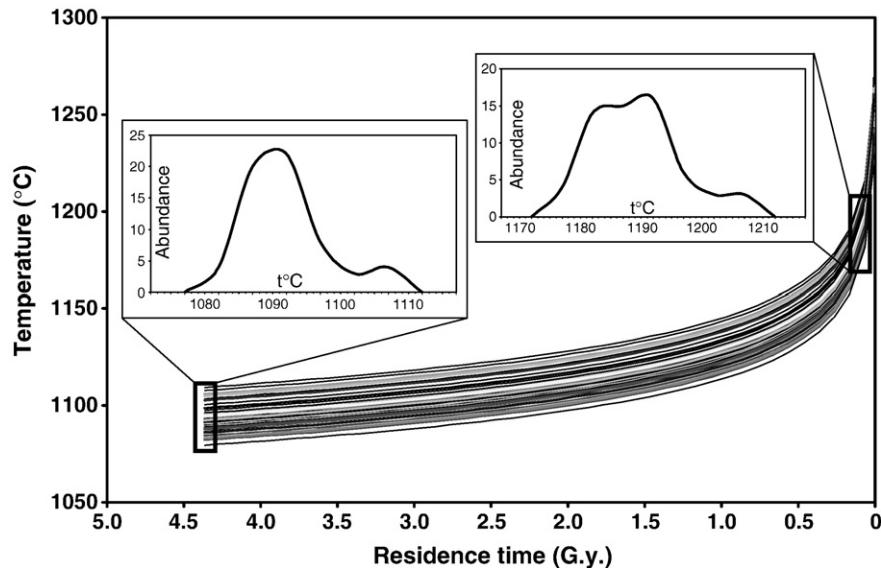

Fig. 1. Diamond nitrogen aggregation plotted as a function of average mantle residence time, and calculated utilising second order reaction kinetics (Chrenko et al., 1977). Temperature distributions have been calculated for assumed mantle residence times of 4365 M.y. and 80 M.y. Note that temperature is a little dependent on time over a wide spread of residence time but are sensitive for very small residence time in the mantle. Each solid line represents a single FTIR measurement on one diamond.

capacitance manometer, and the nitrogen isotopic composition was determined with a home-made triple collector static vacuum mass spectrometer connected directly to the extraction line. Isotopic compositions are expressed using the conventional delta notation (defined for carbon as $\delta^{13}C = [(^{13}C/^{12}C)_{sample} / (^{13}C/^{12}C)_{V\text{-}PDB} - 1] \times 1000$, and for nitrogen as $\delta^{15}N = [(^{15}N/^{14}N)_{sample} / (^{15}N/^{14}N)_{air} - 1] \times 1000$).

4. Results

Nitrogen contents in the diamonds analysed (as determined by infrared spectroscopy) range from 239 to 1272 ppm (Table 1). Average nitrogen content (839 ppm) is 3× higher than the worldwide average of about 300 ppm (e.g. Deines et al., 1987, 1993, 1997; Cartigny, 2005; Donnelly et al., 2007). Nitrogen aggregation states (%B defects, Table 1) vary from 11.5% to 43.7% of IaB. Nitrogen content is positively correlated with N aggregation state (Fig. 2). These infrared characteristics are broadly similar to that of other diamonds described previously from a further 10 eclogite xenoliths from Kaalvallei (Kiviets, 2000).

Carbon isotopic compositions of the diamonds analysed (Table 1) cover a narrow range from −6.0‰ to −4.2‰ (Fig. 3) with an average $\delta^{13}C$ of −5.2‰. This range covers only 5% of the worldwide spread in carbon isotopic compositions for diamonds (Cartigny, 2005), but are comparable to the observed range of mantle-derived carbon (i.e. $\delta^{13}C = -4 \pm 2‰$; Javoy et al., 1986). Nitrogen isotopic compositions (Table 1) show very little variation, ranging from $\delta^{15}N = -8.9‰$ to −4.1‰ (Fig. 4) with an average of −6.9‰. This range in $\delta^{15}N$ covers only 15% of the total observed spread in $\delta^{15}N$ for eclogitic diamonds worldwide, and falls within the so-called mantle range (i.e. $\delta^{15}N_{mantle} = -5 \pm 2‰$; Javoy et al., 1984; Javoy and Pineau, 1991; Cartigny, 2005).

Diamond nitrogen content as determined by combustion and manometry (i.e. [N]$_{comb}$; Table 1) is positively correlated (1:1) with diamond contents determined by FTIR (Table 1), suggesting that the diamonds analysed are probably homogeneous in terms of nitrogen content. This is substantiated by the limited spread in $\delta^{13}C$ and $\delta^{15}N$. In contrast to the diamonds analysed previously from a diamond-bearing peridotite (Premier Mine; Thomassot et al., 2007), there is no clear correlation between $\delta^{13}C$, $\delta^{15}N$ and N content in diamonds from Kaalvallei eclogite xenolith K8/109.

5. Discussion

5.1. Diamonds, xenoliths, and geothermometry

Nitrogen is the main crystallographic lattice impurity in diamond (Kaiser and Bond, 1959) and enters the carbon structure through single atom substitution of carbon to form Ib-type diamond. Initially, this singly-substitutional nitrogen diffuses fairly rapidly (i.e. over millions of years) to form atomic pairs (A defects in IaA diamond) due to a low activation energy associated with this process. Following this, these N-pairs diffuse to form clusters of 4 N-atoms surrounding a vacancy (B defects in IaB diamond). This takes billions of years to accomplish due to a higher activation energy for the reaction relative to the Ib to IaA conversion in diamond (Evans and Qi, 1982; Evans and Harris, 1989; Taylor et al., 1990).

The conversion of A defects (IaA diamond) to B defects (IaB diamond) can be modelled using the following equation (see Chrenko et al., 1977; Evans and Qi, 1982):

$$1 / [\text{IaA}] - 1 / [\text{N}] = \left(A \cdot Exp^{-\text{Ea}/RT} \right) \cdot t$$

where N is the total nitrogen content ([N] = [IaA] + [IaB]), A and R are constants with $A = 294{,}000$ ppm s^{-1} and $R = 8.317$ kJ/mol/K, Ea is the activation energy in eV (7 eV; Cooper et al., 1989), t is time in seconds and T is temperature in Kelvin.

Table 1

Diamond weight, $\delta^{13}C$, $\delta^{15}N$, nitrogen aggregation state (% B), and N contents (as determined by infrared spectroscopy as well as bulk combustion, followed by manometry) for diamonds from Kaalvallei eclogite xenolith K8/109.

Sample	Weight (mg)	N_{FTIR} (ppm)	N_{FTIR} (at ppm)	%B	N_{comb} (ppm)	N_{comb} (at ppm)	$\delta^{15}N$ (‰)	$\Delta^{13}C$ (‰)
kv 1-1	1.6570	923	791	31.7	842	722	−5.7	−4.9
		898	770	29.1				
kv 1-2	1.3360	560	480	29.9	698	598	−6.2	−5.2
		944	809	32.3				
kv 1-3	0.1338	1213	1040	34.1	511	438	−8.2	−6.0
		1133	971	35.5				
kv 1-4	0.6367	449	385	29.9	220	189	−6.7	−5.1
		411	352	30.2				
kv 1-5	1.5486	682	585	24.1	700	600	−6.8	−5.2
		1142	979	32.9				
kv 1-6	0.4280	662	568	27.6	515	441	−5.1	−5.2
		565	484	26.9				
		669	573	32.1				
kv 1-7	0.1910	914	783	38.6	n.a	n.a.	n.a.	n.a.
kv 1-8	0.1595	719	616	28.9	456	391	−7.8	−5.5
		777	666	31.4				
kv 2-1	0.2567	239	205	22.6	176	151	−6.7	−5.2
kv 2-2	0.5061	561	481	39	712	610	−5.8	−4.9
kv 2-3	0.1684	863	740	46.6	546	468	−8.6	−5.6
kv 2-4	0.6776	971	832	33.7	741	635	−7.0	−5.5
		1013	868	36				
kv 2-5	0.1640	744	638	31.3	387	332	−7.9	−5.1
		899	771	36.3				
kv 2-6	1.0994	874	749	28.8	751	644	−6.4	−5.2
kv 2-7	0.4117	912	782	29.9	924	792	n.a.	−5.0
		1035	887	39				
kv 2-8	0.4730	894	766	40.8	748	641	−6.3	−5.3
kv 2-9	0.6341	899	771	25.3	949	813	−7.2	−5.0
		894	766	27.8				
kv 2-10	0.2351	851	729	34.8	510	437	−8.9	−5.2
		824	706	34.3				
kv 3-1	1.1546	884	758	26.9	857	735	−6.6	−5.0
		861	738	28.8				
kv 3-2	0.6662	811	695	29.9	774	663	−6.2	−5.0
kv 3-3	1.2295	592	507	30.4	679	582	−6.2	−4.9
		683	585	28.3				
kv 3-4	0.2609	1017	872	37.2	706	605	−7.3	−5.3
		879	753	32.4				
kv 3-5	0.1610	1037	889	41.8	783	671	−8.1	−5.8
kv 3-6	0.2251	888	761	29.7	642	550	−6.9	−5.1
		828	710	30.7				
kv 3-8	0.8411	1218	1044	42.1	1390	1191	−6.7	−5.6
		1272	1090	43				
kv 3-9	0.5409	840	720	34.6	821	704	−7.3	−4.2
		913	783	28.4				
kv 3-10	0.1995	614	526	32.1	568	487	−6.7	−5.2
kv 4-1	0.6274	1056	905	34.1	912	782	−7.7	−5.1
		920	789	33.5				
kv 4-2	0.6124	998	855	32.4	1011	867	−6.6	−5.0
kv 4-3	0.7205	332	285	11.5	688	590	−6.9	−5.3
		1068	915	40.7				
kv 4-4	0.1592	783	671	30.7	398	341	−7.0	−5.3
		755	647	30.8				
kv 4-5	0.4231	1266	1085	33	1030	883	−7.0	−5.5
		1050	900	26				
kv 4-6	0.4968	467	400	17.9	635	544	−6.4	−4.7
		523	448	19.4				
kv 4-7	1.3690	949	813	31.6	902	773	−5.4	−5.4
		1030	883	31.3				
kv 4-8	0.2114	846	725	43.7	765	656	−8.9	−5.5
kv 4-9	0.1244	672	576	36	408	350	−4.1	−5.6

Note that several FTIR measurements were performed on the same diamond, and these are referred to in the table (i.e. they are not separate measurements on individual fragments).

Although the nitrogen aggregation state of diamond which is stored in the mantle over a very short interval (i.e. a few M.y.) will be a function of mantle residence time as well as mantle residence temperature, most natural diamonds reside in the mantle at long, geological time scales (>10 M.y.) and in this case the resulting nitrogen aggregation

state depends chiefly on temperature, with only a minor contributory effect from mantle residence time (Fig. 1).

The age(s) of the diamonds as well as that of the diamond-bearing eclogites from Kaalvallei is unknown. Griffin and O'Reilly (2007) is of the opinion that some (many?) mantle-derived eclogites worldwide may be comparatively young. Richardson et al. (1990, 1999)) and Richardson (1986) obtained Proterozoic ages of diamond crystallisation for eclogitic diamonds from other kimberlites on the Kaapvaal/Kalahari Craton. For instance, the Jwaneng, Orapa, Premier and Finsch kimberlites yield Sm–Nd ages for eclogitic inclusions in diamonds which are on the order of 0.99 to 1.58 G.y. Re–Os analysis of eclogitic sulphides in diamond have also resulted in older ages on the order of 2.9 G.y. (Shirey et al., 2004). It is therefore clear that the age of eclogitic diamonds, as well as that of diamond-bearing eclogites may be highly variable on a worldwide scale, with no clear consistency. In view of this we do not assume a specific mantle residence time for xenolith K8/109, but consider a number of possible mantle residence scenarios (Fig. 1).

The observed positive correlation between diamond N content and %B (Fig. 2) is consistent with a single diamond population being present in the diamond-bearing eclogite from Kaalvallei. The limited dependence of diamond nitrogen aggregation state on mantle residence time unfortunately does not allow the recognition of multiple diamond populations, unless there are very large differences in the age of diamond crystallisation for each population. In the present case, a minimum average mantle residence temperature of 1090 ± 10 °C is calculated from an assumed mantle residence time of 4.365 G.y, while a mantle residence temperature of 1190 ± 10 °C is calculated if mantle residence of 80 M.y. is assumed (Fig. 1). It is therefore clear that it would be extremely difficult to recognise multiple populations of diamond, based on calculated mantle residence time utilising infrared data. However, in any event, multiple populations of diamond in Kaalvallei eclogite K8/109 would be difficult to reconcile with the observed small ranges of $\delta^{15}N$ and $\delta^{13}C$ in the diamonds from the xenolith (Fig. 3).

The inferred mantle residence temperature of diamonds from xenolith K8/109 (<1190 °C) is significantly lower than the 1243 °C equilibration temperature for the xenolith, calculated from Fe–Mg exchange between garnet and clinopyroxene (Ellis and Green, 1979) at an assumed pressure of 59 kbar (pressure estimated using the regional

Fig. 3. Histogram of $\delta^{13}C$ isotopic compositions for 35 diamonds from Kaalvallei eclogite xenolith K8/109, and compared to the worldwide range. Each diamond locality has been weighted, to take the number of samples into account (as more than 10% of all published data on eclogitic diamonds are from Argyle). Modified from Cartigny (2005).

geotherm for the area surrounding Kaalvallei; Griffin et al., 2003). This difference in xenolith equilibration and diamond mantle residence temperature is highly significant, particularly as all Fe in garnet and clinopyroxene is assumed to be in the divalent form (Fe^{2+}), resulting in calculated *minimum* temperatures. Furthermore, this difference between xenolith temperature and diamond temperature is not unique to Kaalvallei xenolith K8/109, but is also seen in all diamond-bearing eclogites previously studied from Kaalvallei (Viljoen, 1994; Kiviets, 2000; Viljoen, 2005), where differences in temperature between diamonds and host xenoliths may vary from 50 °C to as much as 154 °C. The absence of agreement between the diamond-derived and xenolith-derived temperatures may result from a number of factors. For instance, the differences may be the result of the under-estimation of the activation energy for the nitrogen-in-diamond thermometer (Ea). However this is unlikely as previous studies on other xenolith suites have reported fairly good correlation between xenolith- and diamond-derived temperatures (Viljoen et al., 2004; Creighton et al., 2007; Cartigny et al., 2004b). An alternative possibility could be that the eclogitic diamonds at Kaalvallei are comparatively young (e.g. a short mantle residence time on the order of 30 M.y. or less), in which case substantially higher mantle residence temperatures are calculated (on the order of 1250 °C). In addition, it is also possible that the Ellis and Green thermometer may lead to an overestimate of mantle temperature associated with thermal perturbation during transport in the kimberlite, which is probably not reflected in the diamonds resident in the enclosing xenolith.

5.2. Crystallisation of diamond in a pre-existing eclogite host rock

Based on trace element evidence (e.g. europium anomalies in garnet and clinopyroxene) as well as stable isotope studies (e.g. oxygen) it is likely that many mantle-derived eclogites may represent subducted, hydrothermally altered oceanic crust (reviewed by Jacob, 2004), or, alternatively, that they are high-pressure cumulates from eclogitic melts (Barth et al., 2002; Griffin and O'Reilly, 2007). In the case of Kaalvallei, Viljoen (1994), Kiviets (2000) and Viljoen (2005) is of the opinion that these diamond-bearing xenoliths represent the metamorphosed products of subducted oceanic crust, while Griffin and O'Reilly (2007) indicate that they may also represent the crystallised products of high-pressure mantle melts. Small europium
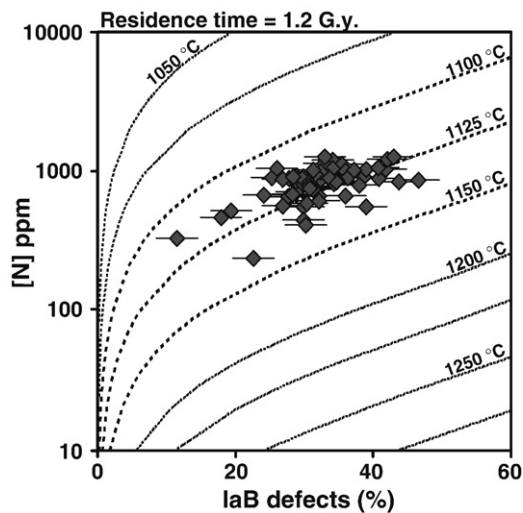

Fig. 2. Nitrogen content and aggregation state (%B) of diamonds from Kaalvallei eclogite xenolith K8/109. Isotherms are based on second order kinetics for nitrogen diffusion in diamond (Chrenko et al., 1977), and have been calculated for a mantle residence of 1.2 G.y. Note the large dependency of aggregation state on temperature, when compared to mantle residence time in Fig. 1. All the diamonds analysed are characterised by a small range of nitrogen aggregation state which is generally less than 60% of the B defect in IaB diamond. Accuracy for nitrogen aggregation state as well as N content is on the order of ± 3% (about the size of the symbol) and 10%, respectively (2σ).
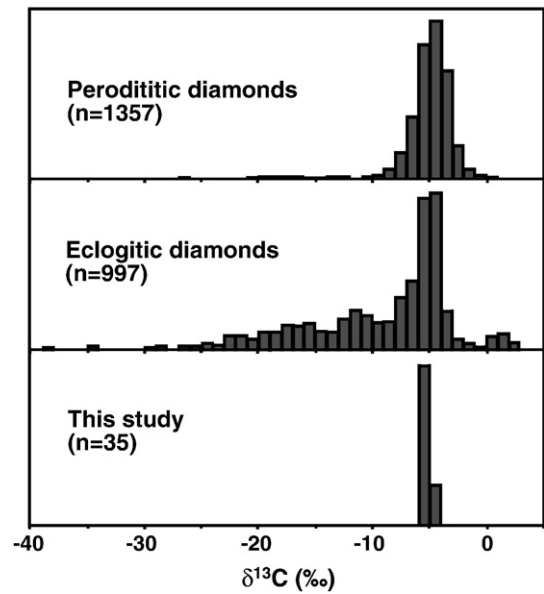
anomalies (Eu*/Eu = 1.2) in garnets from some of the Kaalvallei diamond-eclogites, including K8/109, is consistent with plagioclase fractionation and/or plagioclase accumulation during the formation of crustal protoliths to these xenoliths. Depletion or enrichment in Eu, when compared to the rest of the rare earth elements in eclogite minerals, is generally attributed to preferential incorporation of Eu into plagioclase, followed by accumulation or separation of plagioclase in the eclogite protolith (Weill and Drake, 1973; Jacob, 2004; references therein). In our view, the observed positive Eu anomalies in garnets from the Kaalvallei diamond-bearing eclogites are consistent with a metamorphosed, crustal (oceanic) origin for these eclogites. Furthermore, Jacob (2004; and references therein) argue that the nearly flat $HREE_N$ pattern (~10) of many eclogitic garnets (including K8/109; Fig. 4) is very unlike equilibrium REE patterns for garnet from high-pressure rocks, due to its mineral-melt partitioning characteristics. This, in association with bulk positive Sr anomalies in eclogites (also seen in K8/109), are interpreted by Jacob (2004) as evidence for a subducted and metamorphosed oceanic crust model for these rocks.

Oxygen isotopic compositions of garnets in Kaalvallei eclogite xenoliths range from +4.3‰ to +7.2‰ (Fig. 5), with +5.8‰ for garnets from xenolith K8/109. These compositions deviate substantially from the accepted mantle range (typically $\delta^{18}O_{grt} = +5$ to $+6$‰, Muehlenbachs and Clayton, 1972; Mattey et al., 1994; Eiler, 2001). Such variations in oxygen isotopic compositions for eclogites are commonly interpreted as due to interaction of the protolith (oceanic crust) with seawater, resulting in both lower oxygen isotopic compositions ($\delta^{18}O < +5$‰ in oceanic gabbros) as well as higher oxygen isotopic compositions ($\delta^{18}O > +6$‰ in oceanic basalts) when compared to the 'mantle' range (Gregory and Taylor, 1981). This range in eclogite oxygen isotopic compositions is comparable to that seen for ophiolites (Gregory and Taylor, 1981) and suggests that all layers of oceanic crust (e.g. from shallow basalt to deep gabbro) are possible precursors to mantle-derived eclogites (Jacob, 2004). Although 'mantle-like', the $\delta^{18}O$ composition of garnet in Kaalvallei eclogite K8/109 is considered to not be a reflection of that of a mantle-derived protolith, as the trend in $\delta^{18}O$ of basalt–seawater alteration shows a cross-over with magmatic ('mantle') fractionation (Gregory and Taylor, 1981; Jacob, 2004). However, it is noteworthy that Williams et al. (2007) do suggest that apparent O isotope depletion may be related to a mantle processes, and thus that the $\delta^{18}O$ values of rocks derived from lithospheric mantle may not necessarily reflect those of their low-pressure protoliths. Williams et al. (2007) propose that the positive correlation between $\delta^{18}O_{bulk}$ and $\delta^{57}Fe_{bulk}$ found in some Kaalvallei eclogites may be related to isotopic fractionation during open-system processes operating within the lithospheric mantle. If this is really the case then it would not be

Fig. 5. $\delta^{18}O$ compositions of garnet and clinopyroxene in Kaalvallei eclogite xenolith K8/109, as well as other diamond-bearing xenoliths from Kaalvallei. Also shown are $\delta^{18}O$ values for eclogite and peridotite xenoliths from kimberlites worldwide, and for the mantle (as defined by Mid Ridge Oceanic Basalts; Mattey et al., 1994). Diagram modified from Jacob (2004; and references therein) as well as Cartigny (2005).

possible to prove either a crustal or a mantle origin for Kaalvallei eclogites. In addition this model cannot explain O isotope enrichment (i.e. $\delta^{18}O > +6$‰) for some Kaalvallei eclogites. Therefore, these Kaalvallei diamond-bearing eclogites may be more likely related to a crustal protolith rather than mantle origin.

If all diamond-bearing eclogites at Kaalvallei do have an ultimate origin involving subducted oceanic crust as seem to be suggested by trace element and isotopic data, then it could be argued that the source of the carbon for the diamonds might be closely related to the original (crustal, oceanic) protolith. However, it is also possible that no relationship exist, e.g. if the diamonds are related to a subsequent, metasomatic process, with diamond formation therefore completely unrelated to the formation of the eclogite host (Taylor et al., 1998; Loest et al., 2003; Stachel et al., 2004; Thomassot et al., 2007, 2009). The role of subducted carbon in the formation of eclogitic diamonds is still the subject of much debate. Diamonds from K8/109 have $\delta^{13}C$-values falling within the so-called 'main mantle range' of -5 ± 2‰ (Fig. 3) as determined from mantle-related samples which include mid-oceanic ridge basalts, carbonatites, kimberlites and diamonds (Javoy et al., 1986). However, when viewed in isolation, variations in $\delta^{13}C$-values are not sufficient to constrain the origin of the carbon, as carbon is efficiently cycled between 'internal' and 'external' Earth reservoirs, and is thus likely in equilibrium (Javoy et al., 1982) — hence at geological times scales the amount and isotopic composition of degassed and subducted carbon is likely the same. In view of this a seemingly mantle-like $\delta^{13}C$ signature does not necessarily exclude a subduction-related origin for the carbon.

Additional information can be obtained from nitrogen isotopic compositions in diamond. In contrast to carbon isotopic compositions, there is a nitrogen isotopic contrast between 'inner' and 'outer' earth reservoirs (as illustrated in Fig. 6). Most mid-ocean-ridge basalts (MORB), and also many diamonds, are characterised by negative $\delta^{15}N$ with an average of -5 ± 2‰, while metasediments show positive value of $\delta^{15}N$. It is noteworthy that it is not possible to create negative $\delta^{15}N$ values from positive $\delta^{15}N$ through subduction and recycling, as devolatilization results in light ^{14}N being lost preferentially over ^{15}N — thus leading to even more positive $\delta^{15}N$ (Bebout and Fogel, 1992). Diamond appears to be a good indicator of the source of its carbon and nitrogen, as supported by data on metamorphic diamonds from ultra-high-pressure metamorphic terranes (Cartigny et al., 2001b, 2004a). These are characterised by positive $\delta^{15}N$ (e.g. up to 12.4‰), as would be expected for subduction-related nitrogen. In contrast, diamonds
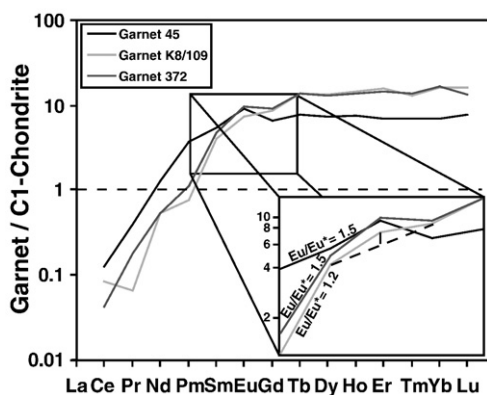

Fig. 4. Chondrite-normalised rare earth element abundance patterns of three garnets from Kaalvallei diamond-bearing eclogites (Viljoen, 2005), using the C1 chondrite values of McDonough and Sun (1995). Eu* is the value obtained for the Eu anomaly by linking samarium and gadolinium, and measuring the height of the Eu anomaly from this line.
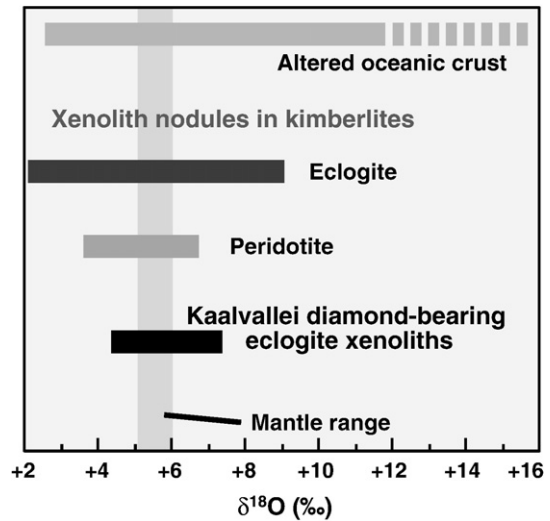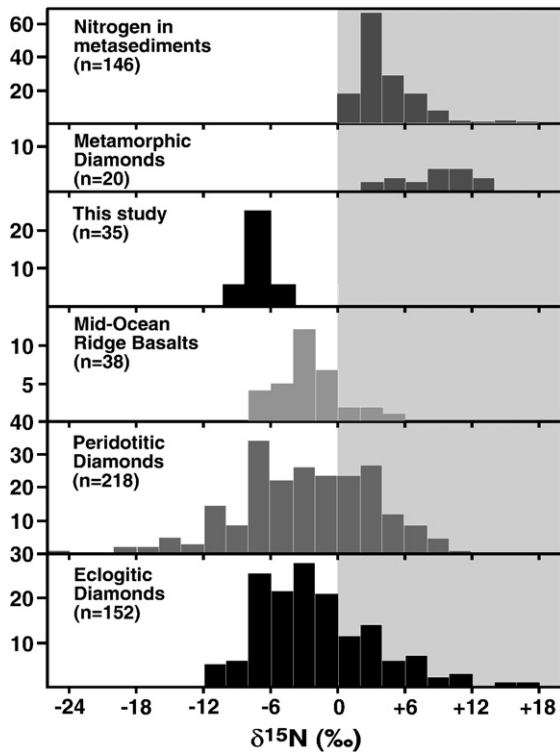
Fig. 7. Nitrogen and carbon isotopic compositions of 35 diamonds from Kaalvallei eclogite xenolith K8/109. Note the lack of any clear correlation. Accuracies for δ^{13}C and δ^{15}N are ± 0.1‰ and ± 0.5‰ (2σ) respectively.

from Kaalvallei xenolith K8/109 show strictly negative δ^{15}N values centred on −6.9‰, and this is clearly within the 'mantle' range of nitrogen isotopic compositions. Negative δ^{15}N values for these diamonds are therefore symptomatic of their mantle origin.

5.3. Diamond genesis as a consequence of metasomatism

The conflicting evidence for a subduction-related origin for many diamond-bearing eclogites (Eu and O isotope anomalies, Jacob, 2004; Viljoen et al., 2004) and the seemingly mantle-related origin of their diamonds (e.g. Kaalvallei xenolith K8/109) can be reconciled in a scenario where diamond growth occurs through one or more stages of metasomatism. This is indeed supported by the apparent close spatial relationship of diamonds in eclogite xenoliths to metasomatic veins within the host eclogite (Schulze et al., 1996; Taylor et al., 2000), and suggests that diamond precipitation occurred during the infiltration of metasomatic fluids. Furthermore several studies extended this process to peridotitic sources using trace elements (Stachel et al., 2004 for review), stable isotopes (Taylor et al., 1998; Thomassot et al., 2007, 2009) and inclusion mineralogy (Loest et al., 2003). Although no clear trend of δ^{13}C and δ^{15}N could be identified for the diamonds from Kaalvallei eclogite xenolith K8/109, the small range in C and N isotopic data for these diamonds (Fig. 7) are, however, compatible with a model of diamond formation through metasomatism by a single, homogeneous fluid, rather than e.g. through a process of solid state diffusion and transformation, as solid diffusion of carbon would result in significant isotopic and chemical heterogeneity.

5.4. Fluid speciation

Diamond may precipitate from either reduced or oxidised fluids (Fig. 8). In the case of a reduced fluid (e.g. methane-bearing fluids),
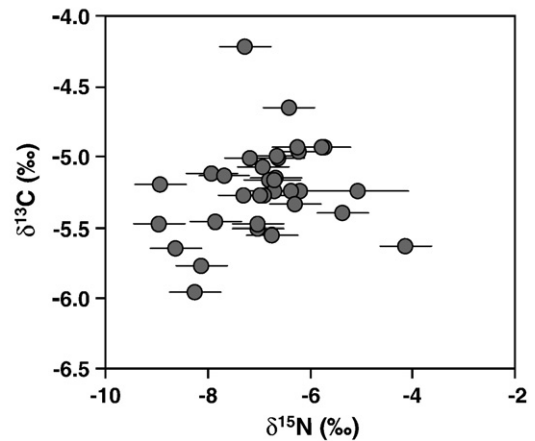
nitrogen is compatible with any crystallising diamond, leading to correlated δ^{13}C–δ^{15}N–N covariations (Thomassot et al., 2007). In the case of oxidised fluids or melts (i.e. carbonate- or CO_2-bearing fluids or melts), the situation is more complex. It has been suggested that nitrogen would tend to behave in an incompatible manner (Boyd et al., 1994a; Cartigny et al., 2001a), resulting in uncorrelated δ^{13}C–δ^{15}N–N. This view has, however, been challenged by Stachel et al. (this issue), who suggests compatible-behavior of nitrogen, and predicts that correlated δ^{13}C–δ^{15}N–N covariation in crystallising diamond will result.

It should be possible to distinguish between these various fractionation trends (Fig. 8) because of opposing methane–diamond and carbonate–diamond fractionation factors ($\alpha_{\mathrm{diamond-methane}} > 1$ and $\alpha_{\mathrm{diamond-carbonate/CO2}} < 1$, Bottinga, 1969). However, diamonds from the present study are characterised by rather small variations of δ^{13}C–δ^{15}N–N (Figs. 2, 3 and 7), and therefore no clear trend as calculated for the various fractionation models can be recognised (Fig. 8).
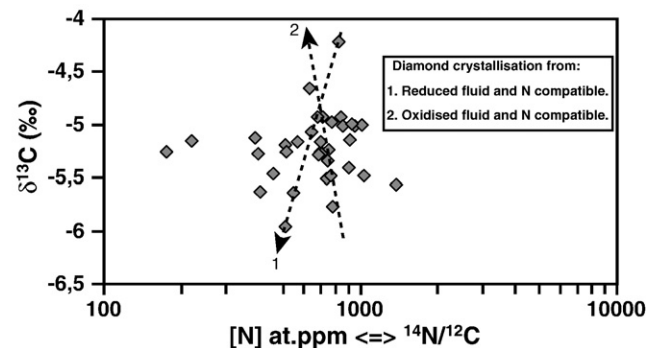

Fig. 8. Plot of the expected (calculated) variation in diamond δ^{13}C (‰) as a function of diamond nitrogen content during diamond crystallisation via Rayleigh distillation, where the carbon isotopic composition is related to the N content by the following equation: $\ln(\mathrm{N/C}) = \ln(\mathrm{N/C_0}) \cdot [(K_N/K_C - 1)^*(\delta^{13}\mathrm{C} - \delta^{13}\mathrm{C_0})/(\Delta_C)]$. K_N and K_C are the partition coefficients for nitrogen and carbon respectively, $\Delta^{13}\mathrm{C_0}$ is the initial delta carbon isotopic composition for diamond or fluid, and Δ_C is the isotopic fractionation between diamond and fluid (note that $\Delta_C \sim 1000 \ln(\alpha)$). The model is based on the following: 1) a reduced fluid (methane-like) with compatible behaviour of nitrogen in diamond, 2) an oxidised fluid (CO_2/carbonate) with compatible behaviour of nitrogen in diamond. The dashed black lines illustrate the chemical evolution of the crystallising diamond, when crystallised in equilibrium with the evolving fluid. A positive fractionation coefficient (i.e. $\alpha_{\mathrm{diamond-CH4}}$) implies that the δ^{13}C of the fluid (and the crystallising diamonds) evolves toward more negative values as diamond crystallisation proceeds. A negative fractionation coefficient (i.e. $\alpha_{\mathrm{diamond-CO2/carbonate}}$) results in fluid and diamond evolution proceeding in the opposite direction towards less negative values.

Fig. 6. Comparative histograms of δ^{15}N values for metasedimentary nitrogen (Haendel et al., 1986; Bebout and Fogel, 1992; Boyd and Philippot, 1998; Mingram and Bräuer, 2001; Sadofsky and Bebout, 2003), metamorphic diamonds from Akluilâk, Canada (Cartigny et al., 2004a), Kaalvallei eclogite xenolith K8/109, mid-ocean ridge basalts (Javoy and Pineau, 1991; Marty and Humbert, 1997; Marty and Zimmerman, 1999; Nishio et al., 1999; Cartigny et al., 2001a) and worldwide peridotitic and eclogitic diamonds (Cartigny et al., 2004b; Cartigny, 2005).

Overall, the lack of a clear correlation between $\delta^{15}N$, $\delta^{13}C$ and N content would seem to indicate that diamond crystallisation in Kaalvallei eclogite xenolith K8/109 results from the metasomatic infiltration of a carbonate/CO_2-like fluid (Boyd et al., 1994a; Cartigny et al., 2001a), with incompatible behaviour of nitrogen during diamond growth. Fairly rapid diamond growth is indicated by the relatively high nitrogen content of the diamonds.

5.5. Implications for all diamonds from Kaalvallei

The diamond-bearing eclogite xenoliths from Kaalvallei exhibit broadly similar characteristics and are clearly of the Group I variety (Viljoen, 1994, 2005). Major element compositions in garnets and clinopyroxenes also do not show any consistent heterogeneity amongst these eclogites. Garnet and clinopyroxene compositions show a general evolutionary trend ranging from Mg-rich compositions to Ca- and Fe-enrichment. Garnets have Cr- and Mn-poor compositions and are pyrope-rich (py_{44}–py_{70}), with similar almandine (al_{18}–al_{35}) and grossular (gr_{23}–gr_{29}) contents. Magnesium numbers range from 55.1 to 72.8 and from 62 to 83.7 for garnets and clinopyroxenes respectively. Low TiO_2 concentrations are present in amounts of 0.14 to 1.01 wt.% for garnet, and 0.10 to 0.53 wt.% for cpx. Chromium contents are consistently low, as is typical for most eclogitic garnets and clinopyroxenes worldwide (a maximum of 0.89 wt.% Cr_2O_3 in garnet and 0.26 wt.% Cr_2O_3 in clinopyroxene, respectively). Na_2O concentrations range from 0.04 to 0.19 wt.% in garnets and 1.26 to 6 wt.% in omphacitic clinopyroxenes.

The diamonds in the eclogite xenoliths from Kaalvallei all exhibit similar $\delta^{13}C$ and FTIR-derived mantle residence temperatures (Viljoen, 1994, 2005; Kiviets, 2000), with the exception of diamonds in Kaalvallei xenolith K5 which have $\delta^{13}C \approx -11.4‰$ — suggesting formation at a different time and/or temperature, from a distinct fluid (Kiviets, 2000).

Based on petrographic, mineralogical, and geochemical similarities, including comparable thermobarometry, the known diamond-bearing eclogites from Kaalvallei compare favourably with sample K8/109. In view of this, we suggest that the majority of the diamonds from Kaalvallei result from a metasomatic process of diamond crystallisation involving the infiltration of fluids into a pre-existing eclogite substrate. Although the nature and speciation of the fluid remains unclear, our data do suggest that mantle-related fluids contributed to a very large extent to the genesis of eclogitic diamonds in the mantle below this kimberlite.

5.6. Implications for diamond genesis worldwide, and for the geochemistry of the Kaapvaal craton

Based on evidence suggesting that many mantle-derived eclogite xenoliths may represent subducted and recycled oceanic crust (Jagoutz et al., 1984; Jacob et al., 1994; Barth et al., 2000, 2002; Spetsius et al., this issue), possibly of even Archean age (Shirey et al., 2002), it has been proposed that diamonds in eclogite nodules may represent carbon which have been subducted along with associated oceanic crust (Gurney, 1991; references therein). However, evidence for the de-coupling of diamond formation from the formation of the host xenolith through a process of metasomatic diamond formation, includes 3D X-ray tomography of eclogite xenoliths (Schulze et al., 1996; Keller et al., 1999) which demonstrate that diamonds may occur in metasomatic veins; various trace element studies of inclusions in diamond (Stachel et al., 2004); the chemistry of fluids trapped during the growth of fibrous and/or coated diamonds (Navon, 1999); the presence of a metasomatic suite of mineral inclusions in diamond (Loest et al., 2003); and evidence for diamond crystallisation in a peridotite xenolith related to an infiltrating methane-rich fluid (Thomassot et al., 2007). All of these studies considered together imply that either carbonate/CO_2 or methane-bearing fluids (or melts) are widespread in the subcratonic lithosphere and is a key component of the diamond crystallisation process.

Of the three diamond-bearing xenoliths that have been investigated thus far (Thomassot et al., 2007; this study; Ishikawa et al., 2008), all are characterised by diamonds with enriched ^{13}C and comparatively small variations in $\delta^{13}C$, with comparatively high N content. Values of $\delta^{15}N$ range from $\sim -7‰$ in the present study to $\sim +8‰$ in some instances (Thomassot et al., 2007; Ishikawa et al., 2008). More studies of diamond populations from xenoliths are required, particularly in the case of diamonds with comparatively low nitrogen content.

All of these studies have recognised a role for metasomatism as an agent in diamond crystallisation. Although the involvement of methane-rich fluids is clearly indicated (Thomassot et al., 2007), neither the present study nor the study of Ishikawa et al. (2008) provide formal proof for the involvement of carbonatitic metasomatism in diamond crystallisation. However, some recent studies (e.g. Schrauder and Navon, 1993; Loest et al., 2003; Klein-BenDavid et al., 2004) have hinted at evidence for the existence of this type of fluid during diamond crystallisation.

It is therefore clear that not all eclogitic diamonds form directly from the recycling of oceanic crust, and associated carbon.

6. Conclusions

Nitrogen thermometry of multiple diamonds in a unique diamond-bearing eclogite xenolith from the Kaalvallei kimberlite in South Africa supports a single diamond growth event. The xenolith therefore provides an opportunity to study a single diamond population in a typical eclogite locality. Although $\delta^{18}O$ and trace element compositions of constituent garnets and clinopyroxene in the xenolith can be reconciled with a recycled hydrothermally altered oceanic crust origin, the carbon and nitrogen isotopic composition of the diamonds, and observed compositional ranges in nitrogen are consistent with a model of diamond genesis from a mantle-related fluid with a high C/N ratio. Our data therefore reinforce the model of metasomatic diamond crystallisation, and places the origin of the carbon source to eclogitic diamonds within the Earth's mantle.

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