Silicate and oxide inclusion characteristics and infra-red absorption analysis of diamonds from the Klipspringer kimberlites, South Africa

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ABSTRACT
The diamonds associated with the 148 Ma Group II Klipspringer kimberlite dyke system emplaced on the Thabazimbi-Murchison Lineament are predominantly of eclogitic origin, and in a parallel study have been demonstrated to have a late Archean origin. Fourier Transform Infra-Red (FTIR) analysis of diamond plates demonstrates complex intergrowth of N-rich and N-poor diamond. Two groups of diamonds occurring in both the Main Fissure and the Sugarbird Blow have been recognised with time averaged mantle residence temperatures (MRT) based on nitrogen aggregation of approximately 1090°C (low-T) and 1170°C (high-T) respectively. In some cases a core of high-T diamond is enclosed within an envelope of low-T diamond. At Marsfontein, a third diamond population with an MRT < 1070°C is present that has not been recorded in diamonds from the Main Fissure or the Sugarbird Blow. Observed lamination lines attest to a deformation event having affected most of the high-T diamonds. A correlation between hydrogen and the ratio between nitrogen present in B aggregates and platelet peak intensity suggests that the presence of hydrogen affects the formation of platelets.

Mineral inclusions in the diamonds are predominantly eclogitic (sulfide, garnet, clinopyroxene, kyanite, coesite and rutile). The garnets and clinopyroxenes have a wide range in compositions, extending the worldwide fields for diamond inclusions. The garnets define four groups, one of which is grospyditic and the individual groups display inter-element correlations, which are consistent with magmatic fractionation. The clinopyroxenes include a high aluminium group exhibiting cation site deficiencies (7 to 28% pseudojadeite). Garnets from all four groups, the high aluminium clinopyroxenes and other clinopyroxenes of widely different compositions occur in both the high-T and low-T diamonds. Estimated bulk compositions for diamond bearing eclogite are akin to MOR cumulates from the S.W. Indian Ridge. Thermobarometric estimates for four non-touching garnet-clinopyroxene inclusion pairs in low-T diamonds are within the range 1152 to 1235°C at 50kb.

It is considered that the high-T Klipspringer diamonds formed in the Archean and underwent deformation followed by the low-T diamond formation in the host-rock to the high-T diamonds. The deformation event might have been associated with reactivation of the Thabazimbi-Murchison Lineament. The most likely protolith for the diamonds is subducted oceanic crust in which the inclusions of the low temperature diamonds formed by re-crystallisation of pre-existing minerals. At or shortly after the low-T diamond formation, a cool (37 to 39mW/m²) geotherm was established within this part of the Kaapvaal craton. The diamonds survived the emplacement of the Bushveld Igneous Complex and were subsequently sampled and transported by their host kimberlites in the late Jurassic.

Introduction
Most syngenetic mineral inclusions in diamonds can be assigned to either a peridotitic or an eclogitic paragenesis (e.g. Gurney, 1989). For eclogitic diamonds, which are the focus of this study, an igneous (Boyd and Gurney, 1986; Kesson and Ringwood, 1989) or solid-state metamorphic (Haggerty, 1986) origin has been proposed, as well as metasomatic formation through an open-system fluid-flux into an eclogitic protolith (e.g. Griffin et al., 1988; Deines and Harris, 1995; Taylor et al., 1998; Keller et al., 1999). An increasing amount of evidence points to a genetic link between upper mantle eclogites/eclogitic diamonds and subducted oceanic crust (reviewed by Navon, 1999). The chemical composition and highly fractionated oxygen isotope compositions of upper mantle eclogites may indicate that they represent metamorphosed fragments of oceanic lithosphere and/or oceanic crust with or without associated sediments (e.g. Helma1stedt and Doig, 1975; Jagoutz et al., 1984; MacGregor and Manton, 1986; Helma1stedt and Schulze 1989). In other situations the subducted oceanic crust may be remelted (Hofmann and White, 1982; Ringwood, 1982) or melt incongruently (Ireland et al., 1994; Rudnick, 1995) and subsequently underplate the lithosphere. Eclogitic diamonds are commonly depleted in 13C, which may suggest an input from organic carbon (e.g. Frank 1959; Kirdley et al., 1991). An organic input and hydrothermally altered mid-ocean ridge basalt source may also be implied from the observed concurrent depletion in 13C and enrichment in 15N in eclogitic diamonds and the positive and negative S isotope excursions of their
The Klipspringer kimberlites are located south of the southern margin of the Limpopo mobile belt and close to the Bushveld Igneous Complex in the northeastern part of the Kaapvaal craton (Figure 1). The kimberlites intrude the Thabazimbi-Murchison Lineament (TML), which is a major ENE-WSW striking terrain boundary on the craton. The earliest movements recorded in the TML have been dated at ~2.96 Ga and it may represent the boundary between a Kaapvaal granite-greenstone terrain and the southern margin of the Limpopo mobile belt (Good, 1997; Good and de Wit, 1997). Two major reactivations of the TML occurred at ~2.7 Ga and ~2 Ga. Seismic anisotropy data has shown that the lithosphere beneath the TML contains an east-west fast polarisation direction in contrast to the NE-SW direction generally observed for the Kaapvaal craton (Vinnik et al., 1995; Silver et al., 2001). This has been interpreted to mean that formation and/or reactivation of the TML recorded in the crustal rocks can be extrapolated down to the lithospheric mantle. The lithospheric and crustal weakness in the TML may therefore have facilitated the emplacement of the Klipspringer kimberlites.

Diamonds from the Main Fissure, the Sugarbird Blow (which occurs on the Sugarbird Fissure) and the Marsfontein pipe are included in the present study. The Main and Sugarbird Fissures intrude the Malmani dolomites of the Transvaal sequence, which was deposited onto the basement in the early Proterozoic. Both kimberlites are en-echelon dykes, which strike parallel to the TML, and the Sugarbird Fissure is located about 750 metres north of the Main Fissure. The two dykes have been dated at 148±4 Ma and classify isotopically as Group II kimberlites (Westerlund et al., this volume). The Marsfontein kimberlite intrudes the Meinhardskraal basement granite about 10 kilometres east of the two dykes. Field relations suggest that it constitutes a blow on a continuation of the Main Fissure and th600 Mt formed contemporaneously with the two dykes.

The lithosphere sampled by the Klipspringer kimberlites is dominated by eclogite and lherzolite, with minor harzburgite and dunite (Westerlund, 2000). Group 1 eclogites (with elevated Na contents in the garnets; McCandless and Gurney, 1989) believed to originate from within the diamond stability field are more common than Group II eclogites. Equilibration temperatures for Group 1 eclogites range up to 1078°C and 1119°C (using Krogh, 1988) at assumed pressures of 50 kbars and 60 kbars respectively. A geotherm (at 148 Ma) inferred from eclogite equilibration temperatures corresponds to a conductive model geotherm of 37-39 mW/m², which is indicative of a fairly cool lithosphere favourable for diamond preservation.

Analytical techniques

FTIR analysis of the diamonds

Spectra were measured at Anglo American Research Laboratories (currently De Beers GeoScience Centre), Johannesburg, using a Nicolet Magna-IR 760 spectrometer and at the Department of Geology, University of Cape Town, using a Nicolet Magna-IR 560

**Figure 1.** Outline of the Kaapvaal-Zimbabwe craton with the location of the Klipspringer kimberlites (TML=Thabazimbi-Murchison Lineament).
Figure 2. Cathodoluminescence images of polished diamond plates with analysis locations. The plates are ~4 mm across the longest direction. Front side images (left) were captured with a scanning electron microscope and rear side (right) through an optical microscope attached to a cold cathode cathodoluminescence generator.
EMP analysis of diamond inclusion minerals
The diamonds were examined visually to ensure there were no cracks connecting the inclusions to the exterior of the diamonds before they were liberated from the diamond. The inclusions were analysed at the University of Cape Town using a Cameca Camebax electron microprobe (EMP). Natural standards of similar compositions to the unknowns were used. Counting times were 10 seconds for peaks and backgrounds except for sodium in garnet and potassium in clinopyroxene for which peaks were measured for 30 seconds and backgrounds for 15 seconds.

IR absorption characteristics of the diamonds
Several studies indicate that the occurrence of nitrogen in diamonds of types Ib (single N atoms substituting for C), IaA (pairs of N atoms) and IaB (four N atoms arranged around a vacancy) represents a sequence of progressive time- and temperature-dependent aggregation. Type II diamonds are deficient in infra-red active nitrogen (e.g. Clark et al., 1992; Evans, 1992). When the correct activation energy for the aggregation reaction is known, the interdependent parameters of time and temperature of mantle residence for the diamond can be estimated (e.g. Mendelssohn and Milledge, 1995). Temperature is the more sensitive parameter and if the mantle residence time can be roughly estimated (at a scale of hundreds of millions or even a billion years), the time-averaged temperature at which the diamond resided can be constrained. Sulfide bearing eclogitic Klippspringer diamonds have been assigned a formation age of 2554 ± 150 Ma on the basis of Re-Os systematics (Westerlund et al., this volume).

Since the diamonds were removed from the lithosphere by the kimberlites at ~150 Ma, some diamonds resided at mantle temperatures for about 2.5 billion years. In the absence of more detailed information, a mantle residence time of 2.5 billion years has been used in the derivation of all temperatures discussed below, and in the interpretation of diamond formation processes in the discussion section. The temperature estimations are based on a value of 7.03 eV for the IaA-IaB activation energy (Taylor et al., 1990).

Platelets are planar features occurring in the cubic planes of the diamond and range in size from 8 nm up to a few nm (Evans and Qi, 1982). There is a direct correlation between the intensity of the platelet peak and X-ray spike intensity (Sobolev et al., 1968) and thus the platelet peak intensity is an indication of the platelet concentration.

Experimental data on the correlation between hydrogen peak intensities and hydrogen concentrations are non-existent. However, hydrogen peak intensities are used in a semi-quantitative way in the present study to evaluate the hydrogen content.

Diamond plates
IR absorption data for the three analysed diamond plates are given in Table 1 and cathodoluminescence images of the plates (with analysis locations) are shown in Figure 2. In the centre of diamond P6-9 is a discernible rounded seed, which is surrounded (at E on P6-9, Figure 2) by several thin semi-circular zones reminiscent of “agate texture” (Seal, 1965; Bulanova and Griffin, 1995; Zezin et al., 1990). This is succeeded by irregular

Table 1. Fourier-transform infra-red absorption data for diamond plates.

<table>
<thead>
<tr>
<th>Plate/Analysis N (ppm)</th>
<th>%NaB</th>
<th>T(°C)</th>
<th>Platelet Hydrogen μ(3107)</th>
<th>μ(3106)</th>
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<td>P6-9B 1098 0.177 0.092</td>
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<td>P6-9C 1097 0.187 0.245</td>
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<td>P6-9E 1102 0.339 1.016</td>
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<td>P6-9F 1108 0.184 1.464</td>
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<td>P6-9G 1116 0.213 0.491</td>
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</table>

%NaB is the percentage of the total nitrogen, which occurs in B aggregates. The temperatures were estimated assuming a mantle residence time of 2.5 Ga. µ = absorption coefficient (cm⁻¹).

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Figure 3. Nitrogen concentration versus platelet peak intensity for diamond plates. P6-9= open squares, A-3=crosses, 17-30=solid diamonds.

Figure 4. Hydrogen peak intensity versus platelet peak intensity for a) Plates P6-9 and 17-30 and b) Plate A-3. Symbols as in Figure 3.

octahedral zones, which are locally disrupted, suggestive of either brittle fracturing or partial etching/resorption while the remainder of the diamond was protected by its host rock. The rest of the plate displays alternating zones (A-F) of luminescent and non-luminescent diamond (diamond that is very dark in the CL images is from now on referred to as non-luminescent). The growth zones are in places complex but generally the luminescent diamond displays a rounded or hummocky outline typical of cuboid growth while the non-luminescent diamond often tends towards octahedral growth, best displayed in the upper left parts of the plate. Analyses B and C of plate P6-9 partially sample the non-luminescent diamond. They display low nitrogen concentrations of 373 ppm and 482 ppm respectively (Table 1, Figure 3) and low hydrogen peak intensities compared to the other analyses (Figure 4a). Analyses A, F, G and J sample predominantly the luminescent zones of the alternating luminescent/non-luminescent zones and yield enriched levels of both nitrogen (~ 680-780 ppm) and hydrogen (cluster of four analyses in Figure 4a) compared to analyses B and C. This suggests that the non-luminescent diamond is depleted in hydrogen as well as nitrogen compared to the luminescent diamond of the alternating luminescent/non-luminescent zones. Comparing the CL images of the front and rear sides of plate P6-9, it is evident that the brightly-luminescent octahedral zones dip steeply inwards and the “agate-texture” core does not penetrate the plate. Further, only minor non-luminescent diamond is present in the central parts of the diamond. These features imply that a single FTIR transmission point will sample more than one zone. Thus, analysis D samples partly the octahedral part of the core but perhaps mainly the adjacent poorly-

luminescent (slightly darker) zone. This would explain its similar platelet peak intensity, and similar but slightly higher nitrogen and hydrogen contents compared to analyses A, F, G and J. Analysis E samples the octahedral/agate texture zones of the core and it yields a similar but slightly higher nitrogen concentration (900 ppm) than analysis D. Although the level of aggregation for analysis E is similar to the rest of the plate, it displays a comparatively strong platelet peak and it is also comparatively depleted in hydrogen.

Plate A-3 displays an “agate texture” core similar to Plate P6-9. The core is surrounded by luminescent diamond, which either has been resorbed or represents hummocky cuboid growth. Outwards follow irregular and partly resorbed octahedral zones of luminescent and non-luminescent diamond. The intermediate parts of the plate display alternating zones of luminescent and non-luminescent diamond similar to those of Plate P6-9 and the peripheral part of the plate consists of a broad rim of type I diamond. Analyses J to O (referred to as Group 1) from the central octahedral (and agate texture) parts yield hydrogen peak intensities between 0.3 and
Thus, analysis N has likely sampled substantial amounts of A-3 and P6-9. Comparing the front and rear CL images strongly alternating luminescence reminiscent of Plates Tlie intermediate parts of the plate display reasonably homogeneous luminescence and cubo-octahedral growth under high magnification. Tlie core is surrounded by a thin zone of non-luminescent diamond. The intermediate parts of the plate display reasonably homogeneous luminescence and cubo-octahedral diamond, which is followed outwards by zones of strongly alternating luminescence reminiscent of Plates A-3 and P6-9. Comparing the front and rear CL images of Plate 17-30 it is evident that the alternating luminescent zones dip gently inwards (from the front to the rear side) along the sides of the diamond while the zones sampled by analysis N appear to dip vertically. Thus, analysis N has likely sampled substantial amounts of non-luminescent diamond and yields the lowest nitrogen content. Analyses A, F, G, H, L, M and N display a positive correlation between nitrogen and hydrogen (Figure 5). From the symmetrical consideration mentioned, this can be explained by sampling of different mixtures of luminescent and non-luminescent diamond. Plate 17-30 is very rich in hydrogen (hydrogen peak intensity = 0.5-2.2 absorption units) compared to the other plates. Hydrogen peak intensities for all analyses (except analysis N) are negatively correlated with platelet peak intensity (Figure 4) as observed for Group 2 of Plate A-3. This correlation is not obviously mirrored by a correlation between the nitrogen concentration and platelet peak intensity. Combining data from three plates, a strong correlation between the hydrogen peak intensity and the ratio between the amount of nitrogen present in B aggregates and platelet peak intensity is observed (Figure 6).

All three plates display considerable variations in nitrogen (P6-9: 373 to 900 ppm, A-3: 351 to 703 ppm, 17-30: 552 to 1154 ppm) for very restricted amounts of nitrogen aggregation (Figure 7) and it has been shown that partial analysis of non-luminescent diamond yields low nitrogen contents. The horizontal trends in Figure 7 can be explained by partial analysis of non-luminescent and nitrogen poor diamond, which would "dilute" the nitrogen concentration, whilst the estimation of nitrogen aggregation will be based on nitrogen-rich zones because of the very fact that they are rich in nitrogen (Fitzsimons et al., 1999). The nitrogen rich zones will also be ones where nitrogen aggregation proceeds most quickly (Evans, 1992). As a consequence, most analyses based on mixed nitrogen-rich and nitrogen-poor zones yield spurious over-estimations of mantle residence temperatures.

**Figure 5.** Nitrogen concentration versus hydrogen peak intensity for analyses A, F, G, H, L, M and N of Plate 17-30.

with platelet peak intensity (Figure 4) as observed for Group 2 of Plate A-3. This correlation is not obviously mirrored by a correlation between the nitrogen concentration and platelet peak intensity. Combining data from three plates, a strong correlation between the hydrogen peak intensity and the ratio between the amount of nitrogen present in B aggregates and platelet peak intensity is observed (Figure 6).

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**Rough diamonds**

Some 129 diamonds were analysed either as rough stones or, mostly, as fragments of diamonds cracked to recover mineral inclusions. Pieces from cracked diamonds were selected to sample both the interior and the rim of the diamond. Most of the diamonds from these kimberlites (termed the low-T group) range from about 400 to 1200 ppm in nitrogen and display low nitrogen aggregation of 10 to 40 % Nitrogen as B aggregates, which yields time-averaged mantle residence
temperatures of 1075 to 1115°C (Figure 8; the Main Fissure and Sugarbird Blow diamonds display similar characteristics and are, for simplicity, plotted together). The data from diamond plates cover most of the range in nitrogen concentration and aggregation state displayed by the low-T group (compare Figures 7 and 8; note the different scales). This suggests that much of the scatter of the low-T diamonds can be attributed to partial sampling of low-nitrogen diamond (see above), which is supported by multiple analyses on some individual rough diamonds that yield a wide range in nitrogen content for a constant level of aggregation (not shown in figure). Thus, the best temperature estimation for the low-T diamonds is -1075 to 1100°C. A smaller number of Main Fissure and Sugarbird Blow rough or fragmental diamonds (termed the high-T group) display similar nitrogen concentration to the low-T group, but exhibit significantly higher aggregation states (Figure 8) with time-averaged temperatures of 1150 to 1180°C. The high-T diamonds frequently display lamination lines indicative of plastic deformation. Six diamonds have core fragments displaying high-T type nitrogen aggregation and rim fragments with low-T type aggregation. Diamonds that straddle the two groups may be due to analysis of multiple growth zones of mixed high-T/low-T diamonds. Many Marsfontein diamonds are similar in nitrogen concentration and aggregation state to the Main Fissure and Sugarbird Blow diamonds and others yield temperatures below 1060 to 1070°C (Figure 8). The latter suggests that the Marsfontein kimberlite has sampled a third diamond population that is not present in the Main Fissure and Sugarbird Blow kimberlites.

Figure 9 shows that the increase in platelet concentration relative to the increase in the amount of nitrogen present in B aggregates for the Klipspringer high-T group is slightly higher (lower slope) than that for the low-T group. The hydrogen intensities for the high-T group are generally below 0.1 absorption units while a high proportion of the low-T diamonds display hydrogen intensities above 0.1.

**Diamond Inclusion minerals**

Some 101 silicate or oxide inclusions have been recovered from a total of 40 diamonds. Thirty-five silicate-bearing diamonds have been assigned to an eclogitic paragenesis whereas 3 diamonds are classified as peridotitic and 2 as websteritic. A strong predominance of the eclogitic paragenesis is confirmed by a further 42 investigated diamonds that all contain low-Ni eclogitic sulfide inclusions (Westerlund, 2000). Only the eclogitic/grospyditic inclusions are described in this paper.

**Diamond Inclusion compositions**

**Garnets**

Garnet inclusion compositions (CaO=3.2 to 22.5 wt.%, FeO=8.7 to 21.2 wt.%, MgO=5.5 to 19.1 wt.%) span most compositions displayed by eclogitic garnet inclusions worldwide and extend to compositions highly enriched in the grossular component (Figure 10). Four different populations can be distinguished by their chemical compositions (Figure 11a-d). (i) GT-1 garnets form a tightly coherent group, with intermediate Ca, Mg and Fe contents, and a trend towards lower Ca with increasing Mg-number (Figure 11 a-d). The most Ca-rich garnets are compositionally similar to garnets in diamond-bearing kyanite eclogite xenoliths (Hatton, 1978; Shee,
SILICATE AND OXIDE INCLUSION CHARACTERISTICS AND INFRA-RED ABSORPTION ANALYSIS OF DIAMONDS

Figure 8. Nitrogen aggregation state (the percentage of the total nitrogen present as B aggregates) versus the nitrogen content for rough diamonds. Main Fissure/Sugarbird Blow=solid triangles, Marsfontein=open squares. Inserted isotherms were estimated with an assumed mantle residence time of 2.5 Ga and range from 1060°C to 1180°C. Tie lines connect individual diamonds displaying high-T cores and low-T rims.

Figure 9. Nitrogen concentration in B aggregates versus platelet peak intensity for rough diamonds. Low-T group=open circles, high-T group=solid circles.

1978). (ii) GT-II garnets trend away from GT-I garnets towards more refractory compositions (Mg=#62-72) and are compositionally similar to garnets from bimineralic eclogite xenoliths (Hatton, 1978; Shee, 1978). Ca, Fe and Mg inter-element variations display a continuous evolution from the more refractory compositions of GT-II to relatively evolved compositions of GT-I, suggesting that these groups are petrogenetically linked. (iii) GT-III garnets are distinctly depleted in Fe and enriched in Ca at any Mg-number compared to the other groups. (iv) GT-IV garnets are enriched in Fe and depleted in Mg (Mg=#41-44) compared to the other groups. As with GT-I and GT-II, both the GT-III and GT-IV garnets display Fe-Mg-Ca inter-element correlations, which could be compatible with magmatic fractionation. Garnets from all groups contain high levels of Na (Na2O=0.14 to 0.29 wt.%), which is common for eclogitic garnet inclusions in diamond and garnet in diamondiferous xenoliths (McCandless and Gurney 1989).

Two diamonds (P5-2 and P8-2; both occurring in the high-T nitrogen aggregation group) contain multiple garnets, some of which fall into GT-I and others into GT-II. This further suggests that the two groups are petrogenetically related. However, GT-I displays a negative correlation between Fe and Ca in contrast to GT-II, and Mg is depleted at a higher rate in GT-II compared to GT-I (Figures 11c and d). This suggests that the end of GT-II crystallisation and the onset of crystallisation of GT-I garnets (or their protolith) was marked by the disappearance of a Mg-rich phase such as orthopyroxene. Four inclusions from two diamonds contain very high levels of about 22 wt.% CaO (Ca=1.8 in Figures 11b and 11c), a grossular component of more than 60%. This level of CaO is distinctly lower than the
Figure 10. Fe-Mg-Ca compositions (atomic proportions) for garnet and clinopyroxene diamond inclusions. Garnet—open squares, clinopyroxene—open triangles. Tie lines connect pairs of non-touching garnet and omphacite from individual diamonds. The dotted lines define fields for worldwide compositions (from Meyer, 1985).

CaO content of ~32 wt.% observed in garnet inclusions of the calc-silicate suite from south-eastern Australia (Sobolev et al., 1984) but higher than for garnets from diamond-bearing kyanite eclogite xenoliths (Hatton, 1978; Shee, 1978). The composition is similar to garnets in grospydite xenoliths (Lappin, 1978; Smyth and Hatton, 1977). From major element variations it may be inferred that these high-Ca inclusions constitute an end-member of GT-III.

Omphacites
Klipspringer omphacite inclusions plot partly within and partly outside the Fe-poor side of the field for eclogitic clinopyroxene in diamond worldwide (Figure 10). The bulk of the omphacites (termed the Main group) plot below the diopside-hedenbergite join in Figure 10 and display a positive Al-Na correlation indicative of a substantial jadeite component. Unlike the garnets, the Main group omphacites do not show clear geochemical subgroups. Distinct from the Main group, there are nine omphacites plotting on or above the diopside-hedenbergite join in Figure 10, which are referred to as the high-Al group (solid symbols in Figure 12). They carry up to 16.3 wt.% CaO and they display extremely high Al contents (Al₂O₃ ~17 to 19 wt.%). The high-Al omphacites, unlike the Main group, do not have sufficient Na to balance Al and cannot support the accommodation of Al entirely as jadeite. Some of the Al is hosted by the Ca-tschermak end-member, which is present in amounts up to 12 mole %. The high-Al clinopyroxenes show various amounts of site deficiency as evident from cation totals lower than four and contain 7-18% pseudojadeite (Ca₆Si₂O₈) with sample P9-2e showing an extremely high pseudojadeite content of 28%. The high-Al group displays very low and constant levels of Fe while Ca and Mg decrease with increasing Na.

The high Al contents together with very low Fe and Mg contents of the High-Al group omphacites suggest that they may be genetically linked to the GT-III garnets with grospyditic compositions. Six of the high-Al omphacites are from diamond P9-2 and they display "large-scale" disequilibrium analogous to the garnets from diamonds P5-2 and P8-2, which belong to the high-T nitrogen aggregation group. Diamond P9-2 displays both high-T and low-T nitrogen aggregation characteristics. The omphacites carry 0.10 to 0.42 wt.% K₂O, which partly exceeds commonly observed concentrations (e.g. Gurney et al., 1979a; b; Gurney et al., 1985). There is no difference in K between the Main group and high-Al omphacites but the most Na-poor/pseudojadeite-rich clinopyroxene in the High-Al group (P9-2e) is slightly depleted in K compared to other High-Al omphacites.

Other phases
Kyanite has only been found as two inclusions present in diamond SB-1, and since this diamond has no other inclusions, kyanite cannot be directly associated with any garnet or omphacite compositions. The kyanites may be related to the GT-I garnets which mirror the compositions of kyanite-bearing eclogites or the most Ca-rich garnets of group GT-III that were classified as grospydite garnets. One inclusion with a composition close to pure CaO has been recovered from diamond P9-3, and two such inclusions were found in diamond 17-7. They are believed to be coesite rather than quartz from their primary setting within the diamond. In diamond P9-3, the coesite occurred as a single inclusion and cannot be associated with any garnet or omphacite inclusions. However, diamond 17-7 also contained a clinopyroxene assigned to a websteritic paragenesis. Otter and Gurney (1989) reported on a coesite inclusion coexisting with a pyrope-almandine with a grossular component of 35% and Sobolev (1983) defined a coesite-eclogite diamond-inclusion paragenesis devoid of kyanite. Coesite has been reported from a grospydite xenolith with garnet containing about 19 wt.% CaO (Smyth and Hatton, 1977) and is common throughout the entire compositional range of Roberts Victor group 1 eclogites (Schulze et al., 2000). Two rutile inclusions were found in diamonds that also contained garnets, which are amongst the less evolved group GT-I garnets. This may suggest that rutile is not associated with kyanite.

Estimation of bulk rock compositions from mineral inclusion compositions
Three diamonds (950W-2, P8-2 and SB-2) carry both pyrope-almandine and omphacite as non-touching inclusions. In diamond P8-2, multiple inclusions of both
Silicate and oxide inclusion characteristics and infra-red absorption analysis of diamonds

Pyrope-almandine and omphacite display two distinctive compositions. In Figure 10, tie lines connecting the different pairs are sub-parallel, compatible with equilibrium crystallisation. Bulk compositions of hypothetical diamond host-rocks have been estimated from these pairs, and also from GT-III garnets and High-Al omphacites, which may be petrogenetically related as suggested above. In this second case, estimations were made for the most evolved minerals from each group. Bulk rock compositions have been estimated assuming equal modal amounts of garnet and clinopyroxene. Although this assumption may not be correct, the major element compositions of these minerals are broadly similar and a modal garnet/omphacite ratio of 50/50 instead of the assumed 50/50 would not affect the estimated bulk rock compositions significantly. The minerals from diamond 950W-2 are similar in composition to their counterparts in kyanite eclogites, and the most evolved GT-III garnet (P3-1) and High-Al omphacite (P7-3) are similar in composition to these minerals in grospydites. Kyanite eclogites and grospydites commonly carry between 5 and 20 modal per cent kyanite (e.g. Ater et al., 1979; Shee, 1978; Smyth and Hatton, 1977; Lippin, 1978). Therefore, bulk rock estimations based on inclusions from 950W-2 and P3-1/P7-3 were also performed assuming 10 and 20 modal % kyanite. Similar to the Al dependence on kyanite, Ti and Si contents are dependent on the assumed amount of rutile and coesite respectively. Potassium and Na are sensitive to the assumed modal abundance of clinopyroxene since K exclusively and Na mainly occurs in clinopyroxene (assuming a phlogopite-free environment). In addition, large-ion lithophile elements like K and high field strength elements like Ti are very sensitive to partial melting and/or metasomatism of the protolith. Therefore we place emphasis on Fe, Ca, Mg and Al (which has been accounted for through the addition of kyanite) as the elements, which best can reflect the compositions of hypothetical protoliths.

The estimated eclogite compositions are presented in Table 2. Representative compositions for mid-ocean
ridge basalts (MORB), mid-ocean ridge (MOR) cumulates and komatiites, which have been suggested as protoliths for mantle eclogites, are given in Table 3. SB-2 displays the most refractory composition and is compositionally similar to the most refractory MOR cumulates. Its MgO (15 wt.%) content is higher than commonly observed for MORB. Komatiites may range down to ~15 wt.% MgO (and down to ~10 wt.% MgO for basaltic komatiites) but the Al$_2$O$_3$ content of SB-2 is distinctly higher than that generally displayed by komatiites.

All compositions displayed by 950W-2 are too fertile to be akin to komatiite. Further, even the most refractory composition (950W-2(0); kyanite-free estimation) displays distinctly higher Al$_2$O$_3$ than is commonly displayed by MORB. All estimated compositions are however covered by the compositional range displayed by the MOR cumulates. 950W-2(0) is similar in composition to kyanite-bearing eclogite (Hatton, 1978; Shee, 1978) but if 10 to 20 modal % kyanite is added, the Al$_2$O$_3$ distinctively exceeds the range observed for kyanite eclogite and enters that of grospydite (Smyth and Hatton, 1977; Lappin, 1978). Since garnet from 950W-2 is akin to kyanite-bearing eclogite garnet rather than grospydite garnet, this suggests that only minor kyanite was associated with the 950W-2 paragenesis. Thus, the composition of a hypothetical protolith for this paragenesis is probably closer to that of 950W-2(0) than those of 950W-2(10) and 950W-2(20).

Chemical compositions for P8-2(I) and P8-2(II) are similar to each other and intermediate between those of SB-2 and 950W-2(0). P8-2(I) and P8-2(II) are much too elevated in Al$_2$O$_3$ to resemble even basaltic komatiites while they are fairly similar to MORB in composition. However, their MgO and Al$_2$O$_3$ contents are slightly higher than commonly observed for MORB and they are compositionally akin to some MOR cumulates.

In a similar way to 950W-2, the estimated bulk rock chemistry based on P3-1 (garnet) and P7-3 (omphacite) is dependent on the assumed modal content of kyanite. These compositions are all distinctly higher in CaO and Al$_2$O$_3$ and lower in FeO and MgO compared to MORB.
and komatite. The whole estimated compositional range however falls within that of MOR cumulates. Analysis P3-1/P7-1(20) with 20 modal % kyanite is very similar in composition to a gosspylite from Roberts Victor, which contains 20 modal % kyanite (Lappin, 1978).

**Diamond inclusion geothermometry**

While no reactions involving garnet and clinopyroxene result in sufficient volume change to yield information on the pressure of equilibration, the four non-touching garnet-omphacite pairs in diamonds 950W-2, P8-2 and SB-2 may be used to estimate the temperature of diamond formation. The basis for garnet-clinopyroxene geothermometry is the temperature dependence of Fe" and Mg partitioning between the two minerals. Chemical equilibrium cannot simply be assumed since the inclusions may have been incorporated into the diamond at different times, in different chemical environments and/or under different temperature conditions. However, in Figure 10, tie-lines connecting the garnets and omphacites are not crossing which suggests, or at least does not preclude, that the different mineral pairs crystallised under potentially similar equilibrium conditions. Four experimentally calibrated and commonly used geothermometers were evaluated in detail by Westerlund (2000): Ellis and Green (1979), Krogh (1988), Ai (1994) and Berman et al. (1995). Based on the results from the application of these geothermometers on Klipspringer eclogitic diamond inclusions and xenoliths, it was proposed that Krogh (1988) yields the most realistic temperatures for the current range in composition. The obtained temperature ranges are 1152 to 1233°C at an assumed pressure of 50 kbars and 1200 to 1278°C at an assumed pressure of 60 kbars (Table 4).

**Discussion and conclusions**

Woods (1986) suggested that platelets are formed from carbon atoms expelled from the diamond lattice during the formation of B aggregates. However, platelet peak development may occur at different rates relative to the amount of B aggregates (Mendelsohn and Milledge, 1989).
While platelet degradation may be explained by catastrophic heating events (Woods, 1986), Mendelsohn and Milledge (1995) suggest that a lower rate of platelet development may be expected during nitrogen aggregation at higher temperatures from the higher reluctance for carbon atoms to relax back into the diamond lattice at higher temperatures. The correlation between the hydrogen peak intensity and the ratio between the amount of nitrogen occurring in B aggregates and the platelet peak for the diamond plates as well as the comparatively lower hydrogen content of the high-T diamonds, which display a higher increase in platelet peak intensity relative to B aggregates than the low-T diamonds, suggest that hydrogen also may affect the formation or degradation of platelets.

Silicate inclusion compositions indicate that eclogite parageneses strongly dominate amongst Klipspringer diamonds. Based on garnet and clinopyroxene inclusion compositions, the presence of both rutile and garnet in two individual diamonds, and the occurrence of kyanite inclusions, three parageneses have been recognised: eclogite ± rutile ± kyanite paragenesis (GT-I/GT-II), a grospydite paragenesis (GT-III/High-Al omphacites) and an Fe-rich eclogitic paragenesis (GT-IV). The major element variations suggest that the garnets within each individual group may be linked by magmatic fractionation. However, the grospydite and Fe-rich parageneses cannot be related to the first eclogite paragenesis by a simple petrogenetic process.

A level of 28 mole % pseudojadeite has not previously been reported for either clinopyroxene inclusions or xenolithic clinopyroxene. Since the inclusions are protected by the diamond host from re-equilibration with the surrounding environment, the observed pseudojadeite contents of the high-Al omphacites may be indicative of intrinsic compositions that cannot be observed in xenolithic omphacite due to decomposition breakdown (Smyth, 1980; Smyth et al., 1989). Experiments in the system Na2O-CaO-Al2O3-SiO2 show that the pseudojadeite content of clinopyroxene is strongly pressure dependent and increases with increasing pressure up to ~35 kbars (Gasparik, 1985). The comparatively small cell volume of non-stoichiometric clinopyroxene would also favour increased stability at higher pressures (Wood and Henderson, 1978). The solubility of K in clinopyroxene increases with increasing pressure under upper mantle conditions (Harlow, 1992). Thus, assuming that K is buffered, the concurrent low level of K and high level of pseudojadeite in P9-2e compared to the rest of the High-Al omphacites suggests that the elevated pseudojadeite content is not reflecting a higher pressure. Rather the amount of pseudojadeite is determined by the bulk composition of the environment of formation. Since the Al2O3 content of garnet is fairly constant at different eclogitic whole-rock compositions, the variations in bulk Al2O3 of the environment are reflected in the Al2O3 content of clinopyroxene and the possible presence of kyanite and/or corundum. The very high Al2O3-levels of the reconstructed grospydite bulk composition and particularly the constant level of Al in the High-Al omphacites with increasing and decreasing contents of other elements, indicate that the environment was buffered with respect to Al2O3. This suggests that kyanite was present, as one would expect for a grospydite paragenesis. Both the GT-III garnets and the high-Al omphacites display distinctive inter-element variations that can be reconciled with magmatic fractionation. Although kyanite is expected to be present in the grospydite paragenesis, it is suggested that excessive amounts of Al in the formation environment were initially accommodated partly in pseudojadeite. While Ca increases with decreasing Mg for the GT-III garnets, Ca (and the pseudojadeite content) decreases and Na increases with decreasing Mg for the high-Al omphacites. Clinopyroxene is the only phase beside melt in a deep lithospheric environment that can host Na to a significant extent. Thus, as Na becomes concentrated in a magma due to fractionation of garnet and Na-deficient clinopyroxene, at some point it starts to enter the clinopyroxene. Garnet and clinopyroxene are the only phases to accommodate Ca. Therefore Ca will increase in the garnet as Na enters the clinopyroxene. Thus, the observed range in pseudojadeite content (2-28 mole %) of the clinopyroxene is proposed to be dependent on the composition of the protolith and perhaps magmatic fractionation of a partial melt of the protolith rather than the prevalent pressures of formation of the clinopyroxene. Bulanova et al. (1988, in Russian, cited by Bulanova, 1995) interpreted a decrease in the pseudojadeite content of clinopyroxene diamond inclusions as a decrease in pressure of formation based on a qualitative estimation of the pressure sensitivity of pseudojadeite (Jarkov et al., 1984, in Russian, cited by Bulanova, 1995). We suggest that any information on the pressure of equilibration based on the level of pseudojadeite in clinopyroxene may be in error if the bulk composition and whole mineral assemblage are not known.

The low-T and high-T nitrogen aggregation group diamonds are well separated in Figure 8 indicating that they are two petrogenetically unrelated populations representing two discrete diamond formation events. However, the presence of six individual diamonds, which are mixtures of low-T and high-T diamonds,
suggests that the two populations were spatially related in the upper mantle. The central location of the high-T analyses and the peripheral location of the low-T analyses implies that the former predate the latter and it suggests that in some cases the high-T diamonds have acted as nucleation sites for the low-T diamonds. A time gap of 50 to 200 million years between the high-T and low-T diamond formation with temperatures in the range of 1220 to 1260 °C would allow for the former to achieve their comparatively enhanced nitrogen aggregation state. A time gap of less than 10 million years would demand unreasonably high temperatures. However, many high-T diamonds show evidence of high-temperature deformation in the form of lamination lines (Westerlund, 2000). Plastic deformation may enhance nitrogen aggregation (Evans, 1992) in which case the estimated time-averaged mantle residence temperatures for the high-T diamonds would be spurious. Westerlund et al. (this volume) propose that the low-T diamonds are related to the ~2.7 Ga Ventersdorp event. It may be speculated that plastic deformation of the high-T diamonds occurred just prior to the formation of the low-T diamonds and was associated with a tectonothermal event responsible for the reactivation of the Thahazimbi-Murchison Lineament at 2.7 Ga. The “large-scale” disequilibrium displayed by inclusions from three high-T nitrogen aggregation group diamonds is difficult to reconcile with a metamorphic origin through solid state diffusion or simple recrystallisation of pre-existing garnet and clinopyroxene since this would require a substantial chemical disequilibrium on a micrometre scale in the eclogitic host-rock. The “large-scale” disequilibrium trends are concordant with the magmatic fractionation trends displayed by the respective parageneses which suggests an igneous or metasomatic origin for the high-T diamonds.

Based on a detailed study of the low-T diamond internal growth characteristics and the Re-Os and S isotope systematics of their sulfide inclusions, Westerlund et al. (2004) argue for an origin of the diamonds by the remobilization of fluids in or proximal to a pre-existing eclogite host rock. Some diamonds from each of the three garnet inclusion parageneses occur in the high-T nitrogen aggregation group while other diamonds from each paragenesis occur in the low-T nitrogen aggregation group. The inclusions from the high-T and the low-T diamonds conform to the same compositional trends which suggest that the low-T diamonds formed in the host-rock for the high-T diamonds and their silicate inclusions acquired their compositions from the surrounding host eclogite/grospydite. The inclusions in the low-T group diamonds may have precipitated from a partial melt of the host eclogite/grospydite. However, in such a scenario one would expect the silicate inclusions from the low-T diamonds to consistently display more evolved compositions than the silicate inclusions from the high-T diamonds, which is not the case. We propose that the silicate inclusions in the low-T diamonds originate from recrystallisation of pre-existing minerals in connection with the late-Archean metasomatic event.

Several lines of evidence point at subducted oceanic crust as a protolith for upper mantle eclogites and eclogitic diamonds (see Introduction). Hypothetical reconstructed eclogite/grospydite protoliths for the silicate inclusions display a wide range in FeO, MgO, CaO and Al₂O₃. Despite the wide compositional range, none of the estimated bulk rock compositions is akin to those of MORB or komatite. However, the estimated abundances of most elements are covered by the range displayed by MOR cumulates from the Southwest Indian Ridge. This may suggest that while the different observed garnet inclusion groups are not directly petrogenetically related, their protoliths may be different types of mid-ocean ridge layer 3 cumulates. However, all estimated compositions display low levels of SiO₂ compared to MOR cumulates. If MOR cumulates are indeed protoliths for the inclusions, it may be that coesite was present in the different parageneses which has not been accounted for in the bulk rock chemistry estimations. Alternatively, any silica present as a SiO₂ phase may have been lost during subduction and partial melting of the oceanic crust as suggested by Rudnick (1995). The reconstructed bulk composition for the grospydite paragenesis, based on the high-Ca garnets and high-Al omphacites, would have been derived from a close to pure anorthosite cumulate as has previously been suggested for mantle grospydites (Jagoutz et al., 1984).

The time-averaged mantle residence temperatures for the low-T diamonds (~1075 to 1100°C) are similar to the equilibrium temperatures for the Group I eclogites (see Geological setting and the Klipspringer kimberlites), which are believed to have recorded the temperatures that prevailed in the lithosphere within the diamond stability field at the time of kimberlite eruption 148 Ma ago. This suggests that the diamondiferous part of the lithosphere at the time of low-T diamond formation (2.5±0.15 Ga) cannot have been much hotter than at 150 Ma ago. Thus, a cratonic geotherm of 37 to 39 mW/m² was already established around the Proterozoic/Archaean boundary. The equilibration temperatures for non-touching garnet and omphacite inclusions are some 80 to 150°C higher than those of the Group I eclogites and the time-averaged mantle residence temperatures for the low-T group diamonds. While it cannot be excluded that the recorded temperature difference reflects a mechanical transport of the diamonds to a shallower lithospheric level subsequent to diamond formation, a metasomatic process of formation was more probably associated with a heating event and a temporarily increased geotherm. The implications are that the low-T diamonds were formed during a thermal perturbation of the lithosphere and were stored under thermal conditions similar to those prevalent in the mantle ~150 Ma ago.
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