

Diamond formation and kimberlite-clan magmatism in cratonic settings

STEPHEN E. HAGGERTY

Department of Geosciences, University of Massachusetts, Amherst, MA 01003, U.S.A.

Abstract—The global distribution of diamonds, and the host rocks transporting diamond, are preferentially concentrated in Archean cratons and in Paleoproterozoic mobile belts surrounding cratons. Kimberlites and lamproites (kimberlite-clan rocks, KCRs) form intrusive clusters that are globally synchronous and temporally punctuated, with major eruptive episodes in the Mesoproterozoic, Paleozoic, Mesozoic, and Cenozoic. From several lines of reasoning and based on the geology of cratons, the mantle geology of diamonds, and the chemistry of KCRs, diamonds and xenoliths, it is concluded that diamond formation in the lower mantle, the transition zone, and the lithosphere results from fluid and gas interactions, and possibly from melt precipitation; and these diamonds were all precipitated from primordial carbon introduced over long periods of time by mantle plumes. In evaluating models of diamond formation and KCR magmatism, and taking all of the above into consideration, the conclusion is that there is no substantial evidence for subduction recycling, but there is relatively strong evidence that superplumes, originating at the D'' core-mantle layer, triggered eruptions during superchron events of the geomagnetic field.

INTRODUCTION

DIAMOND IS an impervious time capsule, and is a window to the geodynamics of the mantle and possibly the core. Diamond-bearing volcanism has been operative since at least the early part of the Proterozoic (JANSE and SHEAHAN, 1995), and some diamonds are >3 Ga (RICHARDSON *et al.*, 1984). Diamond eruptions provide an unprecedented sample of the mantle and this sample is of enormous interest because it is the only solid material of the deep Earth that is available for direct analysis in the laboratory. The formation of diamond, the transport of diamond, and the chemistry of mantle-derived xenoliths have been major research challenges for many decades. F. R. BOYD, in no small measure, has made significant contributions in unravelling the mineralogy and chemistry of the subcontinental lithospheric mantle, and has provided us with a magnificent P-T vista of its interior (BOYD, 1973; BOYD and FINNERTY, 1980). The present contribution will draw upon many of BOYD's insights, and it is hoped will take some of these observations a step further, specifically in the realm of the origin of carbon in diamond, the possible geophysical implications, and information that diamond in KCR magmatism may hold for the history of the bulk Earth.

DISTRIBUTION OF CRATONS, KIMBERLITES AND DIAMONDS

It is now firmly established that the major resources of mantle-derived diamonds in kimberlites are located directly on cratons, whereas lamproites have a preferred concentration in mobile belts adjacent to cratons. The petrology, mineral chemistry, and bulk chemical compositions of kimberlites and lamproites are covered in detail in a series of volumes by MITCHELL (1986; 1996), MITCHELL and BERG-

MAN (1991), and by ROCK (1991), but consensus on the origin of these exotic rocks, since the problem was first fully reviewed by DAWSON (1980), has yet to be made. One view is that kimberlites and lamproites and other closely-related rocks form a single clan (and the term kimberlite-clan rocks is adopted here), with subtle distinctions in petrochemistry (ROCK, 1991), that may merely be functions of degrees of metasomatism (DAWSON, 1987), accentuated by sub-lithospheric craton geometry (HAGGERTY, 1986).

Craton is defined as "a relatively immobile part of the Earth, generally of large size", described initially by KOBER in 1921 as *kratogen*, modified in 1936 by STILLE to *kraton*, and subsequently to the currently preferred spelling of *craton* (HOWELL, 1960). Cratons consist of exposed *shields*, and areas of cratons blanketed by sediments, extrusives, and metamorphic thrust sheets are termed *platforms*. Although cratons are typically described as old (Archean), cold (low heat flow), and stable, there is abundant evidence for intra-cratonic volcanism and seismicity (SYKES, 1978). As outlined elsewhere in this volume there is considerable debate on the origin and long term preservation of cratons, but from xenolith studies (*e.g.*, BOYD and GURNEY, 1986), mineral inclusions in diamonds (*e.g.*, SOBOLEV, 1977; MEYER, 1987; GURNEY, 1989), seismology (DURRHEIM and MOODY, 1991; JORDAN, 1988; POLET and ANDERSON, 1995), heat flow (SCLATER and FRANCHETEAU, 1970; POLLACK and CHAPMAN, 1977; DAVIES, 1979), isostasy (NISBET, 1984), field geology (BURKE *et al.*, 1986; DE WIT *et al.*, 1992), models for the lithosphere (BAER, 1977; HERZBERG, 1993), and early crustal genesis (*e.g.*, TAYLOR and MCCLENNAN, 1985; CONDIE, 1986; DAWSON *et al.*, 1986; BICKFORD, 1988; DE WIT and HART, 1993; FOUNTAIN *et al.*, 1992; RUDNICK and FOUNTAIN, 1995), there are several observations, including those discussed in greater detail in subsequent sections, that point to a commonality among cratons. These are: (1) a predominance of the tonalite-trondhjemite-granodiorite (TTG) suite, a virtual absence of ophiolites and blueschist facies metamorphic rocks, and very minor andesites; (2) cratons have internally-controlled structural domains, and cratons are typically surrounded by Proterozoic mobile belts; (3) cratons have geochemically depleted, low density *keels* that are at least 200 km in thickness, and >3 Ga in age; (4) the characteristic volcanics are Archean komatiites, Protero-

zoic, Paleozoic, Mesozoic and Cenozoic flood basalts in large igneous provinces (LIPS) at craton margins, clusters of diamond-bearing, KCR intrusives in the interior confines of cratons, and along cratonic margins; (5) cratons have acted as buoyant metamorphic core complexes that on amalgamation led to the formation of microcontinents, and ultimately the assembly of supercontinents.

Among the numerous implications of these observations, the following are particularly noteworthy: (1) cratonic crust grew very rapidly in the Archean and was the product of multiple extraction episodes, and of multiple melting events of fertile and reprocessed upper mantle; and (2) continental crusts and cratonic keels, although physically and chemically distinct, behave as a single and mechanical robust unit (lithosphere) of closely comparable age, that differ markedly from the convective and ductile asthenosphere that surrounds the lithosphere.

JANSE (1992) divided cratons on the basis of age into Archons (>2.5 Ga), Protons (2.5–1.6 Ga), and Tectons (1.6–0.8 Ga) as shown schematically in Fig. 1. This is a very useful chronological division because the vast majority of diamondiferous intrusives are into basement Archons, with fewer present in Protons, and none presently recognized in Tectons. The terms Protons and Tectons, however, are less useful: Protons because of the atomic connotation, and Tectons because although the lower age (1.6 Ga) division starts at the Paleoproterozoic boundary, the upper limit arbitrarily ends partway through the Neoproterozoic (1.0–0.54 Ga). The following alternative is proposed: maintain

Archon (>2.5 Ga); but replace *Protons* by *Orotons* (derived from the Orosirian Period, and meaning mountain range with inferences to a "Global orogenic period" in the Paleoproterozoic, 2.5–1.6 Ga (HARLAND *et al.*, 1989); and replace *Protons* by *Stenotons*, meaning *narrow*, for narrow belts of intense metamorphism and deformation, and after Stenian in the Mesoproterozoic Period between 1.2–1.0 Ga (HARLAND *et al.*, 1989). These alternatives maintain the spirit of intent in JANSE's (1994) tecto-chronological division.

MANTLE ROCK TYPES

The distribution of rocks and minerals in mantle xenoliths that are sampled by KCRs in cratons, and for comparison by alkali basalts (and related rocks) in rift zones, are illustrated in a cross-section of an idealized Archon in Fig. 2 (HAGGERTY, 1995). The end members of the three modal ternary diagrams are olivine (Ol), clinopyroxene (Cpx), and orthopyroxene (Opx); ternary diagrams in the lithospheric keel and in the asthenosphere are high pressure projections from garnet, whereas the ternary diagram in the rift zone is at lower pressures and is a projection from spinel. The asthenosphere between ~100 and 410 km is dominantly garnet lherzolite, with possibly large isolated volumes of high-MgO eclogite of komatiitic composition (HAGGERTY *et al.*, 1993). At shallower asthenospheric depths, and sampled mostly by alkali basalt, the major rock type is spinel lherzolite with trapped partial melts of wherlite and websterite. The lithospheric keel is dominantly depleted harzburgite.

GLOBAL DISTRIBUTION OF CRATONS, AGE DIVISION, AND THE LOCATION OF MAJOR DIAMOND DEPOSITS

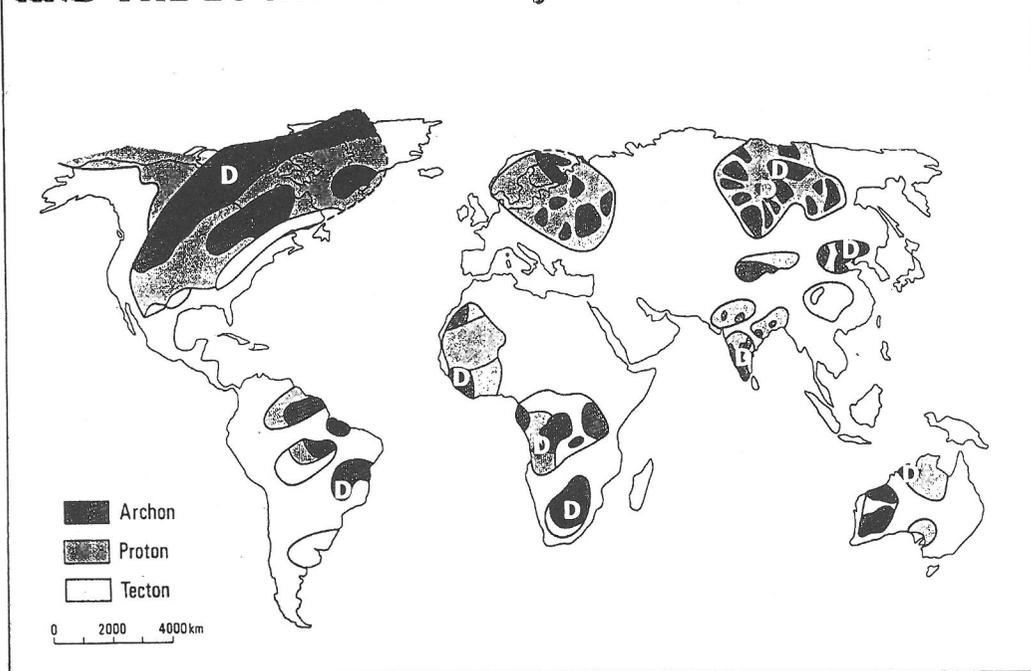


FIG. 1. Global distribution of cratons, craton divisions, and diamonds. See text for explanation of age divisions and nomenclature alternatives. Modified from JANSE (1992), and LEVINSON *et al.* (1992).

ROCKS AND MINERALS IN MANTLE XENOLITHS

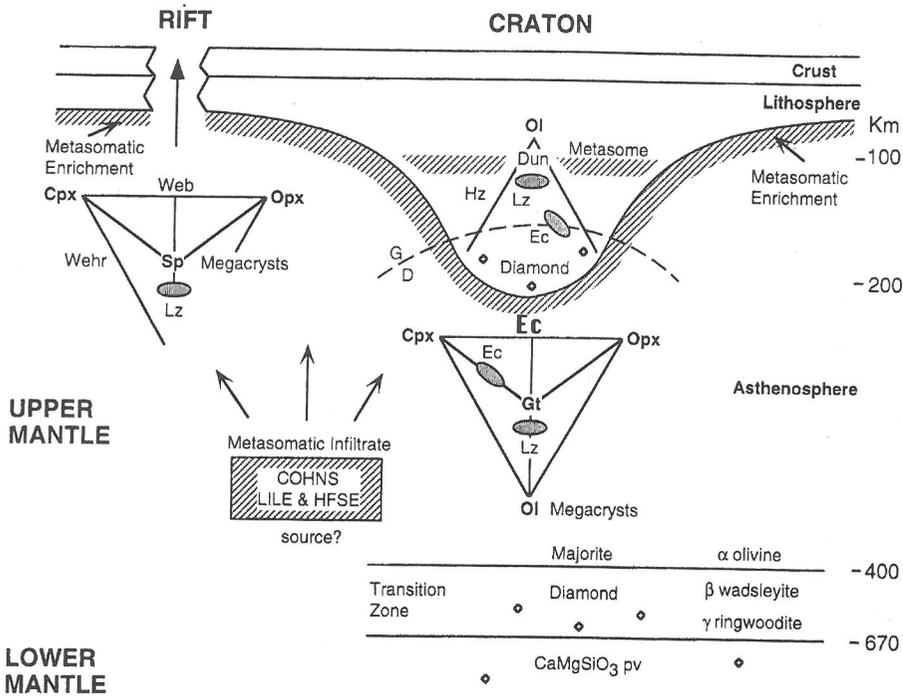


Fig. 2. Schematic cross-section of the mantle showing the major minerals and rock types from the top of the lower mantle, through the transition zone and the asthenosphere, to the lithosphere. The ternaries and partial ternaries define lherzolite (Lz) with mineral endmembers of olivine, orthopyroxene, and clinopyroxene; the ternary in the deeper asthenosphere is a projection from garnet, and at shallower depths is a projection from spinel. Metasomes are shown at the lithosphere-asthenosphere boundary, and in the lithosphere at 75–100 km. The metasomatic infiltrates are charged with C-O-H-N-S gas species, large-ion-lithophile-elements (LILE), and high-field-strength-elements (HFSE). Hz harzburgite; Dun dunite; Ec eclogite; Web websterite; G-D graphite-diamond stability curve. Modified from HAGGERTY (1995).

and dunite; eclogites are also prominent as residues of possible TTG crustal extraction (ROLLINSON, 1997), and as high pressure, trapped and crystallized partial melts of basaltic composition. Discrete megacrystic xenoliths (some as large as 20 cm in diameter) of olivine, orthopyroxene, clinopyroxene, garnet, ilmenite and phlogopite are abundant in kimberlites, and rare to absent in lamproites; kaersutite, Al-clinopyroxene, and anorthoclase, are the characteristic megacrysts in alkali basalts and related rift volcanics. Diamond formed and is stored in the base of the lithosphere, and graphite crystallizes at lower P and T (Fig. 2). Metasomatic xenoliths are pervasive in the upper mantle sample (MENZIES and HAWKESWORTH, 1987; NIXON, 1987; MORRIS and PASTERIS, 1987), and two prominent horizons (metasomes) of metasomatism have been proposed based on the P-T stabilities of minerals (HAGGERTY, 1989), on the form of the C-O-H peridotite solidus (WYLLIE, 1989), and on the thermal, physical, and chemical contrasts that exist between the lithosphere and the asthenosphere (HAGGERTY, 1989; WYLLIE, 1989). One of the proposed metasomes within the keel (Figs. 2 and 3) has a distinctive and compositionally unusual mineralogy of LILE (Ba, K, Na, Ca, Sr, LREE), and HFSE (Ti, Zr, Nb) oxides that include armalcolite, lindsleyite, mathiasite, yimengite, hawthorneite and Nb-Cr-rutile

in association with Ti-ferri-phlogopite and K-richterite in substrates of harzburgitic olivine plus orthopyroxene (HAGGERTY, 1991). The second and deeper proposed metasome (Fig. 2) is along the lithosphere-asthenosphere boundary (LAB), and xenoliths derived from this horizon are glimmerite, a sheared phlogopite-rich rock that may be accompanied by clinopyroxene and ilmenite, but is amphibole-free; such xenoliths are distinctive and differ from polyhedral MARID (mica, amphibole, rutile, ilmenite, diopside) xenoliths, in fabric and mineralogy. It is proposed here that the keel and LAB metasomes may correspond respectively, to the Hale and the Lehmann seismic discontinuities (GAHERTY and JORDAN, 1995). At greater depths in the asthenosphere, majorite appears at ~300 km (AGEE, 1993 and refs. therein). Majoritic garnet is recorded as primary inclusions in diamond (MOORE and GURNEY, 1985), and as equilibrated garnet plus exsolved pyroxene in lherzolite, garnet harzburgite, eclogite, and websterite (HAGGERTY and SAUTTER, 1990; HAGGERTY, unpublished). Majorite extends into the transition zone (TZ = 410–660 km), where the mineral is predicted, based on high P-T experiments, to be accompanied by the transformation of olivine(α) \rightarrow wadsleyite(β) \rightarrow ringwoodite(γ) (RINGWOOD and MAJOR, 1966). Although the β and γ polymorphs of olivine

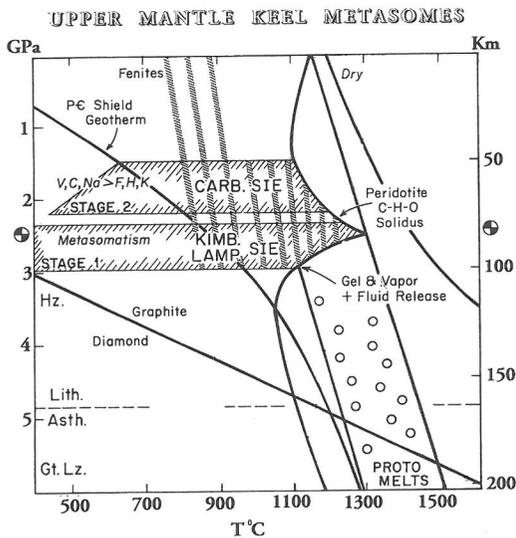


Fig. 3. P-T schematic for the development of metasomes in subcratonic upper mantle lithosphere. Melts originating in the asthenosphere (Asth) from garnet lherzolite (Gt Lz) will partially crystallize on intersection with the C-O-H peridotite solidus if $T < 1400^{\circ}\text{C}$. Fluid and vapor release will take place, metasomatising previously depleted harzburgite (Hz). A subdivision of metasomes is implied from mineral assemblages and mineral stabilities: a Stage 1 horizon enriched in fluid, water (H), and K_2O (K); and a Stage 2 horizon, considered to form by fractional distillation, and characterized by vapor (V), CO_2 (C), carbonate, Na_2O , and associated SIE, specifically LREE. Stage 1 and Stage 2 metasomes, and the metasome at the base of the lithosphere (Fig. 2), provide the petrochemical distinctions of KCR silicate incompatible elements (SIE) that are acquired through assimilation by rising, highly refractory proto-KCR melts generated in the lower mantle and the asthenosphere by superplumes. Varying degrees of metasome assimilation and craton geometry (see Fig. 4), results in a petrochemical spectrum in the kimberlite-lamproite clan; hence, KCR. Modified from HAGGERTY (1989).

have not been recognized in the mantle sample, these polymorphs, and wadsleyite in particular are possibly in the hydrous state (SMYTH and KAWAMOTO, 1997), and several oceans of water may reside in the TZ (SMYTH, 1994). The TZ samples are characterized by majoritic garnet, and by mineral inclusions in diamond of Na pyroxene ($\text{Na}_2\text{MgSi}_2\text{O}_{12}$) solid solution in enstatite (WU and SUENO, 1996). Evidence of direct sampling of the lower mantle (>660 km) is recorded in diamond inclusion assemblages of: enstatite plus magnesiowustite (MW) or ferropericlaase (FP); CaSiO_3 plus FP (HARTE and HARRIS, 1994; DAVIES *et al.*, 1998; STACHEL *et al.*, 1998 and refs. therein); and tetragonal garnet (HARRIS *et al.*, 1997).

DIAMOND FORMATION

The mantle geology of diamond

Subcraton, lithospherically derived-diamonds from KCRs, range from smooth faced octahedra to hopper

crystals, and from fibrous diamond in cubes (and ballas) to polycrystalline framesite. Single crystals of diamond range in body color from colorless, through to either yellows or to browns and pinks. Very occasionally diamond is sapphire blue or ruby red. Green transparent diamonds show radiation damage, whereas green opaque, or green opaque coated diamonds contain abundant mineral and fluid inclusions. Brown and pink diamonds usually exhibit lamination lines because of plastic deformation (HARRIS, 1992). Yellow and greenish yellow diamonds contain nitrogen (mass # = 7) substituting for carbon (mass # = 6), although some colorless and brown diamonds may contain this atomic impurity as well (EVANS, 1992). Semi-conducting blue diamonds have trace amounts of boron (mass # = 5). Diamonds are spectroscopically classified into Type I (nitrogen-bearing), and Type II (nitrogen-free). Subdivision of Type I diamonds is based on the state of N site occupancy (DAVIES, 1976; BIBBY, 1982). Type Ib has N randomly replacing C (typical of rapidly quenched synthetic diamond), but is very rare among natural diamonds. In Type Ia ($\sim 98\%$ of cratonic macrodiamonds), N is present in aggregation, as A-centers (a pair of nitrogen atoms), in N3-centers (three nitrogens and a vacancy), and in B-centers (four nitrogens and a vacancy). Nitrogen aggregation is temperature dependent (EVANS and QI, 1982), with Type IaA diamonds forming at lower temperatures ($1050\text{--}1100^{\circ}\text{C}$), than Type IaB ($1200\text{--}1400^{\circ}\text{C}$).

The distribution of diamond crystal morphologies, diamond types, and diamond host rocks are shown in a thermal cross-section of a generalized lithospheric keel in Fig. 4. Considerable progress has been made over the past several decades that has led to a reasonable understanding of the geological setting of diamond in the mantle, and of the conditions of diamond growth and residency; and this has been accompanied by modelling the growth of diamond in natural settings (DEINES, 1980; BOYD *et al.*, 1994). All of this has been possible from quantitative analyses of mineral inclusions in diamond, and from morphological, spectroscopic, and isotopic studies of diamond (*e.g.*, FIELD, 1979; 1992). Some of these advances followed early work by MEYER and BOYD, (1972), or were made directly by BOYD and coworkers (*e.g.*, BOYD and NIXON, 1975; BOYD and GURNEY, 1982; 1986; BOYD and DANCHIN, 1980; BOYD *et al.*, 1985; GURNEY and BOYD, 1982). The most striking highlights have been: (1) the dating of mineral inclusions in diamond that demonstrate the antiquity of diamond (~ 1 to ~ 3 Ga) (RICHARDSON *et al.*, 1984; 1990; 1993; RICHARDSON and HARRIS, 1997) with implications for specific diamond-forming events, long term storage of diamond in the lithosphere, and

DIAMOND GENESIS IN EVOLVED UPPER MANTLE KEEL

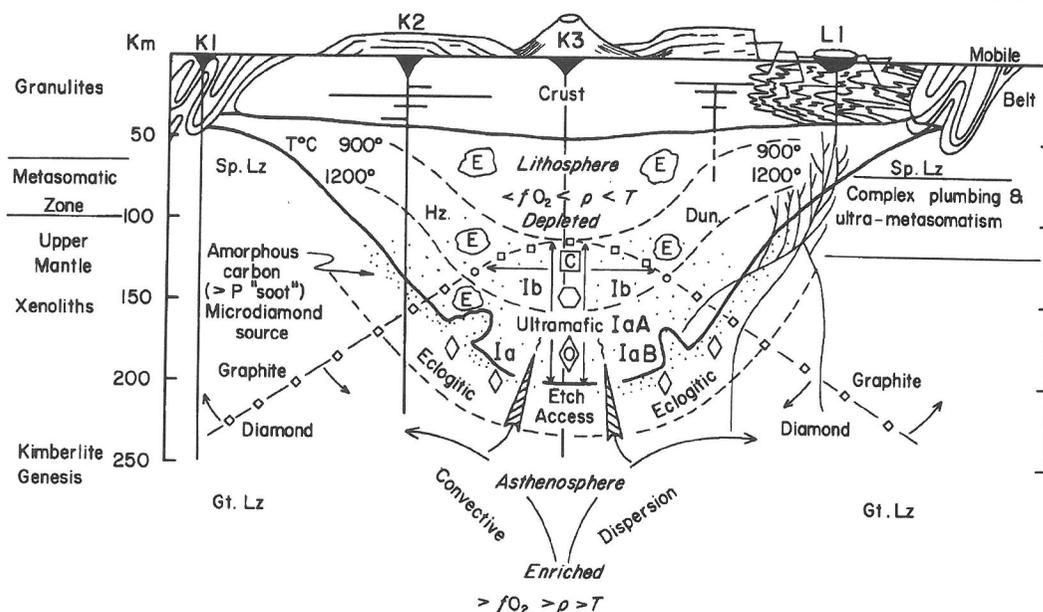


FIG. 4. A schematic cross-section of a depleted subcratonic lithospheric keel, showing the distribution of ancient diamond host rocks (peridotitic and eclogitic), diamond morphologies (octahedron, cubo-octahedron, and cube), and diamond types (Ia, Ib), including young microdiamonds (carbon soot). Diamond corrosion takes places over periods of time in the lithosphere from infiltrating asthenospheric melts (etch access). K1 (non-diamondiferous), K2, and K3 (diamond-bearing), refer to typical kimberlite intrusions into cratons; L1 is representative of lamproites into circum-cratonic mobile belts, with complex plumbing and associated ultra-metasomatism. From HAGGERTY (1986).

growth of the lithosphere to depths of ~ 200 km in the first 1 Ga of Earth's history; (2) macrodiamonds are xenocrysts, and diamond host rocks may now be classified into major populations of P-type (peridotitic, but harzburgitic, *sensu stricto*), and E-type (eclogite) parageneses (Fig. 4); (3) mineral inclusions in diamond from the TZ and the lower mantle place an entirely new constraint on the dynamics of models invoked for the magmatic transport of solids from depths of >660 km, and on the origin of kimberlite-clan rocks; (4) from cathodoluminescence observations (e.g., BULANOVA, 1995), diamonds are complexly zoned, have re-entrant angles resulting from corrosion and multiple overgrowths from sequential carbon precipitation that may be isotopically variable, implying dissolution and deposition over long periods of time in the mantle (SWART *et al.*, 1983; JAVOY *et al.*, 1984; MILLIDGE *et al.*, 1989; HARTE and OTTER, 1992; BOYD and PILLINGER, 1994); (4) Type Ib diamond (quenched), may anneal over millions of years, transforming the diamond into Type IaA or IaB, which at high pressure for a given temperature allows the duration of annealing (which is typically of the order of Ma to Ga), of Ib \rightarrow IaA to be qualita-

tively determined (TAYLOR *et al.*, 1996); (5) cores of high temperature octahedral diamond may be coated by fluid-saturated, lower temperature cuboidal diamond, which has implications for fluid compositions in the mantle, and for the hydrothermal growth of diamond at high P and T (NAVON *et al.*, 1988).

Mineral inclusions in the two dominant rocks hosting diamond (P and E) are given in Table 1. P-type diamond inclusions are highly depleted, are enriched in Mg and Cr, and by association with harzburgitic and dunitic xenoliths are lithospheric in origin (Fig. 4). By contrast, E-type diamonds are typically younger (~ 1 Ga) than P-type (>3 Ga) diamonds (RICHARDSON and HARRIS, 1997 and refs. therein), are geochemically enriched, may be associated with minor coesite, corundum, sanidine, or kyanite, and are either of lithospheric or asthenospheric origin (Fig. 4), with inferred temperatures (900 – 1400°C at 5 GPa) from coexisting mineral inclusions being typically higher for E-type than P-type diamonds (GURNEY, 1989). The geochemical distinction in silicate mineralogy between P- and E-type diamonds is also evident in coexisting sulfide inclusions: P-type diamonds have high-Ni (16–34 wt%) sulfides and high

Table 1. Inclusions in Diamond

Peridotitic	Eclogitic
Olivine	Omphacite
Enstatite	
Diopside	
Cr-pyrope	Pyrope-almandine
Mg-Cr-Spinel	Chromite
Mg-Cr-ilmenite	Ilmenite
Ni-sulfides	Fe-sulfides
	Kyanite
	Sanidine
	Coesite
	Corundum
	Rutile
Diamond	Diamond
Uncertain Paragenesis	
Metallic Fe; FeC; SiC; dry ice	

modal olivine; and E-type diamonds have high-Fe sulfides (0.5–8 wt% Ni) in the presence of garnet plus omphacite; these differences are in accord with the geochemical partitioning of Ni between mafic and ultramafic liquids. As a discrete mineral in diamond, sulfide is orders of magnitude more abundant than any other mineral inclusion; these are S-type diamonds (DEINES and HARRIS, 1995). The chemistry of other silicate mineral inclusions point to rare parageneses in lherzolites (L-type ~2 Ga, RICHARDSON, 1993), and websterites (W-type). Of uncertain paragenesis, but of considerable importance, are inclusions in diamond of Fe, FeC, and SiC (implying extremely low redox conditions, HAGGERTY, 1990; 1994, and refs. therein), zircon (which may be of metasomatic origin and is possibly dateable KINNEY and MEYER, 1994), and solid carbon dioxide, which has implications for mantle fluids (SCHRAUDER and NAVON, 1993).

The source of carbon in diamond

Carbon is the fourth most abundant element in the solar system, and from this vast reservoir it would seem quite natural to assume that the carbon in diamond is primordial. However, with the acceptance of plate tectonics, and given the widespread association of eclogites and diamonds in KCRs it is, in the view of many, a distinct possibility that the carbon in diamond is recycled biological matter. There are two factors that require to be considered in evaluating the recycled model for the source of carbon in diamond: the first is the antiquity of diamond (1.5–3.5 Ga) in

relation to the fossil record; and the second is that the principle of uniformitarianism may not have been applicable in the Archean, when because of high heat flow, subducted oceanic plates were possibly melted at shallow depths rather than being transformed from basalt → amphibolite → eclogite in the deeper mantle (McCULLOCH, 1993).

The compositions of the stable isotopes of carbon (as a major element), and of nitrogen (as a trace constituent), in diamond have been used in efforts to constrain the source of C and N in the mantle, and by extension to model the formation processes of diamond in the mantle (BOYD *et al.*, 1994; CARNIGNY *et al.*, 1998). Interpretation of the stable isotopic ratios of $^{12}\text{C}/^{13}\text{C}$ (expressed as $\delta^{13}\text{C}$ ‰), and $^{14}\text{N}/^{15}\text{N}$ (expressed as $\delta^{15}\text{N}$ ‰) fall into two camps: one interpretation of the data is that C and N are primordial; and the alternative view of the same data concludes that some C and N is biologically fractionated, and that these elements are recycled into the mantle by subduction. The latter interpretation relies upon two factors: the preference of lighter isotopes by biologically-driven processes; and the small (generally 1–2 ‰) isotopic fractionation effects that are considered possible at high temperatures, specifically at $T = 900\text{--}1600^\circ\text{C}$ in the diamond stability field, or possibly at higher P and T in the lower mantle.

Carbon isotopes

The C isotopic distribution of a sample of 2946 petrogenetically *unclassified* diamonds (Fig. 5a), shows a prominent $\delta^{13}\text{C}$ peak at -4 to -7 ‰, but with a range from 0 ‰ to -35 ‰ (VAN HEERDEN *et al.*, 1997). Similar peaks at $\delta^{13}\text{C} = -5$ to -8 ‰ are also displayed (Fig. 5b) in a separate group of 1592 petrogenetically classified diamonds of which 543 are P-type and 1049 are E-type (VAN HEERDEN *et al.*, 1997). It is particularly noteworthy that the distribution patterns of $\delta^{13}\text{C}$ values for E-type diamonds are very similar (i.e. diminishing to more negative, lighter isotopic compositions), to the genetically unclassified diamond isotopic histogram shown in Fig. 5a; both groups have comparable values to -35 ‰, and with some diamonds that are marginally positive. This skewness has been modelled by DEINES (1980) for a variety of reactions and gas compositions, with the conclusion that the frequency distribution profile is most reasonably ascribed to redox-dependency. Subduction of oceanic crust and organically mediated, recycled C is favored by KIRKLEY *et al.* (1991), McCANDLESS and GURNEY (1997), and is considered a possibility by VAN HEERDEN *et al.* (1997), among others, to account for the ~5% of E-type diamonds that are isotopically light (<15 ‰).

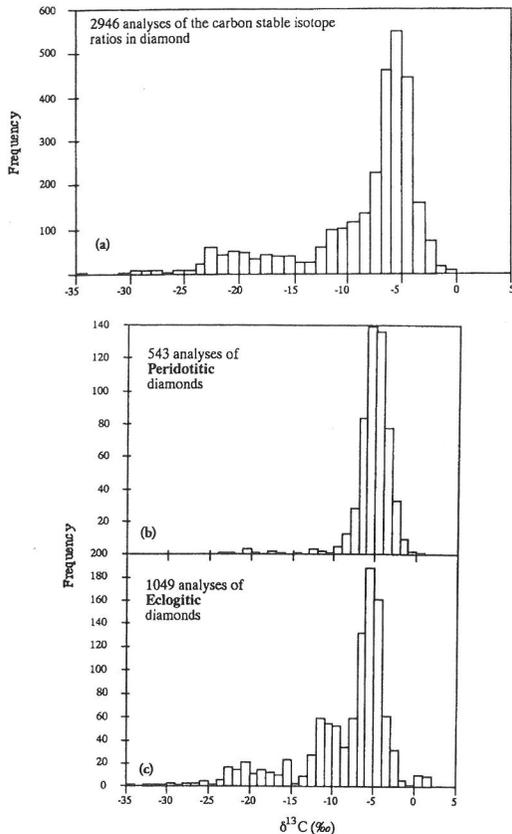


FIG. 5. (a) Carbon isotopic data for a batch of 2,946 diamonds, classified where possible into peridotitic (b), and eclogitic (c), genetic groups. It is not known whether sulfides, which may have a different origin from P- and E-type diamonds, were used in distinguishing the suites. Note that diamonds in the eclogite class have light isotopic values, but note also that the number of diamonds of eclogite affinity that have been measured is a factor of two larger than diamonds in the peridotitic suite. This bias, along with the use of sulfides may significantly affect the true eclogite isotopic distribution. Modified from VAN HEERDEN *et al.* (1997).

There are several problems in the bio-subduction scenario, not the least of which is that biological C was limited in supply, and restricted to prokaryotic bacteria and archaea lineages in the Archean and to primitive eukaryotic cells in the Neoproterozoic (SCHOLF, 1983). Therefore, unless E-type (and also some P-type) diamonds are shown to be younger than the Ediacaran organic bloom at 540–560 Ma in the Cambrian, any appeal to biological C must necessarily be moderated. Moreover, the ratio of carbonate C to organic C (but not always demonstrated to be of biological origin, POPP *et al.*, 1997), was $\sim 80:20$ in the Precambrian (SCHIDLowski, 1988). The average $\delta^{13}\text{C}$ of C_{carb} is +2 ‰, and the average for C_{org} is

–27 ‰, which by simple mixing yields a value of $\delta^{13}\text{C} = -3.8$ ‰, a value that is very different from some E-type diamonds of –10 ‰ to –35 ‰. Present day, but taxonomically primitive cyanobacteria (modern and ancient stromatolites), and methanogenic bacteria yield gas compositions that have $\delta^{13}\text{C}$ between –40 and –60 ‰ (e.g., KVENVOLDEN, 1993; PRINZHOFER and PERNATON, 1997), and this range, either as an isolated bacterial entity or by mixing with C_{carb} (+2 ‰) adds nothing to an explanation for the lighter C isotopic region for E-type diamonds in Fig. 5c. This conclusion is supported by the C isotopic compositions of ubiquitous carbonate in kimberlites, and carbonatites. Because kimberlite-clan volcanics are substantially younger (see a later section) than diamonds (50 Ma to 1 Ga vs 1 to 3 Ga), the chances of identifying marine carbonate in the mantle, possibly subducted since the Archean, is greatly enhanced by C_{kimb} . The carbonates in kimberlites and carbonatites, however, with few exceptions, are resolutely in accord with the mantle $\delta^{13}\text{C}$ range of –5 to –7 ‰ (KIRKLEY *et al.*, 1989; HORTSMANN and VERWOED, 1997, and refs. therein). The most compelling evidence that the carbon in diamond is primordial is derived from the C isotopes of carbon and carbon-bearing phases in stony and iron meteorites, that show a well defined $\delta^{13}\text{C}$ mantle peak at –5 to –7 ‰, other lesser peaks at –18, –22, and –26 ‰, and with a smaller number of lighter values decreasing to –31 ‰ (DEINES, 1989). In addition, composite analyses of *presolar* diamonds in primitive carbonaceous chondrites, have a range of $\delta^{13}\text{C}$ between –32 and –38 ‰ (ANDERS and ZINNER, 1993). Fractionation of this isotopically light C was clearly abiogenic, and it is, therefore, unnecessary to appeal to recycled C as a source for the formation of diamond in the mantle.

Nitrogen isotopes

The interpretation of N isotopes in diamond (JAVOY *et al.*, 1984; BOYD and PILLINGER, 1994; CARTIGNEY *et al.*, 1998), is that N is either primordial or is processed and is derived by subduction. There are, however, considerable uncertainties in defining source regions, and these are due in part to the unknowns of primary heterogeneities in the mantle, and to the possible isotopic fractionation of N and C at high pressures (DEINES *et al.*, 1991). Other interesting features that may have significant isotopic effects are the bulk separation of C and N in marine sediments: the former combines with hydrogen or oxygen, the latter is fixed in clays, and subsequently in feldspar and mica as ammonia; and the expectation in a subduction model is that graphite and ammonia

are recombined to ultimately crystallize N-bearing diamond (BOYD and PILLINGER, 1994). The mantle value of $\delta^{15}\text{N}$ is generally taken to be -5‰ , organic nitrogen in modern marine sediments is 2 to 12 ‰, and ammoniacal nitrogen in subduction zone sediments is 0 to 7 ‰ (BOYD and PILLINGER, 1994). Diamonds have a range from -10 to $+20\text{‰}$, and there is an interesting separation in C-N space in which mantle $\delta^{13}\text{C}$ (-5‰) diamonds are generally low in $\delta^{15}\text{N}$, whereas much lighter C (-10 to -20‰) correlates with heavier N (BOYD and PILLINGER, 1994; CARNIGNY *et al.*, 1998). This relation could argue for two populations of C in diamond, one mantle-derived, the other from recycling. There are, however, significant and poorly understood differences in the isotopic behavior of C and N in single crystals of diamond: C is typically isotopically homogenous whereas N may show extreme variations from core to rim, and with isotopic differences between octahedral and cube faces that may differ by $\sim 40\text{‰}$ $\delta^{15}\text{N}$. In addition, $\delta^{15}\text{N}$ increases with decreasing N abundance (MILLEDGE *et al.*, 1989; BOYD and PILLINGER, 1994). These patterns are, furthermore, compounded rather than resolved by the isotopic distribution of N in meteorites. For example, C1, C2, and ordinary chondrites are enriched in $\delta^{15}\text{N}$ (0 to 170 ‰), relative to C3 and enstatite chondrites (-10 to -40‰) which are highly depleted, indicating there may be significant heterogeneities in primordial N in the Earth (JAVOY *et al.*, 1986).

Sulfur isotopes

Sulfur isotopes ($^{32}\text{S}/^{34}\text{S}$ expressed as $\delta^{34}\text{S}$ ‰) for sulfide inclusions in diamond (CHAUSSIDON *et al.*, 1987; ELDRIGE *et al.*, 1991; RUDNICK *et al.*, 1993; DEINES and HARRIS, 1995), are also interpreted as having either a primordial or a subduction origin. In the recycled interpretation, the source of sulfur is from oceanic basalt, from sulfides in marine hydrothermal vent systems, from sulfur in sediments, or from sulphate reduction of sea water (OHMOTO, 1986; TAYLOR, 1987). The range in isotopic compositions for sulfur in these sources is extreme and varies from very light $\delta^{34}\text{S}$ values (-5 to -20‰) in biologically mediated S in shales, to MORB (-0.1‰) and OIB (-0.5‰) glasses that are close to the meteoritic value of 0‰ , to hydrothermal vent systems (1 to 10 ‰), and to isotopically heavy ($+21\text{‰}$) sea water sulfate. This spectrum represents a range in redox conditions, and redox also affects magmatic systems where loss of H_2S leads to $\delta^{34}\text{S}$ -enrichment, and degassing of SO_4 results in $\delta^{34}\text{S}$ -depletion (KYSER, 1986); and oxidation of basaltic sulfide results in depletion of ^{34}S in the residue, and enrichment in the

resulting sulfate (ALT *et al.*, 1989). Sea water altered oceanic crust may increase $\delta^{34}\text{S}$ by 3 to 5 ‰, but this increase is typically off-set by $\delta^{34}\text{S}$ depletions, so that unless there has been a significant influx of highly fractionated sulfur, altered ocean floor basalts differ very little in $\delta^{34}\text{S}$ from MORB (ALT *et al.*, 1993). From the relatively few S isotopic studies of mantle-derived samples, the $\delta^{34}\text{S}$ range for the majority of kimberlites, xenoliths, and sulfide inclusions in diamond is -5 to $+5\text{‰}$, with a peak that is close to 0‰ (CHAUSSIDON *et al.*, 1989), and a mantle origin. It should be noted that there is isotopic fractionation during cooling and unmixing of monosulfide solid solutions (TAYLOR, 1987), and instrumental fractionation where proton beams are used in analyses (CHAUSSIDON *et al.*, 1987). It is also of interest that there have been dramatic excursions of $\delta^{34}\text{S}$ values for sulfides (-10 to $+10\text{‰}$) and sulfates ($+10$ to $+30\text{‰}$) in oceanic environments over the past 500 Ma (EASTOE and GUSTIN, 1996), and extending back to 1.6 Ga (CANFIELD and TESKE, 1996). Given the ages of diamond (1.5–3.5 Ga) the realm of uncertainty is considerable for similar or larger excursions in the Paleoproterozoic and Archean.

With the variety of fractionation mechanisms that exist for S isotopes, it comes as a surprise that ocean floor hydrothermal vent systems continue to be invoked as a source of S in diamond inclusions (MCCANDLESS and GURNEY, 1977). Black and white ocean floor smokers are charged with Cu, Pb and Zn sulphides, and Ba, Ca, and Pb sulphates (*e.g.*, RONA, 1988 and refs. in this vol.), but neither base metal sulfides nor sulfates have been reported as mineral inclusions in diamond. Sulfides are intensely susceptible to oxyhydration reactions during sea floor alteration with the transformation of pyrite and pyrrhotite to sulfates and goethite. Although locally anoxic conditions may exist in vent systems and in shales, the regional oceanic environment is oxic, and would become more so as slabs are subducted and temperatures rise; and because there is a thermal gradient and differential degassing, pristine stable isotopic signatures of the protolith are unlikely to be preserved. For advocates of biologically mediated isotopic fractionation of sulfides in marine sediments, similar reactions to those in basalt occur, and because grainsizes are small, and mineral surface areas are large, reaction kinetics are fast and sulfide survival or isotopic preservation is severely diminished. Moreover, species such as CO_2 (from amorphous carbon, C-H complexes, or graphite), and SO_2 (from sulfides and sulfates), would expectedly form and should escape *upward*, along with other volatiles, specifically pore water, from *downgoing* slabs as is the case for arc volcanism. But if these sulfides did survive

subduction, one would assume that the metasedimentary host would also have survived. There is, however, no evidence for diamond-bearing sedimentary protoliths in the mantle that is sampled by KCRs.

In summary, the weight of evidence is that the C in diamond is primordial, whereas the isotopes of N and S offer non-unique solutions to the sources of these two elements in diamond and sulfides, respectively.

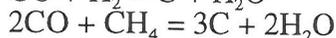
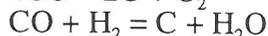
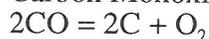
MODELS FOR THE FORMATION OF DIAMOND

Although it is argued here that all, or a vast majority of C in cratonic diamond is primordial, an issue of considerable interest and uncertainty is the physical state of carbon in the mantle: as a stable or metastable gas species in the system C-O-H-N-S; as C dissolved in a fluid; as C in a melt; discrete amorphous C; presolar and solar nebula C-complexes, cryptocrystalline graphite, or nanometer diamond. There are two contrasting views in the gas model: in the first, diamond condensation is considered to occur from oxidized C species (Table 2), on interaction with reduced lithosphere (HAGGERTY, 1986); and in the second, reduced gas species (Table 2) precipitate diamond by redox melting of oxidized subcontinental lithosphere (TAYLOR and GREEN, 1987). Both models are possible and this may be the distinction between P- and E-type diamonds. Alternatively, diamond may also possibly be precipitated from a mixture of CH_4 + CO_2 by rapidly decreasing pressure and tempera-

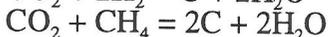
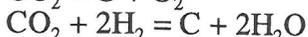
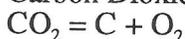
ture (DEINES, 1980). In the fluid model, fluids are in a supercritical state with H and $\text{C} \gg \text{O}$, and with significant S (HAGGERTY, 1986; 1996; DEINES, 1996). This model is supported by the fluid-rich coats of rapidly grown, fibrous cube diamond on single crystals of octahedral diamond substrates (NAVON *et al.*, 1988). In the oxidation of CH_4 , or possibly CO, water is produced in the reaction (Table 2), and water may be responsible for the local dissolution of minerals that are ultimately trapped as inclusions in diamond (EGGLER, 1987). In the magmatic model, diamond is precipitated from C-rich, or C-saturated high P-T melts. Carbon is a silicate incompatible element and would fractionate strongly into low degree partial melts, so that some E-type diamonds in low MgO eclogites of basaltic composition, and W- and S-type diamond may have formed in this way. Oscillatory zoning, displayed by cathodoluminescence and X-ray section tomography (*e.g.*, LANG *et al.*, 1992), in many single crystals of diamond point to slow growth (fast crystal growth is fibrous, SUNAGAWA, 1990), in a changing physiochemical environment. Complex zoning in diamond perhaps more strongly favors the gas and fluid models but equally does not eliminate magmatic nucleation and growth. P-type diamond inclusions have a close compositional affinity to highly depleted subcontinental lithosphere, but C would have been removed during komatiite extraction and early crustal formation in the Archean. Therefore, P-type diamond, must be paragenetically later than the garnet harzburgitic rocks that host these diamonds. The secondary introduction of C was more likely from supercritical gases and fluids, and not from silicate liquids or silicate melts because these would have led to extensive refertilization and metasomatism of the style that is prevalent in the lithosphere (Figs. 2 and 3). Cryptic (rather than modal) metasomatism, in the form of isotopic enrichment, is reported in garnet inclusions from diamond (RICHARDSON *et al.*, 1984). Metasomatic silicate melts were undoubtedly introduced at a later time, and were largely responsible for the mechanical degradation of lithosphere, the release of diamonds over periods of time to passing KCR magmas, and to the precipitation and growth of melt-rich coated diamonds. Microdiamonds (<1 mm in size), are unetched, unzoned, are typically high temperature octahedra, and are widespread in KCRs on cratons (Fig. 4). These diamonds were previously modelled as condensates of young age related to KCR volcanism (HAGGERTY, 1986). The model is supported experimentally by the growth of microdiamond in kimberlite (ARIMA *et al.*, 1993), and it is supported by the demonstration that microdiamonds are Type Ib, consistent with quenching or brief residence in the mantle (TAYLOR *et al.*,

Table 2. Diamond Recipes

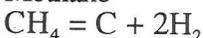
Carbon Monoxide



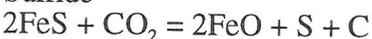
Carbon Dioxide



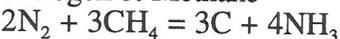
Methane



Sulfide



Nitrogen & Methane



1996). Transition zone diamonds may have formed by similar mechanisms to those modelled for E- and S-type diamonds (melt and fluid related). The upper portion of the transition zone may be an important repository for diamond, given that diamond is shown experimentally to float in mafic melts at 16–20 GPa (SUZUKI *et al.*, 1995). Lower mantle, diamond-inclusion assemblages are either depleted (Opx + MW), or moderately enriched (CaSiO₃ + FP), and by analogy with P- and E-type diamonds, all of the above models may be applicable. Plumes from the core-mantle boundary are considered to be the driving force for depletion and enrichment of the mantle, the transfer of carbon for the precipitation of diamond, and the thermal energy required for KCR volcanism as outlined in the following section.

KIMBERLITE-CLAN MAGMATISM

The increasing recognition of xenoliths and mineral inclusions in diamonds from kimberlites worldwide having an origin close to, or in the transition zone (TZ = 410–660 km) requires that magmas transporting these samples must originate either in the TZ or in the lower mantle (660–2900 km). As noted above, the characteristic mineral inclusions in diamond from the TZ are majoritic garnet and Na pyroxene - enstatite solid solutions, and majorite that has exsolved to pyrope garnet + pyroxene in eclogites, peridotites, and related rocks. Mineral inclusions in diamond that support a lower mantle origin are listed above, but in addition to these are widespread, and as yet unexplained inclusions of monosulfide solid solutions, reduced metallic iron, and extremely reduced SiC and FeC (HAGGERTY, 1994).

There has been considerable debate and little consensus in the classification of kimberlites, lamproites, lamprophyres, and closely related kalsilitic, melilitic, and leucitic rocks. In their Subcommission recommendations to the IUGS, after six years of deliberation, WOOLLEY *et al.* (1996), note: "This contribution brings together the findings of the working groups and Subcommission on these topics, and is presented as the best *compromise* currently available. The recommendations are presented for discussion and should *not* be regarded as the definitive statement on the topic" (page 176, column 1); and . . ." It must be stressed that the hierarchical system presented here is *not* definitive and has *minimal* genetic content. Any classification of a rock as a lamprophyre, kimberlite, or lamproite using this system should be considered *provisional* until further investigations have been undertaken . . ." (page 176, column 2).

The major difficulty in classification, and in the

interpretation of experimental data (FOLEY, 1990), is that these rocks are hybrid. Diamonds are present in kimberlites and olivine lamproites and neither of these rocks are primary melts: both have primitive (high Mg), evolved (high Fe, Al), and highly enriched mineral (LILE and HFSE) constituents, and both are high in volatiles. There is a continuum in Nd and Sr isotopes (DAWSON, 1987), from depleted to enriched mantle, that includes ocean island basalts, mantle metasomites, kimberlites, and lamproites. While acknowledging that there are petrochemical differences in these rocks, there are also similarities, and in view of the uncertainties expressed by the IUGS Subcommission, the term kimberlite-clan rock (KCR) as adopted here, neither affects the theme of the contribution, nor alters the conclusions.

Kimberlite-clan rocks are complex, polymict (macrocrysts, xenocrysts, microcrysts) assemblages that have wide variations in grainsize and texture of the coarse grained components and the crystalline groundmasses. The bulk composition (20–30 wt% MgO), and major mineralogy of KCRs that host diamond (60–90 modal % olivine in two compositional populations, one anhedral Fo_{90–94}, the other euhedral Fo_{84–86}), requires large degrees of partial melting to produce refractory olivine, typical of komatiites, and lower degrees of partial melting, or melting at lower P and T (TAKAHASHI and SCARF, 1985) of fertile mantle to form more Fe-rich melts. Assimilation of early trapped, high pressure melts (specifically eclogite), and previously depleted metasomatized mantle (specifically harzburgite and dunite), however, are also required to account for LILE (K, Na, Ba, Rb, Sr, REE) and HFSE (Ti, Zr, Nb) enrichment in KCRs. These rocks also have 10–15 wt% CO₂ + H₂O; kimberlites are typically carbonated, whereas lamproites are more hydrous. Metasomatized rocks with unusual chemistries and mineralogies (Tiphlogopite, K-richterite, and alkali titanates), are present as xenoliths and partially digested fragments in kimberlites, and the same mineral assemblage in these metasomites appears in the groundmasses of lamproites. These metasomatic constituents, satisfy the levels of enrichment required in hybrid KCRs and point to long term fluid-melt interactions that were globally pervasive and most intense at depths of 75–100 km within the keel and at the base of sub-cratonic lithospheres (Figs. 2 and 3). These metasomes are considered to be an essential source of constituents for kimberlites, and are even more so for lamproites (HAGGERTY, 1986; 1989; DAWSON, 1987), that have higher concentrations of LILE and HFSE (MITCHELL and BERGMAN, 1991). Varying degrees of assimilation of common metasomatic sources into mafic melts is considered here to be the only genetic

distinction between kimberlites and lamproites that evolve in cratonic settings (Fig. 4).

All diamond-bearing kimberlites are in provinces (50–150 km in diam.) or fields (5–50 km in diam.) of intrusive clusters (<5–>100) in ancient (>2 Ga) cratons. A focal or centralized heat source is required to produce these large numbers of intrusions in single provinces and a high thermal flux with sustained energy is necessary because intrusions must penetrate ~200 km (diamond stability) of cool subcratonic lithosphere, and an additional ~50–60 km of even cooler and rheologically robust continental crust (Fig. 4). The number of intrusions that ultimately reach the surface is possibly very small because of *thermal trauma* of low heat capacity melts in contact with cool lithosphere (SPERA, 1984). All KCR intrusives are multiple injections, that attest to stoping in restricted diatremes under a sustained thermal source. For successful high level intrusions, volcanism is violently explosive, a most unusual feature for an ultramafic magma but consistent with the inference that the crystal mushes are gas charged. Neither the walls of conduits, nor the margins of xenoliths are thermally metamorphosed, and crustally-derived limestone, coal, salt, and even wood, are preserved.

Although models have been presented for deep rifts as sources of alkali volcanism (*e.g.*, LE BAS, 1971; PHIPPS, 1988; MCHONE, 1996), the geological settings for diamond-bearing kimberlite-clan rocks *at the time of intrusion* are neither arc (subduction volcanism) nor rift (extension and decompression melting) related, and are in non-collisional terranes. Hence, the heat source is constrained to one of three models that place the driving force for diamond magmatism at three depths: the first model is thermal accumulation and incubation beneath supercontinents with implied depths of KCR genesis at 200–250 km (ANDERSON, 1994); the second is the diapiric model originating in the TZ as a consequence of subduction, slab accumulation, and density separation (KESSON and RINGWOOD, 1989; RINGWOOD *et al.*, 1992); and the third is by hotspots (CROUGH *et al.*, 1980), plumes (HAGGERTY, 1986; WYLLIE, 1989), and superplumes that provide a continuous sample of the lower and upper mantles in KCRs that are synchronously intruded on a global scale (HAGGERTY, 1994). Incubation in model 1 is likely to destroy diamonds in the lithospheric keel and is unlikely to yield deep mantle melting, melt assimilation at a variety of mantle depths, or the transport of ultradeep xenoliths (including diamond) from the TZ and the lower mantle. In model 2, oceanic KCRs should form but are not found, and a convincing case has yet to be made for either KCR genesis in the TZ, or a mechanism to forcefully inject KCRs by any process related to

localized subduction. There is simply a lack of sustained energy in the TZ, and even if 'back-filling' is invoked from density separation and the catastrophic avalanching of slabs through the 660 km discontinuity (TACKLEY *et al.*, 1993), the event is localized and not global. In model 3, non-continental analogs of KCR intrusives are ocean island basalts (LE ROEX, 1986; DAWSON, 1987; KESSON and RINGWOOD, 1989), that lack the subcontinental contribution of metasomatism; and TZ and lower mantle diamonds are absent because of high thermal gradients and high states of oxidation (HAGGERTY, 1990). The weight of evidence currently available, therefore, is decidedly in favor of mantle plumes from the D'' core-mantle boundary layer at 2900 km depth as summarized in Fig. 6.

The D'' layer is either a residue (matte) from the gangue (C-O-H-N-S, Si and K, which are all possible low density dilutants of the core, POIRIER, 1994) of outer core cooling and inner core crystallization, or is a zone of reaction between the silicate lower mantle and the metallic outer core (Fig. 6). Note that the gangue constituents are significant components in diamond, diamond inclusions, and in KCRs. Ultralow seismic velocities are recorded in the D'' layer (WEN and HELMBURGER, 1998), which is consistent with the presence of liquid in this horizon (REVENAUGH and MEYER, 1997). This interpretation is supported by a correlation between ultralow seismic velocities in D'' and hot spots in the crust (WILLIAMS *et al.*, 1998), and by the experimental demonstration that partial melting of silicate mantle in the vicinity of D'' is possible under present day geothermal conditions (ZERR *et al.*, 1998). Plumes may arise from the D'' at instabilities created during growth of the layer, or on disruption, having reached a critical threshold thickness of ~200 km (LARSON and OLSON, 1991). In the present model, plumes are considered to be responsible for mantle melting to produce protokimberlite-clan rocks approaching komatiites in composition, and plumes are a possible source for the chemical agents of metasomatism, and the reduced carbon in diamonds and mantle carbides. The carbon in diamond and the C in kimberlites, as concluded above is primordial, and pumping pristine C from the core that is unfettered by recycled contaminants is intuitively more appealing in a global framework, and over geological timescales, than having the source of carbon be either fortuitously isolated or specifically located in keels and along conduit paths. Plumes transgress the entire vertical extent (2900 km) of the mantle (GRIFFITHS and CAMPBELL, 1990). With a stem and mushroom-like head there are large thermal gradients, and the sequestering of incompatible and compatible elements is greatly enhanced by

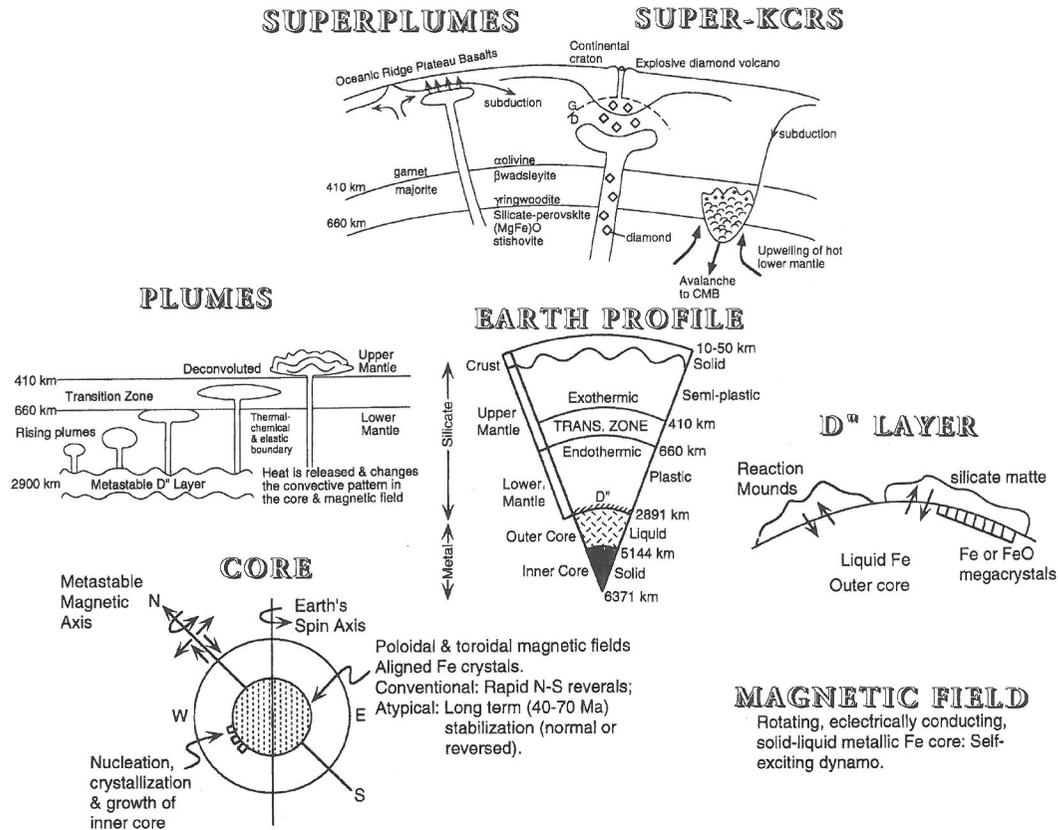


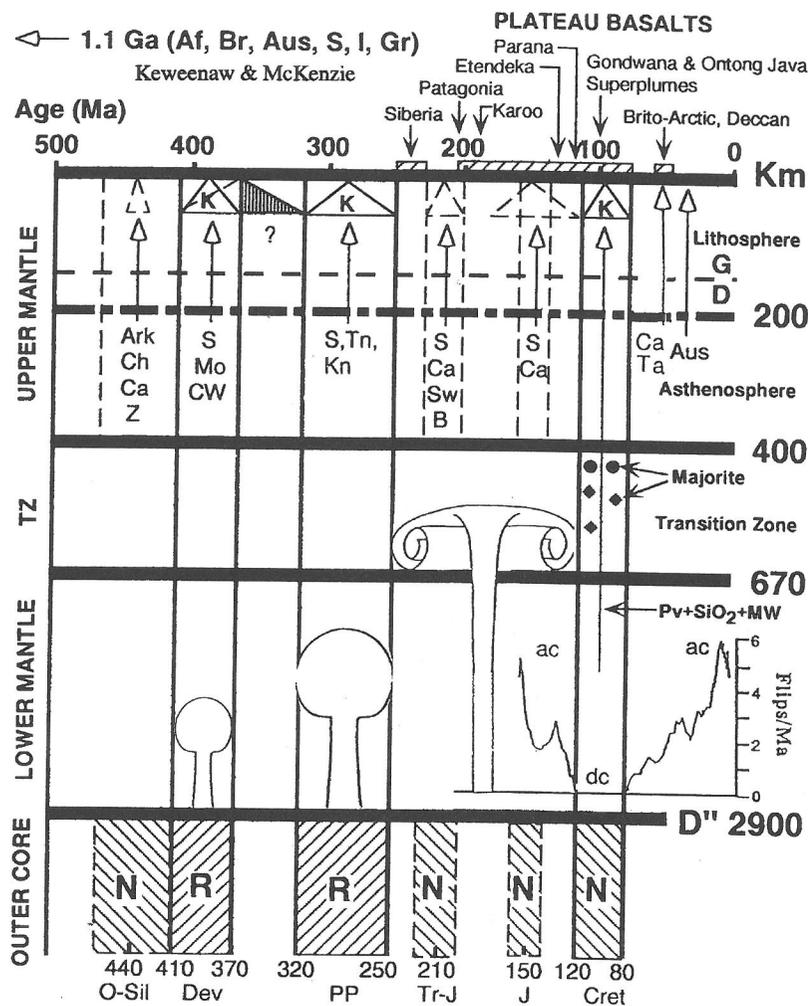
FIG. 6. Properties of the core, the geomagnetic field, and the D'' layer in the context of plume development, and plume modification in sampling the lower and upper mantles and in generating diamondiferous KCRs in subcontinental, subcratonic lithospheres.

this thermal structure, and by the relatively slow upward movement (5–30 cms/yr COURTILOT and BESSE, 1987; LARSON and OLSON, 1991) of plumes through the mantle; and “heads its basalt, tails its komatiite” (CAMPBELL *et al.*, 1989), could account for the two populations of olivine in KCR magmas. The lateral flattening of plume heads at the 660 km discontinuity may accentuate the siphoning off of water held in the TZ by wadsleyite and ringwoodite; and this water will expectedly lower liquidus and induce melting of the asthenosphere. The budding or branching of some plumes is also expected at the 410 km discontinuity (Fig. 6). These miniplumes are less energetic, are prone to impedance in the lithosphere, and are prime candidates for the subsequent deposition of volatile-rich metasomatic melts.

There are two obvious tests that examine the probability of a relation between plumes and KCR intrusives; firstly, if plumes are core-related, this internal control should have a global rather than an isolated expression in the distribution of KCR volcanism; and

secondly, if the core-mantle boundary is invoked, there ought to be some geophysical expression of rising plumes and subsequent eruptions. Both tests are satisfied insofar as KCR volcanism is globally synchronous, and this synchronicity correlates with superchron behavior of the geomagnetic field (HAGGERTY, 1994). The plumes are superplumes (LARSON, 1991) and the products are superkimberlites and related clan intrusives. The major eruptive events (Fig. 7) are at: ~1 Ga (Africa, Brazil, Australia, Siberia, India, Greenland); ~450–500 Ma (Archangel on the White Sea, China, Canada, South Africa, Zimbabwe); 370 and 410 Ma (Siberia, USA); 250–320 Ma (Siberia, USA); ~200 Ma (Botswana, Canada, Swaziland, Tanzania); 80–120 Ma (southern, central, and west Africa, Brazil, Canada, India, Siberia, USA.); ~50 Ma (Canada, Tanzania); with minor fields such as Ellendale at 22 Ma in NW Australia. Geomagnetic-time scale data are well documented over the past 500 Ma (*e.g.*, OGG, 1995; COWLEY and BASSETT, 1989) during which typical normal and

SUPER-KCRS, SUPERCHRONS, SUPER-LIPS



Superchrons

Af-Africa, Ark-Archangelsk, Aus-Australia, B-Botswana, Br-Brazil, Ca-Canada, Ch-China, CW-Colorado-Wyoming, Gr-Greenland, I-India, K-Kentucky, Mo-Missouri, S-Siberia, Sw-Swaziland, Tn-Tennessee

FIG. 7. An orthogonal cross-section of the Earth showing the principal and lesser periods of geomagnetic superchrons (N and R), the timing of globally synchronous KCR diamond intrusions, and globally related large-igneous-provinces of plateau basalt (LIPS). Flips/Ma refers to geomagnetic field reversal frequency shown in greater detail in Fig. 8. Modified from HAGGERTY (1994).

reverse magnetic directional cycles occurred, but atypical superchrons (relatively low reversal rate or no reversals) also existed (Fig. 8). Theory holds that on disruption of the D'' mat, heat is released to the mantle and creates more vigorous convection in the outer core (LARSON and OLSEN, 1991). This results in instabilities and lower intensities of the geomagnetic

field, with constant directions rather than high frequencies in reversal rates. Five of the seven globally synchronous KCR events correlate with superchrons (Fig. 8); the ~450–500 Ma event, and the ~50 Ma event can be accounted for by late release plumes, slower moving plumes, or transiently impounded plumes. There are expected time lags between plume

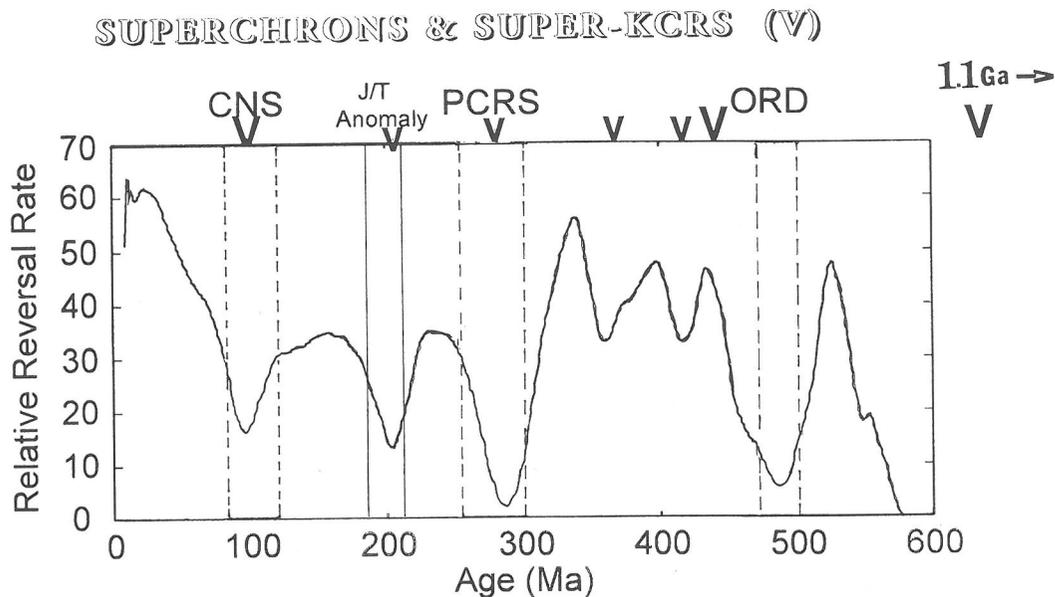


FIG. 8. Relative reversal rate of the geomagnetic field for the Phanerozoic using long (20 Ma) and short (3 Ma) wavelength mean filters (JOHNSON *et al.*, 1995). Four major superchrons are present: the Cretaceous Normal Superchron (CNS); the Jurassic Triassic anomaly (J/T); the Permian-Carboniferous Reversal Superchron (PCRS); and the Ordovician (ORD) Reversed Superchron; other minorchrons are also present. Globally synchronous super-KCR (V) events, taken from Fig. 7, show a close correspondence to periods of low reversal frequency. This relation is considered to be linked to superplumes originating at the D'' core-mantle boundary layer (see Fig. 6). The KCR diamondiferous intrusive event at 1.1 Ga is predicted to be a magnetic superchron.

release and clan volcanism (depth/velocity ~ 25 Ma), and on closer inspection (Fig. 8) we find that some events correlate with the shoulder of gradual decreases in the geomagnetic field reversal rate, whereas other events coincide with superchron maxima. This implies that all plumes are not exactly equal, and nor should thermal equality be expected. The geomagnetic field switches on and off from normal to reverse on short (10–100 Ka) time scales, but the approach to superchron dormancy, or the emergence from a superchron event, takes place by a progressive change in reversal frequencies over ~ 25 Ma (JOHNSON *et al.*, 1995); this alleviates the perceived lag effect between events in the core and surface eruptions. The Tertiary, Cretaceous, Jurassic, and Permo-Triassic KCR events are preceded by, or are directly related to, large igneous provinces (LIPS) of plateau basalt; the timing of LIP events is shown in Fig. 7. LIPS (COFFIN and ELDHOLM, 1994) are voluminous ($1\text{--}40$ Mkm³), eruptions that took place over short periods of time (5–10 Ma), and in all cases the basalts are genetically related to the activity of plumes and the possible mantle melting of up to 30% eclogite (CORDERY *et al.*, 1997).

The Mid-Cretaceous, superkimberlite-clan episode between 80 and 120 Ma is the most widespread and best documented of the KCR diamond intrusive

events that have been recognized to date. This global event is related to the supercontinent breakup of Pangea: rifting was initiated at ~ 200 Ma, and this was followed by the onset of drifting and the intrusions of LIPS along major fracture zones (STOREY, 1995); KCRs followed between 80–120 Ma. It is relevant to note that this plume event produced large volumes of oceanic plateau basalt, and plume activity continued into the Cenozoic with LIPS in the Deccan Traps at ~ 64 Ma, and throughout the North Atlantic between 50 and 60 Ma (including the Skaergaard Layered Intrusion at 55 Ma). The timing of KCR intrusives in Tanzania, Montana and the Slave Province at ~ 53 Ma is considered to be part of this major plume and LIP episode. The next most important event, both in the context of global distribution and diamond economics, but unfortunately not amenable to superchron evaluation (because the data are limited, and the magnetic record becomes weaker and more complex with age), is the KCR diamond event at ~ 1 Ga (Figs. 7–8).

An additional test of the correlation between KCRs and superplumes for the Proterozoic is, however, possible and is presented in Fig. 9 on a base map of the supercontinent of Rodinia (UNRUG, 1996). Because of the rather small number of dated KCRs

DIAMONDS IN THE RODINIA SUPERCONTINENT ASSEMBLED AT ~ 1000 Ma

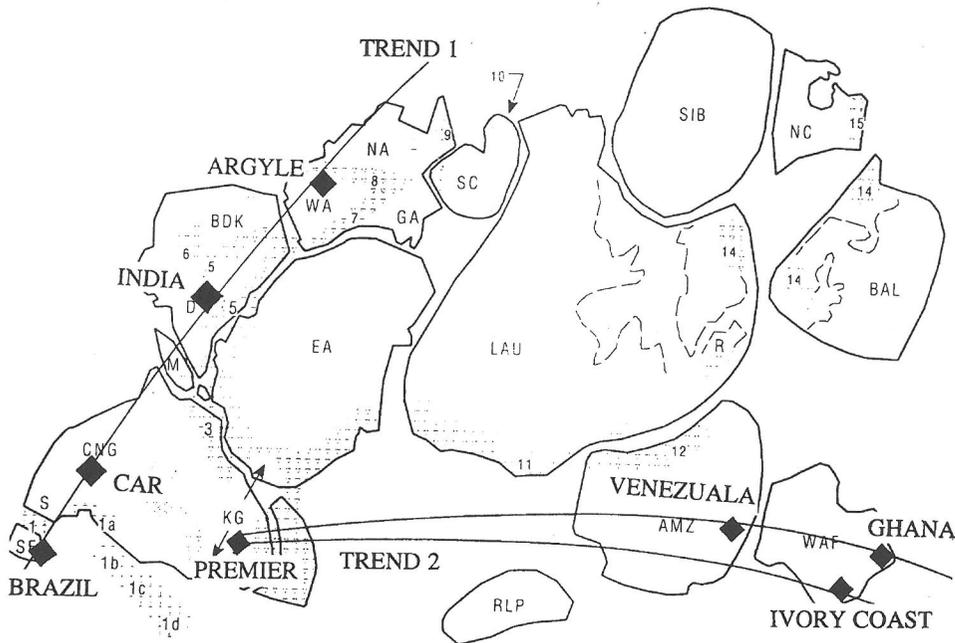


FIG. 9. The distribution of major diamond deposits throughout cratons in the supercontinent of Rodinia at ~1 Ga. The two arcuate trends are interpreted to result from plume tracks, or from two areally extensive superplumes. The base map is from UNRUG (1996).

(Australia, South Africa, India, Ivory Coast and Venezuela, JANSE and SHEAHAN, 1995), Proterozoic alluvial diamond deposits in Brazil, Central African Republic, and Ghana have also been included in this test. The result is that the diamond locations lie on two major arcs: one that is fairly tight and has a NE trend, and the other, less well defined, that lies on an E-W trend in assembled Rodinia at ~1 Ga (Fig. 9). The non-random distribution of diamonds in the NE trend is permissive evidence for migrating superplumes across a supercontinent, consonant with the Pangea episode in the Mesozoic. The interpretation by WHITE and MCKENZIE (1989), for Gondwanaland in particular and other areas in general, is that continental fragmentation in the Mesozoic was related to plumes with heads that were 1000–2000 km across. In the absence of high precision ages for Proterozoic diamond deposits, an alternative to migrating plumes is that a single plume produced the NE trend, but also included Premier in the Kalahari-Grunahogna (Kapaavaal) craton to the east of the NE trend (Fig. 9). This is a reasonable assumption because Premier is 1.1 Ga, Muligiripalle in India is 1.15 Ga, and Argyle in NW Australia is 1.2 Ga; and this plume, or a

temporally-related plume, produced the Keweenaw and Great McKenzie Dike Swarm, a LIP of considerable magnitude, in Laurentia at 1.1 Ga (HUTCHINSON *et al.*, 1990). In this interpretation, the intrusives in the Amazonia craton (Bolivar in Venezuela is 1.7 Ga), are more closely related to the 2 Ga Birrimian alluvial diamonds in Ghana, and this could possibly represent a second superplume. An interesting diamond prospecting consequence of this test is that Proterozoic KCRs are predicted in Madagascar, East Antarctica, South China, and elsewhere in Amazonia; and from a geodynamic standpoint, the period around 1 Ga is predicted to be a superchron.

CONCLUSIONS

As mantle probes, kimberlite-clan rocks (KCR) are paradoxical: these rocks are ultramafic yet geochemically enriched; volcanically explosive yet low in SiO₂; mantle-derived at high temperatures, yet with cool emplacement into crustal diatremes; volatile-rich yet sufficiently reduced to preserve diamond during transport from the lower mantle, the transition zone, and the subcontinental lithosphere; intrusives

are punctuated in time yet synchronously so through thick subcratonic lithosphere and ancient continental crust; there has been substantial recycling of crust into the mantle yet primordial carbon persists in Archean and Proterozoic diamonds, and in Proterozoic through Cenozoic carbonates in KCR intrusives.

In the absence of substantial evidence for subduction-related processes in the genesis of diamond, or in the origin of rocks transporting diamonds from Earth's interior, the only other, seemingly viable mechanism is the partisan view that diamond intrusions are driven by superplumes during superchrons; these superkimberlite-clan rocks are exclusively subcratonic. With globally distributed diamond intrusives dating back to the Paleoproterozoic, and diamonds having even older (>3 Ga) ages, we may conclude that plumes and mineralization, with possible sampling of the D" core-mantle boundary, has taken place over a substantial part of Earth's history.

Acknowledgments—It is with considerable pleasure that this contribution is dedicated to the recognition of the major in-roads that Joe Boyd has made to our understanding of the petrochemistry of the mantle. Joe suggested to me in 1970 that: "it might be fun to look at the opaque minerals in kimberlites" while I was a Carnegie fellow at the Geophysical Laboratory, and following on the lab's collaborative study of the Apollo lunar samples in which we described two new spinels and armalcolite from Mare Tranquillitatis. On reflection, it was not only fun but a sound research suggestion that has allowed me to see and study an enormous number of diamond deposits around the world, many in the wonderful company of Joe Boyd. Thanks a lot Joe, and thanks to Yingwei Fei and Charlie Prewitt for the invitation to the Boyd Fest. The manuscript was thoroughly reviewed with suggestions for improvement by Jeff Harris and R. H. Anon. The NSF is gratefully acknowledged for research support, most recently under EAR 98-05091.

REFERENCES

- AGEE C. B. (1993) Petrology of the mantle transition zone. *Ann. Rev. Earth Planet. Sci.* **21**, 19–41.
- ANDERS E. and ZINNER E. (1993) Interstellar grains in primitive meteorites: Diamond, silicon carbide, and graphite. *Meteoritics* **28**, 490–514.
- ANDERSON D. (1994) Superplumes or supercontinents? *Geology* **22**, 39–42.
- ARIMA M., NAKAYAMA K., AKAISHI M., YAMAOKA S., and KANDA H. (1993) Crystallization of diamond from a silicate melt of kimberlite composition in high-pressure and high-temperature experiments. *Geology* **21**, 968–970.
- BAER A. J. (1977) Speculations on the evolution of the lithosphere. *Precamb. Res.* **5**, 249–260.
- BIBBY D. M. (1982) Impurities in natural diamond. In: *Chemistry and Physics of Carbon* (ed. P. A. THROWER), Marcel Dekker.
- BICKFORD M. E. (1988) The formation of continental crust. *Geol. Soc. Amer.* **100**, 1375–1391.
- BOYD F. R. (1970) A pyroxene geotherm. *Geochim. Cosmochim. Acta* **37**, 2533–2546.
- BOYD F. R. and DANCHIN R. V. (1980) Lherzolites, eclogites, and megacrysts from some kimberlites of Anglo. *Amer. J. Sci.* **280A**, 528–549.
- BOYD F. R. and FINNERTY A. A. (1980) Conditions of origin natural diamonds of peridotite affinity. *J. Geophys. Res.* **85**, 6911–6918.
- BOYD F. R. and GURNEY J. J. (1986) Diamonds and the African lithosphere. *Science* **232**, 472–477.
- BOYD F. R. and GURNEY J. J. (1982) Low-calcium garnets: keys to craton structure and diamond crystallization. *Carnegie Inst. Wash. Yr. Bk.* **81**, 261–267.
- BOYD F. R., GURNEY J. J., and RICHARDSON S. H. (1985) Evidence for a thick 150–200 km thick Archean lithosphere from diamond inclusion thermobarometry. *Nature* **315**, 387–389.
- BOYD F. R. and NIXON P. H. (1975) Origins of the ultramafic nodules from some kimberlites of northern Lesotho and the Monastery Mine, South Africa. *Phys. Chem. Earth* **9**, 431–454.
- BOYD S. R. and PILLINGER C. T. (1994) A preliminary study of ¹⁵N/¹⁴N in octahedral growth form diamonds. *Chem. Geol.* **116**, 43–59.
- BOYD S. R., PINEAU F., and JAVOY M. (1994) Modelling the growth of natural diamonds. *Chem. Geol.* **116**, 29–42.
- BULANOVA G. P. (1995) The formation of diamond. *J. Geochem. Explor.* **53**, 1–23.
- BURKE K., KIDD W. S. F., and KUSKY T. M. (1986) Archean foreland basin tectonics in the Witwatersrand, South Africa. *Tectonics* **5**, 439–456.
- CAMPBELL I. H. and GRIFFITHS R. W. (1990) Implications of mantle plume structure for the evolution of flood basalts. *Earth Planet. Sci. Lett.* **99**, 79–93.
- CAMPBELL I. H., GRIFFITHS R. W., and HILL R. I. (1989) Melting in an Archean mantle plume: Heads it's basalts, tails it's komatiites. *Nature* **339**, 607–699.
- CARTIGNY P., HARRIS J. W., and JAVOY M. (1998) Eclogitic diamond formation at Jwaneng: No room for a recycled component. *Science* **280**, 1421–1424.
- COFFIN M. F. and ELDHOLM O. (1994) Large igneous provinces: Crustal structure, dimensions and external consequences. *Reviews Geophys.* **32**, 1–36.
- CONDIE K. C. (1986) Origin and early growth rate of continents. *Precamb. Res.* **32**, 261–278.
- COURTILLOT V. and BESSE J. (1987) Magnetic field reversals, polar wander, and core-mantle coupling. *Science* **237**, 1140–1147.
- COWIE J. W. and BASSETT M. G. (1989) Global stratigraphic chart with geochronometric and magnetostratigraphic calibration. *International Union Geol. Sci.*
- DAVIES G. F. (1979) Thickness and thermal history of continental crust and root zones. *Earth Planet. Sci. Lett.* **44**, 231–238.
- DAVIES R., GRIFFIN W. L., PEARSON N. J., ANDREW A., DOYLE B. J., and O'REILLY S. Y. (1998) Diamonds from the deep: Pipe DO-27, Slave Craton, Canada. *7th Int Kimberlite Conf.*, 170–172.
- DAWSON J. B. (1980) *Kimberlites and Their Xenoliths*. Springer-Verlag.
- DAWSON J. B. (1987) The kimberlite clan: Relationship with olivine and leucite lamproites, and inferences for upper mantle metasomatism. In *Alkaline Igneous Rocks*. (eds. J. G. FITTON and B. G. J. UPTON) *Geol. Soc. Spec. Pub.* **30**, 95–101.
- DAWSON J. B., CARSWELL D. A., HALL J., and WEDEPOHL K. H. (1986) *The Nature of the Lower Continental Crust*. Blackwell Scientific.
- DEINES P. (1980) The carbon isotopic composition of dia-

- monds: Relationship to shape, color, occurrence and vapor composition. *Geochem. Cosmochim. Acta* **44**, 943–961.
- DEINES P. (1989) Stable isotope variations in carbonatites. In *Carbonatites: Genesis and Evolution*. (ed. K. BELL), pp. 301–359.
- DEINES P. (1996) The role of mantle fluids in the growth of diamonds. *Proc. 3rd Int. Symp. Advanced Materials*, Tsukuba, Japan 61–64.
- DEINES P., HARRIS J. W., and GURNEY J. J. (1991) The carbon and nitrogen content of lithospheric and asthenospheric diamonds from the Jagersfontein and Koffiefontein kimberlite, South Africa. *Geochem. Cosmochim. Acta* **55**, 2615–2625.
- DE WIT M. J. and HART R. A. (1993) Earth's earliest continental lithosphere, hydrothermal flux and crystal recycling. *Lithos* **30**, 309–335.
- DE WIT M. J. *et al.* (1992) Formation of an Archean crust. *Nature* **357**, 553–562.
- DURRHEIM R. J. and MOONEY W. D. (1991) Archean and Proterozoic crustal evolution: Evidence from crustal seismology. *Geology* **19**, 606–609.
- EGGLER D. H. (1987) Solubility of major and trace elements in mantle metasomatic fluids: Experimental constraints. In *Mantle Metasomatism* (eds. M. A. MENZIES and C. J. HAWKESWORTH), pp. 21–41. Academic Press.
- ELDRIDGE C. S., COMPSTON W., WIKKIAIS I. S., HARRIS J. W., and BRISTOW J. W. (1991) Isotope evidence for the involvement of recycled sediments in diamond formation. *Nature* **353**, 649–653.
- EVANS T. (1992) Aggregation of nitrogen in diamond. In *The Properties of Natural and Synthetic Diamond* (ed. J. E. FIELD), pp. 259–290. Academic Press.
- EVANS T. and QI Z. (1982) The kinetics of aggregation of nitrogen atoms in diamond. *Proc. Roy. Soc. (Lon.) A* **381**, 159–178.
- FIELD J. E. (1979) *The Properties of Diamond*. Academic Press.
- FIELD J. E. (1992) *The Properties of Natural and Synthetic Diamond*. Academic Press.
- FOLEY S. F. (1990) A review and assessment of experiments on kimberlites, lamproites, and lamprophyres as a guide to their origin. *Proc. Indian Acad. Sci. (Earth Planet. Sci.)* **99**, 57–80.
- FOUNTAIN D. M., ARCULUS R., and KAY R. W. (1992) *Continental Lower Crust*. Developments in Tectonics Vol. **23**. Elsevier.
- GAHERTY J. B. and JORDAN T. H. (1995) Lehmann discontinuity at the base of an anisotropic layer beneath continents. *Science* **268**, 1468–1471.
- GRIFFITHS R. W. and CAMPBELL I. H. (1990) Stirring and structure in mantle plumes. *Earth Planet. Sci. Lett.* **99**, 66–78.
- GURNEY J. J. (1989) Review paper: Diamonds. In *Kimberlites and Related Rocks* (ed. J. ROSS) *Geol. Soc. Australia*, Spec. Pub. **14**, 935–965. Blackwell Scientific.
- GURNEY J. J. and BOYD F. R. (1982) Mineral intergrowths with polycrystalline diamond from the Orapa mine, Botswana. *Carnegie Inst. Wash. Yr. Bk.* **81**, 267–273.
- HAGGERTY S. E. (1986) Diamond genesis in a multiply-constrained model. *Nature* **320**, 34–38.
- HAGGERTY S. E. (1989) Mantle metasomes and the kinship between carbonatites and kimberlites. In *Carbonatites: Genesis and Evolution*. (ed. K. BELL), pp. 546–560. Unwin Hyman.
- HAGGERTY S. E. (1990) Redox state of the continental lithosphere. In *Continental Mantle*. (ed. M. A. MENZIES), pp. 87–109. Clarendon Press.
- HAGGERTY S. E. (1991) Oxide mineralogy of the upper mantle. In *Oxide Minerals: Petrologic and Magnetic Significance*. (ed. D. H. LINDSLEY), pp. 355–416. Mineralogical Society America.
- HAGGERTY S. E. (1994) Superkimberlites: A geodynamic diamond window to the Earth's core. *Earth Planet. Sci. Lett.* **122**, 57–69.
- HAGGERTY S. E. (1995) Upper mantle mineralogy. *J. Geodynam.* **20**, 331–364.
- HAGGERTY S. E. (1996) Genesis of natural diamond. *Proc. 3rd Int. Symp. Advanced Materials*. Tsukuba, Japan, 65–68.
- HAGGERTY S. E., FUNG A. T., and PYLE J. M. (1993) The mantle array and geochemistries of high pressure and high temperature eclogites from the West Africa (Koidu) and Kaapvaal (Jagersfontein) cratons. *Russian Geol. Geophys.* **34**, 51–65.
- HARLAND W. B., ARMSTRONG R. L., COX A. V., CRAIG L. E., SMITH A. G., and SMITH D. G. (1989) *A Geologic Time Scale*. Cambridge University Press.
- HARTE B., HARRIS J. W., and HUTCHISON M. T. (1996) Mineral association in diamonds from across the mantle transition zone. *Proc. 3rd Int. Symp. Advanced Materials*. Tsukuba, Japan, 81–86.
- HARTE B. and OTTER M. (1992) Carbon isotope measurements on diamond. *Chem. Geol. (Isotope Geosci. Sec.)* **101**, 177–183.
- HARRIS J. W., HUTCHISON M. T., HURSTHOUSE M., LIGHT M., and HARTE B. (1997) A new tetragonal silicate mineral occurring as inclusions in lower-mantle diamonds. *Nature* **387**, 486–488.
- HORSTMANN U. E. and VERWOED A. R. (1997) Carbon and oxygen isotope variations in southern African carbonatites. *J. African Earth Sci.* **25**, 115–136.
- HOWELL J. V. (1960) *Glossary of Geology*. American Geological Institute.
- HUTCHINSON D. R., WHITE R. S., CANNON W. F., and SCULZ K. J. (1990) Keweenaw hot spot: Geophysical evidence for a 1.1 Ga mantle plume beneath the midcontinent rift system. *J. Geophys. Res.* **95**, 10869–10884.
- JANSE A. J. A. (1992) New ideas on subdividing cratonic areas. *Russian Geol. Geophys.* **33**, 9–25.
- JANSE A. J. A. and SHEAHAN P. A. (1995) Catalogue of world wide diamond and kimberlite occurrences: A selective and annotative approach. *J. Geochem. Explor.* **53**, 73–111.
- JAVOY M., PINEAU F., and DEMAIFF D. (1984) Nitrogen and carbon isotopic composition in the diamonds of Mbuji Mayi (Zaire). *Earth Planet. Sci. Lett.* **68**, 399–412.
- JOHNSON H. P., VAN PATTE N., TIVEY M., and SAGER W. W. (1995) Geomagnetic reversal rate for the Phanerozoic. *Geophys. Res. Lett.* **22**, 231–234.
- JORDAN T. H. (1988) Structure and formation of the continental tectosphere. *J. Petrol. Spec. Vol.* **1988**, 11–37.
- KESSON S. E. and RINGWOOD A. E. (1989) Slab-mantle interactions 2. The formation of diamonds. *Chemical Geol.* **78**, 97–118.
- KIRKLEY M., GURNEY J. J., OTTER M. L., HILL S. J., and DANIELS L. R. (1991) The application of C isotope measurements to the identification of the sources of C in diamonds: A review. *Applied Geochem.* **6**, 477–494.
- KIRKLEY M., SMITH H. S., and GURNEY J. J. (1989) Kimberlite carbonates—a carbon and oxygen stable isotope study. *Geol. Soc. Australia Spec. Vol.* **14**, 264–281.

- KVENVOLDEN K. A. (1993) Gas hydrates— geological perspective and global change. *Rev. Geophys.* **31**, 173–187.
- LANG A. R., MOORE M., and WALMSLEY J. C. (1992) Diffraction and imaging of diamond. In *The Properties of Natural and Synthetic Diamond*. (ed. J. E. FIELD) Academic Press.
- LARSON R. L. (1991) Latest pulse of Earth: Evidence for a Mid-Cretaceous superplume. *Geology* **19**, 547–550.
- LARSON R. L. and OLSON P. (1991) Mantle plumes control magnetic reversals. *Earth Planet. Sci. Lett.* **107**, 437–447.
- LE BAS M. J. (1971) Per-alkaline volcanism, crustal swelling, and rifting. *Nature* **230**, 85–87.
- LE ROEX A. P. (1986) Geochemical correlation between southern African kimberlites and South Atlantic hotspots. *Nature* **324**, 243–245.
- LEVINSON A. A., GUNNEY J. J., and KIRKLEY M. B. (1992) Diamond sources and production: Past, present, and future. *Gems & Gemology* Winter, 234–253.
- MCCANDLESS T. E. and GURNEY J. J. (1997) Diamond eclogites: Comparison with carbonaceous chondrites, carbonaceous shales, and microbial carbon-enriched MORB. *Russian Geol. Geophys.* **38**, 394–404.
- MCCULLOCH M. T. (1993) The role of subducting slabs in an evolving Earth. *Earth Planet. Sci. Lett.* **115**, 89–100.
- McHONE J. G. (1996) Constraints on the mantle plume model for Mesozoic alkaline intrusions in northeastern North America. *Can. Mineral.* **34**, 325–334.
- MENZIES M. A. and HAWKESWORTH C. G. (1987) *Mantle Metasomatism*. Academic Press.
- MEYER H. O. A. (1987) Inclusions in diamond. In *Mantle Xenoliths* (ed. P. H. NIXON), John Wiley & Sons.
- MEYER H. O. A. and BOYD F. R. (1972) Composition and origin of crystalline inclusions in natural diamonds. *Geochim. Cosmochim. Acta* **36**, 1255–1273.
- MILLEDGE H. J., MENDELSSOHN M. J., BOYD S. R., PILLENGER C. T., and SEAL M. (1989) Infrared topography and carbon and nitrogen isotope distribution in natural and synthetic diamonds in relation to mantle processes. In *Diamond Workshop* (eds. F. R. BOYD *et al.*). 28th Int. Geol. Congress.
- MITCHELL R. H. (1986) *Kimberlites. Mineralogy, Geochemistry, and Petrology*. Plenum Press.
- MITCHELL R. H. and BERGMAN S. C. (1991) *Petrology of lamproites*. Plenum Press.
- MOORE R. O. and GURNEY J. J. (1985) Pyroxene solid solution in garnets included in diamond. *Nature* **318**, 553–555.
- NAVON O., HUTCHEON I. D., ROSSMAN G. R., and WASSERBURG G. J. (1988) Mantle-derived fluids in diamond micro-inclusions. *Nature* **335**, 784–789.
- NISBET E. G. (1984) The continental and oceanic crust and lithosphere in the Archean: Isostatic, thermal, and tectonic models. *Can. J. Earth Sci.* **21**, 1426–1441.
- NIXON P. H. (1987) *Mantle Xenoliths*. John Wiley & Sons.
- PHIPPS S. P. (1988) Deep rifts as sources for alkaline intraplate magmatism in eastern North America. *Nature* **334**, 27–31.
- POIRIER J. -P. (1994) Light elements in the Earth's outer core: A critical review. *Phys. Earth Planet. Inter.* **85**, 319–337.
- POLET J. and ANDERSON D. (1995) Depth extent of cratons as inferred from tomographic studies. *Geology* **23**, 205–208.
- POLLACK H. N. and CHAPMAN D. S. (1977) On the regional variation of heat flow, geotherms, and lithospheric thickness. *Tectonophysics* **38**, 279–296.
- POPP B. N., PAREKH P., TILBROOK B., BIDIGARE R. R., and LAWS E. A. (1997) Organic carbon $\delta^{13}\text{C}$ variations in sedimentary rocks as chemostratigraphic and paleoenvironmental tools. *Paleogeog. Paleoclim. Paleoecol.* **132**, 119–132.
- PRINZHOFER A. and PERNATON E. (1997) Isotopically light methane in natural gas: bacterial imprint or diffusive fractionation? *Chem. Geol.* **142**, 193–200.
- REVENAUGH J. and MEYER R. (1997) Seismic evidence of partial melt within a possibly ubiquitous low-velocity layer at the base of the mantle. *Science* **277**, 670–673.
- RICHARDSON S. H., GURNEY J. J., ERLANK A. J., and HARRIS J. W. (1984) Origin of diamond in old enriched mantle. *Nature* **310**, 198–202.
- RICHARDSON S. H., ERLANK A. J., HARRIS J. W., and HART S. R. (1990) Eclogitic diamonds of Proterozoic age from Cretaceous kimberlites. *Nature* **346**, 54–56.
- RICHARDSON S. H., HARRIS J. W., and GURNEY J. J. (1993) Three generations of diamonds from old continental mantle. *Nature* **366**, 256–258.
- RINGWOOD A. E., KESSON S. E., HIBBERSON W., and WARE N. (1992) Origin of kimberlites and related magmas. *Earth Planet. Sci. Lett.* **113**, 521–538.
- RINGWOOD A. E. and MAJOR A. (1966) High-pressure transformation in pyroxenes. *Earth Planet. Sci. Lett.* **1**, 351–357.
- ROCK N. M. S. (1991) *Lamprophyres*. Blackie & Sons.
- ROLLINSON H. (1997) Eclogite xenoliths in west African kimberlites as residues from Archean granitoid crust formation. *Nature* **389**, 173–176.
- RONA P. A. (1988) Hydrothermal mineralization at oceanic ridges. *Can. Mineral.* **26**, 431–465.
- RUDNICK R. L., ELDRIDGE C. S., and BULANOVA G. P. (1993) Diamond growth history from in-situ measurement of Pb and S isotopic compositions of sulfide inclusions. *Geology* **21**, 13–16.
- RUDNICK R. L. and FOUNTAIN D. M. (1995) Nature and composition of the continental crust: A lower crustal perspective. *Rev. Geophys.* **33**, 267–309.
- SCHOPF J. W. (1983) *Earth's Earliest Biosphere*. Princeton University Press.
- SCHIDLowski M. (1988) A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature* **333**, 313–318.
- SCHRAUDER M. and NAVON O. (1993) Solid carbon dioxide in a natural diamond. *Nature* **365**, 42–44.
- SCLATER J. G. and FRANCHETEAU J. (1970) The implications of terrestrial heat flow observations on current tectonic and geochemical models of the crust and upper mantle of the Earth. *Geophys. J. R. Soc.* **20**, 509–542.
- SMYTH J. R. (1994) A crystallographic model for hydrous wadsleyite: An ocean in the Earth's interior? *Amer. Mineral.* **79**, 1021–1024.
- SMYTH J. R. and KAWAMOTO T. (1997) Wadsleyite II: A new high pressure hydrous phase in the peridotite-H₂O system. *Earth Planet. Sci. Lett.* **146**, E9-16.
- SOBOLEV N. V. (1977) *Deep Seated Inclusions in Kimberlites and the Problem of the Composition of the Upper Mantle*. American Geophysical Union.
- SPERA F. J. (1984) Carbon dioxide in petrogenesis III: Role of volatiles in the ascent of alkaline magma with special reference to xenolith-bearing mafic lavas. *Contrib. Mineral. Petrol.* **77**, 56–65.
- STOREY B. C. (1995) The role of mantle plumes in continental breakup: Case histories from Gondwanaland. *Nature* **377**, 301–308.
- SUNAGAWA I. (1990) Growth and morphology of diamond

- crystals under stable and metastable conditions. *J. Crystal Growth* **99**, 1156–1161.
- SUZUKI A., OHTANI E., and KATO T. (1995) Flotation of diamond in mantle melt at high pressure. *Science* **269**, 216–218.
- SWART P. K., PILLINGER C. T., MILLEDGE H. J., and SEAL M. (1983) Carbon isotopic variation within individual diamonds. *Nature* **303**, 793–795.
- SYKES L. R. (1978) Intraplate seismicity, reactivation of preexisting zones of weakness, alkaline magmatism, and other tectonism postdating continental fragmentation. *Rev. Geophys. Space Phys.* **16**, 621–688.
- TACKLEY P. J., STEVENSON D. J., GLATZMAIER G. A., and SCHUBERT G. (1993) Effects of an endothermic phase transition at 670 km depth in a spherical mode of convection in the Earth. *Nature* **361**, 699–704.
- TAKAHASHI E. and SCARFE C. M. (1985) Melting of peridotite to 14 Gpa and the genesis of komatiite. *Nature* **315**, 566–568.
- TAYLOR S. R. and MCLENNAN S. M. (1985) *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific.
- TAYLOR W. R. and GREEN D. H. (1987) The petrological role of methane: Effect on liquid phase relations and the solubility mechanism of reduced C-H volatiles. In *Magmatic Processes: Physicochemical Principles*. Geochem. Soc. Spec. Pub. 1 (ed. B. O. MYSEN) pp 121–138. Geochemical Society.
- TAYLOR W. R., CANIL D., and MILLEDGE H. J. (1996) Kinetics of Ib to IaA nitrogen aggregation in diamond. *Geochem. Cosmochim. Acta* **60**, 4725–4733.
- UNRUG R. (1996) *Geodynamic map of Gondwana*. Council of Geoscience, Pretoria.
- VAN HEERDEN L. A., DEINES P., and GURNEY J. J. (1995) The carbon isotopic composition of harzburgitic, lherzolitic, websteritic, and eclogitic paragenesis diamonds from southern Africa: A comparison of genetic models. *S. Afr. J. Geol.* **98**, 119–125.
- WANG W. and SUENO S. (1996) Discovery of a Na Px-En inclusion in diamond: possible transition zone origin. *Mineral. J.* **18**, 9–16.
- WEN L. and HELMBERGER D. V. (1998) Ultra-low velocity zones near the core-mantle boundary from broadband PKP precursors. *Science* **279**, 1701–1703.
- WHITE R. S. and MCKENZIE D. P. (1989) Magmatism at rift zones: The generation of volcanic continental margins and flood basalts. *J. Geophys. Res.* **94**, 7685–7730.
- WILLIAMS Q., REVENAUGH J., and GARNERO E. (1998) A correlation between ultra-low basal velocities in the mantle and hot spots. *Science* **281**, 546–549.
- WOOLLEY A. R., BERGMAN S. C., EDGAR A. D., MITCHELL R. H., ROCK N. M. S., and SCOTT-SMITH B. H. (1996) Classification of lamprophyres, lamproites, kimberlites, and the kalsilitic, melilitic, and leucitic rocks. *Can. Mineral.* **34**, 175–186.
- WYLLIE P. J. (1989) The genesis of kimberlites and some low SiO₂, high alkali magmas. In *Kimberlites and Related Rocks*. (ed. J. ROSS) Geol. Soc. Australia Spec. Pub. 14, pp. 603–615. Blackwell Scientific.
- ZERR A., DIEGELER A., and BOEHLER R. (1998) Solidus of Earth's deep mantle. *Science* **281**, 243–246.

