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Archean diamonds from Wawa (Canada): samples from deep cratonic roots predating cratonization of the Superior Province

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Abstract With an age of ca. 2.7 Ga, greenschist facies volcaniclastic rocks and lamprophyre dikes in the Wawa area (Superior Craton) host the only diamonds emplaced in the Archean available for study today. Nitrogen aggregation in Wawa diamonds ranges from Type IaA to IaB, suggesting mantle residence times of tens to hundreds of millions of years. The carbon isotopic composition ($\delta^{13}C$) of cube diamonds is similar to the accepted mantle value (− 5.0‰). Octahedral diamonds show a slight shift (by + 1.5‰) to isotopically less negative values suggesting a subduction-derived, isotopically heavy component in the diamond-forming fluids. Syngenetic inclusions in Wawa diamonds are exclusively peridotitic and, similar to many diamond occurrences worldwide, are dominated by the harzburgitic paragenesis. Compositionally they provide a perfect match to inclusions from diamonds with isotopically dated Paleo- to Mesoarchean crystallization ages. Several high-Cr harzburgitic garnet inclusions contain a small majorite component suggesting crystallization at depth of up to 300 km. Combining diamond and inclusion data indicates that Wawa diamonds formed and resided in a very thick package of chemically depleted lithospheric mantle that predates stabilization of the Superior Craton. If late granite blooms are interpreted as final stages of cratonization then a similar disconnect between Paleo- to Mesoarchean diamondiferous mantle lithosphere and Neoarchean cratonization is also apparent in other areas (e.g., the Lac de Gras area of the Slave Craton) and may suggest that early continental nuclei formed and retained their own diamondiferous roots.

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Introduction

Radiometric dating of silicate (e.g., Richardson et al. 1984, 1990, 1993) and sulfide (e.g., Pearson et al. 1999; Shirey et al. 2002) inclusions in diamonds from kimberlites indicates that the bulk of diamonds of harzburgitic paragenesis formed during the Paleo- (3.6–3.2 Ga) and Mesorchean (3.2–2.8 Ga), whereas lherzolitic and eclogitic diamonds were added during later events of craton modification extending into the Neoarchean and Proterozoic. The validity of diamond ages derived from mineral inclusions has been challenged though (e.g., Navon 1999; Spetsius et al. 2002), casting some doubt on the widely accepted model of ancient peridotitic diamonds. Based on the assumption that the subcratonic lithospheric mantle evolves over time, the case for Archean formation of harzburgitic diamonds would be strengthened, if a study on diamonds with Archean host rock emplacement ages showed that the thermal regime and chemical environment for such "proven" Archean diamonds coincides with that for radiometrically dated Archean diamonds that resided in the Earth's mantle for several more billion years.

The oldest known diamonds on the Earth surface come from the gold-bearing sediments of the Witwatersrand Basin in South Africa (3.0–2.8 Ga; Robinson 1979; Poujol et al. 2003). Due to fine crushing in modern gold mining these diamonds are no longer recovered and systematic collections of Witwatersrand diamonds have not been preserved. The next oldest diamond deposits are in the Abitibi–Wawa greenstone belts (Superior Craton) in Canada (ca. 2.7 Ga; Wyman and Kerrich 1993; Wilson 2004). During the current exploration in the Wawa area in excess of 20,000 diamonds have been

recovered (Ayer and Wyman 2003), making it now possible to study the mantle sources of "proven" Archean diamonds.

Geological setting

The Wawa diamond deposits are located ca. 20 km north of the town Wawa (Ontario) along the Trans-Canada Highway. The area represents a section of the Michipicoten greenstone belt within the Wawa (or Abitibi–Wawa, e.g., Thurston 2002) subprovince of the Superior Craton (Fig. 1). The Wawa subprovince has been interpreted as an allochthonous island arc terrain (e.g., Hoffman 1989) that experienced greenschist to amphibolite facies metamorphic overprint during the Wawan phase (2.67 Ga) of the Kenoran orogeny (Stott 1997). Wyman et al. (2002) suggested that the greenstone belts at Abitibi–Wawa resulted from subduction tectonics modified by mantle plume processes with a late, post-tectonic (2650–2550 Ma) coupling of greenstone belt crust and lithospheric mantle roots. As an alternative to the allochthonous terrane model, Thurston (2002) proposed that greenstone belts in the central and southern Superior Province (including Aibitbi–Wawa) originated from (par-)autochthonous progression from platforms through rifting of continental fragments and late assembly during the Kenoran orogeny.

Williams et al. (1991) recognized three bimodal volcanic assemblages (Hawk, Wawa and Catfish, equivalent to cycles 1–3 of Sage et al. 1996) in the Michipicoten greenstone belt, with ages of about 2.90, 2.75 and 2.70 Ga, respectively (Turek et al. 1984, 1992). Field relationships show that the diamond-bearing lamprophyric rocks in the Wawa area are synchronous with the Catfish assemblage. Diamonds for this study come from upper greenschist facies, metavolcaniclastic rocks (subaqueous lahars or debris flows) on the Festival claim block of Pele Mountain Resources. U–Pb dating of zircons from the Genesis diamond occurrence on this property indicates a volcanic emplacement age of 2744 ± 44 Ma (Stachel et al. 2004a). A detailed account of the diamond-bearing metavolcanic rocks (breccias and dikes) at Wawa is given by Lefebvre et al. (2005) who established a classification as calc-alkaline lamprophyres based on the presence of coarse oscillatory-zoned edenitic and pargasitic amphibole. Breccias and dikes both contain xenoliths composed of secondary hornblende and actinolite. Based on, in part, high Cr and Ni contents, these xenoliths are identified as mantle inclusions (Lefebvre et al. 2003, 2005). Details on the geology and geochemistry of the volcaniclastic host rocks for the diamonds studied here will be presented elsewhere (Walker et al., in preparation).

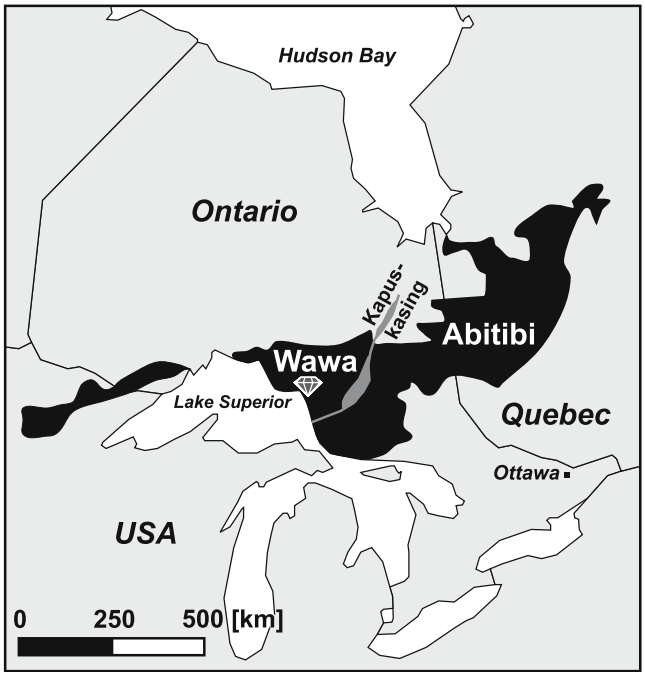

Fig. 1 The Wawa and Abitibi subprovinces of the Superior Craton, separated by the Kapuskasing Uplift. Location of Wawa diamond deposits is indicated

Samples

Rugged terrain and complexly folded, overturned stratigraphy make a correlation of the numerous individual diamond occurrences on the Festival claim block difficult. Currently two main zones (South and North) of volcaniclastic deposits, tens of meters in thickness, are recognized in the western part of the property (Walker et al., in preparation), with diamonds mainly occurring within discrete layers at the base of these zones. Diamonds for the present study were recovered from bulk samples taken at two locations, "Genesis" (South Zone) and "Cristal" (a stratigraphically older occurrence in the south-east of the property).

The size distribution for Wawa diamonds is distinctly skewed towards finer stone sizes with > 95% being microdiamonds (Ayer and Wyman 2003; microdiamonds are < 0.5 mm in the two largest dimensions). Micro- and commercial size diamond results for Genesis obtained by Pele Mountain Resources showed ca. 12% of the diamonds to be larger than 0.3 mm (sieve size) and just over 2% to be larger than 0.425 mm. We studied 57 diamonds from Genesis in a size range of 0.3–1.7 mm (largest dimension). Micro- and commercial size diamond results from Cristal indicated that 8% of the diamonds are larger than 0.3 mm (sieve size) and 2.4% exceed 0.425 mm. We examined 270 diamonds from Cristal ranging from 0.4 to 3.0 mm in size (largest dimension) and selected 45 inclusion-bearing diamonds for further analytical studies.

Analytical methods

Nitrogen concentrations and aggregation states were determined by micro-FTIR (Thermo-Nicolet Nexus 470

Fourier transform infrared spectrometer fitted with a Continuum infrared microscope with a KBr beam splitter). For Genesis, spectra were taken from whole diamonds (57 samples); for Cristal cleavage fragments of 37 diamonds were used after breakage for inclusions. Using an aperture size of 50–100 μm, spectra (4,000–600 cm^{-1}) were collected for 200 s with a resolution of 4 cm^{-1}. After conversion to absorption coefficient the spectra were de-convoluted into the A, B and D components (e.g., Boyd et al. 1995) using least square techniques. Nitrogen concentrations (atomic ppm) were calculated using the absorption strength at 1,282 wave numbers for the A-center (Boyd et al. 1994: 16.5 ± 1) and the B-center (Boyd et al. 1995: 79.4 ± 8). The detection limit for nitrogen is about 10 ppm, analytical precision is 10–20% of the concentration.

For carbon isotopic analyses, fragments (ca. 1 mg) of 15 diamonds from Genesis and 25 diamonds from Cristal were combusted using a conventional sealed tube technique. Carbon isotope ratios were subsequently determined with a Finnigan Mat 252 Mass Spectrometer and are reported relative to the V-PDB standard. Analytical precision is ± 0.1‰; from analyses of reference standards, analytical accuracy is estimated to be ± 0.2‰.

Thirty-four mineral inclusions were liberated from 29 diamonds from the Cristal occurrence, embedded in epoxy resin and polished. Major and minor element analyses were performed by EPMA (Jeol JXA−8900 RL) at 20 kV gun potential and 20 nA beam current using silicate, oxide and metal standards. Count times range between 30 and 90 s to ensure detection limits of 200 ppm or better for all oxides. To improve precision for Zn-in-spinel thermometry, peak and background count times for Zn were the same (100 s) and five analyses per spinel were averaged.

References for the database of diamonds and their inclusions from worldwide sources are given in Stachel et al. (2000) and Tappert et al. (2005). This database has been expanded by the incorporation of analytical data of Appleyard et al. (2004), Cartigny et al. (2004), Davies et al. (2003, 2004a, b), Deines and Harris (2004), Griffin et al. (2001), Harris et al. (2004), Kaminsky et al. (2001), Leost et al. (2003), Logvinova et al. (2001), Mc Kenna et al. (2004), Phillips et al. (2004), Pokhilenko et al. (2004), Promprated et al. (2004), Sobolev et al. (2000, 2004), Stachel et al. (2004b), Taylor et al. (1996a), and Wang et al. (2000).

Diamonds from Genesis and Cristal

Morphology and coloration

At Genesis the sampled stratigraphic horizon yielded almost exclusively cube diamonds (Fig. 2), including some fragmented, twinned and moderately resorbed cubes. The cube faces are often slightly concave (“re-entrant cubes”) and distorted and may display fine

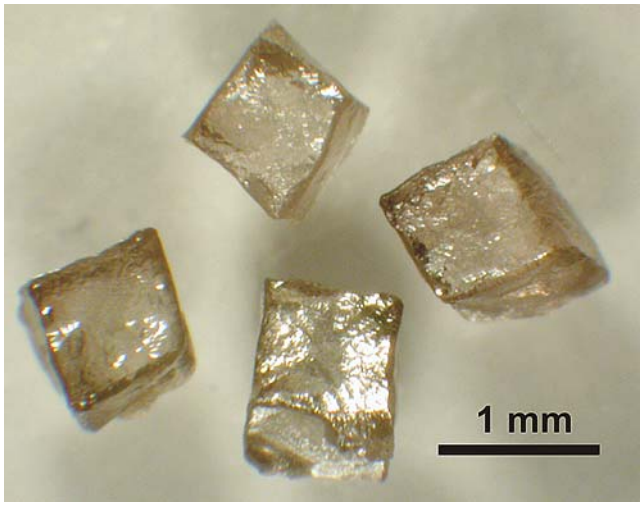

Fig. 2 Diamonds from Genesis: transparent cubes with slightly concave crystal faces

textured tetragons (an etch feature equivalent to trigons on octahedral faces). About 5% of the Genesis diamonds show extensive dodecahedral resorption, 10% classify as irregular crystals. Most (about two-thirds) of the cubes contain clouds composed of innumerable sub-micrometer inclusions. FTIR spectra taken through clouded areas show a broad absorption peak at around 3,420 cm^{-1}, suggesting the presence of water, and two more peaks at 1,430 and 876 cm^{-1}, indicative of carbonate (Navon et al. 1988). The fully transparent stones are dominated by browns of variable intensity followed by colorless and, in the case of one diamond, yellow coloration.

Diamonds from Cristal range from un-resorbed octahedra to highly resorbed dodecahedra (Fig. 3). Overall, octahedral and mildly resorbed octahedral diamonds dominate. About 25% of the samples from Cristal are irregular crystals (mainly broken diamonds, some aggregates and highly irregular shapes), macles (octahedral twins) are common (ca. 15%) and about 5% of the diamonds have minor {100} faces, i.e., represent cubo-octahedral growth. Half the diamonds are colorless, the rest covers a range from very light to intense brown coloration. Plastic deformation lines can only be observed on dodecahedral faces and, therefore, were only recognized on a few highly resorbed samples. Using brown body color as an indication of plastic deformation (Orlov 1977; Harris 1992) as much as half the diamonds from Cristal are strained.

Surface features typical for diamonds from alluvial deposits, such as percussion and scratch marks, edge abrasion and ground crystal faces are absent both at Genesis and Cristal.

Nitrogen characteristics

Nitrogen concentrations in diamonds from Genesis (Table 1) range from below detection (i.e., < 10 ppm,

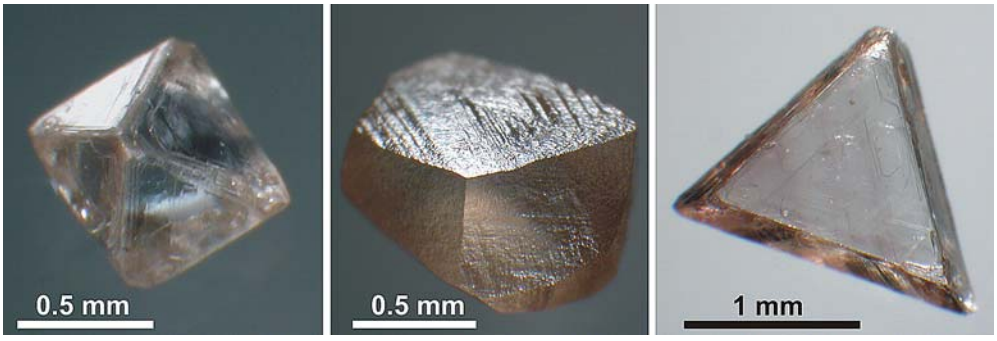

Fig. 3 Diamonds from Cristal: colorless octahedron (*left*), brown dodecahedron with plastic deformation lines in two directions (*center*) and triangular macle with plastic deformation indicated by stripes of brownish coloration (*right*)

two samples) to 600 atomic ppm. Nitrogen aggregation, measured as the relative percentage of nitrogen in the fully aggregated B-center, is very low (0–11% B).

At Cristal nitrogen contents range from < 10 (seven diamonds) to 170 ppm, with the exception of one diamond with 560 ppm (Table 2). Nitrogen aggregation varies between 0 and 97% B-center. Compared to Genesis, where few Type II (4%, N below detection) and predominantly Type IaA diamonds (95%, Type IaA has ≤ 10% B-center) are found, Cristal contains more Type II diamonds (19%) and covers the full range from Type IaA (16%) through IaAB (59%) to IaB (5%, Type IaB has ≥ 90% B-center).

The time needed for the transition from the A-center (pairs of nitrogen) to the B-center (rings of four nitrogen surrounding a vacancy) depends on the absolute nitrogen concentration and time-averaged mantle residence temperature. Assuming geologically reasonable residence times, the aggregation state of nitrogen in diamonds may thus be employed as a geothermometer (Evans and Harris 1989; Taylor et al. 1990). Alternatively, if the residence temperature is known, crude estimates of the mantle residence time may be derived (the result is extremely dependent on temperature). The potentially accelerating effect of plastic deformation on nitrogen aggregation has not been experimentally studied but overall good agreement with mineral inclusion thermometry (Taylor et al. 1995; Leahy and Taylor 1997) suggests that nitrogen aggregation indeed provides a robust geothermometer. On this background, the poor aggregation state of diamonds from Genesis reflects (1) formation and storage at low temperatures (≤ 1,100°C), (2) short mantle residence or (3) a combination of both. Experimental studies point to the formation of cube diamonds at temperatures lower than those for octahedra (Yamaoka et al. 1977).

Mantle residence temperatures for Cristal are evaluated based on residence times of 100 and 500 Ma (Fig. 4), corresponding to crystallization ages at about 2.8 and 3.2 Ga, respectively. With their low nitrogen contents, the Type IaA diamonds from Cristal then suggest mantle residence at around 1,150°C. A cluster of diamonds extending from intermediate aggregations states (ca. 30% B-center) at very low nitrogen contents (< 20 ppm) to high aggregation states and elevated nitrogen contents (≤ 170 ppm) implies distinctly higher mantle residence temperatures of about 1,250–1,300°C. Although dodecahedral diamonds are somewhat more abundant in this high temperature group no significant correlations between physical characteristics (diamond morphology and coloration) and residence temperature have been found.

Carbon isotopic composition

In their carbon isotopic composition ($\delta^{13}C$) the cube diamonds from Genesis form a narrow distribution (−5.3 to −3.4‰) with a distinct mode at −5.0 to −4.5‰ (Fig. 5). This coincides with the mode for diamonds from worldwide sources (Fig. 5). Fibrous cubes and cubic coats from the Republic of Congo show a similarly narrow distribution ($\delta^{13}C$ range −5.9 to −7.5‰; Boyd et al. 1987) near the assumed mantle value at −5‰ (e.g., Deines 2002).

Diamonds from Cristal display a wider range in carbon isotopic composition (−5.5 to −1.1‰) with a well-defined mode at −3.5 to −3.0‰ (Fig. 5). Relative to Genesis and worldwide data this corresponds to a shift in mode by about 1.5‰ to isotopically heavier compositions (i.e., less negative $\delta^{13}C$ values).

Discussion

Based on morphology, nitrogen characteristics and carbon isotopic composition diamonds from Genesis and Cristal are entirely different. Genesis contains cubes, typically with intermediate concentrations of nitrogen almost entirely in the A-center and with a carbon isotopic composition corresponding to the mantle value. This suggests crystallization from a mantle-derived fluid/melt not too long (< 100 Ma) before eruption of the host magma.

Diamonds from Cristal formed with octahedral morphology. Variable nitrogen aggregation states (IaA to IaB) at generally low nitrogen contents indicate diamond formation at temperatures between 1,150 and 1,300°C. The upper end of this temperature range is unusually high and points to diamond sources that either extended to great depth (assuming diamond formation along a geothermal gradient) or became

Table 1 Physical characteristics, nitrogen content and aggregation state and carbon isotopic composition for diamonds from Genesis

Sample	Shape	Color	$\delta^{13}C$	Type	N	Percent B
GEN-500	c	cldy, b	−4.91	IaA	380	0
GEN-501	c	cldy, c	−4.65	IaA	339	0
GEN-502	c	b	−4.68	IaA	295	0
GEN-503	c	c	−4.89	IaA	343	0
GEN-504	c	cldy, b	−4.79	IaA	356	6
GEN-505	c	cldy, b	−5.14	IaA	408	7
GEN-506	c	cldy,	−4.81	IaA	426	10
GEN-507	c	cldy, b		IaA	186	0
GEN−508	c	c	−4.66	IaA	600	5
GEN−509	c	c	−4.67	IaA	329	7
GEN-510	c	cldy, b		IaA	317	0
GEN-511	c	cldy, c	−3.48	IaA	244	0
GEN-512	i/c	cldy, b		IaA	417	10
GEN-513	c	Light b	−4.85	IaA	340	5
GEN-514	c	cldy, b	−5.15	IaA	341	0
GEN-515	c	cldy, b		IaA	218	1
GEN-516	c	cldy, c		IaA	329	6
GEN-517	c	Light b	−4.67	IaA	348	4
GEN-518	c	c	−5.28	IaA	207	0
GEN-519	i	cldy, b		IaA	337	0
GEN-520	c	cldy,	−3.37	IaA	277	8
GEN-521	c	b		IaA	335	6
GEN-522	c	cldy, b		IaA	492	9
GEN-523	c	b		IaA	295	0
GEN-524	c	cldy, b		IaA	378	9
GEN-525	c	cldy, b		IaA	336	0
GEN-526	i/c	cldy, b		IaA	351	8
GEN-527	i/c	b		IaA	372	0
GEN-528	c	cldy, c		IaA	254	10
GEN-529	c	cldy, b		IaA	337	9
GEN-530	c	b		IaA	342	10
GEN-531	c	cldy, b		IaA	351	0
GEN-532	c	cldy, b		IaA	340	0
GEN-533	c	cldy, b		IaA	570	7
GEN-534	i/c twin	cldy, b		IaA	364	5
GEN-535	d/i/c	cldy, b		IaA	251	0
GEN-536	c	cldy, b		IaA	282	0
GEN-537	i/c	cldy, b		IaA	212	0
GEN-538	i/d	cldy, c		IaAB	226	11
GEN-539	o/c	cldy, b		IaA	182	0
GEN-540	c	cldy, b		IaA	301	0
GEN-541	c	cldy, b		IaB	198	5
GEN-542	i/c	cldy, b		IaA	189	7
GEN-543	d twin	c		IaA	231	6
GEN-544	c	cldy, gray		IaA	192	7
GEN-545	i	Light b		II	0	
GEN-546	c	c		IaA	217	8
GEN-547	i	cldy, light b		II	0	
GEN-548	d	cldy, b		IaA	258	0
GEN-549	i	y		IaA	155	0
GEN-550	c	cldy, y		IaA	18	3
GEN-551	c	cldy, gray		IaA	515	0
GEN-552	c	b		IaA	448	7
GEN-553	i/c	cldy, b		IaA	211	10
GEN-554	c	cldy, gray		IaA	525	0
GEN-555	c	b		IaA	330	9
GEN-556	i	c		IaA	411	9

Shape: *c* cube, *i* irregular, *d* dodecahedron, *o* octahedron; color: *cldy* cloudy, *c* colorless, *b* brown, *y* yellow

Table 2 Physical characteristics, nitrogen content and aggregation state, carbon isotopic composition and recovered inclusion content for diamonds from Cristal

Sample	Shape	Color	$\delta^{13}C$	Type	N	Percent B	Recovered
CRI-1	i/d	c	−5.22	IaAB	107	63	
CRI-4	o	b	−3.40	IaAB	95	11	ol
CRI-5	d	Light b	−1.20	IaAB	13	35	2 ol
CRI-6	o	Light b	−3.47	IaA	106	7	opx
CRI-9	d	c	−2.92	IaAB	27	47	
CRI-10	i/d	c	−4.59	IaAB	69	57	2 chr
CRI-11	o-m	c	−3.29	IaAB	157	80	2 chr
CRI-16	(d)/o	Light b	−2.16	IaAB	9	41	ol
CRI-17	(i)/d	c	−2.90	IaA	94	8	ol
CRI-19	o	b	−1.94	IaA	52	9	2 ol
CRI-31	d	b	−2.43	IaAB	88	82	ol
CRI-41	i/o	c	−3.30	IaAB	41	82	Fe-chr
CRI-47	o	Light b	−2.36				ol
CRI-49	d-m	Light b		IaA	59	5	ol
CRI-51	d/o	Light b	−2.85	IaAB	140	85	maj grt
CRI-57	o	b	−3.76	IaAB	40	24	2 ol
CRI-59	i/d	b	−3.40	IaAB	168	73	
CRI-67	(d)/o/a	Light b	−1.10	IaAB	68	65	Altered
CRI-70	i/o/a	b	−3.49	IaAB	37	14	ol
CRI-72	i/d	Light b	−3.21	IaB	138	92	Altered
CRI-86	d/o	Light b		IaAB	17	30	maj grt
CRI−90	d/o	c	−3.64	II	0		2 maj grt
CRI-95	o	Light b	−3.13	IaAB	38	29	ol
CRI-201	d	c		IaB	140	97	chr
CRI-202	d-m	Light b	−4.01	IaAB	58	67	Altered
CRI-203	d-m	c		II	0		ol
CRI-204	o-m	c		IaAB	88	87	ol
CRI-205	i-m	c		IaA	25	0	ol
CRI-206	d-m	c	−2.97	II	0		ol
CRI-207	c-o	c		IaAB	10	61	opx
CRI-208	d/o	c	−3.59	II	0	0	ol
CRI-209	d/o	Light b	−5.50				
CRI-210	i/o	c		IaAB	13	25	
CRI-211	o twin	Light b		IaAB	9	87	
CRI-212	c-o twin	c					cpx
CRI-213	o/d	c		II	0		
CRI-214	Twin	c		IaA	53	0	
CRI-301	d/o-m	c		II	0		grt
CRI-302	i/d/o	c		II	0		Altered
CRI-303	i/o	b		IaAB	557	18	

Shape: *c* cube, *i* irregular, *d* dodecahedron, *m* macle, *o* octahedron; color: *c* colorless, *b* brown; mineral inclusions: *grt* garnet, *ol* olivine, *cpx* clinopyroxene, *opx* orthopyroxene, *chr* chromite, *maj* majoritic

thermally perturbed during transient heating events (i.e., absence of a single geotherm). A shift in $\delta^{13}C$ of + 1.5‰ relative to the mode of diamonds worldwide may either indicate crystallization from a mixed fluid/melt containing an isotopically heavy, slab-derived component or reflect the presence of a carbon isotopic heterogeneity beneath the southern Superior Craton during the Archean. Minor deviations in mode from the established mantle value have been observed for a number of diamond deposits worldwide (Kirkley et al. 1991).

Mineral inclusions in diamonds from Cristal

Microscopically visible mineral inclusions were absent at Genesis but 34 inclusions from 29 diamonds from Cristal were successfully recovered and polished (Table 3). Two of these inclusions consist of a soft whitish mass and represent alteration products of former syngenetic

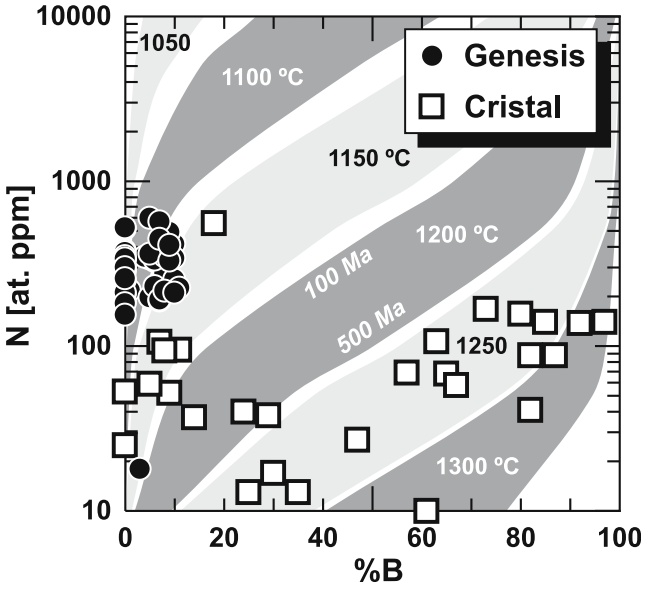

Fig. 4 Nitrogen content versus nitrogen aggregation state (measured as percent nitrogen in the B-center, assuming that only nitrogen A- and B-centers are present) for diamonds from Genesis and Cristal. *Y*-axis is cut off at 10 ppm (detection limit), hence Type II diamonds (two for Genesis, seven for Cristal) are not shown. Isotherms are calculated for mantle residence times of 100 and 500 Ma using the thermodynamic data of Evans and Harris (1989) and (Taylor et al. 1990)

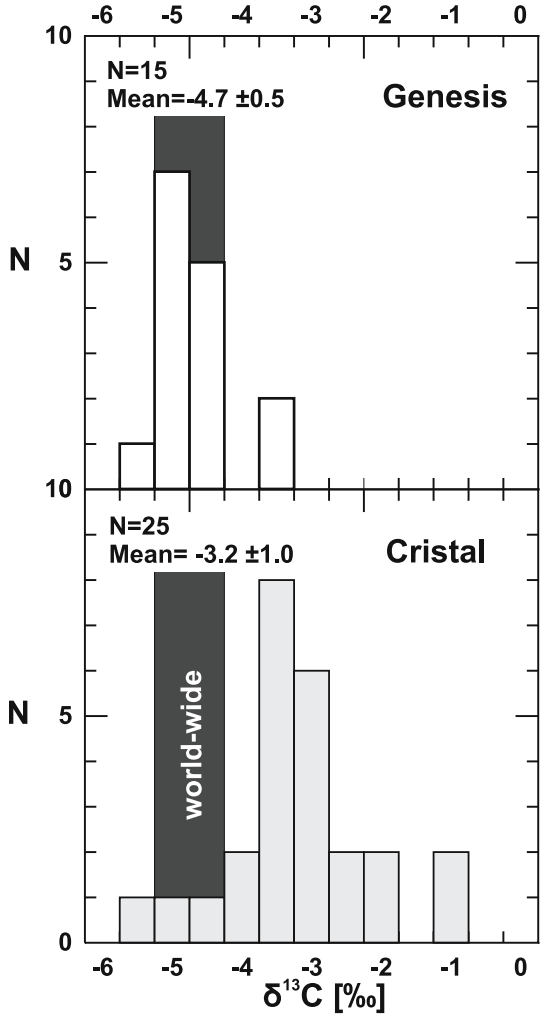

Fig. 5 Carbon isotopic composition ($\delta^{13}C$) of diamonds from Genesis and Cristal. Class (bin) size is 0.5‰, so, e.g., class −5.0‰ contains all samples falling between −5.25 and −4.75‰. *Dark band* represents mode of 567 peridotitic and eclogitic diamonds from worldwide sources

phases. A third diamond (CRI−41) contained a Fe-chromite inclusion with an Mg number of 8.8 and high MnO (1.6 wt%, see Table 5) and ZnO (2.9 wt%). This composition is typical for metamorphic spinels and the inclusion is regarded as having been affected by Kenoran age metamorphic fluids penetrating the diamond along fine fractures.

Chemical composition

Garnet

Five garnets (Fig. 6, Table 4) were released from four diamonds. All are harzburgitic in composition and four have a small majorite component [$M_6(Al_2MSi)^{[VI]}Si_6^{[IV]}O_{24}$ end-member, Ringwood 1967] signified by an excess of silicon over the available tetrahedral sites (6.18–6.25 cations of Si per formula unit). Elevated Na_2O (0.09 and 0.12 wt%) at low TiO_2 ($\leq$ 0.02 wt%) in two majoritic garnets included in diamond CRI−90 indicates minor occurrence of a second pressure-dependent substitution: $M^{2+}Al^{3+} = Na^{+}Si^{4+}$ (Ringwood and Major 1971; Irifune et al. 1989). Very Cr-rich (12–13 wt% Cr_2O_3) harzburgitic garnets with a majorite component were first recognized at Snap Lake (southern Slave Craton) and because of their depleted nature were interpreted to reflect a very deep lithospheric source (Pokhilenko et al. 2004). Using experimental data (Akaogi and Akimoto 1977; Irifune 1987) as an *approximate* indication of depth, Wawa majoritic garnets are derived from 250 to 300 km, slightly shallower than the deepest value for Snap Lake (Fig. 7).

Comparing garnet inclusions from Wawa and from the southern (Snap Lake) and central Slave (Panda) shows

Table 3 Inclusion types and abundances at Cristal

	Diamonds	Inclusions
Epigenetic inclusions		
Altered (soft)	2	2
Fe-chromite	1	1
Syngenetic inclusions		
Garnet (pyrope)	4	5
Cpx (Cr-diopside)	1	1
Opx (enstatite)	2	2
Olivine	16	19
Mg-chromite	3	4
Total	29	34

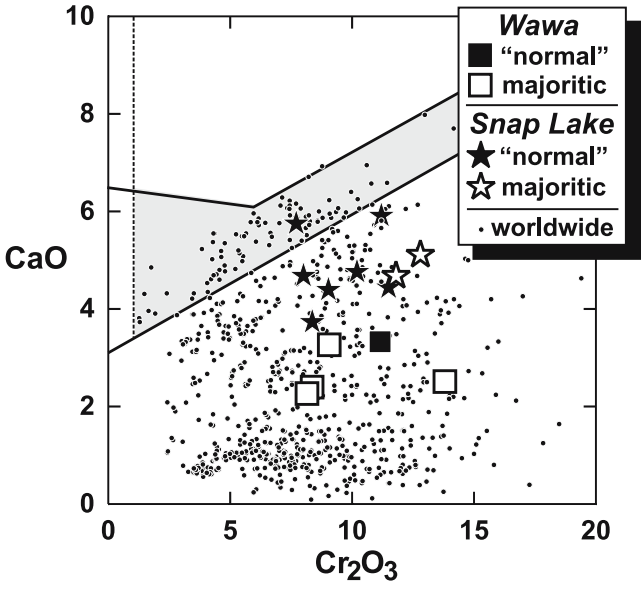

Fig. 6 Ca–Cr plot for garnets from Wawa and peridotitic (> 1 wt% Cr_2O_3) garnet inclusions from worldwide sources. Snap Lake is highlighted as the only other source of Cr-rich harzburgitic garnets with a majorite component. Lherzolite field is from Sobolev et al. (1973)

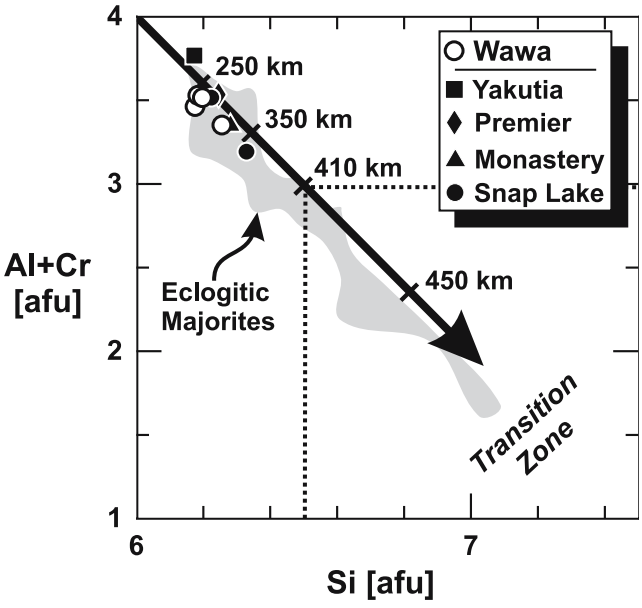

Fig. 7 Atomic proportions (at [O] = 24) of Al + Cr versus Si for harzburgitic majorite garnets. Lherzolitic majoritic garnets have not yet been observed, the field of eclogitic majorites is given for reference. *Arrow* indicates increasing majorite component with increasing pressure. Depth estimates are derived from high-pressure experiments at 1,200°C (Akaogi and Akimoto 1977; Irifune 1987) and should only be taken as a first approximation since the effect of variations in temperature and composition is not considered

that Wawa garnets are lower in CaO (2.2–3.3 wt%) but similar in both high Cr_2O_3 content (8.2–13.8 wt%, see Fig. 6) and Ca-corrected Mg numbers (86.0–87.5, for calculation see Stachel et al. 2003). By comparison, garnet inclusions from the Kaapvaal Craton have distinctly higher Ca-corrected Mg numbers (mode around 89, Stachel et al. 2003).

Pyroxene

A single clinopyroxene inclusion of presumably peridotitic paragenesis is characterized by relatively low Cr_2O_3 (1.09 wt%, see Table 4) and Mg number (89.8) and unusually high TiO_2 (0.40 wt%), Al_2O_3 (2.54 wt%) and Na_2O (2.88 wt%). High Na and Al are characteristic of websteritic clinopyroxene inclusions, and although usually their Mg number and Cr content are still lower there is similarity to the Cr-rich websteritic paragenesis at Orapa (Gurney et al. 1984), in particular inclusion OR42-b (coexisting with websteritic garnet).

Two single orthopyroxene inclusions have Mg numbers typical for the peridotitic suite (93.9 and 94.6) and are low in CaO (0.32 and 0.15 wt%, see Table 4) and Al_2O_3 (0.37 and 0.16 wt%). Low calcium suggests a

Table 4 Representative analyses (EPMA) of silicate inclusions from Cristal

Mineral	Garnet	Majoritic garnet	Majoritic garnet	Majoritic garnet	Clinopyroxene	Orthopyroxene	Orthopyroxene	Olivine	Olivine	Olivine	Olivine
Sample	CRI-301	CRI-51	CRI-86	CRI-90A	CRI-212	CRI-6	CRI-207	CRI-5	CRI-16	CRI-17	CRI-205
P_2O_5	0.02	0.02	≤ 0.01	0.02	0.02	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	0.02
SiO_2	41.09	42.99	42.64	42.48	54.46	57.21	57.86	40.36	40.11	40.78	39.88
TiO_2	≤ 0.01	0.03	0.04	−0.00	0.40	≤ 0.01	≤ 0.01	0.01	≤ 0.01	≤ 0.01	≤ 0.01
Al_2O_3	15.19	13.40	11.19	14.53	2.54	0.37	0.16	0.05	0.03	0.05	0.05
Cr_2O_3	11.15	9.07	13.81	8.36	1.09	0.33	0.09	0.01	0.02	0.04	0.05
V_2O_3	0.06	0.04	0.06	0.05	0.03	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01
FeO	6.44	7.01	6.44	7.16	3.38	4.14	3.73	7.63	6.95	6.66	7.90
MnO	0.36	0.34	0.31	0.36	0.12	0.11	0.09	0.09	0.10	0.10	0.11
NiO	≤ 0.01	≤ 0.01	0.02	0.01	0.05	0.12	0.13	0.34	0.35	0.33	0.33
MgO	21.87	23.28	23.60	23.78	16.72	35.63	37.01	50.96	52.32	51.91	50.67
CaO	3.33	3.27	2.51	2.40	16.64	0.32	0.15	0.02	0.03	0.01	0.06
Na_2O	≤ 0.02	0.05	≤ 0.02	0.12	2.88	0.05	0.04	0.04	0.03	≤ 0.02	0.04
K_2O	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	0.09	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01
Total	99.62	99.56	100.72	99.33	98.49	98.37	99.33	99.59	99.99	99.97	99.17

harzburgitic paragenesis for both inclusions. The very low Al content of the Mg-rich and Ca-poor orthopyroxene (it also has low Cr_2O_3 of 0.09 wt%) points to a garnet-free paragenesis; alternatively a very low geothermal gradient combined with formation at great depth (> 200 km) would be required.

Olivine

Nineteen inclusions were released from 15 diamonds, making olivine the most abundant inclusion phase at Cristal. The olivines, with a mode in Mg number at around 92.5 and an average of 92.8, match the distribution of olivine inclusions worldwide (Fig. 8). With one exception, CaO contents are below 0.04 wt% (Fig. 9, Table 4), implying a clinopyroxene-free harzburgitic (or dunitic) source. Olivine from CRI-205, with 0.06 wt% CaO, also shows the lowest Mg number (92.0) and may possibly be of lherzolitic paragenesis.

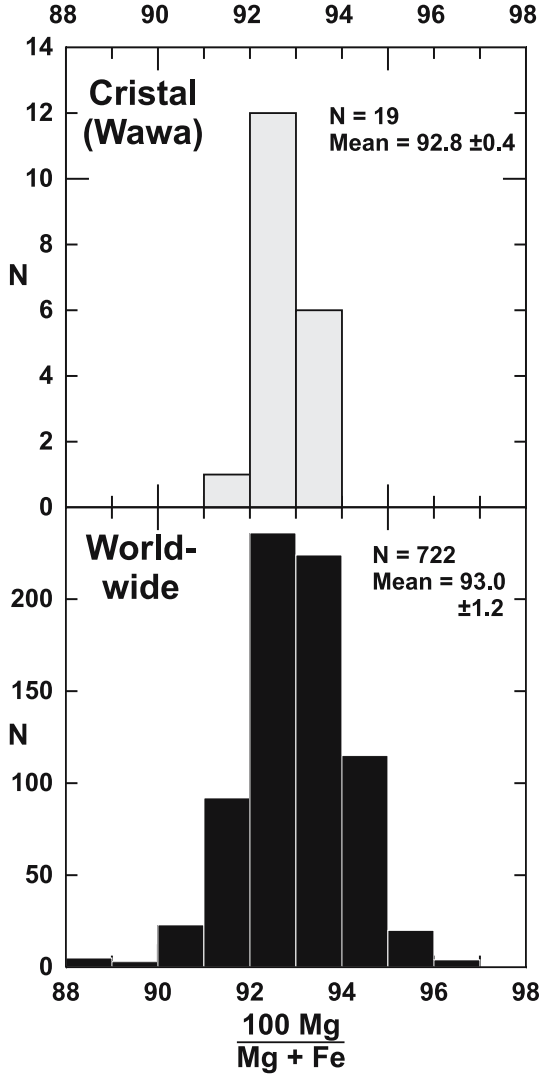

Fig. 8 Histogram of forsterite content for olivine inclusions in diamonds from Cristal and worldwide. Class size is 1 (i.e., the mode at 92.5 covers samples with Mg numbers between 92.0 and 93.0)

Mg-chromite

Four spinel inclusions were recovered from three diamonds (Table 5). The two Mg-chromites included in CRI-10 fall right in the middle of the worldwide database with respect to their FFM (molar $100Fe^{2+}$ / $[Fe^{2+} + Mg]$), Cr / Al and Fe^{3+} / Fe^{2+} ratio. The other two spinels have a lower FFM ratio (28.5 and 23.6) and significantly lower Cr number [100Cr / (Cr + Al) of 69.9 and 72.0], compared to CRI-10 (87.8–88.2). Based on

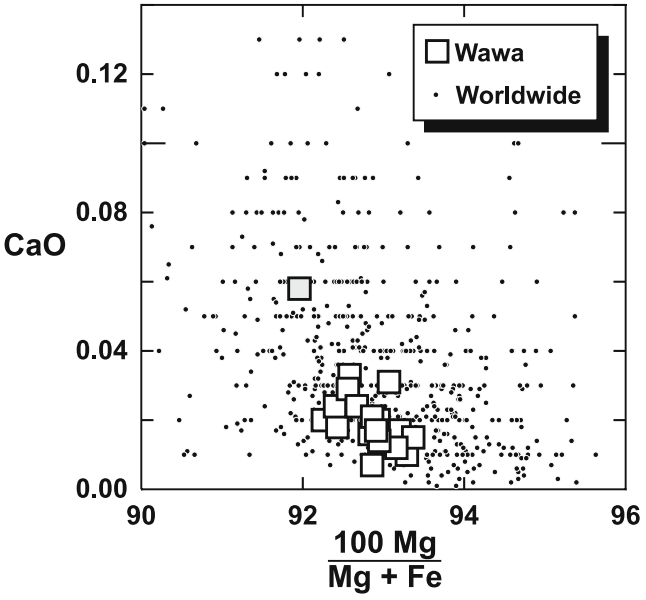

Fig. 9 Calcium content versus Mg number for olivine inclusions from Cristal and worldwide sources. Only one olivine from Cristal (*gray square*) contains high enough calcium to allow for possible equilibrium with clinopyroxene (i.e., a possible lherzolitic paragenesis), the rest (*white squares*) is so low in CaO that a harzburgitic/dunitic paragenesis is implied

Table 5 Analyses (EPMA) of oxide inclusions from Cristal

Mineral Sample 2	Mg-chr WW-10A	Mg-chr WW-10B	Mg-chr WW-11A	Mg-chr WW-201	Fe-chr WW-41
SiO_2	0.28	0.29	0.36	0.28	0.38
TiO_2	0.02	≤ 0.01	0.09	0.06	0.16
Al_2O_3	5.80	5.93	15.44	14.61	14.53
Cr_2O_3	64.54	63.87	53.53	55.90	50.09
V_2O_3	0.22	0.22	0.16	0.20	0.15
Fe_2O_3	3.03	3.92	4.37	3.46	1.29
FeO	11.89	11.04	9.09	10.97	28.73
MnO	0.26	0.25	0.23	0.25	1.62
NiO	0.10	0.09	0.12	0.12	0.11
MgO	13.65	14.26	16.49	15.47	1.56
ZnO	0.06	0.05	0.05	0.06	2.88
Na_2O	0.02	0.02	0.06	0.03	≤ 0.02
Total	99.87	99.95	100.00	101.43	101.51

experimental data on the distribution of Cr and Al between spinel and garnet (Doroshev et al. 1997), at the pressure and temperature conditions within the diamond stability field, such low Cr numbers imply a pyroxene and garnet-free source. Dunites can be under-saturated in silica to the extent that garnet is not stable anymore, allowing for the existence of Al-rich spinels outside the "spinel stability field". One of the Al-rich spinels contains detectable Na_2O (0.06 wt%), an unusual feature previously known only from two inclusions from the Venetia Mine (Aulbach 1999).

Geothermometry

In the few cases where two inclusions were recovered from the same diamond, it invariably was a compositionally homogenous (within error of EPMA analyses) pair of the same mineral species. Inclusion thermometry is thus restricted to the application of the Zn-in-spinel thermometer of Ryan et al. (1996). Calculated temperatures (Table 6) for four Mg-chromites range from 1,070 to 1,210°C with an average (based on the three host diamonds) of 1,140°C. This result coincides well with an average of 1,150°C obtained for Zn-in-spinel thermometry of Mg-chromite inclusions in diamonds worldwide (Stachel et al. 2003).

All three Mg-chromite bearing diamonds belong to a group of samples where nitrogen concentrations and aggregation states suggest mantle residence at temperatures around 1,250–1,300°C. Table 6 gives nitrogen-based temperatures for the three diamonds calculated for a range of residence times. Zn-in-spinel temperatures are systematically lower than nitrogen-based estimates but for sample CRI-201 alone this difference (Δ = 220°C at an assumed mantle residence of 500 Ma) clearly exceeds combined uncertainties derived from sample analyses (EPMA, FTIR) and the thermometers themselves. None of the spinel-bearing samples shows visible signs of plastic deformation (the diamonds are colorless and free of lamination lines) rendering possible acceleration of nitrogen aggregation during strain unlikely. Without putting much emphasis on the single sample CRI-201, the observation of generally higher nitrogen temperatures may indicate that mantle residence occurred at higher temperatures than diamond formation or reflect accelerated nitrogen B-center formation during transient heating events.

Discussion

The mineralogy and chemical composition of inclusions in diamonds from Cristal documents a common, exclusively peridotitic source, strongly dominated by harzburgite and probable dunite. Lherzolitic parageneses are virtually absent. Compositionally the inclusions fall within the normal ranges established for inclusions in diamonds worldwide. Garnet and olivine Mg numbers are lower than observed for the highly depleted diamond sources on the Kaapvaal (Stachel et al. 2003) but match inclusions from other cratons, including the Slave. The similarity to worldwide occurrences includes evidence for mantle metasomatism, such as a spinel inclusion with elevated Na content and a clinopyroxene with increased Ti, Al and Na. Although only available for three diamonds, Zn-in-spinel temperatures also coincide with the average conditions of diamond formation for worldwide sources. The only "unusual" observation is the presence of high-Cr garnets containing a small majorite component.

Origin and exhumation of Wawa diamonds

Lamprophyres and subduction zone diamonds

Presumed primary magmatic amphiboles (edenite, pargasite, Mg-hornblende; Lefebvre et al. 2003) at Wawa bear no resemblance to richteritic amphiboles occasionally associated with diamond occurrences. Whole rock chemical data suggest derivation from a calc-alkaline, basic magma (Lefebvre et al. 2005). Ayer and Wyman (2003) agree with this notion of Ca-alkaline (shoshonitic) lamprophyres as the magmatic component for the diamond-bearing rocks at Wawa but suggest hybridization of the primary magma with an (ultra)-mafic component similar to komatiite. Mineral and whole rock chemical data indicate hydrous melting of relatively shallow upper mantle sources (probably within the spinel peridotite field), compatible with a convergent margin setting (Wyman and Kerrich 1993; Ayer and

Table 6 Zinc content and zinc-in-spinel and nitrogen-in-diamond (for a range of mantle residence times from 100 to 1,000 MA) temperatures for three Mg-chromite bearing diamonds from Cristal

Sample	ZnO (wt%)	T-Zn (°C)	T-N (0.1 Ga; °C)	T-N (0.5 Ga; °C)	T-N (1 Ga; °C)
CRI-10a	0.058 ± 0.008	1,120 ± 70	1,260	1,220	1,200
CRI-10b	0.052 ± 0.003	1,180 ± 40	1,260	1,220	1,200
CRI-11	0.049 ± 0.006	1,210 ± 70	1,270	1,230	1,210
CRI-201	0.064 ± 0.004	1,070 ± 40	1,340	1,290	1,270

For Zn analyses five spots per sample were averaged; errors (1 sigma) are derived from the variance among individual spots and thus are purely a measure of the analytical precision of EPMA analyses

Wyman 2003; Lefebvre et al. 2005). This likely shallow origin of the primary magmas at Wawa appears to be at odds with their diamond-bearing nature. Ayer and Wyman (2003) point to the supposedly subduction-related diamond occurrences in eastern Australia as a precedent for a relatively shallow mantle origin. Based on a detailed study of diamonds from alluvial showings in New South Wales, Griffin et al. (2000) proposed diamond formation in the cool upper portions of subducting slabs that enter the diamond stability field at shallow depth of about 100 km. Storage of diamonds at this shallow depth is precluded by thermal re-equilibration with the surrounding mantle that drives the slabs back into the graphite stability field within about 10–35 Ma (Griffin et al. 2000). As a consequence, to avoid graphitization the diamonds must be exhumed directly after their formation, either through a detachment-obduction process without heating or through entrainment in a rapidly ascending magma.

To assess the proposed subduction origin of diamonds in the Abitibi–Wawa greenstone belts (Ayer and Wyman 2003; Lefebvre et al. 2003), the feasibility of diamond formation at low temperatures within slabs needs to be evaluated. If external carbon sources are excluded then two possible processes have to be considered in such a scenario: (1) carbon present in the form of carbonates may form diamond via a reduction process; (2) graphite derived from subducted organic matter could directly convert to diamond.

With carbonate minerals being thermally stable in descending slabs till the onset of partial melting (Yaxley and Green 1994; Wood et al. 1996) a reduction process cannot be linked with decarbonation reactions (i.e., cannot entail CO_2) but has to involve a solid carbonate phase. Based on experimental data and a thermodynamic analysis of the system $CaCO_3$–FeO–H_2O, Scott et al. (2004) showed that carbonate reduction at low temperatures (500°C, 1–80 kbar) directly leads to methane-bearing equilibria without involving the presence of native carbon (graphite or diamond).

Diamond formation through direct conversion from graphite is plausible but in order to create shallow subduction-related diamonds the conversion has to occur almost immediately after a slab enters the diamond stability field. Diamond formation proceeds via puckering of graphite bonds and may require martensitic transitions, depending on the type of stacking of layers within graphite (Sung 2000). Activation energies are exceedingly high and, therefore, in a static compression process require overstepping of the graphite–diamond transition by > 30 kbar, aided by high temperatures (≫ 1,000°C; Sung 2000). Shearing, a process likely to occur in subducting slabs, may aid the martensitic transition from hexagonal to rhombohedral graphite and reduce the required overstepping of the graphite–diamond transition. Nevertheless, conversion of graphite to diamond at 100 km depth and temperatures of about 500°C seems unlikely. In addition, the kinetically caused overstepping of the transition suggests that the conversion will occur instantaneously (catastrophic) resulting in microscopic crystallites rather than well-developed octahedral diamonds. Experiments by Irifune et al. (2004) simulated the graphite–diamond transition in descending slabs and showed it to occur under conditions corresponding to the deep upper mantle and transition zone with diamonds forming as polycrystalline aggregates. In conclusion, although cold portions of subducting oceanic plates may encounter the graphite–diamond transition at depth of only 100 km it appears highly unlikely that diamond formation takes place before the descending slabs penetrate deep into the upper mantle.

Evidence for a cratonic origin

The mineralogy and the chemically depleted harzburgitic composition of inclusions from Cristal match the characteristics established for typical cratonic diamond deposits around the world (Meyer 1987; Gurney 1989; Harris 1992). High-Cr garnets are a hallmark of cratonic peridotites (e.g., Sobolev 1977; Gurney 1984; Griffin et al. 1999) and relate to chemical depletion during partial melting of a protolith in the spinel stability field (Stachel et al. 1998; Grütter 2001). The bulk rock Cr–Al ratio cannot be efficiently changed during partial melting or cumulate formation in the garnet stability field (Stachel et al. 1998 and references therein), making the presence of high-Cr garnets at Genesis crucial evidence against a plume origin of their diamond source. High-Cr garnets may form in highly depleted oceanic mantle lithosphere subducting into the garnet stability field. For Wawa the thermal history of inclusions and host diamonds precludes a subduction scenario directly preceding exhumation. The average temperature of diamond formation obtained from three spinel-bearing diamonds (1,140°C) matches the mean for cratonic diamonds worldwide, suggesting formation under ''normal'' conditions along a cratonic mantle geotherm. Formation in a slab immediately followed by exhumation also is inconsistent with the nitrogen characteristics observed for Genesis and Cristal. If mantle residence of the diamonds had been restricted to a short period in a ''cold'' slab environment then the presence of single substitutional N in form of the C-center (Type Ib diamonds) would be expected (Taylor et al. 1996b). Diamonds with short mantle residence times (< 1 Ma), e.g., from the komatiitic occurrences in the Dachine region of French Guiana (Capdevila et al. 1999; Magee and Taylor 1999), typically classify as mixed Type Ib–IaA, i.e., show incomplete aggregation from the C- to the A-center. Genesis diamonds are Type IaA and for some nitrogen-poor diamonds from Cristal aggregation proceeded even to fully aggregated Type IaB diamonds, suggesting a deep lithospheric section and mantle residence over tens to hundreds of millions of years. The possible accelerating effect that transient heating events and plastic deformation may have had on nitrogen aggregation does

not affect the principal conclusion that formation of Wawa diamonds in a cold subducting slab briefly before exhumation is not viable. We thus have to conclude that a typical section of subcratonic lithospheric mantle extending into the stability field of majoritic garnet (possibly as deep as 300 km) existed beneath the Wawa subprovince even before cratonization of the Superior Province in the course of the Kenoran orogeny was completed. Following the model that final cratonization of the Slave Province occurred only at about 2.58 Ga with the termination of the late "granite bloom" (Davis et al. 2003; Bleeker 2003), a similar situation appears to apply for the Lac de Gras area, where diamond formation at about 3.41 ± 0.28 Ga (Westerlund et al. 2003, Re–Os dating of sulfide inclusions) and residence in cool cratonic lithosphere (Stachel et al. 2003) preceded final cratonization by almost 1 Ga.

Possible mechanisms for exhumation

A primary origin of Wawa diamonds in deep lithospheric mantle and their crustal occurrence within volcaniclastic rocks and intrusive lamprophyres leaves two alternative scenarios for their exhumation:

1. The relationship of Wawa diamonds to their volcanic host rocks is purely accidental. The observation that significant diamond grades are restricted to the base of volcaniclastic sequences (Walker et al., in preparation) appears to support this notion. Low diamond grades in lamprophyre dikes may have been picked up from diamondiferous country rocks. The fine skewed size distribution of Wawa diamonds may thus reflect a sedimentary sorting process. However, the absence of surface features reflecting extended transport on the Earth's surface is difficult to reconcile with an interpretation as placer deposits. Short transport distances may explain the absence of percussion and abrasion features but during active deposition of supracrustal rocks (Catfish assemblage) exhumation of old primary diamond deposits close by is not feasible. In consequence, if the diamonds were derived from erosion of nearby "kimberlites", then volcanic emplacement would need to be penecontemporaneous with the lamprophyric activity and had to occur in a convergent margin setting. A placer origin of Wawa diamonds is thus unlikely.
2. If the Ca-alkaline (shoshonitic) volcanics at Wawa indeed represented the volcanic host rock, then a two-stage exhumation process would be required, since such magmas are not derived from depth that would allow them to sample diamonds containing majoritic garnet inclusions (i.e., 250–300 km deep). A magma mixing model is not preferred, since Wawa diamonds (including the study of Lefebvre et al. 2003) are only mildly resorbed whereas mixing with and continued transport in a hydrous lamprophyric magma should have caused extensive resorption and etching. Alternatively, diamondiferous peridotitic lithosphere may have been delivered directly to the magma source. Detachment and upward transport of diamondiferous lithosphere would need to occur rapidly, to preserve diamonds and to prevent exsolution of pyroxene from majoritic inclusions. Exhumation of peridotite complexes remaining in garnet facies (e.g., Alpe Arami, Brenker and Brey 1997) and the diamondiferous crustal rocks at Kokchetav and Dabie Shan (e.g., Ernst and Liou 1999) provide evidence that rapid upward transport may occur. In such a scenario the diamonds may have been released from entrained peridotite into the lamprophyric magma only near the surface. This could explain the low degree of resorption and would suggest a link to the common ultramafic inclusions at Wawa (as suggested by Vaillancourt et al. 2004). Problematic with this exhumation mechanism is that it would have been unique in Earth history as no other cases of significantly diamond-bearing volcanics of presumed shallow origin have been established so far.

The exhumation mechanism for Wawa diamonds and the origin of these deformed and metamorphosed deposits thus remain enigmatic.

Conclusions

Diamonds from Archean metavolcanic rocks at Wawa (Genesis and Cristal showings) have nitrogen characteristics and carbon isotopic compositions that are not in support of a proposed derivation from a subducting slab (Ayer and Wyman 2003; Lefebvre et al. 2003). Syngenetic mineral inclusions in diamonds from Cristal provide a perfect match to harzburgitic inclusion suites from cratonic diamond deposits worldwide. Including the presence of mildly majoritic high-Cr garnets, Wawa diamonds document the existence of a thick package of depleted lithospheric mantle already before stabilization of the Superior Province during the Kenoran orogeny was completed. The presence of a thick mantle lithosphere supports the autochthonous formation of the Aibitbi–Wawa greenstone belt proposed by Thurston (2002).

Presupposing that the composition of the subcratonic lithosphere is not static but evolves over time, the observation that proven Archean diamonds from Wawa are a perfect compositional match to isotopically dated Archean diamonds of harzburgitic paragenesis (but residing in the Earth's mantle for several more billion years) backs the notion that isotopic dating of inclusions yields diamond formation ages.

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References

Akaogi M, Akimoto S (1977) Pyroxene–garnet solid-solution equilibria in the systems $Mg_4Si_4O_{12}$–$Mg_3Al_2Si_3O_{12}$ and $Fe_4Si_4O_{12}$–$Fe_3Al_2Si_3O_{12}$ at high pressures and temperatures. Phys Earth Planet Inter 15:90–106

Appleyard CM, Viljoen KS, Dobbe R (2004) A study of eclogitic diamonds and their inclusions from the Finsch kimberlite pipe, South Africa. Lithos 77(1–4):317–332

Aulbach S (1999) The chemistry of syngenetic mineral inclusions in diamonds from Venetia and the stable isotope composition of diamonds from Mwadui and the Kankan district. MSc thesis, J.W. Goethe University, 104 pp

Ayer JA, Wyman DA (2003) Origin of diamondiferous Archean Lamprophyres in the evolution of the Michipicoten and Abitibi greenstone belts. In: Extended abstracts of the eighth international kimberlite conference, Victoria, BC, Canada, 5 pp (CD, not paginated)

Bleeker W (2003) The late Archean record: a puzzle in ca. 35 pieces. Lithos 71(2–4):99–134

Boyd SR, Mattey DP, Pillinger CT, Milledge HJ, Mendelssohn M, Seal M (1987) Multiple growth events during diamond genesis: an integrated study of carbon and nitrogen isotopes and nitrogen aggregation state in coated stones. Earth Planet Sci Lett 86(2–4):341–353

Boyd SR, Kiflawi I, Woods GS (1994) The relationship between infrared absorption and the A defect concentration in diamond. Philos Mag B 69(6):1149–1153

Boyd SR, Kiflawi I, Woods GS (1995) Infrared absorption by the B nitrogen aggregate in diamond. Philos Mag B 72(3):351–361

Brenker FE, Brey GP (1997) Reconstruction of the exhumation path of the Alpe Arami garnet-peridotite body from depths exceeding 160 km. J Metamorphic Geol 15:581–592

Capdevila R, Arndt N, Letendre J, Sauvage JF (1999) Diamonds in volcaniclastic komatiite from French Guiana. Nature 399(6735):456–458

Cartigny P, Stachel T, Harris JW, Javoy M (2004) Constraining diamond metasomatic growth using C- and N-stable isotopes: examples from Namibia. Lithos 77(1–4):359–373

Davies RM, Griffin WL, O'Reilly SY, Andrew AS (2003) Unusual mineral inclusions and carbon isotopes of alluvial diamonds from Bingara, eastern Australia. Lithos 69(1–2):51–66

Davies RM, Griffin WL, O'Reilly SY, Doyle BJ (2004a) Mineral inclusions and geochemical characteristics of microdiamonds from the DO27, A154, A21, A418, DO18, DD17 and Ranch Lake kimberlites at Lac de Gras, Slave Craton, Canada. Lithos 77(1–4):39–55

Davies RM, Griffin WL, O'Reilly SY, McCandless TE (2004b) Inclusions in diamonds from the K14 and K10 kimberlites, Buffalo Hills, Alberta, Canada: diamond growth in a plume? Lithos 77(1–4):99–111

Davis WJ, Jones AG, Bleeker W, Grütter H (2003) Lithosphere development in the Slave craton: a linked crustal and mantle perspective. Lithos 71:575–589

Deines P (2002) The carbon isotope geochemistry of mantle xenoliths. Earth Sci Rev 58(2002):247–278

Deines P, Harris JW (2004) New insights into the occurrence of C-13-depleted carbon in the mantle from two closely associated kimberlites: Letlhakane and Orapa, Botswana. Lithos 77(1–4):125–142

Doroshev AM, Brey GP, Girnis AV, Turkin AI, Kogarko LN (1997) Pyrope-knorringite garnets in the earths mantle: experiments in the MgO–Al_2O_3–SiO_2–Cr_2O_3 system. Geol Geofiz 38(2):523–545

Ernst WG, Liou JG (1999) Overview of UHP metamorphism and tectonics in well-studied collisional orogens. Int Geol Rev 41(6):477–493

Evans T, Harris JW (1989) Nitrogen aggregation, inclusion equilibration temperatures and the age of diamonds. In: Ross J et al (eds) Kimberlites and related rocks. GSA Spec Publ 14, vol 2. Blackwell, Carlton, pp 1001–1006

Griffin WL, O'Reilly SY, Ryan CG (1999) The composition and origin of subcontinental lithospheric mantle. In: Fei Y, Bertka CM, Mysen BO (eds) Mantle petrology: field observations and high pressure experimentation: a tribute to Francis R. (Joe) Boyd. The Geochemical Society, Houston, pp 13–45

Griffin WL, O'Reilly SY, Davies RM (2000) Subduction-related diamond deposits? Constraints, possibilities, and new data from Eastern Australia. Rev Econ Geol 11:291–310

Griffin WL, Win TT, Davies R, Wathanakul P, Andrew A, Metcalfe I, Cartigny P (2001) Diamonds from Myanmar and Thailand: characteristics and possible origins. Econ Geol 96(1):159–170

Grütter HS (2001) The genesis of high Cr/Al garnet peridotite, with implications for cratonic crust–mantle architecture. In: The Slave–Kaapvaal workshop, Merrickville, Ontario, 3 pp

Gurney JJ (1984) A correlation between garnets and diamonds in kimberlites. In: Glover JE, Harris PG (eds) Kimberlite occurrence and origin; a basis for conceptual models in exploration, vol 8. Geology Department & University Extension, University of Western Australia, pp 143–166

Gurney JJ (1989) Diamonds. In: Ross J et al (eds) Kimberlites and related rocks. GSA Spec Publ 14, vol 2. Blackwell, Carlton, pp 935–965

Gurney JJ, Harris JW, Rickard RS (1984) Silicate and oxide inclusions in diamonds from the Orapa Mine, Botswana. In: Kornprobst J (ed) Kimberlites II: the mantle and crust–mantle relationships. Elsevier, Amsterdam, pp 3–9

Harris JW (1992) Diamond geology. In: Field JE (ed) The properties of natural and synthetic diamond, vol 345–393. Academic, London, pp 345–393

Harris JW, Stachel T, Leost I, Brey GP (2004) Peridotitic diamonds from Namibia: constraints on the composition and evolution of their mantle source. Lithos 77(1–4):209–223

Hoffman PF (1989) Precambrian geology and tectonic history of North America. In: Bally AW, Palmer AR (eds) The geology of North America—an overview, vol A. The Geological Society of America, Boulder, pp 447–511

Irifune T (1987) An experimental investigation of the pyroxene–garnet transformation in a pyrolite composition and its bearing on the constitution of the mantle. Phys Earth Planet Inter 45(4):324–336

Irifune T, Hibberson WO, Ringwood AE (1989) Eclogite–garnetite transformation at high pressure and its bearing on the occurrence of garnet inclusions in diamond. In: Ross J et al (eds) Kimberlites and related rocks. GSA Spec Publ 14, vol 2. Blackwell, Carlton, pp 877–882

Irifune T, Kurio A, Sakamoto S, Inoue T, Sumiya H, Funakoshi K (2004) Formation of pure polycrystalline diamond by direct conversion of graphite at high pressure and high temperature. Phys Earth Planet Inter 143–144:593–600

Kaminsky FV, Zakharchenko OD, Khachatryan GK, Shiryaev AA (2001) Diamonds from the Coromandel Area, Minas Gerias, Brazil. Rev Bras Geoci 31(4):583–596

Kirkley MB, Gurney JJ, Otter ML, Hill SJ, Daniels LR (1991) The application of C isotope measurements to the identification of the sources of C in diamonds: a review. Appl Geochem 6(5):477–494

Leahy K, Taylor WR (1997) The influence of the Glennie domain deep structure on the diamonds in Saskatchewan kimberlites. Geol Geofiz 38(2):451–460

Lefebvre N, Kopylova M, Kivi K, Barnett RL (2003) Diamondiferous volcaniclastic debris flows of Wawa, Ontario, Canada. In: Eighth international kimberlite conference, Victoria, BC, Canada, 5 pp (CD, pot paginated)

Lefebvre N, Kopylova M, Kivi K (2005) Archean calc-alkaline lamprophyres of Wawa, Ontario, Canada: unconventional diamondiferous volcaniclastic rocks. Precambrian Res 138(1–2):57–87

Leost I, Stachel T, Brey GP, Harris JW, Ryabchikov ID (2003) Diamond formation and source carbonation: mineral associations in diamonds from Namibia. Contrib Mineral Petrol 145(1):15–24

Logvinova AM, Zedgenizov DA, Sobolev NV (2001) Pyroxenite paragenesis of abundant mineral and probable fluid inclusions in microdiamonds from the Mir kimberlite pipe, Yakutia. Dokl Earth Sci 380(7):795–799

Magee CW, Taylor WR (1999) Diamond and chromite geochemical constraints on the nature of the Dachine complex, French Guiana. In: Experimental Petrology Group, annual report 1999, Research School of Earth Sciences, ANU, Canberra, 1 p

Mc Kenna N, Gurney JJ, Klump J, Davidson JM (2004) Aspects of diamond mineralisation and distribution at the Helam Mine, South Africa. Lithos 77(1–4):193–208

Meyer HOA (1987) Inclusions in diamond. In: Nixon PH (ed) Mantle xenoliths. Wiley, Chichester, pp 501–522

Navon O (1999) Diamond formation in the Earth's mantle. In: Gurney JJ, Gurney JL, Pascoe MD, Richardson SH (eds) The P.H. Nixon volume, Proceedings of the VII international kimberlite conference, Red Roof Design, Cape Town, pp 584–604

Navon O, Hutcheon ID, Rossman GR, Wasserburg GJ (1988) Mantle-derived fluids in diamond micro-inclusions. Nature 335(6193):784–789

Orlov YL (1977) The mineralogy of the diamond. Wiley, New York, p 235

Pearson DG, Shirey SB, Bulanova GP, Carlson RW, Milledge HJ (1999) Re–Os isotope measurements of single sulfide inclusions in a Siberian diamond and its nitrogen aggregation systematics. Geochim Cosmochim Acta 63(5):703–711

Phillips D, Harris JW, Viljoen KS (2004) Mineral chemistry and thermobarometry of inclusions from De Beers Pool diamonds, Kimberley, South Africa. Lithos 77(1–4):155–179

Pokhilenko NP, Sobolev NV, Reutsky VN, Hall AE, Taylor LA (2004) Crystalline inclusions and C isotope ratios in diamonds from the Snap Lake/King Lake kimberlite dyke system: evidence of ultradeep and enriched lithospheric mantle. Lithos 77(1–4):57–67

Poujol M, Robb LJ, Anhaeusser CR, Gericke B (2003) A review of the geochronological constraints on the evolution of the Kaapvaal Craton, South Africa. Precambrian Res 127(1–3):181–213

Promprated P, Taylor LA, Anand M, Floss C, Sobolev NV, Pokhilenko NP (2004) Multiple-mineral inclusions in diamonds from the Snap Lake/King Lake kimberlite dike, Slave craton, Canada: a trace-element perspective. Lithos 77(1–4):69–81

Richardson SH, Gurney JJ, Erlank AJ, Harris JW (1984) Origin of diamonds in old enriched mantle. Nature 310(5974):198–202

Richardson SH, Erlank AJ, Harris JW, Hart SR (1990) Eclogitic diamonds of Proterozoic age from Cretaceous kimberlites. Nature 346(6279):54–56

Richardson SH, Harris JW, Gurney JJ (1993) Three generations of diamonds from old continental mantle. Nature 366(6452):256–258

Ringwood AE (1967) The pyroxene–garnet transformation in the Earth's mantle. Earth Planet Sci Lett 2(3):255–263

Ringwood AE, Major A (1971) Synthesis of majorite and other high pressure garnets and perovskites. Earth Planet Sci Lett 12:411–418

Robinson DN (1979) Surface textures and other features of diamonds. PhD thesis, University of Cape Town, Cape Town (South Africa), vol 1: 221 pp, vol 2: 161 pp

Ryan CG, Griffin WL, Pearson NJ (1996) Garnet geotherms—pressure–temperature data from Cr-pyrope garnet xenocrysts in volcanic rocks. J Geophys Res 101(B3):5611–5625

Sage RP, Lightfoot PC, Doherty W (1996) Bimodal cyclical Archean basalts and rhyolites from the Michipicoten (Wawa) greenstone belt, Ontario: geochemical evidence for magma contributions from the asthenospheric mantle and ancient continental lithosphere near the southern margin of the Superior Province. Precambrian Res 76(3–4):119–153

Scott HP, Hemley RJ, Mao HK, Herschbach DR, Fried LE, Howard WM, Bastea S (2004) Generation of methane in the Earth's mantle: in situ high pressure–temperature measurements of carbonate reduction. Proc Natl Acad Sci USA 101(39):14023–14026

Shirey SB, Harris JW, Richardson SH, Fouch MJ, James DE, Cartigny P, Deines P, Viljoen F (2002) Diamond genesis, seismic structure, and evolution of the Kaapvaal-Zimbabwe craton. Science 297(5587):1683–1686

Sobolev NV (1977) Deep-seated inclusions in kimberlites and the problem of the composition of the upper mantle. Translated from the Russian edition, 1974. AGU, Washington, p 279

Sobolev NV, Lavrent'ev YG, Pokhilenko NP, Usova LV (1973) Chrome-rich garnets from the kimberlites of Yakutia and their paragenesis. Contrib Mineral Petrol 40(1):39–52

Sobolev NV, Logvinova AM, Zedgenizov DA, Yefimova ES, Lavrent'ev YG, Usova LV (2000) Anomalously high Ni admixture in olivine inclusions from microdiamonds, the Yubileinaya Kimberlite pipe, Yakutia. Dokl Earth Sci 375(9):1403–1406

Sobolev NV, Logvinova AM, Zedgenizov DA, Seryotkin YV, Yefimova ES, Floss C, Taylor LA (2004) Mineral inclusions in microdiamonds and macrodiamonds from kimberlites of Yakutia: a comparative study. Lithos 77(1–4):225–242

Spetsius ZV, Belousova EA, Griffin WL, O'Reilly SY, Pearson NJ (2002) Archean sulfide inclusions in Paleozoic zircon megacrysts from the Mir kimberlite, Yakutia: implications for the dating of diamonds. Earth Planet Sci Lett 199(1–2):111–126

Stachel T, Viljoen KS, Brey G, Harris JW (1998) Metasomatic processes in lherzolitic and harzburgitic domains of diamondiferous lithospheric mantle: REE in garnets from xenoliths and inclusions in diamonds. Earth Planet Sci Lett 159(1–2):1–12

Stachel T, Brey GP, Harris JW (2000) Kankan diamonds (Guinea) I: from the lithosphere down to the transition zone. Contrib Mineral Petrol 140:1–15

Stachel T, Harris JW, Tappert R, Brey GP (2003) Peridotitic diamonds from the Slave and the Kaapvaal cratons—similarities and differences based on a preliminary data set. Lithos 71(2–4):489–503

Stachel T, Blackburn L, Kurszlaukis S, Barton E, Walker EC (2004a) Diamonds from the Cristal and Genesis volcanics, Wawa area, Ontario. In: Abstracts of the 32nd annual Yellowknife geoscience forum, Yellowknife, NWT, Canada, pp 74–75

Stachel T, Viljoen KS, McDade P, Harris JW (2004b) Diamondiferous lithospheric roots along the western margin of the Kalahari Craton—the peridotitic inclusion suite in diamonds from Orapa and Jwaneng. Contrib Mineral Petrol 147(1):32–47

Stott GM (1997) The Superior Province, Canada. In: de Wit MJ, Ashwal LD (eds) Greenstone belts. Clarendon Press, Oxford, pp 480–507

Sung J (2000) Graphite $\rightarrow$ diamond transition under high pressure: a kinetics approach. J Mater Sci 35(23):6041–6054

Tappert R, Stachel T, Harris JW, Shimizu N, Brey GP (2005) Mineral inclusions in diamonds from the Panda kimberlite, Slave Province, Canada. Eur J Mineral 17(3):423–440

Taylor WR, Jaques AL, Ridd M (1990) Nitrogen-defect aggregation characteristics of some Australasian diamonds: time–temperature constraints on the source regions of pipe and alluvial diamonds. Am Mineral 75(11–12):1290–1310

Taylor WR, Bulanova GP, Milledge HJ (1995) Quantitative nitrogen aggregation study of some Yakutian diamonds: constraints on the growth, thermal and deformation history of

peridotitic and eclogitic diamonds. In: Sixth international kimberlite conference, Novosibirsk, Russia, pp 608–610
Taylor LA, Snyder GA, Crozaz G, Sobolev VN, Yefimova ES, Sobolev NV (1996a) Eclogitic inclusions in diamonds: evidence of complex mantle processes over time. Earth Planet Sci Lett 142(3–4):535–551
Taylor WR, Canil D, Milledge HJ (1996b) Kinetics of Ib to IaA nitrogen aggregation in diamond. Geochim Cosmochim Acta 60(23):4725–4733
Thurston PC (2002) Autochthonous development of Superior Province greenstone belts? Precambrian Res 115(1–4):11–36
Turek A, Smith PE, Vanschmus WR (1984) U–Pb zircon ages and the evolution of the Michipicoten plutonic volcanic terrane of the Superior Province, Ontario. Can J Earth Sci 21(4):457–464
Turek A, Sage RP, Vanschmus WR (1992) Advances in the U–Pb zircon geochronology of the Michipicoten greenstone-belt, Superior Province, Ontario. Can J Earth Sci 29(6):1154–1165
Vaillancourt C, Ayer JA, Zubowski SM, Kamo SL (2004) Synthesis and timing of Archean geology and diamond-bearing rocks in the Michipicoten greenstone belt: Menzies and Musquash townships. Summary of field work and other activities 2004, Ontario Geological Survey, Open file report 6145, pp 6.1–6.9
Wang WY, Sueno S, Takahashi E, Yurimoto H, Gasparik T (2000) Enrichment processes at the base of the Archean lithospheric mantle: observations from trace element characteristics of pyropic garnet inclusions in diamonds. Contrib Mineral Petrol 139(6):720–733
Westerlund K, Shirey SB, Richardson SH, Gurney JJ, Harris JW (2003) Re–Os isotope systematics of peridotitic diamond inclusion sulfides from the Panda kimberlite, Slave Craton. In: Extended abstracts of the eighth international kimberlite conference, Victoria, BC, Canada, 5 pp (CD, not paginated)
Williams HR, Stott GM, Heather KB, Muir TL, Sage RP (1991) Wawa Subprovince. In: Geology of Ontario, Special volume 4. Ontario Geological Survey, Sudbury, pp 485–539
Wilson AC (2004) Diamond exploration targets, Michipicoten greenstone belt. CIM Bull 97(1077):41–46
Wood BJ, Pawley A, Frost DR (1996) Water and carbon in the Earth's mantle. Philos Trans R Soc Lond Ser A Math Phys Eng Sci 354(1711):1495–1511
Wyman DA, Kerrich R (1993) Archean shoshonitic lamprophyres of the Abitibi Subprovince, Canada—petrogenesis, age, and tectonic setting. J Petrol 34(6):1067–1109
Wyman DA, Kerrich R, Polat A (2002) Assembly of Archean cratonic mantle lithosphere and crust: plume–arc interaction in the Abitibi–Wawa subduction–accretion complex. Precambrian Res 115(1–4):37–62
Yamaoka S, Komatsu H, Kanda H, Setaka N (1977) Growth of diamond with rhombic dodecahedral faces. J Cryst Growth 37(3):349–352
Yaxley GM, Green DH (1994) Experimental demonstration of refractory carbonate-bearing eclogite and siliceous melt in the subduction regime. Earth Planet Sci Lett 128(3–4):313–325