



# Multiple-mineral inclusions in diamonds from the Snap Lake/King Lake kimberlite dike, Slave craton, Canada: a trace-element perspective

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## Abstract

Multiple inclusions of minerals in diamonds from the Snap Lake/King Lake kimberlites of the southeastern Slave craton in Canada have been analyzed for trace elements to elucidate the petrogenetic history of these inclusions, and of their host diamonds. As observed worldwide, the harzburgitic-garnet diamond inclusions (DIs) possess sinusoidal REE patterns that indicate an early depletion event, followed by metasomatism by LREE-enriched, HREE-depleted fluids. Furthermore, these fluids appear to contain appreciable concentrations of LILE and HFSE, based on the increasing abundances of these elements in the olivine inclusion that occurs at the outer portion of a diamond compared to that near the core. The compositions of these fluids are probably a mixture of hydrous-silicic melt, carbonatitic melt, and brine, similar to the compositions of micro-inclusions in diamonds reported by Navon et al. (2003). Comparison between the compositions of majoritic and normal harzburgitic garnets shows that the former are more depleted in terms of major/minor elements (higher Cr#) but significantly more enriched in the REE (up to  $\sim 10\times$ ). This characteristic may indicate the higher susceptibility for metasomatic enrichment of previously more depleted garnets. Garnets of eclogitic paragenesis show strong LREE-depleted patterns, whereas the coexisting omphacite inclusion has relatively flat light- and middle-REE but depleted HREE. Whole-rock reconstruction from coexisting garnet and omphacite inclusions indicates that the protolith of these inclusions was probably the extrusive section of an oceanic crust, subducted beneath the Slave craton.

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## 1. Introduction

Mineral inclusions in diamonds are generally accepted to be pristine samples of the mantle, because

they are protected from retrograde reactions and re-equilibration with the surrounding environment by the extremely strong and chemically inert host diamonds. Unraveling the petrogenetic history of diamond inclusions (DIs) is crucial to understanding the processes involved in diamond formation, as well as the evolution of the mantle beneath a craton. Understanding of the nature of the mantle beneath the Slave craton,

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Northwest Territories, Canada, was limited in the past largely because of lack of direct samples from the mantle. Within the last decade, however, the Slave craton has become the “epicenter” of diamond exploration and mining, including a series of kimberlite dikes; one such dike is highly diamondiferous (Pokhilenko et al., 1998; Carlson et al., 1999). This Snap Lake/King Lake diamondiferous dike has been dated at approximately 540 Ma (Agashev et al., 2001). Limited data on diamonds and diamond inclusions from this kimberlite dike have been presented by Pokhilenko et al. (2001, 1998, 2000).

Pokhilenko et al. (in press) summarize, in a companion paper, the present state of knowledge on Snap Lake/King Lake (SKL) diamonds, their carbon isotope composition, the nature of inclusions in these diamonds (DIs), and their major- and minor-element chemistry. From this DI suite, we have selected for detailed trace-element study those inclusions that were recovered as multiple inclusions by the burning of 11 diamonds. In addition, we present new major- and trace-element data of DIs analyzed in situ on polished surfaces of selected diamonds. This investigation is an attempt to provide new insights into diamond petrogenesis and the nature of the mantle beneath the SE Slave craton.

## 2. Analytical methods

Mineral inclusions were liberated from diamonds both by crushing and burning, as well as by polishing host diamonds exposing inclusions. Twenty-four inclusions (10 garnet—Gt; 4 clinopyroxene—Cpx; 10 orthopyroxene—Opx) from the sample set described by Pokhilenko et al. (in press) were recovered by the “burning” technique. Fourteen additional olivine (Ol), Opx, and Cpx inclusions were examined from five diamonds using an in situ technique (Taylor et al., 2000). As shown earlier by Taylor et al. (1996) in a comparative study of pyroxene inclusions liberated both by diamond burning versus simply crushing, the pyroxene from different fragments of the same diamond showed no differences in major- and trace-element contents—i.e., the burning process did not modify the mineral composition. During the present study, inclusion grains released by burning, as well as minerals exposed on polished

surfaces of diamonds, were mounted in epoxy resin for analysis.

With the in situ technique, the diamonds were polished so as to expose the encapsulated inclusion(s) for analysis with EMP and ion microprobe. Cathodoluminescence (CL) images of the polished surfaces were initially obtained, in an attempt to correlate the inclusion chemistry with the growth features of diamonds. As observed in this study and in the companion paper Pokhilenko et al. (in press), most inclusions showed no petrographic or chemical signs of alteration—e.g., chemical zonation, as determined by electron microprobe analyses. We believe that the chemical characteristics of the DIs reported here are those at the instant of the diamond capture and encapsulation—i.e., the DIs are pristine.

Major-element compositions of DIs were determined with a fully automated CAMECA SX-50 electron microprobe at the University of Tennessee. The EMP analytical conditions employed an accelerating potential of 15 kV, 30-nA beam current, a 5- $\mu$ m beam size, and 20-s counting time. All data were corrected for matrix effects using the CAMECA PAP procedure.

Trace-element analyses of the diamond inclusions were performed with the modified CAMECA IMS-3f ion microprobe at Washington University. Details of the experimental procedures are described by Zinner and Crozaz (1986a,b), Fahey et al. (1987), Alexander (1994), and Hsu (1995). Detection limits are variable, depending on the element and phase being analyzed, but may be as low as a few ppb in favorable cases. The precision of the trace-element measurements is limited primarily by the number of counts obtained. Errors ( $1\sigma$ ) are generally less than 10%, but may range up to 50% for some of the REEs present in low concentrations.

## 3. Chemistry of the mineral inclusions

### 3.1. Garnet

Chondrite-normalized REE (rare earth element) concentrations of harzburgitic-garnet inclusions from two diamonds display sinusoidal patterns that peak at Nd and reach the minimum at Ho or Er (Fig. 1A). The

REE patterns are identical, within error, for garnets from the two individual diamonds. Some differences in the chemistry of garnets from these two diamonds should be noted. First, the garnet inclusions in dia-

mond SL3-31/00 contain significant majoritic components as much as 3.072 pfu Si (Table 1), corresponding to the pressure of around 8 GPa (Irifune, 1987), which suggests the greater depth of origin of this diamond compared to diamond SL3-3/00, whose garnet has no discernable Si excess. Second, garnets in SL3-31/00 diamond are distinctly more enriched in the REEs (up to an order of magnitude), compared to those in SL3-3/00. Third, the REE-elevated garnets in the former are also Cr-rich, with the Cr# (100Cr/Cr + Al) around 40 compared to ~34 in garnets from the latter diamond (Table 1). Moreover, both LILE and HFSE of garnets in diamond SL3-31/00 are noticeably higher, with an exception for Ba in one inclusion (Fig. 1B).

The REE patterns of the multiple eclogitic-garnet inclusions from diamond SL5-6/00 display a strong depletion in LREEs (Fig. 1C), all with identical REE patterns, within errors. Such LREE-depleted patterns are typical for low-Ca eclogitic-garnet DIs from other world localities (e.g., Taylor et al., 1996; Sobolev et al., 1998; Stachel et al., 2000).

### 3.2. Clinopyroxene

Four omphacitic clinopyroxenes were recovered from three Snap Lake/King Lake diamonds, one of which coexists with five eclogitic garnets in diamond SL5-6/00. Chondrite-normalized REE patterns of the Cpx inclusions are distinctly different between the two K<sub>2</sub>O-rich clinopyroxenes versus the two with low K<sub>2</sub>O: (1) the K<sub>2</sub>O-rich clinopyroxenes have a steeply LREE-enriched pattern with a hump at Pr, and (2) the K<sub>2</sub>O-poor pyroxenes have relatively flat light-middle REEs, with negative slopes towards the HREEs (Fig. 2). Similar correlations between the REE patterns and K<sub>2</sub>O contents have also been observed in the clino-

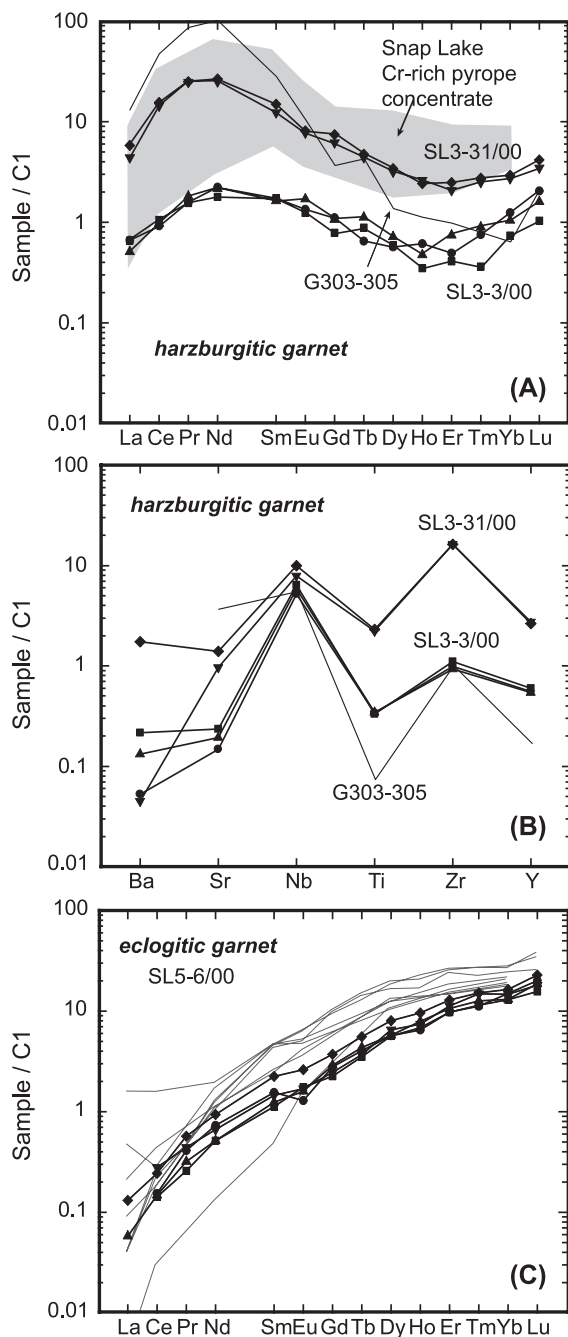


Fig. 1. Chondrite-normalized REE patterns of garnet DIs from the Snap/King Lake kimberlites. (A) The characteristic sinusoidal REE patterns of harzburgitic garnets. Notice the higher REE abundance in “majoritic” garnets (SL3-31/00), compared to the normal ones (SL3-3/00). A majoritic garnet diamond inclusion from Ghana (G303-305; Stachel and Harris, 1997) is also plotted for comparison. The shaded area represents the range of REE patterns of garnet concentrates from SKL kimberlites (Pokhilenko et al., 2001). (B) Plot of LILE and HFSE. (C) LREE-depleted patterns typical for low-Ca garnets. Lines represent DIs from Siberia (Taylor et al., 1996; Sobolev et al., 1998).

Table 1  
Trace-element compositions (ppm) of garnet and clinopyroxene diamond inclusions

Sample	SL3-3/00			SL3-31/00		SL5-6/00					SL3-32/00	SL5-52/00		SL5-6/00
Grain no.	1	2	3	35	36	112	113	114	115	116	39	91	92	117
Mineral	Gt	Gt	Gt	Gt	Gt	Gt	Gt	Gt	Gt	Gt	Cpx	Cpx	Cpx	Cpx
Paragenesis	harz	harz	harz	harz	harz	eclo	eclo	eclo	eclo	eclo	eclo	eclo	eclo	eclo
Sc	156	157	158	148	146	48.0	46.5	47.1	45.3	45.9	14.2	11.9	12.2	14.5
Ti	144	148	150	966	1001	2510	2167	2056	2177	2077	3030	2322	2286	2429
V	297	310	314	341	387	113	118	122	122	125	324	251	247	244
Sr	1.84	1.15	1.50	7.53	10.9	0.79	4.04	0.53	1.93	1.80	177	711	681	71.5
Y	0.93	0.86	0.84	4.29	4.14	15.0	13.2	12.5	13.3	11.8	3.84	3.62	3.02	3.91
Zr	4.32	3.89	3.65	64.0	64.1	28.7	17.1	16.0	17.2	15.9	16.3	13.0	9.58	14.8
Nb	1.58	1.28	1.44	1.94	2.45	0.20	0.17	0.098	0.21	0.19	0.18	0.31	0.18	0.50
Ba	0.50	0.12	0.31	0.11	4.06	0.17	1.25	0.097	6.31	2.42	5.14	11.7	4.54	11.0
La	0.15	0.16	0.12	1.03	1.36	0.031	n.d.	0.014	n.d.	n.d.	0.60	4.27	4.21	0.81
Ce	0.64	0.56	0.59	8.66	9.36	0.15	0.17	0.089	0.093	0.086	1.82	15.0	13.1	5.81
Pr	0.14	0.14	0.16	2.20	2.22	0.051	0.039	0.028	0.037	0.023	0.39	2.45	2.25	0.44
Nd	0.81	1.01	0.97	11.3	12.0	0.42	0.30	0.23	0.33	0.23	1.85	10.9	9.66	2.00
Sm	0.26	0.25	0.24	1.81	2.19	0.33	0.21	0.18	0.23	0.17	0.62	2.01	2.03	0.57
Eu	0.069	0.075	0.095	0.43	0.45	0.15	0.095	0.089	0.07	0.098	0.26	0.58	0.59	0.16
Gd	0.16	0.22	0.21	1.22	1.46	0.73	0.48	0.57	0.55	0.44	0.93	1.32	1.45	0.50
Tb	0.032	0.024	0.041	0.16	0.17	0.20	0.13	0.16	0.15	0.13	0.19	0.18	0.14	0.10
Dy	0.14	0.14	0.17	0.77	0.83	1.95	1.58	1.40	1.38	1.38	0.89	0.77	0.88	0.66
Ho	0.019	0.034	0.026	0.15	0.13	0.53	0.41	0.44	0.36	0.38	0.17	0.14	0.15	0.17
Er	0.065	0.078	0.12	0.33	0.39	2.05	1.79	1.69	1.56	1.55	0.28	0.34	0.42	0.38
Tm	0.009	0.018	0.022	0.060	0.066	0.37	0.36	0.31	0.27	0.28	0.023	0.024	0.060	0.051
Yb	0.12	0.20	0.17	0.44	0.48	2.67	2.39	2.13	2.43	2.11	n.d.	0.19	0.29	0.34
Lu	0.025	0.050	0.039	0.084	0.10	0.56	0.44	0.45	0.49	0.38	0.011	0.028	n.d.	0.047
Si (pfu)	3.004	2.994	2.994	<b>3.050</b>	<b>3.072</b>	3.032	3.023	<b>3.038</b>	<b>3.041</b>	3.035	2.000	1.989	1.990	2.007
Cr#	34.3	34.4	34.1	39.8	39.5	0.21	0.37	0.32	0.27	0.32	0.48	0.26	0.27	0.56

Major-element compositions of these DIs are presented in Pokhilenko et al. (2003). The Si (per formula unit) and Cr# (100Cr/Cr + Al) obtained from the major-element compositions are reanalyzed for this study, which are in general agreement with the analysis done by Pokhilenko et al. (2003). Paragenesis: harz. = harzburgitic, eclo. = eclogitic. Gt = garnet; Cpx = clinopyroxene. n.d. = not detected.

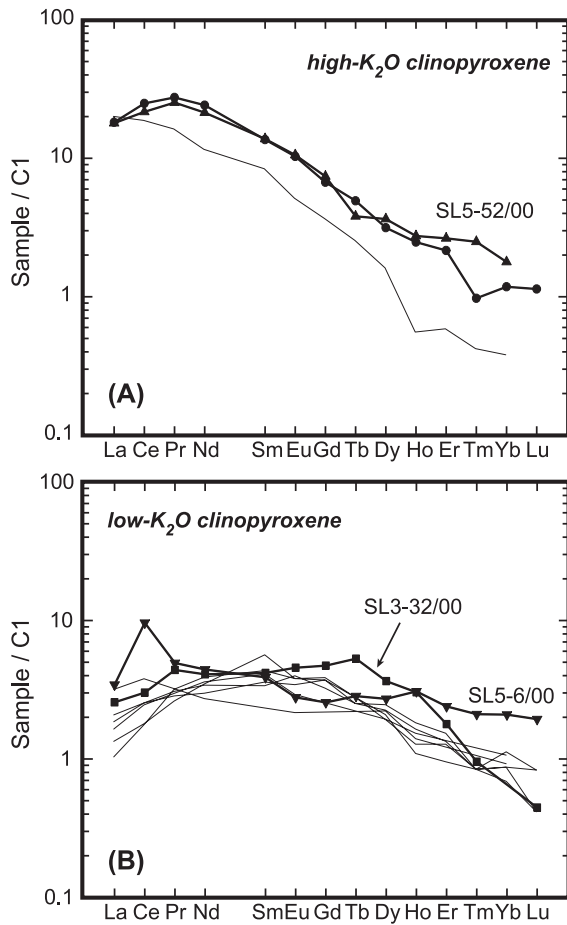


Fig. 2. REE patterns of clinopyroxene DIs from the Snap/King Lake area. (A) LREE-enriched patterns occur in high-K<sub>2</sub>O Cpx. (B) Low-K clinopyroxenes possess flat light-middle REE patterns that become depleted towards HREE. Lines represent DI data from Siberia (Mir and Udachanaya; Taylor et al., 1996; Sobolev et al., 1998).

pyroxene DIs from Siberia (Taylor et al., 1996, 1998, 2000; Sobolev et al., 1998; Anand et al., 2004 this volume). The depletion of Tm for SL5-52/00 is within error of the analysis because of its low abundance approaching the detection limit. In contrast, the Ce spike for SL5-6/00 is difficult to explain but may be attributed to weathering (Floss et al., 2000), in which case, this would appear to be indication of “open-system behavior” of the diamond with respect to the clinopyroxene.

One clinopyroxene was found in contact with Opx and another with Ol during our in situ study of DIs

in polished diamonds, and their major-element compositions are shown in Table 2. The Cpxs are small (< 5 μm) and occur at the edges of the inclusions to which they are attached. These Cpxs have high Mg# (94.2 and 94.6), relatively high Cr- and low Ti-contents, and are classified as Cr-diopsides. Their K<sub>2</sub>O contents (0.14 and 0.33 wt.%) are generally lower than those in the eclogitic counterparts, but high for peridotitic inclusions. *P–T* estimates of the Opx–Cpx pair yield 63 kb (Finnerty and Boyd, 1987) and 1214 °C (Brey and Köhler, 1990).

### 3.3. Orthopyroxene

The composition of the three orthopyroxenes from diamond SL5-75 obtained from the in situ

Table 2  
Major-elements compositions (wt.%) of clinopyroxene and orthopyroxene from diamond SL5-75, analyzed in situ

Mineral	Cpx <sup>a</sup>	Opx <sup>a</sup>	Cpx <sup>b</sup>	Opx	Opx
Grain no.	5	4	6	2	3
SiO <sub>2</sub>	55.1	57.6	55.3	57.7	57.7
TiO <sub>2</sub>	<0.03	<0.03	<0.03	<0.03	<0.03
Al <sub>2</sub> O <sub>3</sub>	0.63	0.46	1.01	0.48	0.48
Cr <sub>2</sub> O <sub>3</sub>	1.03	0.32	1.37	0.32	0.33
MgO	19.3	35.6	17.6	35.8	35.7
CaO	20.6	0.38	20.9	0.37	0.37
MnO	0.08	0.11	0.09	0.11	0.11
FeO	1.98	4.65	1.94	4.63	4.68
Na <sub>2</sub> O	0.48	0.13	0.71	0.13	0.13
K <sub>2</sub> O	0.14	0.03	0.33	0.03	<0.03
Total	99.39	99.31	99.24	99.60	99.52
Oxygen	6	6	6	6	6
Si	1.995	1.986	2.008	1.984	1.984
Ti	0.000	0.000	0.000	0.000	0.000
Al	0.027	0.019	0.044	0.019	0.020
Cr	0.029	0.009	0.039	0.009	0.009
Mg	1.042	1.832	0.952	1.835	1.833
Ca	0.798	0.014	0.812	0.014	0.014
Mn	0.002	0.003	0.003	0.003	0.003
Fe	0.060	0.134	0.059	0.133	0.135
Na	0.034	0.004	0.050	0.004	0.004
K	0.007	0.002	0.015	0.002	0.001
Total	3.995	4.003	3.981	4.003	4.002
Mg#	94.6	93.2	94.2	93.2	93.2
En	54.9	92.5	52.2	92.6	92.5
Wo	42.0	0.7	44.5	0.7	0.7
Fs	3.2	6.8	3.2	6.7	6.8

<sup>a</sup> Touching Opx–Cpx pair.

<sup>b</sup> In contact with olivine.

technique (Table 2) are essentially identical, and fall within the restricted compositional range of the Opx compositions reported by Pokhilenko et al. (in press). However, subtle differences can be seen in some trace elements (Table 3). In the Cr-Ni plot (Fig. 3), the orthopyroxenes DIs can be divided into two distinct groups: low Cr (<2000 ppm) and high Cr (>2000 ppm), each showing a positive slope. Furthermore, the three Opx inclusions analyzed in situ (SL5-75) appear to form extension to the high-Cr group. These differences may indicate compositional variations of harzburgitic source rocks, at least with respect to Ni and Cr, as commonly observed in garnet (Cr) and olivine (Ni) DIs. Significant variations of Ti, Zr, and Sr were observed (6–179, 0.18–16.9, 0.2–9.8 ppm, respectively), and their concentrations are notably higher than those in some Opx DIs from West Africa (Stachel and Harris, 1997).

### 3.4. Olivine

In five of the diamonds polished to expose mineral inclusions for in situ analysis, nine olivines were encountered, whose major-element chemistry (Table 4) generally lies within the range observed for olivines recovered by the burning technique. However, NiO contents mostly fall outside this range, which suggests a higher variation in trace-element abundances among olivine DIs than previously recognized (Fig. 4).

Diamond SL5-62 contains two relatively large (~200 µm) olivine inclusions occurring in the core and intermediate growth zones, as revealed by cathodoluminescence (CL) imaging of the diamond (Fig. 5). Well-defined “stratigraphy” of the diamond is clearly visible; however, the continuity of the growth layers is disrupted by the obscured regions (“dead zones”) surrounding the inclusions, a typical occurrence for DIs (Taylor et al., 2003a). Major-element

Table 3  
Trace-element compositions (ppm) of orthopyroxene diamond inclusions

Sample	SL5-21/00		SL5-39/00			SL5-42/00		
Grain no.	63	64	74	75	76	77	78	79
Ca	2710	2720	1849	2522	3105	3133	2166	4906
Sc	1.24	1.11	1.62	1.88	1.38	1.77	1.47	1.87
Ti	30.9	26.1	5.66	179	102	19.2	31.0	90.7
V	26.1	27.9	27.8	28.8	28.4	28.1	25.4	28.3
Cr	2430	2532	1908	1928	1958	2570	2488	2511
Mn	629	660	541	574	584	699	652	659
Ni	918	973	893	921	968	1033	918	967
Sr	2.90	2.55	0.41	2.29	4.33	4.62	1.07	9.82
Y	0.066	0.073	0.024	0.19	0.061	0.075	0.023	0.065
Zr	0.90	1.33	0.18	16.9	1.39	2.13	0.30	1.15
Nb	0.15	0.20	0.060	1.77	0.089	0.092	0.089	0.20

Sample	SL5-59/00		SL5-54/00		SL3-27/00	SL5-75 <sup>a</sup>		
Grain no.	97	99	104	105	122	2	3	4
Ca	1964	4675	2892	2167	2192	3709	3136	2572
Sc	1.31	1.59	1.80	1.28	1.77	0.60	1.43	1.44
Ti	15.8	20.8	26.1	27.5	40.1	36.1	35.4	43.3
V	24.4	25.8	24.4	23.2	23.7	27.0	25.6	27.6
Cr	1768	1791	2343	2298	1926	1955	1952	1894
Mn	610	622	614	598	620	582	585	575
Ni	847	854	851	847	866	649	730	686
Sr	0.20	7.32	4.32	1.23	1.19	6.86	4.21	2.85
Y	0.022	0.10	0.077	0.050	0.039	0.062	0.056	0.075
Zr	0.19	1.42	1.69	0.76	0.55	4.74	2.98	7.33
Nb	0.032	0.066	0.13	0.11	0.042	0.053	0.089	0.063

<sup>a</sup> Analyzed in situ.

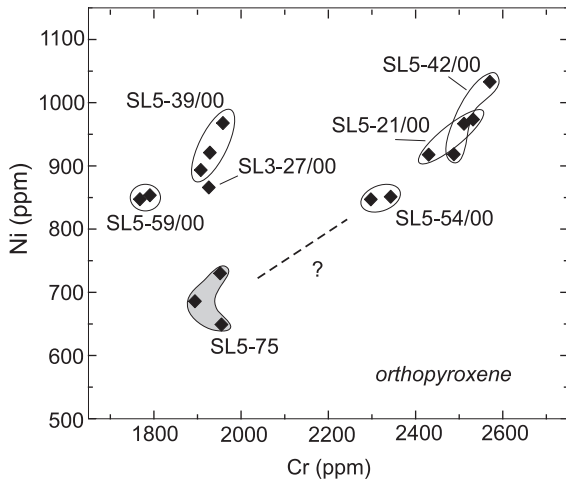


Fig. 3. Cr versus Ni in orthopyroxene inclusions from Snap/King Lake area. Two positive trends can be established from the data points. The three data points within the shaded envelope are in situ analyses of sample SL5-75. These three inclusions are probably part of the high-Cr data array (joined with a dashed line).

chemistry of the two olivine DIs in diamond SL5-62 is essentially identical, but certain trace-element abundances are different (Table 4). That is, OI-2 that occurs in the outer portion of the diamond contains higher abundances of incompatible trace elements (Ca, Sc, Ti, Sr, Y, Zr, Nb, Ba), when compared to OI-1, which resides in the core region (Fig. 6).

Two additional olivine inclusions were analyzed for trace elements (Table 4). With few exceptions, both HFSE and LILE vary in restricted ranges, consistent with the relatively uniform major-element chemistry. The low-Ti contents in conjunction with low- and variable-Sr contents are similar with harzburgitic-olivine DIs from Akwatia, Ghana (Stachel and Harris, 1997).

## 4. Discussion

### 4.1. Constraints from trace-element chemistry

The harzburgitic-garnet diamond inclusions from the Snap Lake/King Lake kimberlites display the sinusoidal REE patterns, typical of garnet diamond inclusions worldwide. It is generally agreed that such REE patterns are the result of metasomatism of depleted garnets by LREE-enriched, HREE-depleted

fluids; however, various models have been proposed. To explain the hump formed by the LREE and HREE, Hoal et al. (1994) and Shimizu and Richardson (1987) invoked disequilibrium processes that imply higher diffusivities of the LREE compared to the MREE. In contrast, Griffin et al. (1999) called for the progressive misfit in the garnet structure of the larger LREE to explain the hump. These two models, however, appear unlikely in light of the recent experiment by Van Orman et al. (2002) that shows no perceptible difference in diffusion rates among the REEs in the garnet structure. Stachel et al. (2003) pointed out that: (1) the apparent complexity of the sinusoidal REE patterns is merely an artifact of rapidly increasing compatibility, from LREE to MREE, within the garnet structure due to decreasing ionic radius, and (2) the consistency of the patterns over the large compositional range, particularly the inflection points on the sinusoidal curve, is difficult to explain by disequilibrium models. Ivanic et al. (2003) have also demonstrated that garnets with the humped REE profiles could be in equilibrium with extremely LREE-enriched melt. The consistency of REE profiles obtained in this study with those of the worldwide data (Stachel et al., 2003) appears to support the view of equilibrium metasomatic enrichment proposed by both Stachel and Ivanic et al. (2003).

Noteworthy in this study is that both “majoritic” and normal garnet inclusions (SL3-31/00 and SL3-3/00, respectively) possess similar REE patterns, although the REE concentrations in the former are significantly more enriched, up to  $\sim 10\times$  higher for LREEs but  $2\times$  for HREEs. It is also important to note that the Cr# (the depletion index) is higher in majoritic garnets compared to the normal ones ( $\sim 40$  versus 34, respectively; Table 1). A number of possibilities may be used to explain this difference in the REE concentrations. As demonstrated by Stachel and Harris (1997), the partition coefficients of REEs, especially the light and middle REE, increase with increasing pressure and temperature (i.e., depth), thus resulting in the higher uptakes of the REEs in the majoritic garnets. This would appear to explain the present situation. However, it should also be pointed out that Stachel et al. (2000), based on the partitioning data of Zack et al. (1997), stated that majoritic garnets typically contain lower REE concentrations, which would seem to be the opposite

Table 4

Compositions of major (wt.%) and trace elements (ppm) in olivine diamond inclusions, analyzed in situ

Sample	SL5-62		SL5-75 <sup>a</sup>	SL5-47			SL3-53	SL00/173	
	1	2		1	2	3		1	2
SiO <sub>2</sub>	40.8	41.0	40.6	40.7	40.6	40.7	41.4	40.8	40.6
Cr <sub>2</sub> O <sub>3</sub>	0.04	0.04	<0.03	0.05	<0.03	0.03	0.03	0.07	0.06
MgO	50.7	51.0	50.52	49.9	49.83	50.3	51.9	50.8	51.0
CaO	<0.03	0.06	<0.03	0.05	<0.03	0.03	0.05	<0.03	0.03
MnO	0.10	0.09	0.10	0.11	0.10	0.10	0.08	0.10	0.10
FeO	7.67	7.80	7.86	8.03	7.85	7.85	6.85	6.37	6.42
NiO	0.39	0.40	0.40	0.38	0.36	0.37	0.32	0.38	0.37
Total	99.7	100.37	99.49	99.20	98.78	99.36	100.58	98.58	98.65
Oxygen	4	4	4	4	4	4	4	4	4
Si	0.994	0.993	0.993	0.998	0.999	0.997	0.996	1.001	0.996
Cr	0.001	0.001	0.000	0.001	0.000	0.001	0.001	0.001	0.001
Mg	1.844	1.844	1.843	1.827	1.829	1.834	1.861	1.856	1.865
Ca	0.000	0.002	0.000	0.001	0.001	0.001	0.001	0.001	0.001
Mn	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Fe	0.156	0.158	0.161	0.165	0.162	0.161	0.138	0.131	0.132
Ni	0.008	0.008	0.008	0.007	0.007	0.007	0.006	0.008	0.007
Total	3.005	3.008	3.006	3.001	2.999	3.003	3.004	2.999	3.004
Fo	92.2	92.1	92.0	91.7	91.9	91.9	93.1	93.4	93.4
Ca (ppm)	281	320	462	366					
Sc	0.44	0.64	0.55	0.54					
Ti	4.83	6.75	4.65	4.67					
V	11.0	9.84	9.92	11.3					
Cr	572	351	298	493					
Mn	559	572	558	581					
Ni	2389	2391	2416	2220					
Sr	0.46	1.16	0.66	0.78					
Y	0.025	0.034	0.016	0.081					
Zr	0.35	0.56	0.18	6.34					
Nb	0.015	0.036	0.030	0.093					
Ba	0.74	1.11	0.22	2.68					

<sup>a</sup> In contact with Cpx.

from that we have observed. Alternatively, the higher degree of depletion of these majoritic garnets results in their greater susceptibility to metasomatic enrichment that significantly increases their trace-element concentrations, without modifying the major-element abundances (Stachel et al., 2003). It may also be possible that the fluids interacting with majoritic garnets in this study contain higher incompatible trace-element concentrations than those interacted with normal garnets.

Nature of the fluids/melts that may have enriched harzburgitic garnets is not well understood at present (e.g., Taylor et al., 2003b). Stachel and Harris (1997) believed that the fluids must be very rich in LREE, and to a lesser degree Rb and Sr, and low or void in HFSE and HREE. These requirements seem to ex-

clude kimberlitic, lamproitic, or carbonatitic melts, and they favored methane-rich fluids as the most likely enriching media, as well as being the carbon source for diamond formation. In contrast, Griffin et al. (1999) interpreted that fluids such as carbonatite cause the depletion in HFSE but enrichment in LREE observed in some harzburgitic garnets from South African ultramafic xenoliths.

The “majoritic” harzburgitic diamond inclusions in this study (SL3-31/00) differ from the previous investigations in their enrichment in HFSE, particularly Zr (Fig. 2B), possibly reflecting the compositions of metasomatic fluids. It is unlikely that the relatively high HFSE concentrations are the inherent nature of pre-metasomatized garnets because the “normal” harzburgitic garnets (SL3-3/00), which are



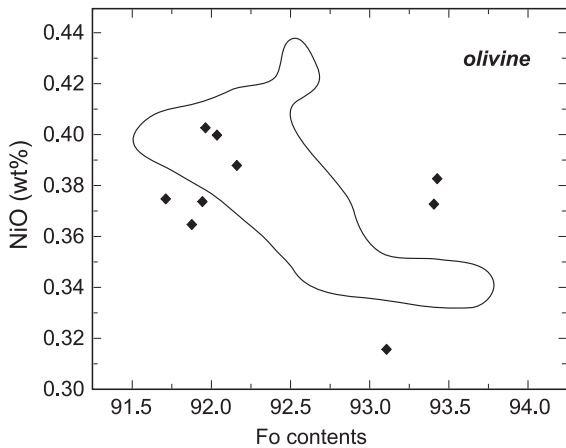


Fig. 4. Fo versus NiO plot of olivine inclusions in this study, compared with the data from Pokhilenko et al. (2003), as denoted by the envelope.

less depleted (lower Cr#), contain lower abundances of these elements. The increase in HFSE in SKL diamond inclusions, perhaps, is best seen in the in situ analysis of two olivines in diamond SL5-62 (Fig. 6). Olivine-2 that occurs in the outer portion of the diamond contains consistently higher abundances of HFSE and LILE than olivine-1 that occurs in the core of the diamond, albeit overlaps in  $2\sigma$  error bars of the analyses. Based on these observations, the fluids that interacted with at least some of the SKL diamond

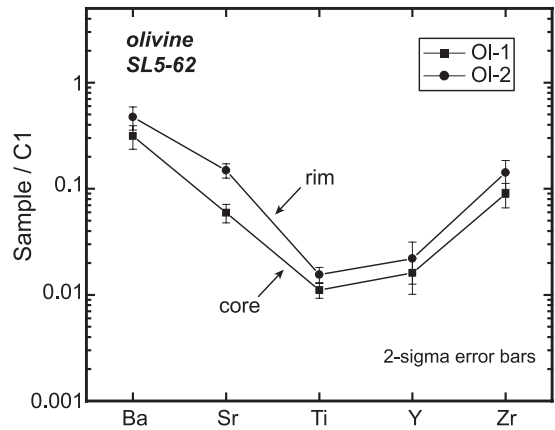


Fig. 6. Plot of LILE and HFSE in olivine inclusions from sample SL5-62 that shows the higher abundances of these elements in olivine-2 (rim), compared to those in olivine-1 (core).

inclusions are probably enriched in LREE, and to a lesser degree LILE and HFSE, and depleted in HREE. Perhaps, these fluids are akin to those occurring as micro-inclusions in diamonds studied by Navon et al. (2003). They suggested that the major-element compositions of these micro-inclusions correspond to three end-members, including hydrous-silicic melt, carbonatitic melt, and brine. The silicic component of this fluid may contain high abundances of HFSE similar to silicate melts, and therefore, may supply HFSE to these SKL diamond inclusions.

#### 4.2. Remnant of oceanic crust beneath SE Slave craton

Eclogitic diamond inclusions and eclogite xenoliths are common in kimberlitic fields worldwide, and kimberlites of the Slave craton have also carried eclogitic materials from the great depths (Pearson et al., 1999a,b; Davies et al., 1999a,b; Pokhilenko et al., 2001). Based on the major-element chemistry of garnets and omphacitic clinopyroxenes (Pokhilenko et al., 2003), E-type diamond inclusions from the Snap Lake kimberlite have been classified as Group B, suggesting their derivation from an ancient oceanic crust. This may have been associated with the 1.9-Ga collision of the Slave craton with the Hottah Terrane, as described by Bowring and Grotzinger (1992).

Eclogites are essentially biminerals rocks, consisting mainly of garnet and omphacitic clinopyroxene,

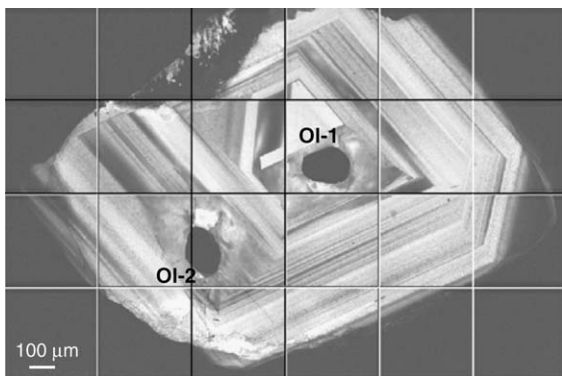
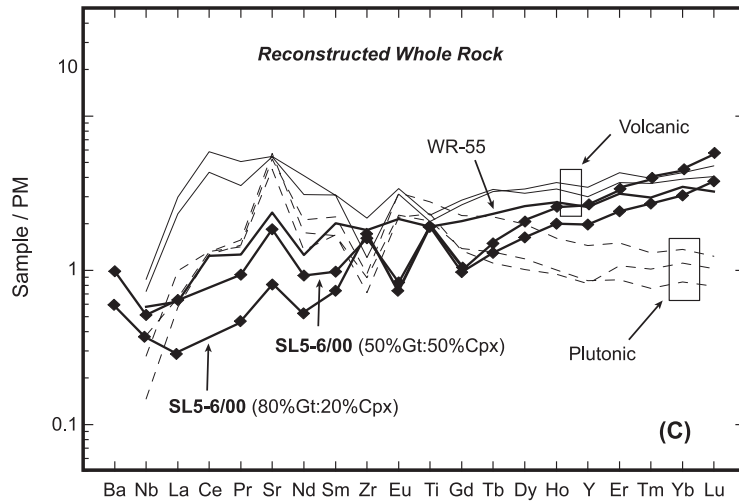
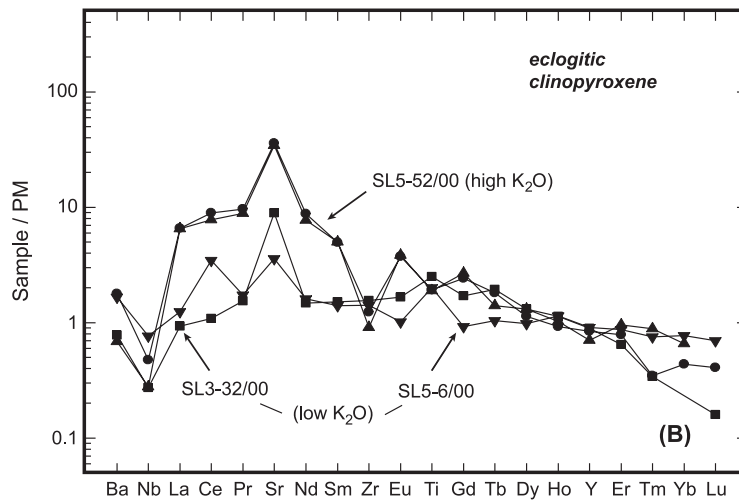
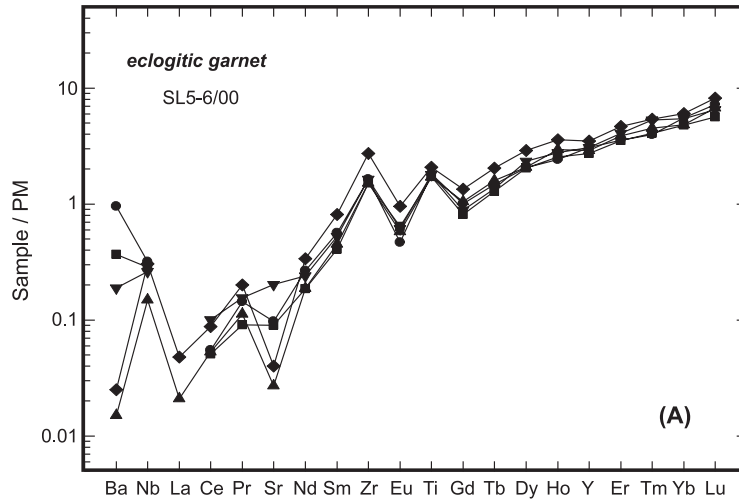


Fig. 5. Cathodoluminescence (CL) image of a plate of diamond SL5-62 polished parallel to (110) plane. Two olivine inclusions occur at core (Ol-1) and at intermediate (Ol-2) growth zones of the diamond. Well-defined growth layers of the diamond are clearly visible, except at the regions surrounding the two DIs.



often with accessory minerals such as rutile, kyanite, coesite, etc. In diamond SL5-6/00, both eclogitic garnets and omphacite were found, thereby enabling the reconstruction of whole-rock composition. The compositions of the five garnet inclusions in this diamond were averaged for reconstruction, since they have similar major- and trace-element compositions. Assuming the modal proportions of garnet/cpx at 50:50 and 80:20 (for comparison), the trace-element pattern for the reconstructed compositions (PM normalized) of the Snap Lake eclogite, along with that of constituent minerals, is illustrated in Fig. 7, together with a similar reconstruction on diamondiferous eclogites from Udachanaya (Jacob and Foley, 1999). This reconstructed composition is generally considered as representative of an oceanic crust that has lost partial melts during subduction to produce trondhjemite–tonalite–granodiorite (TTG) magmas in the Archean (Ireland et al., 1994). In comparison, the composition of the reconstructed eclogite from Snap Lake is very similar to that of WR-55, with the exception of Zr and Ti depletions. This eclogite is believed to be derived from the volcanic section of an ancient oceanic crust (Jacob and Foley, 1999) and, analogously, this may also hold true for the protolith of the inclusions in diamond SL5-6/00.

Trace-element patterns of all eclogitic clinopyroxene diamond inclusions in this study show prominent positive Sr anomaly, which is also present in the reconstructed whole-rock composition (Fig. 7). This anomaly has often been interpreted as the consequence of carbonate depositions on the ocean floor, coupled with remobilization of the Sr during hydrothermal alterations of the eclogite protoliths (Ireland et al., 1994; Jacob and Foley, 1999), and these Sr-enrichment processes may be applicable to the eclogitic clinopyroxenes of the present study as well. Hydrothermal alteration, however, is unlikely to cause positive anomalies of Ti and Zr in eclogitic garnets from diamond SL5-6/00 (Fig. 7A), since these HFSEs are essentially immobile in the hydrothermal fluids (Jacob and Foley, 1999). Metasomatic enrichment by a silicate melt will also

increase the abundances of other incompatible trace elements, such as LREE, which is not observed in the present data. Based on the experiment by Konzett (1997), a possible cause of these HFSE anomalies in garnet is the increase in solubility of these elements in garnets upon increasing  $P$ – $T$  during the subduction (Klemme et al., 2002) that eventually produced the eclogite protoliths of the DIs.

## 5. Conclusion

Trace-element chemistry of multiple diamond inclusions presented here provides insights into the nature of processes involved in the formation of diamonds in the Snap Lake/King Lake area. The harzburgitic-garnet inclusions possess sinusoidal REE patterns that are consistent in both concentrations and shapes (positions of peaks and troughs) with the worldwide data (Stachel et al., 2003). Such consistency most likely suggests the *equilibrium* metasomatic enrichment of pre-existing garnets that previously experienced partial-melting episode(s). The data in this study also support the interpretation that the most-depleted garnets (high Cr#) are most sensitive to metasomatism, thus capable of absorbing high concentrations of incompatible trace-element abundances (Stachel et al., 2003). Moreover, it seems that “majoritic” garnets, which were derived from the greater depths, experience more intense melting and metasomatic enrichment, compared to the normal garnets. The relatively high concentrations of HFSE in majoritic garnets and the increase from core to rim in HFSE and LILE of olivine diamond inclusions may indicate the relatively high abundances of these components in metasomatic fluids. Such fluids may be represented by the three end-member components, including hydrous-silicic melt, carbonatitic melt, and brines (Navon et al., 2003). Reconstructed whole-rock trace-element composition of eclogitic DIs suggests that the eclogite protolith was probably the volcanic layer of an oceanic crust

Fig. 7. Primitive Mantle (PM) normalized trace-element patterns of eclogitic DIs (A and B) and the reconstructed whole-rock compositions, using two different proportions of garnet and Cpx (C). Note that Ce is not included in the whole-rock reconstruction due to its abnormally high concentration in the omphacite. Also plotted for comparison in (C) are the reconstructed compositions of diamondiferous eclogite xenoliths from Udachanaya (WR-55), Siberia, which are separated into volcanic and plutonic suites (Jacob and Foley, 1999).

that had undergone hydrothermal alteration and partial melting during subduction.

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## References

- Alexander, C.M.O.D., 1994. Trace element distributions with ordinary chondrite chondrules: Implications for chondrule formation conditions and precursors. *Geochim. Cosmochim. Acta* 58, 3451–3467.
- Agashev, A.M., Pokhilenko, N.P., McDonald, J.A., Takazawa, E., Vavilov, M.A., Sobolev, N.V., Watanabe, T., 2001. A unique kimberlite-carbonatite primary association in the Snap Lake dyke system, Slave Craton: evidence from geochemical and isotopic studies. The Slave Kaapvaal Workshop, Ext. Abstr. Vol. Merrickville, Canada, unpagged.
- Anand, M., Taylor, L.A., Carlson, W.D., Taylor, D.-H., Sobolev, N.V., 2004. Diamond genesis revealed by X-ray tomography of diamondiferous eclogites. *Lithos*, Proceedings of the 8th International Kimberlite Conference. This volume.
- Bowring, S.A., Grotzinger, J.P., 1992. Implications of new chronostratigraphy for tectonic evolution of Wopmay Orogen, Northwest Canadian Shield. *Amer. Jour. Sci.* 292, 1–20.
- Brey, G.P., Köhler, T., 1990. Geothermobarometry in four-phase lherzolites II: new thermobarometers and practical assessment of existing thermobarometers. *J. Petrol.* 31, 1353–1378.
- Carlson, R.W., Pearson, D.G., Boyd, F.R., Shirey, S.B., Irvine, G.A.H., A.H., Menzies, A.H., Gurney, J.J., 1999. Regional age variation of the southern African mantle: significance for models of lithospheric mantle formation. In: Gurney, J.J., Gurney, M.D., Pascoe, M.D., Richardson, S.H. (Eds.), *Proceedings 7th International Kimberlite Conference vol. 1*. Red Roof Design, Cape Town, pp. 99–108.
- Davies, R., Griffin, W.L., Pearson, N.J., Andrew, A., Doyle, B.J., O'Reilly, S.Y., 1999a. Diamonds from the Deep: pipe DO-27, Slave Craton, Canada. *Proc. of the 7th Int'l Kimberlite Conf.*, vol. 1, pp. 148–155.
- Davies, R.M., O'Reilly, S.Y., Griffin, W.L., 1999b. Growth structures and nitrogen characteristics of group B alluvial diamond crystals from Bingara and Wellington, Eastern Australia. *Proceedings of the 7th International Kimberlite Conference*, vol. 1, pp. 156–163.
- Fahey, A.J., Zinner, E.K., Crozaz, G., Kornacki, A.S., 1987. Microdistribution of Mg isotopes and REE abundances in a Type A calcium-aluminum-rich inclusion from Efremovka. *Geochim. Cosmochim. Acta* 51, 3215–3229.
- Finnerty, A.A., Boyd, F.R., 1987. Thermobarometry for garnet peridotite xenoliths: a basis for upper mantle stratigraphy. In: Nixon, P.H. (Ed.), *Mantle Xenoliths*, vol. 1, 381–402.
- Floss, C., Crozaz, G., Yamaguchi, A., Keil, K., 2000. Trace element constraints on the origins of highly metamorphosed Antarctic eucrites. *Antarct. Meteor. Res.* 13, 222–237.
- Griffin, W.L., Shee, S.R., Ryan, C.G., Win, T.T., Wyatt, B.A., 1999. Harzburgite to lherzolite and back again: metasomatic processes in ultramafic xenoliths from the Wesselton kimberlite, Kimberley, South Africa. *Contrib. Mineral. Petrol.* 134, 232–250.
- Hoal, K.E.O., Hoal, B.G., Erlank, A.J., Shimizu, N., 1994. Metasomatism of the mantle lithosphere recorded by rare earth elements in garnets. *Earth. Plan. Sci. Lett.* 126, 303–313.
- Hsu, W., 1995. *Ion Microprobe Studies of the Petrogenesis of Enstatite Chondrites and Eucrites*. Washington University, St. Louis, MO, United States, p. 380.
- Ireland, T.R., Rudnick, R.L., Spetsius, Z.V., 1994. Trace elements in diamond inclusions from eclogites reveal link to Archean granites. *Earth Planet. Sci. Lett.* 128, 199–213.
- Irifune, T., 1987. An experimental investigation of the pyroxene-garnet transformation in a pyrolite composition and its bearing on the composition of the mantle. *Earth Planet. Sci. Lett.* 45, 324–336.
- Ivanic, T.J., Harte, B., Burgess, S.R., Gurney, J.J., 2003. Factors in the formation of sinuous and humped REE patterns in garnets from mantle harzburgitic assemblages (Abstract). *Proc. 8th IKC*, vol. 4, pp. 14.
- Jacob, D.E., Foley, S.F., 1999. Evidence for Archean ocean crust with low high field strength element signature from diamondiferous eclogite xenoliths. *Lithos* 48, 317–336.
- Klemme, S., Blundy, J.D., Wood, B.J., 2002. Experimental constraints on major and trace element partitioning during partial melting of eclogite. *Geochim. Cosmochim. Acta* 66, 3109–3123.
- Konzett, J., 1997. Phase relations and chemistry of Ti-rich K-rich-terite-bearing mantle assemblages: an experimental study to 8.0 GPa in Ti-KNCMASH system. *Contrib. Mineral. Petrol.* 128, 385–404.
- Navon, O., Izaeli, E.S., Klein-BenDavid, O., 2003. Fluid inclusions in diamonds: the carbonatitic connection. *Proc. 8th Int. Kimb. Conf. long abstracts # 107*.
- Pearson, N.J., Griffin, W.L., Doyle, B.J., O'Reilly, S.Y., Van Acherbergh, E., Kivi, K., 1999a. Xenoliths from kimberlite pipes of the Lac de Gras area, Slave craton, Canada. *Proc. 7th Int'l Kimberlite Conf., Extnd. Abstr.*, vol. 2, pp. 644–658.
- Pearson, D.G., Shirey, S.B., Bulanova, G.P., Carlson, R.W., Milledge, H.J., 1999b. Dating and paragenetic distinction of diamonds using the Re-Os isotope system: application to some Siberian diamonds. *Proceedings of the 7th International Kimberlite Conference*, vol. 2, pp. 637–643.

- Pokhilenko, N.P., McDonald, J.A., Melnyk, W., Hall, A.E., Shimizu, N., Vavilov, M.A., Afanasiev, V.P., Reimers, L.F., Irvin, J., Pokhilenko, L.N., Vasilenko, V.B., Kuligin, S.S., Sobolev, N.V., 1998. Kimberlites of Camsell Lake Field and some features of structure and composition of lithosphere roots of southeastern part of Slave Craton, Canada. *Proc. 7th Int. Kimberlite Conf. Ext. Abstr. Vol.*, Cape Town, pp. 699–701.
- Pokhilenko, N.P., Sobolev, N.V., Cherny, S.D., Mityukhin, S.I., Yanygin, Y.T., 2000. Pyrope and chromite from kimberlites of the Nakyn Field (Yakutia) and the Snap Lake region (Slave Craton, Canada) evidence for anomalous lithospheric structure. *Doklady Earth Sci.* 372, 356–360.
- Pokhilenko, N.P., Sobolev, N.V., McDonald, J.A., Hall, A.E., Yefimova, E.S., Zedgenizov, D.A., Logvinova, A.M., Reimers, L.F., 2001. Crystalline inclusions in diamonds from kimberlites of the Snap Lake area (Slave Craton, Canada): new evidences for the anomalous lithospheric structure. *Dokl. Earth Sci.* 380, 806–811.
- Pokhilenko, N.P., Sobolev, N.V., Reutsky, V.N., Hall, A.E., Taylor, L.A., 2003. Crystalline inclusions and C-isotope ratios of diamonds from the Snap Lake/King Lake kimberlite dyke system: Evidence for an ultradeep and enriched lithosphere mantle, *Lithos. Proceedings of the 8th International Kimberlite Conference. This volume.*
- Pokhilenko, N.P., Sobolev, N.V., Reutsky, V.N., Hall, A.E., Taylor, L.A., 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. *Proc. 8th Int'l. Kimb. Conf., Lithos.* in press.
- Shimizu, N., Richardson, S.H., 1987. Trace element abundance patterns of garnet inclusions in peridotite suite diamonds. *Geochim. Cosmochim. Acta* 51, 755–758.
- Sobolev, N.V., Snyder, G.A., Taylor, L.A., Keller, R.A., Yefimova, E.S., Sobolev, V.N., Shimizu, N., 1998. Extreme chemical diversity in the mantle during eclogite diamond formation: evidence from 35 garnet and 5 pyroxene inclusions in a single diamond. *Int. Geol. Rev.* 40, 567–578.
- Stachel, T., Harris, J.W., 1997. Diamond precipitation and mantle metasomatism: evidence from the trace element chemistry of silicate inclusions in diamonds from Akwatia, Ghana. *Contrib. Mineral. Petrol.* 129, 143–154.
- Stachel, T., Brey, G.P., Harris, J.W., 2000. Kankan diamonds (Guinea): I. from the lithosphere down to the transition zone. *Contrib. Mineral. Petrol.* 140, 1–15.
- Stachel, T., Aulbach, S., Brey, G.P., Harris, J.W., Leost, I., Tappert, R., Viljoen, K.S., 2003. Diamond formation and mantle metasomatism: a trace element perspective. *8th Int'l Kimberlite Conf. Extnd. Abstr.*, Victoria BC, Canada.
- Taylor, L.A., Snyder, G.A., Crozaz, G., Sobolev, V.N., Yefimova, E.S., Sobolev, N.V., 1996. Eclogitic Inclusions in diamonds: Evidence of complex mantle processes over time. *Earth Planet. Sci. Lett.* 142, 535–551.
- Taylor, L.A., Milledge, H.J., Bulanova, G.P., Snyder, G.A., Keller, R.A., 1998. Metasomatic eclogitic diamond growth: evidence from multiple diamond inclusions. *Int. Geol. Rev.* 40, 592–604.
- Taylor, L.A., Keller, R.A., Snyder, G.A., Wang, W., Carlson, W.D., Hauri, E.H., McCandless, T., Kim, K.-R., Sobolev, N.V., Bezborodov, S.M., 2000. Diamonds and their mineral inclusions, and what they tell us: a detailed “pull-apart” of a diamondiferous eclogite. *Int. Geol. Rev.* 42, 959–983.
- Taylor, L.A., Anand, M., Promprated, P., 2003a. Diamonds and their inclusions: are the criteria for syngeneis valid? *8th Internat. Kimb. Conf., Ext Abstr.*
- Taylor, L.A., Anand, M., Promprated, P., Floss, C., Sobolev, N.V., 2003b. The significance of mineral inclusions in large diamonds from Yakutia, Russia. *Am. Mineral.* 88, 912–920.
- Van Orman, J.A., Grove, T.L., Shimizu, N., 2002. Diffusive fractionation of trace elements during production and transport of melt in Earth's upper mantle. *Earth Plan. Sci. Lett.* 198, 93–112.
- Zack, T., Foley, S.F., Jenner, G.A., 1997. A consistent partition coefficient set for clinopyroxene, amphibole and garnet from laser ablation microprobe analysis of garnet pyroxenites from Kakani, New Zealand. *Neues Jahrb. Mineral. Abh.* 172, 23–41.
- Zinner, E., Crozaz, G., 1986a. A method for the quantitative measurement of rare earth elements in the ion microprobe. *Int. J. Mass Spectrom. Ion Process.* 69, 17–38.
- Zinner, E., Crozaz, G., 1986b. Ion probe determination of the abundances of all the rare earth elements in single mineral grains. *Int. J. Mass Spectrom. Ion Process.* 69, 444–446.