

## **Trace element abundances in garnets and clinopyroxenes from diamondites – a signature of carbonatitic fluids**

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### **Summary**

Silicates intergrown with diamonds from 10 diamondites (polycrystalline diamonds, framesites) have been analysed for trace element contents by laser ablation ICP-MS. The diamondites are fine- (<100 µm) to coarse-grained (> 1 mm) rocks with abundant pores and cavities. The walls of the open cavities are covered by euhedral diamond crystals. Silicates (commonly garnets) are mostly interstitial or occupy the space in cavities and often contain inclusions of euhedral diamonds.

Four diamondites contain lilac “peridotitic” garnets with low CaO contents (3.6–5.7 wt%), high Mg-numbers (0.83–0.84) and high Cr<sub>2</sub>O<sub>3</sub> contents (3.9–6.4 wt%). Occasionally, they are accompanied by Cr-diopside. “Peridotitic” garnets have heavy rare earth element-enriched and light rare earth element-depleted chondrite-normalised patterns, occasionally with a small hump at Eu and Sm. The remaining six diamondites contain orange coloured “eclogitic” garnets with low Cr<sub>2</sub>O<sub>3</sub> contents (<1 wt%). “Eclogitic” garnets can be divided into two subgroups: E-I garnets have high Mg-numbers (0.84–0.85, as high as those of the “peridotitic” garnets) and higher Cr<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> and lower heavy rare earth element contents than the E-II garnets. The chondrite-normalised trace element patterns of the two subgroups of “eclogitic” garnets are similar to each other, all are depleted in light rare earth elements with respect to the heavy rare earth elements and show significant positive anomalies of Zr and Hf. “Eclogitic” garnets are more depleted in highly incompatible elements (light rare earth elements, Nb and Ta) than the “peridotitic” garnets. Diamondites and their silicates very likely crystallised from a fluid phase. The trace element contents of the hypothetical fluids in equilibrium with the “peridotitic” garnets are similar to the trace

element contents of kimberlitic and carbonatitic liquids. Thus, crystallisation of these diamondites from a highly alkaline liquid in the presence of carbonates can be suggested. Hypothetical melts in equilibrium with “eclogitic” garnets are highly magnesian but depleted in light rare earth elements and other highly incompatible elements relative to the typical kimberlitic, lamproitic or carbonatitic liquids. This is an unexpected result because eclogites are richer in trace elements than peridotites and fluids in equilibrium with these rocks should reflect this. The different trace element contents of fluids which precipitated, beside diamonds, “peridotitic” and “eclogitic” garnets, respectively, therefore, must be the result of differences in the properties of these fluids rather than of different source rocks, as was already suspected by *Kurat and Dobosi* (2000).

## Introduction

Monocrystal diamonds and their silicate inclusions as well as diamond-bearing peridotitic or eclogitic xenoliths carry essential information about the deeper upper mantle evolution and processes. However, beside monocrystalline diamonds, polycrystalline diamonds (diamondites/framesites/bort) can be abundant in some kimberlites and they occasionally bear silicates, oxides and sulphides. Unfortunately, only few studies were devoted to these rocks so far, although such studies may open a yet unexploited window into the earth’s mantle. A few electron microprobe data are available for garnets, clinopyroxenes and chromites from diamondites originating from the kimberlites of Yakutia (*Sobolev et al., 1975; Sobolev, 1977*), Botswana, Orapa (*Gurney and Boyd, 1982*) and Jwaneng (*Kirkley et al., 1991*). There are also carbon and helium isotope data (*Kirkley et al., 1991; Burgess et al., 1998*). Trace element contents and radio-isotopes of silicates were not reported for diamondites until recently (*Kurat et al., 1999; Kurat and Dobosi, 2000; Jacob et al., 1999*).

In this paper we present major and trace element data for garnets and clinopyroxenes from ten diamondites, analysed *in situ* by electron microprobe and laser ablation ICP-MS. These data extend the existing small data base and allow an improved look into diamond formation and mass transport by fluids in the earth’s upper mantle. They also confirm the previously reached conclusion that monomineralic upper mantle rocks composed mainly of diamond, which were therefore named *diamondites* by *Kurat et al. (1999)* and *Kurat and Dobosi (2000)*, were formed by fluids.

## Samples

The origin of our samples is in the dark. Several kilograms of diamondites (“polycrystalline diamonds”) were offered to the Museum of Natural History in Vienna by a Viennese diamond dealer. Among these, some few (less than 1% by number) contained silicates. The only information that was given about their origin is that these diamondites come from somewhere in southern Africa – presumably from Botswana, because similar rocks were previously described from there (*Gurney and Boyd, 1982; Kirkley et al., 1991*).

From a collection of about 50 samples of diamondite xenoliths ten were selected for detailed major and trace element study. This relatively small sample number is due to the fact that we wanted to investigate the silicate phases in their original textural relationships with the diamonds and with each other on a polished surface rather than crushing the rocks for mineral separation. Naturally, only few samples were suitable for this way of sample preparation which turned out to be a real challenge for our workshop.

Macroscopically the samples have angular shapes and are 12 to 25 mm in their longest dimensions with masses from 13 to 61.5 ct. The colour of the bulk samples varies from medium to dark grey, sometimes almost black; individual diamond grains may have varying shades of grey ranging from almost white to dark grey. All diamondites are complex intergrowths of anhedral diamonds with abundant pore space and cavities. The grain size of diamonds varies from 50 to 1000  $\mu\text{m}$  – fine-grained varieties, like Dia 012 have grain sizes generally smaller than 100  $\mu\text{m}$ , while the relatively coarse-grained ones like Dia 014 have grain sizes varying from 100 to 1000  $\mu\text{m}$ . The grain sizes can vary even within a sample and coarser- and finer-grained portions can be present. Euhedral diamond crystals, either sharp-edged octahedra (e.g., Dia 015) or terraced octahedra (e.g., Dia 012) cover the walls of the cavities (Fig. 1).

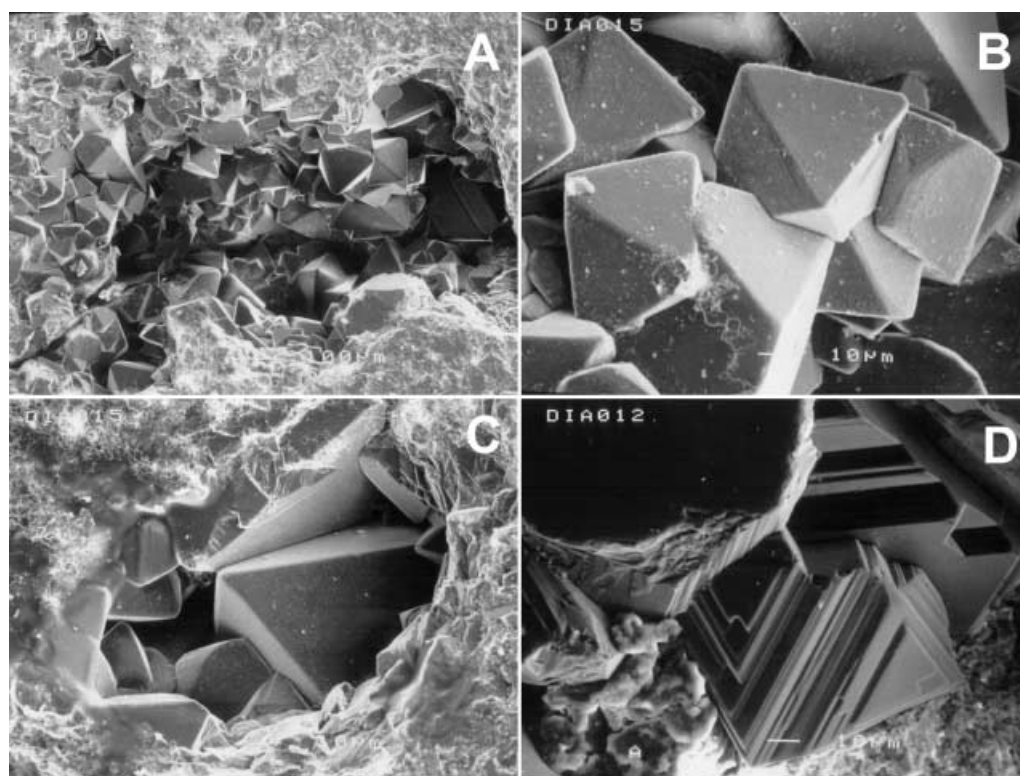


Fig. 1. Diamond crystals in cavities of diamondites; secondary electron scanning microscope images. **A** Octahedral diamond crystals from Dia 015. **B** Detail from A. **C** Octahedral diamond crystals from Dia 015. **D** Terraced diamond octahedra from Dia 012

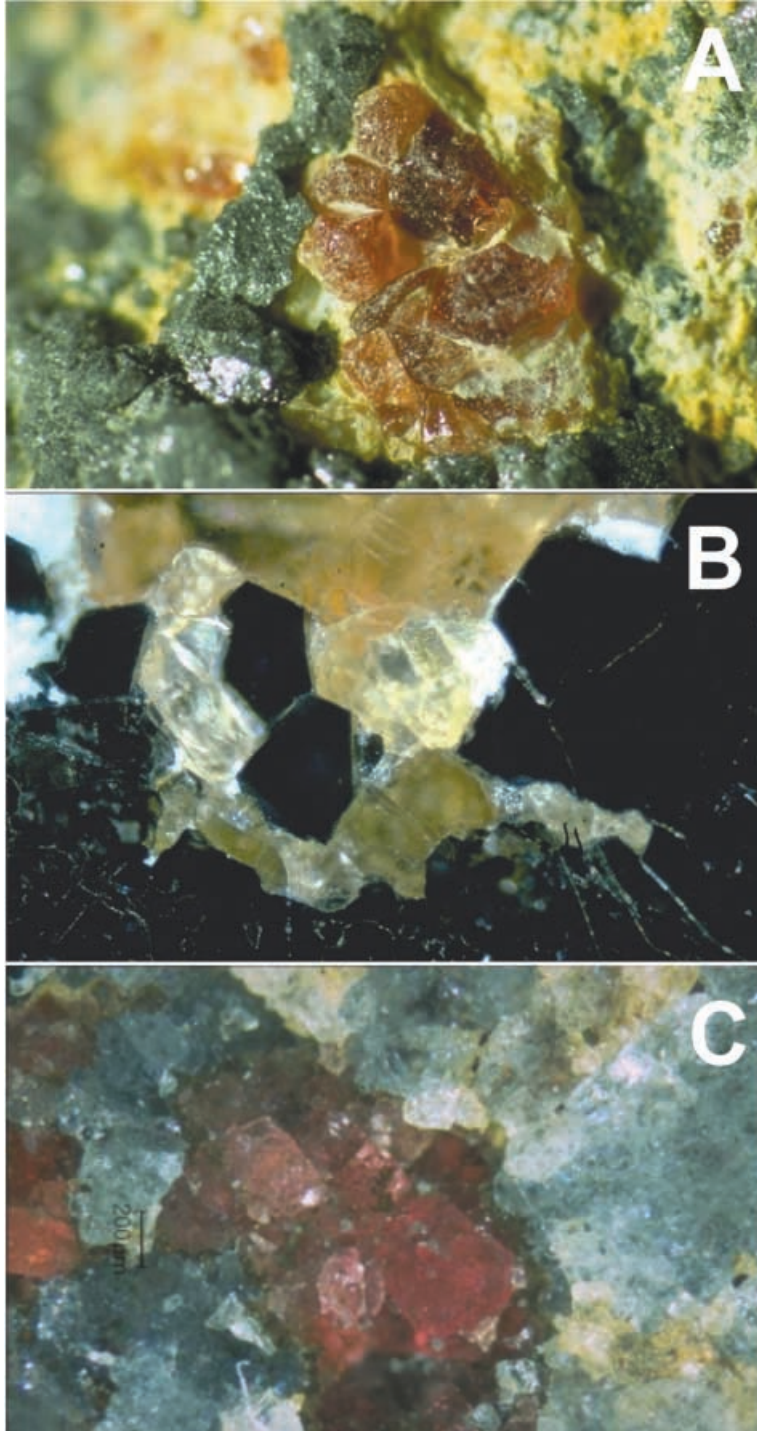


Fig. 2. Garnets in diamondites. **A** Polycrystalline eclogitic garnet (Dia 079) filling a cavity and intergrown with fine-grained diamonds. Length of picture: 2 mm. **B** Polycrystalline eclogitic garnet (Dia 016) intimately intergrown with and including euhedral diamond. Length of picture: 1 mm. **C** Polycrystalline peridotitic garnet (Dia 015) filling cavity and intergrown with diamond

Table 1. *List and brief description of diamondite samples*

Sample	Max. dimension, colour	Texture, grain size	Cavities	Silicates	Type
Dia 001	25 mm, 61.5 ct, medium grey	fine-grained rock with abundant cavities, 100–400 µm	euhedral octahedral diamonds, 100–200 µm	abundant brownish-red garnets in pores, 100–200 µm	eclogitic type I
Dia 002	20 mm, 32.5 ct, medium grey	porous rock, 200–400 µm		abundant, deep honey-yellow garnet, 200–600 µm	eclogitic type II
Dia 012	15 mm, 34 ct, dark grey	fine-grained porous rock, <100 µm	contact twins or terraced octahedra	abundant green clinopyroxene and lilac garnet	peridotitic
Dia 013	18 mm, dark grey almost black	flat porous rock, 100–200 µm	euhedral octahedra, some terraced diamonds, 100–200 µm	abundant dark honey-yellow garnets, up to 200 µm	eclogitic type II
Dia 014	19 mm, 20 ct, dark grey, almost black	granular rock, garnet-diamond contacts with rounded interfaces, 100–1000 µm		abundant yellowish-brown garnet up to 200 µm	eclogitic type II
Dia 015	12 mm, 13 ct, dark grey	granular, highly porous rock, 50–500 µm	sharp edged octahedral diamonds, 50–100 µm	fresh lilac and altered light brownish, rusty garnets with small 50–100 µm clinopyroxenes	peridotitic
Dia 016	17 mm, light grey	granular rock, 200–600 µm	sharp-edged octahedra	brownish-red garnets up to 1000 µm	eclogitic type I
Dia 017	18 mm, 25.5 ct, dark grey, almost black	granular, fine-grained rock, around 100 µm		lilac-violet garnets, 200–300 µm	peridotitic
Dia 021	16 mm, dark grey, black	granular, grains up to 500–1000 µm	terraced octahedra	lilac garnets, 200–300 µm	peridotitic
Dia 030	20 mm, 29.5 ct, medium grey	porous friable rock, fan-like structure at one side, granular texture at the opposite side		abundant brown garnets, from 200 to 1000 µm	eclogitic type I

Silicate phases intergrown with the diamonds are mainly garnets and less frequently clinopyroxenes. They occur interstitially or partly fill the space of cavities and are usually intimately intergrown with each other and with diamonds (Fig. 2). The colours of the garnets are deep honey yellow, brownish-red or lilac and their grain size varies between 200 and 1000  $\mu\text{m}$ . Green clinopyroxene is present in sample Dia 012, where it forms complex intergrowths with garnet, and in sample Dia 015, where it is either associated with garnet or occurs isolated. Both, garnets and clinopyroxenes, contain inclusions of euhedral diamonds; the reverse (silicate inclusions in diamonds) has not been observed. Occasionally, fluid inclusions are also present. The petrography of samples Dia 012 and Dia 016 with illustrations is discussed in Kurat and Dobosi (2000). The list of samples and short descriptions are presented in Table 1.

### Analytical techniques

Electron microprobe analyses of garnets and clinopyroxenes were carried out with a Cameca SX 100 (University of Vienna) and an ARL SEMQ (Natural History Museum, Vienna) electron microprobes. All analyses were made against mineral standards by utilising wavelength-dispersive spectrometers; acceleration voltage and beam current were 15 kV and 15 nA, respectively, and standard correction procedures were applied.

Trace elements were determined *in situ* in garnets and pyroxenes by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland. The details of the laser ablation system and analytical conditions are given in our previous paper (Kurat and Dobosi, 2000). All measurements were carried out using "time-resolved analysis" data acquisition mode which allows us to monitor the progress of the laser ablation and detect inclusions and heterogeneities. The diameter of the ablation pit is between 30–50  $\mu\text{m}$  and the depth after 60 seconds of ablation is typically about 100  $\mu\text{m}$ .

### Results

#### *Major elements*

Major element contents of garnets and clinopyroxenes are presented in Table 2. They are the averages of 10–25 individual spot analyses, depending on the abundance of garnet and clinopyroxene in a given diamondite.

Both, garnets and clinopyroxenes, are relatively homogeneous with respect to major element composition and individual grains in the same samples have about the same compositions. A slight inhomogeneity was observed only in the  $\text{Cr}_2\text{O}_3$  contents of garnets from samples Dia 012 and Dia 021.

All garnets have low CaO (varies between 3.5 and 5.7 wt%) and high MgO (around 20 wt%) contents and they plot into a relatively restricted area in the Ca–Mg–Fe triangle (Fig. 3).

The four lilac garnets from samples Dia 012, Dia 015, Dia 017 and Dia 021 have  $\text{Cr}_2\text{O}_3$  contents between 3.9–6.4 wt%. The highest  $\text{Cr}_2\text{O}_3$  was measured in

Table 2. Major element compositions (in wt%) of garnets and clinopyroxenes from diamondites as determined by electron microprobe

	Dia 001	Dia 002	Dia 012	Dia 013	Dia 014	Dia 015	Dia 016	Dia 017	Dia 021	Dia 030	Dia 012	Dia 015
	gt	gt	gt	gt	gt	gt	gt	gt	gt	gt	cpx	cpx
SiO <sub>2</sub>	42.7	41.8	42.3	41.4	42.0	41.6	43.2	41.4	41.8	41.7	56.0	56.8
TiO <sub>2</sub>	0.64	0.40	0.27	0.43	0.31	0.14	0.61	0.56	0.18	0.63	0.33	0.11
Al <sub>2</sub> O <sub>3</sub>	22.6	22.8	19.5	23.4	22.3	18.8	21.5	20.1	19.4	22.4	3.5	2.96
Cr <sub>2</sub> O <sub>3</sub>	0.73	0.25	5.2	0.33	0.16	6.4	0.71	3.9	6.1	0.70	2.27	2.25
FeO <sub>tot</sub>	7.4	9.6	7.8	9.4	10.6	7.0	7.0	7.4	7.1	7.2	2.44	2.37
MnO	0.29	0.32	0.35	0.33	0.36	0.32	0.28	0.35	0.39	0.29	0.08	0.10
MgO	21.8	19.0	20.8	20.0	18.5	20.8	22.2	21.4	20.4	21.4	15.6	15.9
CaO	3.8	4.6	4.4	4.5	4.9	5.4	3.7	3.6	5.7	3.7	17.1	17.3
Na <sub>2</sub> O	0.11	0.07	0.08	0.08	0.07	0.04	0.12	0.06	0.00	0.08	3.08	2.13
K <sub>2</sub> O	-	-	-	-	-	-	-	-	-	-	0.04	0.07
totals	100.07	98.84	100.70	99.87	99.20	100.50	99.32	98.77	101.07	98.10	100.44	99.99
Si	3.009	3.014	3.017	2.957	3.034	2.986	3.060	2.991	2.983	2.997	2.000	2.028
Ti	0.034	0.022	0.014	0.023	0.017	0.008	0.032	0.030	0.010	0.034	0.009	0.003
Al	1.878	1.938	1.640	1.970	1.899	1.591	1.795	1.712	1.632	1.898	0.146	0.125
Cr	0.041	0.014	0.294	0.019	0.009	0.364	0.040	0.223	0.345	0.040	0.064	0.064
Fe	0.435	0.578	0.464	0.560	0.639	0.419	0.414	0.446	0.423	0.432	0.073	0.071
Mn	0.017	0.020	0.021	0.020	0.022	0.019	0.017	0.021	0.024	0.018	0.002	0.003
Mg	2.289	2.041	2.210	2.128	1.991	2.224	2.343	2.303	2.169	2.291	0.830	0.846
Ca	0.287	0.355	0.336	0.344	0.379	0.415	0.281	0.279	0.436	0.285	0.653	0.662
Na	0.015	0.010	0.011	0.011	0.010	0.006	0.016	0.008	0.000	0.011	0.213	0.147
K	-	-	-	-	-	-	-	-	-	-	0.002	0.003
Oxygen	12.000	12.000	12.000	12.000	12.000	12.000	12.000	12.000	12.000	12.000	6.000	6.000
Cations	8.005	7.992	8.007	8.032	8.000	8.032	7.998	8.013	8.022	8.006	3.992	3.952
Mg-number	0.84	0.78	0.83	0.79	0.76	0.84	0.85	0.84	0.84	0.84	0.92	0.92

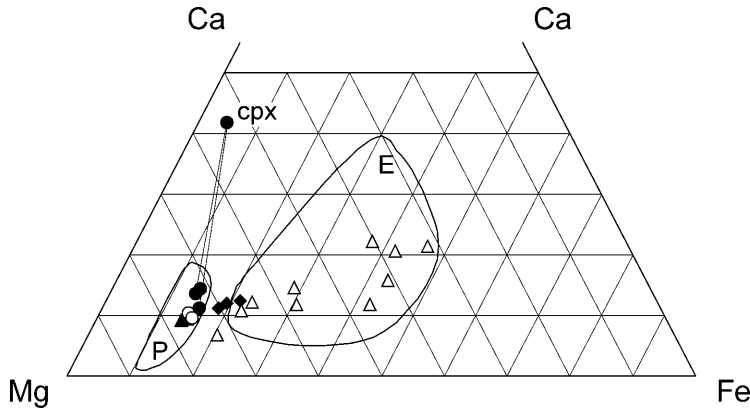


Fig. 3. Projection of diamondite garnet and clinopyroxene analyses onto the Mg–Fe–Ca (atomic) plane. For comparison, analyses of garnets from Orapa and Jwaneng framesites (diamondites) (*Gurney and Boyd, 1982; Kirkley et al., 1991*) are plotted and the fields for eclogitic and peridotitic garnet inclusions from diamonds (*Meyer, 1987*). Clinopyroxenes coexisting with garnets from Dia 012 and Dia 015 samples are also shown. Solid circles: peridotitic (P) garnets and clinopyroxenes; solid triangles: eclogitic (E-I) garnets; solid diamonds: eclogitic (E-II) garnets; open circles and triangles: peridotitic and eclogitic garnets, respectively, from Orapa and Jwaneng framesites

Dia 015 and the lowest in Dia 017 garnets. All high-chromium garnets plot into the fields of peridotitic (P) garnets in the Ca–Fe–Mg triangular plot (Fig. 3) and they fall into the lherzolitic and harzburgitic garnet fields in the CaO vs. Cr<sub>2</sub>O<sub>3</sub> plot (Fig. 4) with positively correlated CaO and Cr<sub>2</sub>O<sub>3</sub> contents. Two of the garnets plot into the harzburgite (H), one into the lherzolite (L) field and one on the H/L boundary line.

The remaining 6 garnets have low Cr<sub>2</sub>O<sub>3</sub> contents (less than 1 wt%). Although their Cr<sub>2</sub>O<sub>3</sub> contents correspond to the eclogitic suit of garnet inclusions in diamonds (Fig. 4), their high MgO and low FeO contents places them outside the

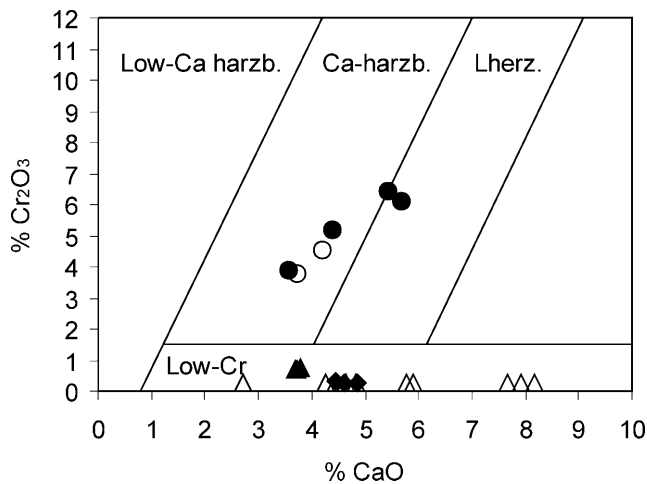


Fig. 4. Cr<sub>2</sub>O<sub>3</sub> vs. CaO contents in garnets from diamondites. For comparison, data from Orapa and Jwaneng diamondites (*Gurney and Boyd, 1982; Kirkley et al., 1991*) are plotted. Diagram modified after *Sobolev (1977)* and *Griffin et al. (1999)*. Symbols as in Fig. 3



eclogitic (E) garnet field of Meyer (1987) in the Ca–Fe–Mg triangular plot (Fig. 3). Low-chromium garnets can be divided into two groups: the first group, eclogitic I (E-I) comprises samples Dia 001, Dia 016 and Dia 030. They are as magnesian as the Cr-rich P garnets, have FeO contents between 7.0 and 7.4 wt%, CaO contents between 3.7 and 3.8 wt% and their Cr<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents cluster around 0.7 wt% and 0.6 wt%, respectively. They plot together with the high-Cr garnets into the peridotitic (P) garnet field of Meyer (1987) in the Ca–Fe–Mg diagram (Fig. 3). Low-Cr garnets of the second eclogitic garnet group (E-II) comprise samples Dia 002, Dia 013 and Dia 014. They are less magnesian than the E-I garnets, are richer in FeO (9.4–10.6 wt%) and contain more CaO (4.5–4.9 wt%) and less Cr<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> (0.2–0.3 and 0.3–0.4 wt%, respectively). These mainly plot in between the peridotitic and eclogitic fields in Fig. 3.

### *Trace elements*

The trace element abundances (Table 3) vary systematically among the garnet groups (all groups have their own compositional characteristics), so they will be described separately.

Peridotitic garnets form a relatively diverse group. The chondrite-normalised rare earth element (REE) patterns of garnets from samples Dia 015 and Dia 021 are very similar to each other (Fig. 5a). They have heavy REE (HREE) abundances around 10 × chondritic, a small “hump” at the medium REE (MREE) (the maximum is at Eu and Sm) and a continuous depletion in the light REE (LREE) region towards La (0.2–0.5 × Cl). The pattern of garnet from Dia 012 is similar to that of the previous garnets but has only a small hump at the MREE and is slightly poorer in LREE than the garnets from Dia 015 and Dia 021. The garnet from Dia 017 has a different REE pattern. It is rich in HREE (more than 20 × chondritic) and shows a continuous depletion towards La (Fig. 5a) with the LREE abundances being identical to those in Dia 012 garnet.

The chondrite-normalised REE abundances of the E garnets show a continuous depletion from the HREE to the LREE (Fig. 5c). Garnets of the two groups identified from major and compatible trace element abundances, E-I and E-II, have about the same level of LREE depletion (La = 0.03–0.08 × Cl) but different HREE contents. The E-I garnets have low, the E-II ones high HREE abundances (9–16 × Cl and 33–36 × Cl, respectively).

Of the other incompatible trace elements, Y always follows the HREE having approximately the same chondritic abundance as Ho and Sr shows negative anomalies relative to the adjacent REE in garnets of all groups (Fig. 5b and d). In P garnets, the chondrite-normalised abundances of Nb and Ta are always significantly higher than those of the LREE and Ti shows negative anomalies. The elemental abundance patterns are practically identical in garnets from Dia 015 and Dia 021 (Fig. 5b). They differ from the rest in higher LREE, Nb and Ta contents. Abundances of Zr and Hf are quite complex: garnet from Dia 021 has both elements slightly depleted relative to the adjacent REE, while the garnet from Dia 017 has positive anomalies for both elements. Garnet from Dia 015 and Dia 017 have a small positive Zr anomaly and a small negative one for Hf. The few available data for Th and U suggest elevated abundances relative to the LREE.

Table 3. Average trace element contents of garnets and clinopyroxenes from diamondites as determined by LA-ICP-MS. The number of analyses are given in brackets

	Dia 001	Dia 002	Dia 012	Dia 013	Dia 014	Dia 015	Dia 016	Dia 017	Dia 021	Dia 030	Dia 012	Dia 015
	gt (5)	gt (12)	gt (4)	gt (8)	gt (4)	gt (4)	gt (5)	gt (10)	gt (6)	gt (8)	cpx (12)	cpx (1)
Sc	114	105	145	87	93	140	94	108	129	72	35	27
V	210	233	220	295	332	325	240	159	281	240	380	408
Co	66	51	71	85	82	74	68	58	47	57	38	58
Ni	121	82	100	119	154	93	124	145	71	105	630	2687
Zn	79	48	55	137	115	65	57	54	43	62	46	47
Ga	11	5	9	13	9	13	11	10	8	9	8	10
Rb												
Sr		0.32		0.41	0.32	0.92	0.42	1.0	1.47	0.54	199	343
Y	11	26	9.9	26	31	12	11	24	9.0	7.6	3.9	4.1
Zr	38	40	27	43	32	45	37	52	32	30	64	30
Nb	0.31	0.28	0.78	0.35	0.55	1.56	0.24	0.89	2.03	0.3	2.2	12.9
Ba							1.0					114
La	0.019		0.036	0.013		0.07		0.041	0.16		3.9	19.5
Ce	0.12	0.095	0.38	0.15	0.14	0.9	0.14	0.35	1.54	0.13	14.9	48.3
Pr	0.046	0.041	0.14	0.051	0.052	0.33	0.04	0.13	0.49	0.038	2.6	6.0
Nd	0.41	0.41	1.3	0.51	0.55	3.2	0.36	1.4	4.3	0.38	12.6	22.9
Sm	0.32	0.4	0.98	0.49	0.49	2.1	0.4	1.2	2.0	0.39	3.1	5.3
Eu	0.19	0.21	0.42	0.27	0.29	0.85	0.2	0.61	0.74	0.19	0.99	1.2
Gd	0.76	1.0	1.2	1.2	1.2	2.3	0.82	2.6	2.1	0.72	2.2	3.4
Tb	0.21	0.32	0.22	0.35	0.41	0.43	0.2	0.59	0.33	0.19	0.27	0.31
Dy	1.5	3.2	1.7	3.3	3.9	2.3	1.5	4.4	1.9	1.4	1.2	1.3
Ho	0.43	0.97	0.37	0.99	1.15	0.47	0.38	1.0	0.41	0.32	0.18	0.21
Er	1.5	3.5	1.2	3.7	4.0	1.4	1.4	3.4	1.3	1.0	0.34	0.22
Tm	0.28	0.64	0.21	0.69	0.71	0.23	0.26	0.54	0.22	0.18	0.04	0.04
Yb	2.2	4.7	1.4	4.9	5.1	1.6	1.8	3.84	1.8	1.28	0.2	
Lu	0.42	0.82	0.27	0.89	0.86	0.28	0.39	0.62	0.3	0.22	0.03	0.03
Hf	1.1	1.0	0.44	1.2	0.73	0.64	1.2	1.3	0.91	0.97	3.2	2.5
Ta	0.021	0.022	0.033	0.024	0.036	0.12	0.012	0.093	0.134	0.014	0.13	0.57
Th						0.05	0.015					2.1
U						0.066	0.007	0.03	0.16	0.014	0.095	0.22

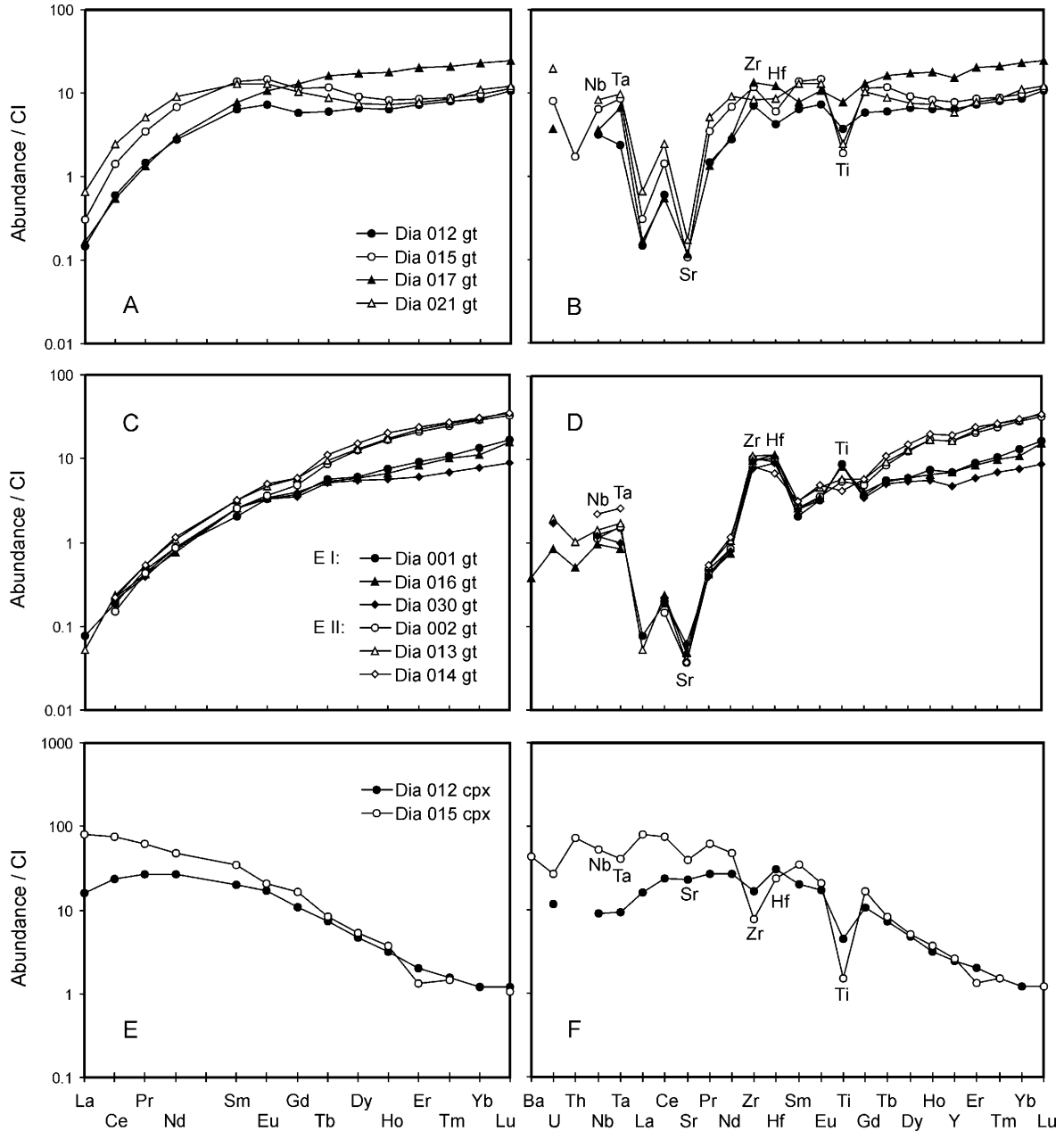


Fig. 5. Chondrite-normalised abundances of trace elements in garnets and clinopyroxenes from diamondites. **A** and **B** peridotitic garnets, **C** and **D** eclogitic (E-I and E-II) garnets; **E** and **F** clinopyroxenes. Normalisation data from *Palme (1988)*

Eclogitic garnets all have positive anomalies in the abundances of Zr and Hf (though their absolute concentrations are similar to their abundances in the P garnets) as well as those of Nb and Ta with respect to elements of comparable compatibility. Titanium is enriched over the adjacent REE in E-II garnets but not in the E-I ones (Fig. 5d). Few data for U and Th shows their normalised abundance are around the level of Nb and Ta.

Clinopyroxene coexisting with garnet in Dia 012 shows a concave upward chondrite-normalised REE pattern (Fig. 5e) which is poor in HREE (about  $1 \times \text{CI}$ ), shows an enrichment towards the LREE with a maximum at Nd and Pr (about  $27 \times \text{CI}$ ) and a slight depletion in Ce and La. Possibly, there is a small depletion in Hf and a small enrichment in Zr relative to the adjacent REE (Fig. 5f). The chondrite-normalised REE pattern of the clinopyroxene in Dia 015 (only one analysis) is similar to that of the former between Lu and Sm but abundances continuously increase towards La. A clear negative anomaly in the abundances of Hf and Zr is present (Fig. 5f). Strong negative anomalies of Ti abundances relative to the adjacent REE can be observed in both clinopyroxenes.

## Discussion

### *Fluid origin and crystallisation of diamondites*

Gurney and Boyd (1982) suggested that polycrystalline diamond aggregates (diamondites) are the product of rapid crystallisation from a fluid and the intergrowths of diamond and silicate clearly indicate that both precipitated in the same crystallisation event. Our observations strongly confirm these suggestions. The high porosity of the diamondite xenoliths and the presence of euhedral diamond crystals on the walls of cavities are indicative of crystallisation from a fluid. The intimate intergrowth of diamonds and silicates and the free-floating euhedral diamond inclusions in clinopyroxenes and garnets suggest that diamond and silicates crystallised from the same fluid during the same rock forming event. Because the silicates in our diamondites crystallised together with the diamond from a fluid phase it can be assumed that the peridotitic and eclogitic character of the garnets (and clinopyroxenes) is a result of the chemical characteristics of the fluids and does not reflect the crystallisation environment. Thus, it cannot be *a priori* assumed that diamondites with peridotitic or eclogitic garnets crystallised in peridotitic or eclogitic environments, respectively.

The silicates in diamondites are predominantly garnets. Olivine, orthopyroxene and omphacite, the major minerals to be expected to coexist with peridotitic and eclogitic garnets, respectively, are missing from the diamondites. Their absence was considered a puzzling feature by Gurney and Boyd (1982) – they explained this by the susceptibility to alteration of these minerals or by non-representative sampling. However, relatively fresh samples of the present study – as judged from the preservation state of garnets – also lack omphacitic clinopyroxene while chromium-rich clinopyroxene coexisting with chromium-rich garnet was found in two samples, indicating that clinopyroxene can survive the possible alterations and possible chemical processing during recovery. Thus, we believe that the absence of these minerals in diamondites is an original feature and omphacitic clinopyroxene, orthopyroxene and very likely also olivine were not present in the primary, unaltered mineral assemblage.

However, the lack of olivine, orthopyroxene and omphacite, main minerals of the most common upper mantle rocks, is in contrast to what is observed in most monomineralic rocks of the uppermost mantle where relictic grains from the wall rock are commonly included by the vein rocks (e.g., Kurat et al., 1993). As vein

rock formation is related to tectonic activity, which opens the space for the fluids to move, relic grains can be expected to be present. However, the absence of the most common minerals of the upper mantle in diamondites indicates an environment different from that of the common upper mantle vein rocks. It possibly indicates precipitation of diamondites in a non-brittle environment and a mechanism for the creation of the necessary space which was different from that which helped to create the common upper mantle vein rocks. As none of the fluids/melts that formed diamondites precipitated olivine, orthopyroxene or omphacite, they apparently were undersaturated in these phases. Consequently, they were capable of dissolving the most common wall rock minerals and thus were able to create the space necessary for the precipitation of the diamondites. Although most diamondites indicate transportation within the upper mantle from a deep-seated formation site (below the asthenosphere) to a shallower depth where they were picked up by the kimberlite magma, they have a granular, tectonically undisturbed texture and undisturbed druse space. We believe that this is a consequence of transportation in a ductile wall rock like those which constitute upper mantle convection currents. Possibly, because of this we do get delivered diamondites only in small pieces as they should be broken up, but not ground up, by differential flow of the convection cell rocks. However, the fine-grained, schistose diamondites (like Dia 013) could be the result of tectonic forces having been active during or after formation of the rock.

#### *Composition and origin of the fluids*

In order to characterise the trace element abundances of the parental fluids, it is useful to transform the trace element concentrations of the minerals into trace element concentrations of the theoretical coexisting melts (*Stachel and Harris, 1997*). Unfortunately, an internally consistent set of trace element partition coefficients for many elements between garnet, clinopyroxene and fluid (melt) at high pressures is not available. We chose to apply the same set of partition coefficients that *Stachel and Harris (1997)* used – for Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu, Zr and Hf the partition coefficients between garnet, clinopyroxene megacrysts and kimberlite melt of *Fujimaki et al. (1984)* were used and for Nb and Ti the partition coefficients of *Green et al. (1989)*. The calculated melt/fluid compositions are plotted in Fig. 6.

The trace element patterns of the hypothetical melts in equilibrium with the peridotitic garnets in diamondites (Fig. 6a) are similar to each other. The HREE abundances are  $2\text{--}3 \times \text{Cl}$  and LREE (Ce) abundances are variable and  $100\text{--}500 \times \text{Cl}$ . There are negative anomalies for Ti, Hf and Zr. Hypothetical melt compositions calculated from clinopyroxenes are similar to those calculated from garnets, except for much higher LREE, Nd and Nb abundances in the former. This can be the result of the “contaminated” clinopyroxene analyses (which is possibly the case of clinopyroxene Dia 015), the lack of equilibrium between clinopyroxene and garnet, or the internal inconsistency of the partition coefficients under the conditions of crystallisation. However, the difference between the hypothetical melt compositions in equilibrium with garnets and clinopyroxenes for most elements is not serious. The general shape of the elemental abundance patterns of the

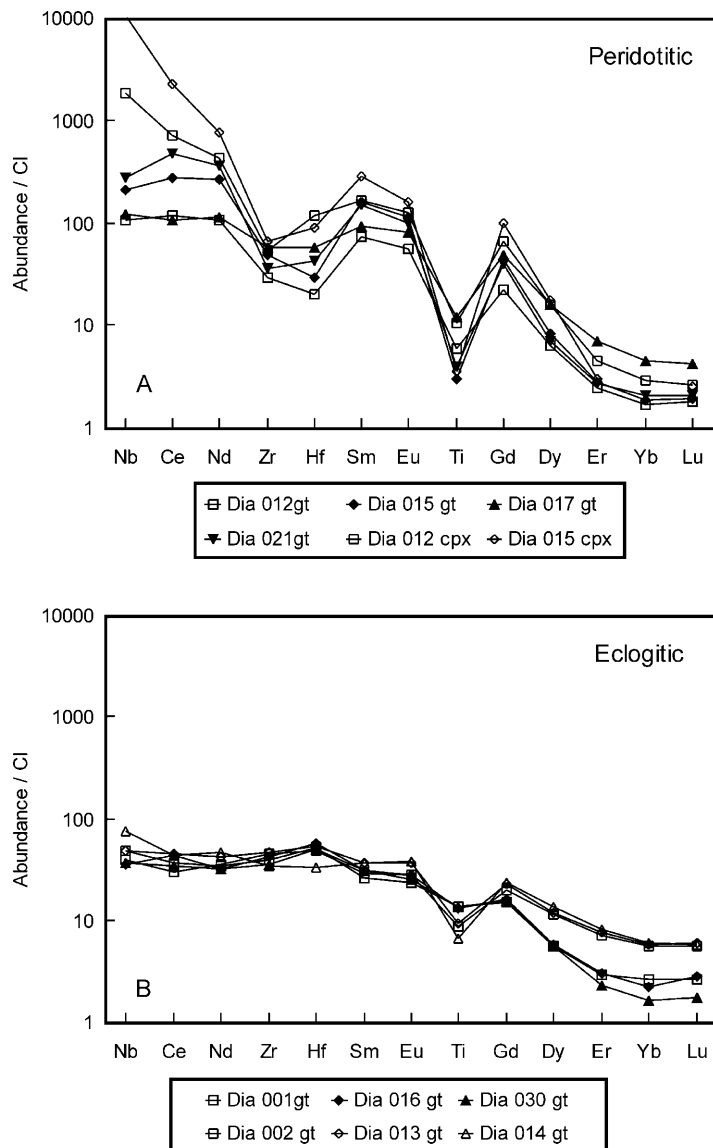


Fig. 6. Chondrite-normalised trace element patterns of hypothetical melts in equilibrium with garnets and clinopyroxenes from diamondites. **A** Peridotitic garnets and clinopyroxenes. **B** Eclogitic garnets. Melt/fluid compositions were calculated using the crystal/melt partition coefficients from *Fujimaki et al. (1984)* and *Green et al. (1989)*. Normalisation data from *Palme (1988)*

hypothetical melts for peridotitic garnets and clinopyroxenes in Fig. 6a is similar to those of hypothetical melts calculated from lherzolitic garnet inclusions in diamonds by *Stachel and Harris (1997)*. The extreme elemental fractionations related to incompatibility indicate that the extraction of these elements from the source was only partial. The low abundances of HREE indicate the presence of residual garnet in the source, the low abundances of Ti, Hf and Zr could indicate a refractory Ti, Zr, Hf phase (ilmenite?) in the source. Solubility of these elements in the

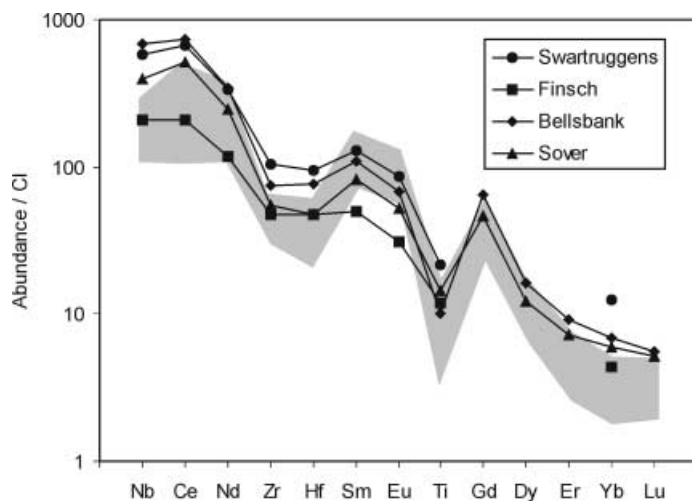


Fig. 7. Compositional fields of hypothetical melts in equilibrium with the peridotitic garnets of diamondites (shaded field) compared with kimberlites/orangeites (Mitchell, 1995). Normalisation data from *Palme* (1988)

fluid clearly was low – in contrast to Cr which must have been highly soluble and consequently was enriched in the fluid.

Comparison of these hypothetical melts with kimberlites/orangeites (Mitchell, 1995) is shown in Fig. 7. The calculated hypothetical melt compositions for peridotitic garnets from diamondites are similar to kimberlite and carbonatite melt compositions, although three of the four are more depleted in HREE than typical kimberlites. The troughs at Zr, Hf and Ti abundances of the hypothetical melt compositions are similar to those in kimberlites but are significantly less pronounced than in carbonatite melts. On the basis of trace element compositions the crystallisation from kimberlitic or carbonatitic melt is a possibility, and this agrees with *Gurney and Boyd* (1982) who suggested that framesites precipitated from carbonatitic or kimberlitic fluids. *Wang et al.* (2000) imply that the trace element characteristics of the harzburgitic garnet inclusions in Chinese diamonds are generally consistent with metasomatism by carbonatite melts. The presence of carbonate during diamond crystallisation is confirmed by fluid inclusion evidence. This evidence comprises the rare carbonate inclusions in diamonds (*Stachel et al.*, 1998), H<sub>2</sub>O-, carbonate- and alkali-bearing micro-inclusions in diamonds (*Navon et al.*, 1988) and carbonate-bearing, incompatible element-rich fluid inclusions from coated diamonds (*Schrauder et al.*, 1996). Recent experimental studies of *Pal'yanov et al.* (1999) and *Sokol et al.* (2000) have demonstrated the possible formation of diamonds in carbonate-carbon systems in the presence of H<sub>2</sub>O–CO<sub>2</sub>-rich fluids. These experimental results confirm that diamond can crystallise in nature in a wide range of redox conditions. Considering fluid inclusion and experimental evidence, *Pal'yanov et al.* (1999) suggested that alkaline carbonate fluids represent the most likely medium for natural diamond formation, a scenario that is perfectly compatible with our results.

Compositions of hypothetical melts in equilibrium with eclogitic garnets from diamondites have much less fractionated REE patterns (especially for E-I garnets

in Dia 001, Dia 015 and Dia 030, samples where the depletion of HREE is less pronounced than in the E-II group garnets) and lower Nb contents than the melts calculated from the peridotitic garnets. There is a small negative anomaly in the abundance of Ti but none for Zr and Hf relative to the adjacent REE (Fig. 6b). The LREE enrichment of the melt is about  $50 \times Cl$ , similar to olivine alkali basalts and not to kimberlites or lamproites. The mostly flat abundance pattern could indicate derivation from a primitive source. The abundances of HREE could indicate residual garnet in the source of E-I garnets or precipitation of garnet from the fluid on its way to the E-I garnet formation site (garnet fractionation). There was probably less residual garnet in the source of E-II garnets. The abundance anomaly of Ti could be due to precipitation of a Ti phase (ilmenite?) or to a refractory Ti phase in the source rock.

Both peridotitic and eclogitic garnet precipitating fluids appear to have a primitive (peridotitic?) source which was sampled in different ways because of the different properties of the fluids involved. The eclogitic garnet fluid/melt had a much lower Cr content but a similar Mg-number than the fluids/melts from which the peridotitic garnets and clinopyroxenes crystallised. Possibly, the high abundance of carbonatitic components in the fluids/melts that precipitated the peridotitic garnets also enabled these fluids to dissolve and carry Cr. Consequently, the formation of "peridotitic" (Cr-rich) or "eclogitic" (Cr-poor) garnet appears to be solely a feature of the fluids and not of the ultimate source of the fluids.

## Conclusions

The high porosity of the diamondites, the presence of euhedral diamonds on the walls of open cavities and the intergrowth relationships between diamonds and garnets (and sometimes clinopyroxenes) suggest an origin by fluid deposition for the diamondites and their silicates. The fluids were of a carbonatitic nature (dolomitic, alkali carbonatitic?) which were derived from primitive, probably peridotitic sources. Strongly carbonatitic fluids/melts, similar in chemical composition to kimberlites and orangeites, are assumed to have formed by low degree partial extraction of elements from a peridotitic source where a refractory Ti, Hf, Zr-phase and garnet kept Ti, Hf, Zr and the HREE, respectively. Such fluids produced diamondites with "peridotitic" (high-Cr) garnets (+/- clinopyroxene). The second type fluid/melt, similar in trace element contents to alkali olivine basalts, has had a primitive, flat trace element pattern indicative of derivation from a primitive (peridotitic) source by high degree of elemental extraction where only small amounts of a refractory Ti phase and garnet were left behind. These fluids precipitated diamondites with "eclogitic" (Cr-poor) garnets of two types: the magnesian E-I garnets with low HREE contents and the slightly less magnesian E-II garnets with high HREE contents.

As peridotitic and eclogitic garnets from diamondites are very similar in chemical composition and differ only in their Cr contents, their nature reflects the nature of the fluid/melt from which they were precipitated rather than the source of the fluid. The high Cr content is likely to be a feature of the highly carbonatitic, kimberlite/orangeite-like fluid/melt which apparently was able to extract Cr from the source(s) to a high degree. In contrast, the fluids/melts which precipitated the



eclogitic garnets were poor in Cr either because of their incapability to extract Cr from the source or because of the high degree of extraction of all elements from the source which resulted in a low, upper mantle-like Cr abundance in the fluid/melt.

All fluids/melts that formed diamondites were undersaturated in the main minerals of the upper mantle, such as olivine, orthopyroxene and omphacite, a fact that possibly enabled them to create the space for diamond precipitation. Diamondites probably formed in the ductile lower upper mantle and were transported in a convection cell to shallower depth where they were ultimately collected by the kimberlite magma.

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