Detailed Pull-Apart of a Diamondiferous Eclogite Xenolith: Implications for Mantle Processes during Diamond Genesis

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ABSTRACT

Two ways to determine the composition of diamondiferous mantle are to study diamond-bearing mantle xenoliths and inclusions contained in diamonds. We have combined these two approaches by examining in detail a diamondiferous eclogite from the Udachnaya kimberlite using high-resolution X-ray tomography and the electron microprobe, and then extracting the diamonds and analyzing the compositions of their mineral inclusions. None of the diamonds is in contact with fresh minerals. Instead, they are preferentially located along secondary mineralization zones within and between clinopyroxenes and between clinopyroxene and garnet. Most of the diamonds contain inclusions, from which we have analyzed, *in situ*, four clinopyroxenes. All of the inclusions are compositionally different from each other and from clinopyroxene in the host xenolith, even in the case of multiple inclusions from the same diamond. The differences are non-systematic, which, in conjunction with the location of the diamonds within secondary mineralization zones, suggest that the diamonds in this eclogite grew during a complex series of metasomatic events.

Keywords: diamond, X-ray computed tomography, eclogite, Udachnaya, Yakutia, metasomatism, diamond inclusions

1. INTRODUCTION

The problem of when and why diamonds crystallize in the mantle can be reduced to a first order question: Do diamonds crystallize at the same time as their host rock (i.e., are they igneous), or are they associated with a metasomatic event (i.e., metamorphic)? To answer this question, nature provides us with two types of samples of the environment in which diamonds form: diamondiferous mantle xenoliths, and inclusions trapped in diamonds. Both of these sample types have been studied by numerous workers (e.g., MacGregor and Carter, 1970; Sobolev et al., 1972; Prinz et al., 1975; Sobolev, 1977; Griffin et al., 1988; Ireland et al., 1994; Sobolev et al., 1994; Bulanova, 1995; Taylor et al., 1996; Kopylova et al., 1997; Snyder et al., 1997). However, a detailed study of multiple inclusions from multiple diamonds within a single, well-characterized sample of diamondiferous mantle has never been performed. We have undertaken such a study in an attempt to merge the two data sets into a single coherent picture of the conditions of diamond genesis.

Detailed examination of the mineral assemblage in a diamond-bearing eclogite xenolith can establish the conditions under which eclogitic diamonds occur. Mineral compositions in the xenolith record information which can be used to determine the conditions under which the diamonds crystallized, unless the xenolith has re-equilibrated at lower pressure, or has been affected by interaction with other mantle domains or with kimberlite. Such late-stage processes can be detected by comparing the compositions of mineral inclusions encapsulated (and, thus, geochemically isolated) within the diamonds to those same mineral phases in the xenolith.

Our approach to studying the nature of diamond-bearing mantle involves a detailed characterization of a 4x5x6 cm diamondiferous eclogite xenolith (U51-3) from the Udachnaya kimberlite (Yakutia). We chose an Udachnayan eclogite because there is an extensive body of previous work on similar xenoliths from this locality, including major- and trace-element mineral compositions (Jerde et al., 1993; Jacob et al., 1994; Sobolev et al., 1994; Snyder et al., 1997), C, O, Sr, and Nd isotopic compositions (Snyder et al., 1993; Jacob et al., 1994; Snyder et al., 1995; Snyder et al., 1997), as well as Re-Os isotopic analyses that yielded a whole-rock isochron age of 2.9 ± 0.4 Ga (Pearson et al., 1995) and a detailed study of the effects of mantle metasomatism in these xenoliths (V.N. Sobolev et al., 1998). Also, previous work on diamonds and diamondiferous eclogites from Udachnaya showed that the compositions of diamond inclusions can be different compared to each other and to the same mineral in the host eclogite (Sobolev et al., 1996; Taylor et al., 1996).

The piece of diamondiferous mantle we chose for this study is a relatively fresh eclogite with 11 diamonds visible on its exterior. The sample was found to contain a total of 30 macrodiamonds of up to 0.6 ct each, nearly all of which contain numerous mineral inclusions up to 300 microns in size. Sulfide inclusions are ubiquitous, whereas clinopyroxene inclusions are less common, and garnets are rare. Many inclusions less than 20 microns in diameter also occur, but the mineralogy of these tiny inclusions has not yet been determined. This plethora of inclusions provides ample opportunities to compare their compositions to the compositions of the host minerals and to each other.

2. PETROGRAPHY AND TOMOGRAPHY

Prior to extracting the diamonds from the xenolith, we created a 3-dimensional digital model of the sample using high-resolution X-ray computed tomography (HRXCT; Carlson and Denison, 1992; Denison et al., 1997; Keller et al., 1997; Rowe et al., 1997). The entire volume of eclogite xenolith U51-3 was scanned in a series of 79 X-ray slices at a slice thickness of 0.5 mm, using a microfocal X-ray source operating at 100 kV and 0.4 mA. This provided optimum contrast between the minerals present, and in-plane resolution of approximately 250 microns. (Higher resolutions are possible with a smaller sample size or a finer tomographic matrix.) Beam-hardening artifacts were minimized by embedding the sample in powdered garnet, and correcting for absorption measured in a scan through the powder alone. This resulted in HRXCT images that clearly resolve the diamonds in
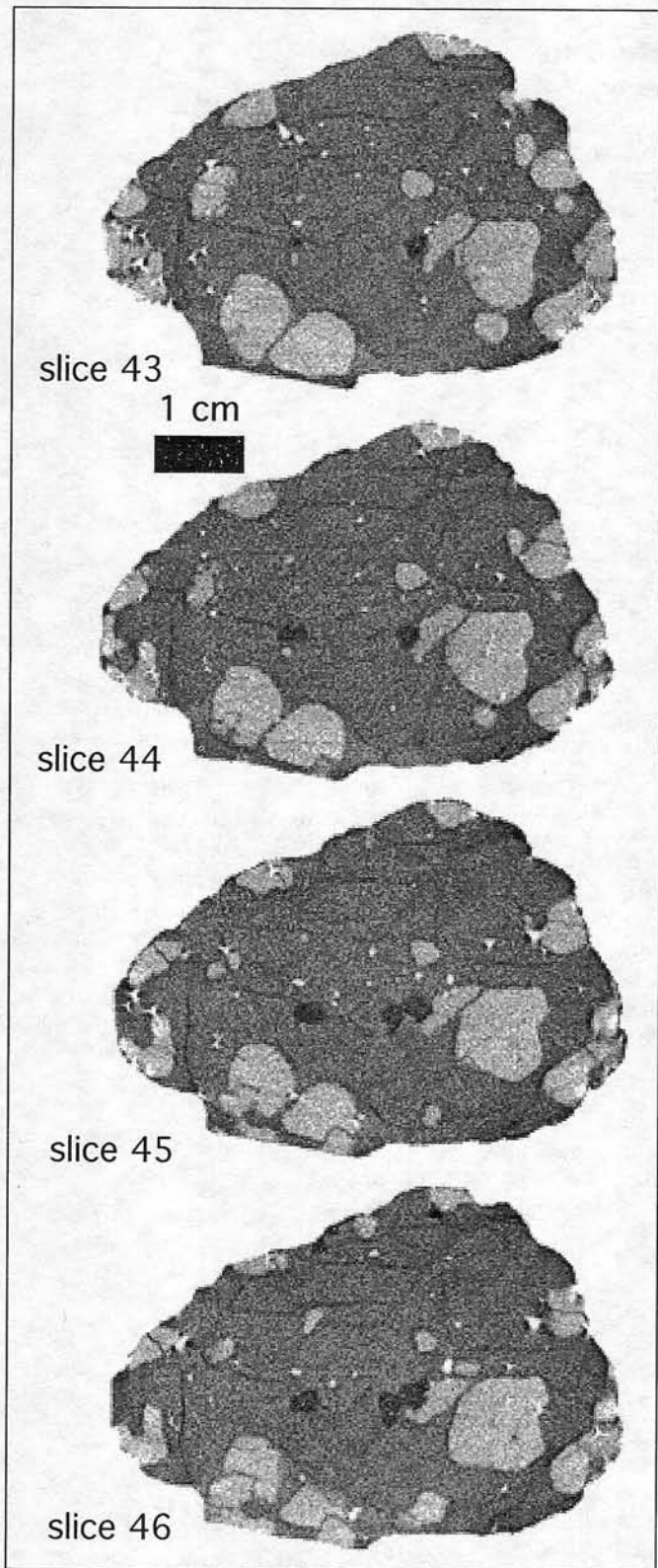
slice 43

1 cm

slice 44

slice 45

slice 46

Figure 1. Four sequential 2-dimensional X-ray tomographic "slices" through Udachnaya eclogite xenolith U51-3 show diamonds (dark gray to black shapes near the center of each image and the top edge of slices 45 and 46), sulfides (small white spots), and garnets (light gray shapes) in a matrix of clinopyroxene (medium gray) with a linear secondary mineralization fabric (thin, slightly darker gray lines). Brightness in these grayscale images correlates with mass density and effective atomic number. These neighboring slices are 500 microns apart. Sequential 2-D slices such as these can be combined into a 3-D digital model.

this sample and the textural details of their surrounding mineral assemblages (Fig. 1). The diamonds are easily distinguished from the other minerals using this high-resolution technique, in contrast to previous XCT experiments on a diamondiferous rock (Schulze *et al.*, 1996), which resolved diamonds only where they were surrounded by a high-density mineral (barite).

Stacking the 79 HRXCT slices into a three-dimensional digital model of the xenolith allowed us to view spatial relationships among the diamonds, to examine textural relationships between the diamonds and the eclogite, to calculate volume percentages of minerals, and to determine the best way to cut the xenolith and extract the diamonds while disturbing their adjacent minerals as little as possible.

The xenolith consists of 26 % red-orange garnets up to 1 cm in diameter, 0.5 % Fe-Ni sulfides up to 3 mm in diameter, and 0.5 % diamonds up to 4 mm in diameter, all dispersed in a matrix of large (>0.5 cm), dark green clinopyroxene that makes up 73 % of the sample. All of the garnets have thin kelyphytic rims (Fig. 2), but are otherwise fresh, and appear to have been euhedral or subhedral. Clinopyroxene is anhedral, and poikilitically surrounds garnet, but also occurs as inclusions in garnet (and vice versa). A fabric of subplanar cracks permeates the clinopyroxene, and is visible in hand-sample, in thin-section (Fig. 2), and in the HRXCT data (Fig. 1). A narrow zone of secondary mineralization surrounds each of these cracks, but the majority of the clinopyroxene remains fresh. There are no systematic petrographic differences between garnet and clinopyroxene grains that abut diamonds and those that do not. Sulfides are mainly pyrrhotite with minor amounts of chalcopyrite and pentlandite exsolution, and occur as spherical to obloidal inclusions in garnet and clinopyroxene, and as xenohedral inclusions in diamond. Diamonds are scattered throughout the sample, and are always associated with secondary mineralization zones within and between clinopyroxene or between clinopyroxene and garnet. All of the diamonds are euhedral and have octahedral growth forms, although many are complexly twinned. Only the smaller diamonds occur as individual octahedra. Growth zonations in the diamonds (as revealed by cathodoluminescence of
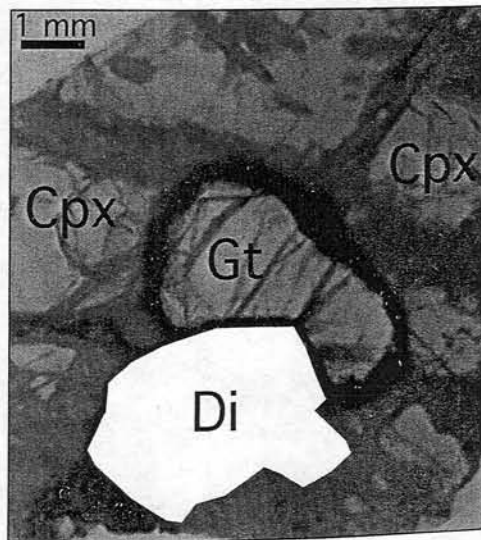

1 mm

Cpx

Cpx

Gt

Di

Figure 2. Thin-section of the area surrounding a diamond in eclogite xenolith U51-3. The diamond was removed prior to thin-sectioning, and nowhere was it in contact with fresh clinopyroxene or garnet. The garnet is surrounded by a dark, kelyphytic rim, including along its interface with the diamond. Subplanar cracks with secondary mineralization are visible in the clinopyroxene.

polished surfaces) are elaborate and discontinuous, indicating extremely complex growth histories.

3. MINERAL CHEMISTRY

3.1. Host minerals

The garnets in the host xenolith are pyropic ($Gr_9Py_{58}Al_{32}$) and mostly unzoned; however, the largest garnets have slightly more magnesian cores ($Gr_7Py_{60}Al_{32}$; Table 1). Garnet compositions plot mostly within the Group B field on the garnet ternary (Fig. 3), with a few of the core analyses just overlapping the boundary of the Group A field. This is within the field of previous analyses of garnets in eclogites from the Udachnaya kimberlite (Sobolev *et al.,* 1994).Clinopyroxenes in the host xenolith are omphacitic ($Wo_{36-37}En_{49-50}Fs_{13-14}$; Na_2O: 5.4–5.7 wt%; Table

2) and unzoned. A clinopyroxene inclusion in a garnet is slightly higher in FeO and Na_2O, and lower in CaO ($Wo_{36}En_{50}Fs_{15}$; Na_2O: 5.8 wt%; Table 2). These compositions plot within the field for Group B clinopyroxene in MgO vs. Na_2O space (all of Fig. 4C is within the Group B field of Taylor and Neal, 1989), and are consistent with previous analyses of clinopyroxene in eclogites from Udachnaya (Sobolev *et al.,* 1994).

3.2. Inclusions in diamonds

Four carefully chosen 50–100 micron clinopyroxene inclusions from crack-free regions of three diamonds from widely separated areas of the xenolith have four distinct compositions (Table 3), which are also distinct from clinopyroxene in the xenolith (Fig. 4). This is consistently true in the lower Na_2O and higher K_2O in the inclusions, but otherwise, there do not appear to be any systematic differences between the inclusions and the host xenolith. Each inclusion is compositionally homogeneous (Table 3), but taken together, the inclusions have both higher and lower TiO_2, Al_2O_3, and MgO compared to the xenolith (Fig. 4). Also, each inclusion is distinct from the others in various ways. Inclusion C has the highest CaO and TiO_2 and lowest Al_2O_3 (Fig. 4), whereas inclusion F has the lowest MgO, and inclusion K2 has the highest MgO. Inclusions K1 and K2, from separate pieces of the same diamond, have similar concentrations of some elements, but K2 has higher MgO and K_2O, and lower Na_2O. Diamond K, as with the other diamonds, has elaborate, patchy growth zonations, so it is difficult to determine unequivocally which of the two K inclusions was entrapped earlier in this diamond's growth history. Nonetheless, inclusion K2 is in a blue (in cathodoluminescence) growth zone that appears to be more central in the diamond than the green growth zone that contains inclusion K1. This is consistent with the higher K_2O content
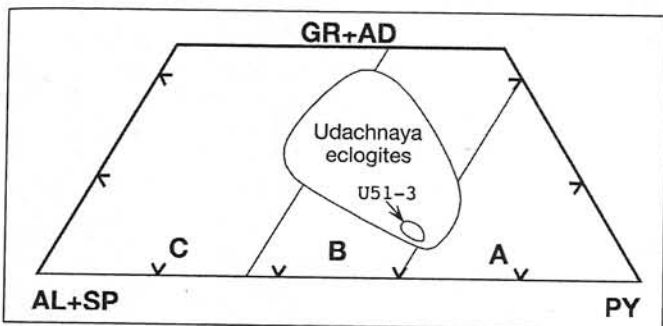

Figure 3. Garnets from eclogite U51-3 plot within the field for Group B eclogites on the garnet ternary, which is consistent with data for the majority of Udachnaya eclogites (field from Sobolev *et al.,* 1994). Group boundaries are from Coleman *et al.* (1965).

Table 1. Garnet compositions in host eclogite xenolith U51-3.

Thin section # of analyses	U51-3b 15 (rims)		U51-3b 3 (cores)		U51-3f 11		U51-3m 22	
SiO_2	40.7	(4)	41.0	(1)	40.5	(4)	40.8	(1)
TiO_2	0.41	(4)	0.28	(3)	0.44	(1)	0.40	(5)
Al_2O_3	22.5	(1)	22.8	(1)	22.6	(2)	22.4	(1)
Cr_2O_3	0.09	(2)	0.09	(3)	0.09	(3)	0.07	(3)
MgO	16.1	(2)	16.7	(2)	16.2	(2)	16.3	(2)
CaO	3.85	(19)	3.15	(4)	3.96	(5)	3.60	(27)
MnO	0.32	(3)	0.31	(3)	0.31	(3)	0.31	(3)
FeO	15.7	(1)	15.7	(2)	15.7	(1)	15.8	(2)
Na_2O	0.16	(1)	0.13	(1)	0.16	(1)	0.20	(11)
total	99.87		100.19		99.96		99.79	
Cations on a 12 <O> basis								
Si	2.988		2.987		2.976		3.000	
Ti	0.024		0.020		0.024		0.023	
Al	1.948		1.950		1.950		1.931	
Cr	0.005		0.004		0.003		0.004	
Mg	1.743		1.779		1.766		1.767	
Ca	0.314		0.291		0.309		0.288	
Mn	0.021		0.020		0.020		0.020	
Fe	0.960		0.955		0.964		0.964	
Na	0.022		0.022		0.021		0.024	
total	8.025		8.028		8.033		8.021	

Analyzed by WDS at the University of Tennessee on a Cameca SX-50 electron microprobe with 20 sec counting times at an accelerating voltage of 15 kV, a beam current of 20 nA, and standard ZAF (PAP) procedures. Reported values are means of the indicated number of analyses. Numbers in parentheses are standard deviations given for the last decimal place.

Table 2. Clinopyroxene compositions in host eclogite xenolith U51-3.

Thin section # of analyses	U51-3b 10		U51-3f 16		U51-3m 6		U51-3m* 5	
SiO_2	55.6	(4)	55.1	(4)	55.2	(2)	55.0	(4)
TiO_2	0.48	(3)	0.47	(3)	0.48	(2)	0.52	(3)
Al_2O_3	8.4	(9)	8.4	(11)	8.4	(5)	8.4	(7)
Cr_2O_3	0.08	(3)	0.09	(3)	0.08	(3)	0.09	(4)
MgO	11.6	(8)	11.7	(16)	11.5	(4)	11.5	(6)
CaO	12.1	(1)	12.0	(2)	12.1	(1)	11.5	(1)
MnO	0.07	(3)	0.08	(3)	0.07	(2)	0.08	(2)
FeO	5.59	(11)	5.59	(15)	5.67	(10)	5.88	(12)
Na_2O	5.56	(7)	5.55	(10)	5.67	(6)	5.77	(1)
K_2O	0.07	(1)	0.08	(1)	0.07	(2)	0.07	(2)
total	99.52		99.01		99.29		98.83	
Cations on a 6 <O> basis								
Si	1.996		1.988		1.994		1.991	
Ti	0.013		0.012		0.012		0.015	
Al	0.356		0.349		0.358		0.361	
Cr	0.002		0.002		0.001		0.003	
Mg	0.617		0.643		0.616		0.621	
Ca	0.465		0.459		0.461		0.441	
Mn	0.002		0.004		0.001		0.003	
Fe	0.166		0.179		0.169		0.175	
Na	0.384		0.374		0.398		0.402	
K	0.003		0.004		0.003		0.003	
total	4.006		4.014		4.013		4.015	

Methods as in Table 1. *This clinopyroxene is an inclusion in a garnet.
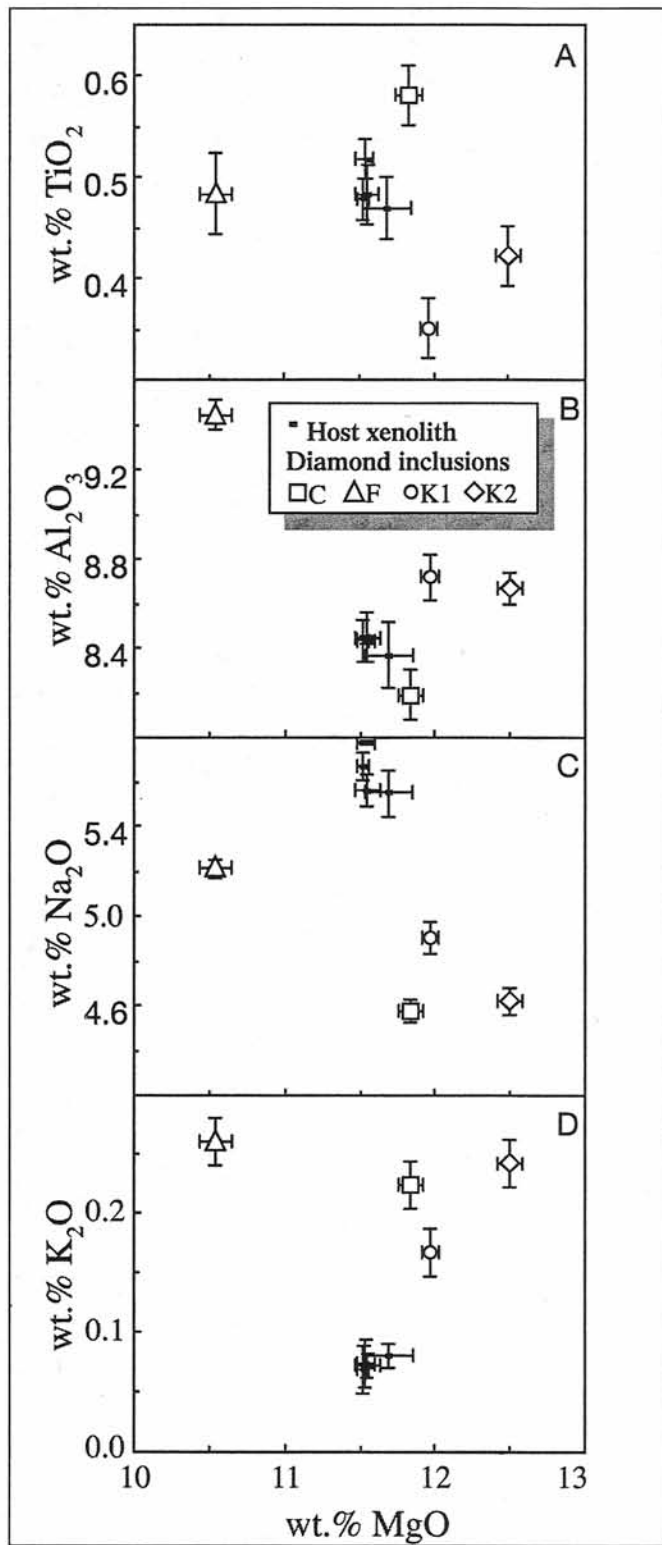
Figure 4. MgO vs. TiO_2, Al_2O_3, Na_2O, and K_2O for clinopyroxene in diamond inclusions and in the host eclogite xenolith. Data are plotted as means of multiple analyses, with error bars representing standard deviations of the multiple analyses (Tables 2 and 3). The host xenolith data are from three thin-sections from widely separated areas of the xenolith. The fourth host xenolith data point (the one with the largest standard deviation) is for a clinopyroxene inclusion within a garnet. Inclusions K1 and K2 are from the same diamond. All of the data plot within the Group B eclogite field on MgO vs Na_2O. (The entire area in Fig. 4C is within the Group B eclogite field of Taylor and Neal, 1989.) This is consistent with many other diamondiferous eclogites from Udachnaya (field from Sobolev et al., 1994).

(indicating higher pressure; Harlow and Veblen, 1991) of inclusion K2 compared to K1.

4. DISCUSSION

Ireland et al. (1994) compared the major- and trace-element compositions of silicate inclusions in diamonds with their host xenolith minerals. Based upon a garnet inclusion from one diamond and a clinopyroxene inclusion from another diamond, they concluded that the inclusion minerals had seen an episode of partial melting prior to incorporation in the diamond, and that the eclogite hosts had been metasomatized (i.e. had higher Mg#s) relative to the inclusions. However, Taylor et al. (1996) analyzed garnet-clinopyroxene pairs from four diamonds and their host xenoliths and found that in two samples the minerals from the host xenoliths had lower MgO and higher FeO contents (and thus, lower Mg#s) than the inclusions. Another sample showed enrichment of the MREE in the inclusion relative to host minerals, suggestive of metasomatism prior to or during diamond growth. Finally, a fourth sample had LREE-depleted garnet and clinopyroxene host minerals relative to the inclusions. This is most readily explained by partial melting of the eclogite after diamond formation. Thus, the study of Taylor et al. (1996), indicated that metasomatism is a pervasive process that must be considered in all eclogite xenolith studies, but in at least some cases, is not a significant contributing factor to the final chemical compositions of eclogite xenoliths.

The only systematic compositional differences between the diamond inclusions and the host xenolith minerals in eclogite U51-3 are that the inclusions are higher in K_2O and lower in Na_2O than the host. Sobolev et al. (1972) reported higher K_2O in clinopyroxene inclusions compared to their host xenoliths, and Taylor et al. (1996) observed similar differences in other dia-

Table 3. Clinopyroxene compositions in diamond inclusions from xenolith U51-3.

inclusion	C		F		K1		K2	
# of analyses	5		3		7		30	
SiO_2	55.5	(2)	54.5	(1)	54.6	(3)	55.9	(1)
TiO_2	0.58	(3)	0.48	(4)	0.35	(3)	0.42	(3)
Al_2O_3	8.19	(6)	9.44	(3)	8.72	(8)	8.67	(6)
Cr_2O_3	0.14	(3)	0.12	(4)	0.09	(2)	0.10	(3)
MgO	11.8	(1)	10.5	(1)	12.0	(1)	12.5	(1)
CaO	12.8	(1)	12.1	(1)	11.8	(1)	11.9	(1)
MnO	0.09	(1)	0.05	(3)	0.08	(4)	0.10	(2)
FeO	5.55	(10)	5.38	(16)	5.61	(14)	5.85	(10)
Na_2O	4.58	(5)	5.21	(4)	4.90	(7)	4.61	(6)
K_2O	0.22	(2)	0.26	(2)	0.17	(2)	0.24	(2)
total	99.45		98.08		98.32		100.28	
Cations on a 6 <O> basis								
Si	1.992		1.979		1.981		1.987	
Ti	0.016		0.014		0.009		0.012	
Al	0.345		0.406		0.376		0.360	
Cr	0.005		0.004		0.003		0.003	
Mg	0.632		0.568		0.648		0.664	
Ca	0.495		0.470		0.456		0.450	
Mn	0.003		0.002		0.002		0.004	
Fe	0.163		0.168		0.167		0.173	
Na	0.321		0.370		0.347		0.321	
K	0.010		0.013		0.008		0.012	
total	3.982		3.994		3.997		3.986	

Methods as in Table 1.

mondiferous eclogites from Udachnaya. Our results show that this phenomenon is true for inclusions from multiple diamonds from a single host xenolith. Higher K_2O in the clinopyroxene inclusions is consistent with crystallization at a higher pressure (Harlow and Veblen, 1991), and suggests that the xenolith clinopyroxenes re-equilibrated at a lower pressure after the diamonds formed. The fact that the clinopyroxene is unzoned, whereas the largest garnets have cores slightly more magnesium-rich than their rims, suggests that re-equilibration was complete for the clinopyroxene, but not for the garnet.

While re-equilibration may explain the systematic differences (e.g., K_2O) between the diamond inclusions and the host minerals, most elements vary in a non-systematic way both between the diamond inclusions and the host, and between individual diamond inclusions (Fig. 4). In no case do the inclusion compositions fall along a trend that can be accounted for by a single process. Instead, it appears that the diamonds in this piece of eclogitic mantle grew in multiple stages during a time when frequent, compositional changes were occurring. Such complex compositional changes are most easily explained by a series of metasomatic fluids passing through the mantle. The fact that the diamonds mainly occur along cracks and grain boundaries within the xenolith also suggests late-stage processes. This result agrees with accumulating evidence from diamond-inclusion work that many diamonds grow during metasomatic events (Griffin *et al.*, 1988; Deines and Harris, 1995; Stachel and Harris, 1997; Spetsius, 1998; Taylor *et al.*, 1998).

That multiple eclogitic diamond inclusions give variable major- and trace-element compositions was also pointed out by Sobolev *et al.* (1996; 1998). Those authors analyzed 35 individual garnet inclusions from a single diamond from the Mir pipe and found that the range in major- and trace-element concentrations was similar to the total range found in all eclogite xenoliths from that pipe (Beard *et al.*, 1996). This startling discovery indicates that the environment of diamond formation changed significantly over the course of diamond crystallization and growth. Such compositional changes are not consistent with crystallization of the diamond from an igneous melt, but suggest a process involving various metasomatic fluids passing through the eclogite. Furthermore, the Sobolev *et al.* (1996; 1998) study suggested that the chemical variation in xenoliths (and diamond inclusions) from a given pipe may be indicative only of changes occurring to the xenoliths within the mantle and during diamond formation, and may not be used, at least in some cases, for protolith information.

5. CONCLUSION

Since multiple inclusions from a single diamond can have various compositions, and inclusions from multiple diamonds from a single eclogite xenolith can also be diverse, analyzing a limited number of diamond inclusions with the expection of characterizing diamond growth conditions, even within a single kimberlite, may be unrealistic. It may also be incorrect to assume that host minerals in a xenolith accurately represent the conditions under which the diamonds grew.

More work is needed on diamond inclusions before we can hope to understand why they vary so much within a single diamond and a single host xenolith. Detailed study of multiple inclusions in-situ in individual diamonds with well-documented growth histories (via cathodoluminescence and infrared spectroscopy) are necessary to determine if there are systematics to how mantle composition varies during diamond growth. Additional studies of diamondiferous eclogite and peridotite xenoliths from different kimberlite pipes are also crucial to developing an appreciation for the relationships between diamond inclusions and their host xenoliths. Complete characterization of these xenoliths using high-resolution X-ray computed tomography, careful petrography, and comprehensive elemental and isotopic analyses are necessary to crack the enigma of diamonds and their inclusions.

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