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Multi-stage metasomatism of diamondiferous eclogite xenoliths from the Udachnaya kimberlite pipe, Yakutia, Siberia

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Abstract The primary garnet (pyrope-almandine)-omphacite (Cpx 1, 6.5–7 wt% Na₂O)-sulfide (Fe-Ni-Co mss) assemblage of the two diamondiferous eclogite xenoliths studied (U33/1 and UX/1) experienced two mantle metasomatic events. The metasomatic event I is recorded by the formation of platy phlogopite (~10 wt% K₂O), prior to incorporation of the xenoliths in the kimberlite. The bulk of the metasomatic alteration, consisting of spongy-textured clinopyroxene (Cpx 2A, 1–3 wt% Na₂O), coarser-grained clinopyroxene (Cpx 2B, 2–5 wt% Na₂O), pargasitic amphibole (~0.8 wt% K₂O; 3–3.5 wt% Na₂O), kelyphite (Cpx 3, mostly <1 wt% Na₂O; and zoned Mg-Fe-Al spinel), sodalite, calcite, K-feldspar, djerfisherite (K_{5.95}Na_{0.02}Fe_{18.72}Ni_{2.36}Co_{0.01}Cu_{4.08}S₂₆Cl) and a small amount of K-Ca-Fe-Mg glass, is ascribed to the metasomatic event II that occurred also in the upper mantle, but after the xenoliths were incorporated in the kimberlite. A pervasive chloritic alteration (mainly clinocllore + magnetite) that overprints earlier assemblages probably took place in the upper crustal environment. The diamonds are invariably associated with secondary clinopyroxene and chlorite, but the diamonds formed before the entrainment of the xenoliths in the Udachnaya kimberlite.

Introduction

Diamond-bearing xenoliths in kimberlites account for less than 1% of all xenoliths in kimberlites, but are particularly valuable samples because of their potential to provide insight into not only the metasomatic processes in the mantle but also the genesis of diamonds. Peridotites (garnet peridotite, lherzolite, and harzburgite) are the most common mantle-derived xenoliths in kimberlites, but they seldom contain diamond. In contrast, eclogite xenoliths, consisting essentially of clinopyroxene and garnet, are much less common, an observation consistent with the conceptual model (Nixon and Davies 1987) that the upper mantle is composed of peridotites with randomly distributed lenses/pods of eclogite. Eclogite xenoliths, however, are exceptionally abundant in some kimberlites, such as Orapa, Botswana (e.g., Shee and Gurney 1979) and Roberts Victor, South Africa (e.g., Hatton and Gurney 1987), and are more likely to be diamondiferous (Reid et al. 1976).

The presence of diamondiferous eclogite xenoliths in South African kimberlites was recognized as early as 1899 (Bonney 1899) and in Yakutian kimberlites (north-central Siberian platform, Russia) much later (Bobrievich et al. 1959). However, such eclogites are rather common in the collected Yakutian mantle xenolith suites, especially from the Mir pipe and the Udachnaya pipe located in the central region of the Siberian Platform, and have been described in a number of recent publications (e.g., Jerde et al. 1993; Ireland et al. 1994; Beard et al. 1996; Snyder et al. 1997). In addition, Sobolev et al. (1994) presented an excellent summary of diamondiferous eclogite xenoliths from the Udachnaya kimberlite pipe (Russia); Taylor et al. (2000) discussed a detailed “pull-apart” of one such xenolith (U51) from the same kimberlite; Misra et al. (2001) reported preliminary results on the characterization of metasomatic alteration in two Udachnaya eclogite xenoliths (U33/1 and UX/1); and Spetsius and Taylor (2002) emphasized the role of

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partial melting in metasomatic alteration of Udachnaya eclogite xenoliths.

Almost all mantle xenoliths, both peridotitic and eclogitic, exhibit some degree of metasomatism as evidenced by the compositions and textures of secondary minerals. An understanding of these metasomatic processes is important not only from the perspective of mantle and crustal metasomatism, but also because of the possible relationship between mantle metasomatism and diamond genesis (Spetsius and Griffin 1998; Spetsius 1999; Taylor et al. 2000; Misra et al. 2001; Spetsius and Taylor 2002). The focus of the present study is to characterize in detail and interpret the metasomatic alteration in two highly diamondiferous eclogite xenoliths (U33/1 and UX/1) from the Udachnaya kimberlite pipe and to examine possible connections between the metasomatism and formation of the associated diamonds.

Samples studied

The two Udachnaya eclogite xenoliths we have studied, U33/1 and UX/1, are ovoid in shape, weighing 42 and 66 g, and with maximum dimensions of 3.5x2.2x3 cm and 4.1x3x3 cm, respectively. Both are highly diamondiferous; diamonds exposed on the surface ranged from five in U33/1 to eight in UX/1 and were predominantly octahedral.

The xenoliths were first examined by high-resolution, X-ray-computed tomography (HRXCT), employing the technique used for U51 as described by Taylor et al (2000). In essence, this non-destructive technique results in the production of a computed 3-D image of an entire sample from X-ray imaging data acquired in a series of 2-D slices through the sample. One such slice from UX/1 is shown in Fig. 1; the resulting 3-D image of the entire sample is much more vivid in colored versions. The software allows the viewer to rotate the 3-D image about a vertical axis, thus permitting a view of the entire volume of the sample in terms of mineralogy and textures, without any physical slicing of the sample. In addition, the 3-D reconstruction renders considerable help in deciding how the sample should eventually be dissected to recover the enclosed diamonds and prepare thin sections for detailed petrologic study.

Several macroscopic features became apparent from the HRXCT 2-D and 3-D images of U33/1 and UX/1. The two xenoliths are composed essentially of four mineral suites, which in order of decreasing abundance are: garnet (and its alteration products), clinopyroxene (and its alteration products), sulfides (and their alteration products), and diamonds. Much of the clinopyroxene is metasomatically altered, whereas the garnet grains are relatively fresh except for peripheral alteration. The sulfides occur as irregularly distributed patches associated with both clinopyroxene and garnet. Octahedral and cubo-octahedral diamond crystals are quite abundant in both xenoliths and are surrounded invariably by secondary clinopyroxenes. Some diamond

crystals seem to occur close to garnet grains but never in direct contact with or as inclusions in garnet. The total number of diamonds of all sizes counted from the 3-D images amounted to 47 in U33/1 and 74 in UX/1, with estimated tenors of 90,000 carats/ton and 144,000 carats/ton, respectively. The largest diamonds in U33/1 and UX/1 are just over 1 carat.

Petrography

Mineralogy

The primary mineralogy of the eclogite xenoliths is essentially a two-phase assemblage consisting of pyrope-almandine garnet (Gt) and omphacitic clinopyroxene (Cpx 1), with small amounts (<3%) of polyphase sulfide grains. Secondary mineral assemblages in the two xenoliths are dominated by Na-depleted secondary clinopyroxenes, relatively K-enriched amphibole (Amph), Mg-Fe-Al spinel (Sp), and chlorite (Chl). The secondary clinopyroxene suite consists of two texturally and compositionally distinct clinopyroxenes (Cpx 2 and Cpx 3) related to the alteration of Cpx 1 and Gt, respectively. As will be discussed later, the Cpx 2 can be further subdivided into two subtypes (Cpx 2A and Cpx 2B) on the basis of texture. Other secondary minerals include K-feldspar (K-fel), calcite (Cal), sodalite (Sod), djerfisherite (Djf), magnetite (Mt), Ba-Sr sulfate, and apatite. A small amount (<1%) of K-Ca-Fe-Mg glass occurs in both xenoliths. As will be elaborated later, the small amount of phlogopite (Phlog) in one of the xenoliths (UX/1) is interpreted to be "modal metasomatic" (as defined by Harte 1983). Serpentine has been

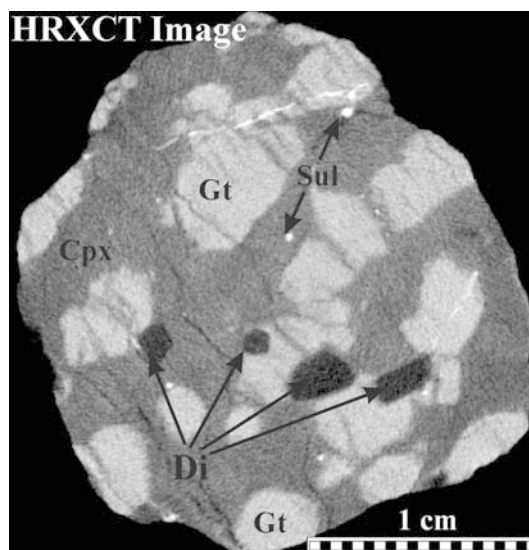


Fig. 1 Example of a two-dimensional HRXCT slice of diamondiferous eclogite xenolith UX/1. *Di* = diamond (dark gray to black, euhedral to subhedral); *Gt* = garnet with altered margins (light gray, subhedral to subrounded); *Cpx* = clinopyroxene and its alteration products (medium gray mass); *Sulf* = sulfide minerals (disseminated white spots)

reported in eclogite xenoliths from Mir and Udachnaya pipes (e.g., Beard et al. 1996; Sobolev et al. 1999) but was not observed in either U33/1 or UX/1.

Textures

In hand specimen, each xenolith is an aggregate of coarse-grained (up to 2 mm across), subhedral to sub-rounded, peripherally altered garnet crystals and a mass of largely altered clinopyroxene, similar in texture to Group I eclogite xenoliths of MacGregor and Carter (1970). However, lamellar exsolution of garnet from clinopyroxene, considered by Smyth and Caporuscio (1984) a characteristic feature of Group I eclogite xenoliths of MacGregor and Carter (1970), was not observed in U33/1 or UX/1. Despite extensive metasomatic alteration, especially of the clinopyroxene, chemical compositions of the primary minerals could readily be obtained from their unaltered remnants. The remnants of primary clinopyroxene (Cpx 1) occur as isolated islands, which in a single clinopyroxene grain are in optical continuity with each other (simultaneous extinction) and are separated by optically continuous secondary clinopyroxenes. The secondary clinopyroxenes may be subdivided into three textural types (Fig. 2a, b): (a) fine-grained, “spongy-textured” clinopyroxene (Cpx 2A) — a term first used by Wilshire and Binns (1961) to describe similar alteration texture at the contact between peridotite xenoliths and host volcanic rock in New South Wales, Australia — with numerous islands of Cpx 1 in optical continuity and small amounts of K-feldspar ± glass (Fig. 3a, b); (b) relatively coarse-grained clinopyroxene (Cpx 2B) that occurs at the outer margins of original Cpx 1 grains; and (c) fine-grained clinopyroxene (Cpx 3), which is invariably associated with garnet and intergrown with spinel (and at places with other secondary minerals) and represents one of the products of kelyphitic alteration of garnet.

The most conspicuous texture in the xenoliths arises from the disposition of the spongy-textured clinopyroxene (Cpx 2A) that occurs as anastomosing veins crisscrossing Cpx 1 in all directions (Fig. 3c), most probably controlled by fractures. Similar alteration textures in eclogite and peridotite mantle xenoliths have been described in many other studies of eclogite and peridotite xenoliths (Donaldson 1978; Kutolin and Frolova 1970; Carswell 1975; Reid et al. 1975; Taylor and Neal 1989; Beard et al. 1996; Sobolev et al. 1999; Taylor et al. 2000; Misra et al. 2001). Texturally, Cpx 2A may be further divided into two subtypes that commonly show a crude zonal pattern (Fig. 2a, b): a finer-grained type (Cpx 2A₁) that occurs at the contact with Cpx 1 islands; and a slightly coarser-grained type (Cpx 2A₂) beyond the immediate contact zone. In veins of secondary clinopyroxene bounded by Cpx 1 islands on two sides, this zonal arrangement results in a crudely symmetrical zoning composed of Cpx 2A₁ at the margins and Cpx 2A₂ in the core zone (Fig. 2a). The com-

monly observed saw-tooth outline of the Cpx 1 islands (Fig. 2a) probably reflects a control of cleavages in the original clinopyroxene. None of the clinopyroxenes contain any exsolution lamellae.

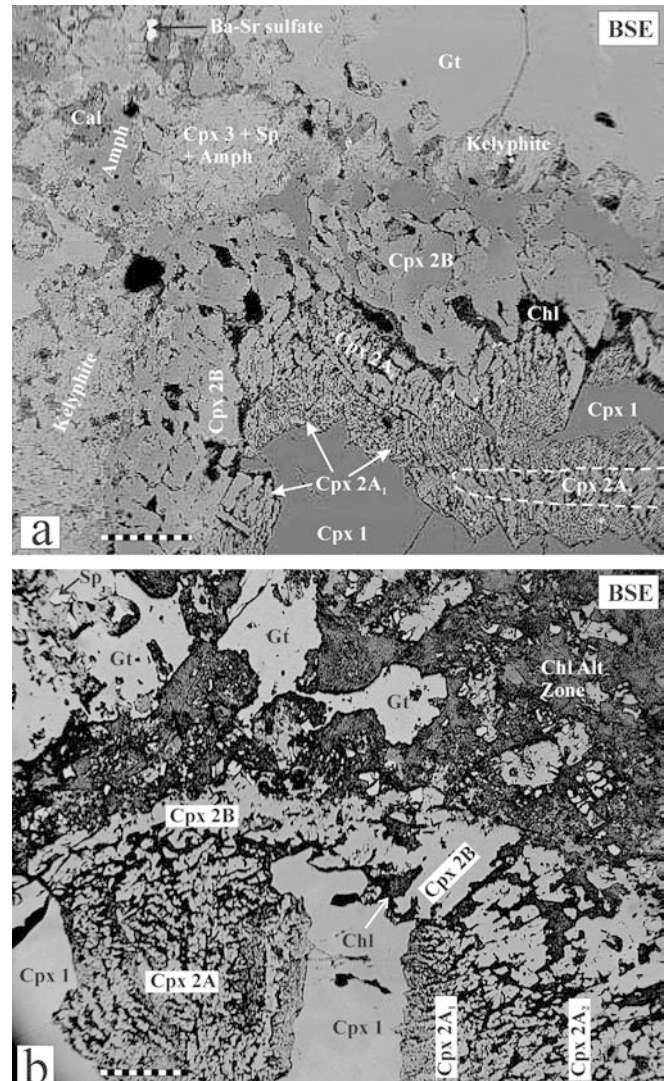


Fig. 2a,b Alteration assemblages and textures near the original contact of *Gt* and *Cpx 1* (U33/1). **a** The secondary pyroxenes show gradational textural zoning, from fine-grained (*Cpx 2A*₁) at the contact with *Cpx 1* island to slightly coarser grained in the middle portion (*Cpx 2A*₂) to relatively coarser-grained near the contact with *Gt* (*Cpx 2B*). A coronitic rim of kelyphitic alteration (*Cpx 3* + *Sp*) marks the original boundary of garnet. Amphibole occurs at the contact between kelyphite and *Cpx 2B*, and also as a narrow lens within the kelyphite. **b** Well developed textural zoning of *Cpx 2A*₁, *2A*₂, and *Cpx 2B*, and pervasive chloritic alteration of both *Gt* and *Cpx*. The chloritic alteration zone (*Chl* + *Mt* + very fine-grained unidentified phases) in *Gt* contains numerous relict islands of *Gt*, *Cpx 3*, *Sp*, and perhaps amphibole adjacent to *Cpx 2B*. The composition of *Gt* occurring as islands in chloritic alteration has been modified. Mineral abbreviations: *Phlog* = phlogopite; *Gt* = garnet; *Cpx 1* = primary clinopyroxene; *Cpx 2* = secondary clinopyroxene; *Cpx 3* = secondary clinopyroxene associated with garnet alteration; *Amph* = amphibole; *Kelyp* = kelyphite (*Cpx 3* + *Sp*); *Sod* = sodalite; *Sp* = spinel; *Chl* = chlorite; *K-fel* = K-feldspar; *Cal* = calcite; *Mt* = magnetite; *Sulf* = sulfide. *BSE* = Back-scattered electron image. The bar scale represents 100 μm

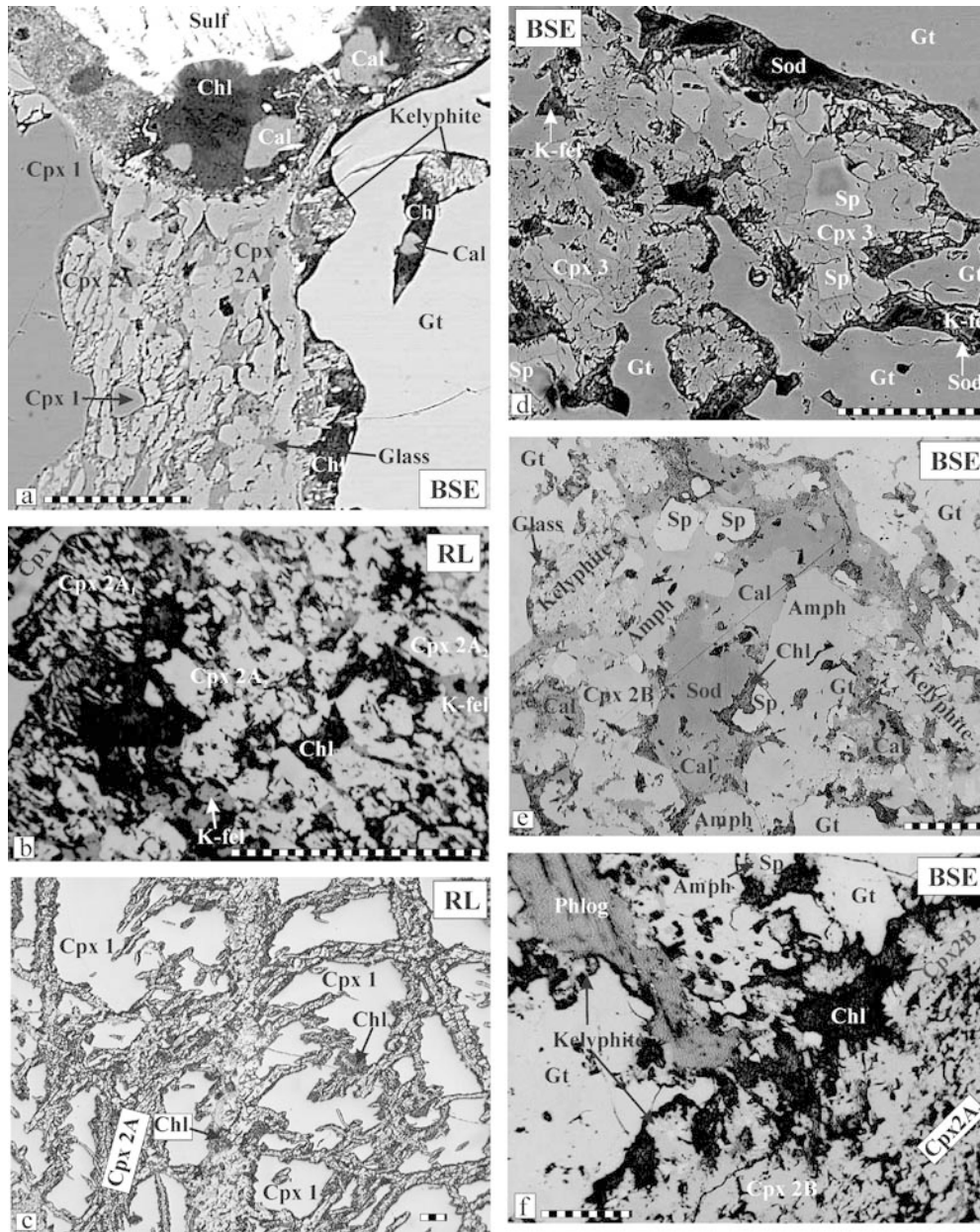


Fig. 3a–f Alteration textures in U33/1 and UX/1. **a** A vein of secondary clinopyroxene, with islands of *Cpx 1* and a small amount of glass, at the original contact between *Cpx 1* and *Gt* (U33/1). Note the well-developed chloritic alteration (*Chl* + *Cal* + very fine-grained mixture of unidentified phases) mantling a sulfide grain. **b** A thin vein of texturally zoned secondary clinopyroxenes (*Cpx 2A₁* and *Cpx 2A₂*) with interstitial *Chl* and *K-fel* (UX/1). **c** Veins of secondary clinopyroxene (*Cpx 2A*), commonly rimmed by *Chl*, and islands of *Cpx 1* (U33/1). **d** Part of a *kelyphite* vein containing an intergrown assemblage of *Cpx 3* and euhedral *Sp*, *Sod*, *Chl*, *Cal*, and a few grains of *K-fel* (U33/1). The *Sp* is optically and compositionally zoned. **e** Part of a *kelyphite* vein in *Gt*, with well-developed *Amph*, *Sod*, *Cal*, and a small amount of glass (U33/1). **f** Platy *Phlog* and *kelyphitic* alteration in garnet (UX/1). Note the textural zoning of secondary clinopyroxenes. Mineral abbreviations as in Fig. 2. The bar scale represents 100 μm

Schrauf (1882) coined the term “*kelyphite*” (derived from the Greek word *kelyphos*, meaning rind or shell) to describe symplectitic intergrowth of amphibole and

spinel in a reaction rim around garnet in serpentinite. We follow the usage of the term in recent literature to describe dominantly peripheral alteration of garnet irrespective of the minerals in the alteration assemblage (Reid and Dawson 1972; Garvie and Robinson 1984; Messiga and Bettini 1990; Obata 1994). Much of the *kelyphitic* alteration in U33/1 and UX/1 occurs as coronitic rims within the limits of original garnet crystals (Fig. 2a), but also common are thin (commonly 50 to 500 μm wide), continuous and discontinuous veins of *kelyphitic* alteration traversing the garnet grains without any preferred orientation, presumably along fractures (Fig. 3d). The alteration product is dominated by nodular masses of intergrown *Cpx 3* and spinel (pleonaste) (Figs. 2a, and 3e). The spinel is invariably euhedral and compositionally zoned, the zoning being optically

discernible in the larger crystals (Fig. 3d). Amphibole (pargasite) occurs typically at the contact zone between the nodular masses of kelyphitic alteration (garnet side) and Cpx 2B (clinopyroxene side). Other associated secondary minerals in small amounts include glass, calcite, sodalite, K-feldspar, and Ba-Sr sulfate (Fig. 3b, e), although all of these do not necessarily represent components of kelyphitic alteration.

Polyphase sulfide grains are disseminated throughout the xenoliths. Most of the sulfide particles occur as subrounded inclusions (up to about 400 μm in maximum dimension) in clinopyroxene. A few occur as inclusions in garnet or are interstitial to the primary garnet-clinopyroxene assemblage; the interstitial sulfide grains commonly have thin tentacles extending into the surrounding silicates (Fig. 4a). The sulfide phases consist of pyrrhotite and pentlandite, the pentlandite occurring predominantly as hair-thin lamellar intergrowths with pyrrhotite, but also as fine-grained granular aggregates at the outer margins of the sulfide grains. The sulfide grains invariably have a partial to complete rind of djerfisherite (Fig. 4a). Spetsius (1999) reported sulfides at the rims of some of the diamonds in eclogite xenoliths and considered this association as evidence for diamond growth in a silicate-sulfide partial melt that was slightly supersaturated in carbon. In the two xenoliths we have investigated there is no specific association between sulfide grains and diamonds (Anand et al. 2003).

A pervasive chloritic alteration overprints both the xenoliths. The chloritic alteration assemblage consists of chlorite (clinocllore), magnetite, calcite, a fine-grained mixture of unidentified minerals, and in a few places tiny needles of apatite. It occurs as interstitial material and veins in clinopyroxenes (Figs. 2a, 3b, and 4b), and as interstitial material within and discontinuous rims at the margins of kelyphitic alteration veins in garnet (Fig. 3a). In U33/1, the chloritic alteration invades large parts of some garnet grains, preserving islands of relict garnet and kelyphitic assemblage (Fig. 2b). The sulfide grains also have been invaded by veinlets of chloritic alteration, and some are largely replaced by an assemblage of chlorite + magnetite. The chloritic alteration cuts and mantles djerfisherite; in the latter case, the chloritic alteration is associated with a small amount of what appears to be a second generation of calcite.

Mineral chemistry

Major- and minor-element compositions of the minerals were determined with a Cameca SX-50 four-spectrometer electron microprobe (EMP) at the University of Tennessee. Minerals and metals were used as standards. All data were collected using wavelength dispersive techniques and corrected with the Cameca PAP procedure. Analytical conditions included an accelerating voltage of 15 keV, a beam current of 20 nA, a beam size of 5 μm , and 20 second counting time for all elements,

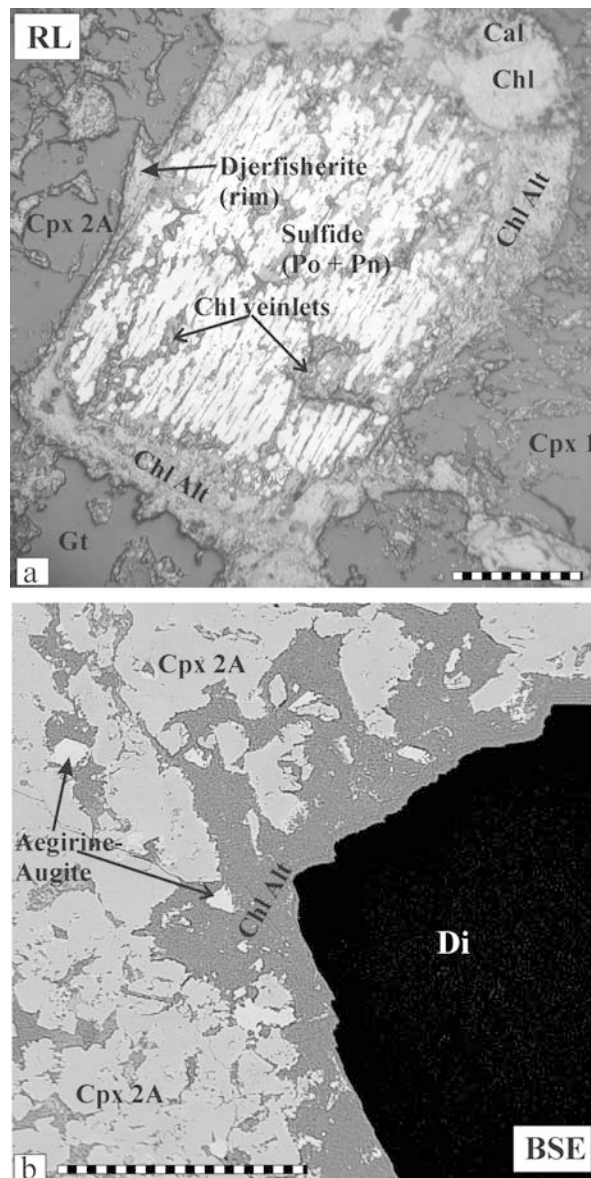


Fig. 4a,b **a** A sulfide grain, consisting of pyrrhotite (*Po*) and hair-thin lamellar intergrowth of pentlandite (*pn*), is partially rimmed by a thin (5 to 30 μm) rind of djerfisherite and a thicker zone of chloritic alteration (*Chl* + *Cal* + fine-grained mixture of unidentified minerals) (U33/1). The sulfide grain is also veined by chloritic alteration. The sulfide grain is interstitial to *Cpx 1* and *Gt*, and has undergone some remobilization. **b** An example from UX/1 of the typical occurrence of diamond crystals in the studied xenoliths. The diamond crystal (*Di*) is surrounded by chloritic alteration and secondary pyroxene (*Cpx 2B*). Note that the composition of *Cpx* occurring as small islands in chloritic alteration has been modified to aegirine-augite. BSE = Back-scattered electron image; RL = Reflected-light photomicrograph. The bar scale represents 100 μm .

except K and Na in clinopyroxene and garnet (40 seconds each). Examples of EMP analytical data for the different minerals are presented in Tables 1, 2, 3, 4, and 5; a complete listing of the analytical data may be viewed at the web-site of the Planetary Geosciences Institute, University of Tennessee (<http://web.utk.edu/~PGI>) or obtained on request from the senior author.

As is the case with other eclogites from Udachnaya (Sobolev et al. 1994; Sobolev et al. 1999; Taylor et al. 2000), the primary minerals in U33/1 and UX/1 do not show discernible zoning within individual grains or significant compositional variation among grains in the same xenolith. The secondary minerals are more variable in composition because of disequilibrium.

Garnet

The garnets are virtually devoid of Cr (<0.1 wt% Cr₂O₃), K (<0.05 K₂O) and P (<0.1 P₂O₅), and contain only small concentrations of Ti (0.3–0.6 wt% TiO₂) and Mn (0.3–0.4 wt% MnO). Considering that the wt%

oxide totals of garnet analyses, with all Fe calculated as FeO, are invariably close to 100 (between 99.5 and 100.5 wt%) and the total cations per 12 oxygen range between 7.98 and 8.04, the Fe³⁺ content of the garnets is inferred to be negligible. The garnets are pyrope in composition, most containing about 20–30% almandine component and about 10–20% grossular component (Fig. 5). The Al₂O₃ content is quite uniform around 22 wt%. Excluding three analyses with unusually high MgO (18.0 to 18.5 wt%), all adjacent to the kelyphitic rim around one garnet crystal, and one analysis with unusually low MgO (10.9 wt%), the MgO concentrations in U33/1 garnets show a continuous spectrum from about 15.5 to 12.0 wt%, with corresponding systematic increase in CaO and FeO* (total Fe calculated as FeO)

Table 1 Selected major-element analyses (wt%) of major minerals in eclogite xenolith U33/1

Mineral	Garnet (Gt)	Clinopyroxenes (Cpx) ^a									Amphibole (Amph)	Spinel (Sp) (zoned)	
		Cpx 1	Cpx 2A ₁	Cpx 2A ₂	Cpx 2A ₂	Cpx 2B	Cpx 2B	Cpx 3	Cpx 3	Cpx 3		Core	Rim
SiO ₂	40.5	55.9	52.2	52.8	53.4	53.9	51.8	48.0	47.6	48.4	40.7	0.21	0.23
Al ₂ O ₃	21.9	11.2	4.92	6.74	2.74	8.83	6.70	8.74	10.8	8.57	17.5	61.6	60.1
TiO ₂	0.55	0.50	0.55	0.71	0.32	0.60	0.44	0.57	1.17	0.70	1.44	0.31	0.47
Cr ₂ O ₃	0.06	0.07	0.09	0.09	0.09	0.04	0.07	0.03	0.05	0.07	<0.03	0.25	0.22
V ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	0.04	0.05
MgO	12.2	9.01	14.4	13.3	15.9	12.1	14.2	18.6	13.0	16.3	14.7	13.6	13.2
CaO	6.95	11.7	18.8	17.4	18.6	14.1	17.3	5.68	17.9	10.5	9.66	0.08	0.07
MnO	0.34	0.04	0.07	0.09	0.08	0.13	0.18	0.50	0.19	0.41	0.13	0.23	0.21
FeO*	17.3	4.87	6.35	5.78	7.10	5.14	6.76	17.5	7.53	14.5	9.54	22.8	24.7
Na ₂ O	0.23	6.67	1.70	2.66	1.11	4.37	2.06	0.11	1.23	0.41	3.46	-	-
K ₂ O	0.04	0.12	0.03	0.02	0.03	0.03	0.03	<0.03	-	-	0.81	-	-
P ₂ O ₅	-	-	-	-	-	-	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	-	-	-	2.07	-	-
Total	100.07	100.08	99.11	99.59	99.37	99.24	99.54	99.73	99.47	99.86	100.01	99.12	99.25
Mg ^b	55.6	76.7	80.1	80.4	80.0	80.8	79.0	65.4	75.4	66.8	73.3		

^aCpx-1 = primary; Cpx 2 = secondary after Cpx 1; Cpx-3 = secondary after garnet;

^bMg = [Mg/(Mg + Fe total)]100; FeO* = total Fe as FeO

Table 2 Selected major-element analyses (wt%) of major minerals in eclogite xenolith UX/1

Mineral	Garnet (Gt)	Clinopyroxenes (Cpx) ^a									Amphibole (Amph)	Spinel (Sp) (zoned)	
		Cpx 1	Cpx 2A ₁	Cpx 2A ₂	Cpx 2A ₂	Cpx 2B	Cpx 2B	Cpx 3	Cpx 3	Cpx 3		Core	Rim
SiO ₂	40.1	55.7	52.9	54.2	53.7	53.3	53.4	49.4	53.1	39.5	42.9	0.33	0.78
Al ₂ O ₃	22.3	11.1	4.10	3.81	4.50	7.44	4.69	9.12	3.35	22.3	14.0	61.5	55.23
TiO ₂	0.52	0.45	0.52	0.45	0.58	0.63	0.58	0.54	0.48	0.50	1.04	0.36	1.86
Cr ₂ O ₃	0.03	0.07	0.09	0.09	0.09	0.09	0.11	<0.03	0.10	0.04	0.03	0.30	0.25
V ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-
MgO	12.6	8.96	15.7	14.8	14.4	12.5	14.4	23.8	15.1	12.8	15.4	18.6	16.6
CaO	6.34	11.8	17.8	18.6	18.2	16.6	18.5	1.94	19.2	6.38	11.5	0.08	0.03
MnO	0.31	0.02	0.13	0.07	0.12	0.11	0.10	0.38	0.12	0.36	0.22	0.10	0.08
FeO*	17.3	5.02	5.92	5.61	5.67	5.31	6.04	13.8	6.14	17.6	9.49	18.2	24.2
Na ₂ O	0.18	6.71	1.76	2.09	2.38	3.59	2.14	0.22	1.52	0.19	2.51	-	-
K ₂ O	-	0.10	0.18	0.03	0.07	0.03	0.03	<0.03	0.03	<0.03	0.75	-	-
P ₂ O ₅	0.06	-	-	-	-	-	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	-	-	-	2.07	-	-
Total	99.74	99.93	99.10	99.75	99.71	99.60	99.99	99.20	99.14	99.67	99.91	99.47	99.03
Mg ^b	56.5	76.1	82.5	82.5	81.9	80.8	81.0	75.5	81.4	56.4	74.3		

^aCpx-1 = primary; Cpx 2 = secondary after Cpx 1; Cpx-3 = secondary after garnet;

^bMg = [Mg/(Mg + Fe total)]100; FeO* = total Fe as FeO

Table 3 Selected major-element analyses (wt%) of phyllosilicates in eclogite xenoliths U33/1 and UX/1

Mineral	Phlogopite		Chlorites			Chlorites		
	UX/1	UX/1	U33/1 Gt association	U33/1 Cpx 2A association	U33/1 Sulfide association	UX/1 Gt association	UX/1 Cpx 2A association	UX/1 Sulfide association
SiO ₂	38.8	39.6	30.9	32.0	32.7	35.7	34.5	34.0
Al ₂ O ₃	15.6	15.3	22.3	20.0	15.0	14.3	16.6	11.7
TiO ₂	3.15	3.25	0.04	0.38	0.45	<0.03	0.32	<0.03
Cr ₂ O ₃	0.05	0.07	<0.03	<0.03	<0.03	0.04	<0.03	<0.03
MgO	20.3	19.7	27.5	25.8	19.6	29.8	23.5	20.2
CaO	<0.03	0.10	0.44	1.53	2.36	2.00	7.63	0.70
MnO	0.07	<0.03	0.19	0.22	0.21	0.39	0.89	0.22
FeO*	7.12	7.45	4.64	5.01	15.7	3.73	2.42	20.8
Na ₂ O	0.25	0.29	0.08	0.30	1.01	0.09	0.29	0.14
K ₂ O	10.2	9.92	0.03	0.24	0.31	0.07	0.95	0.12
H ₂ O	3.97	4.18	12.5	12.3	11.9	12.3	13.07	11.7
F	0.39	0.18	<0.03	<0.03	-	0.37	0.34	0.02
Cl	0.05	0.04	0.29	0.53	0.15	0.43	0.30	0.13
Total	99.95	100.08	98.91	98.31	99.39	99.22	100.81	99.73

FeO* = total Fe as FeO

Table 4 Selected major-element analyses (wt%) of K-feldspar and glass in eclogite xenoliths U33/1 and UX/1

Mineral	K-feldspar		Sodalite		Glass		Glass		
	U33/1	UX/1	U33/1	U33/1	Cpx 2A assoc		Gt assoc		
	U33/1	UX/1	U33/1	U33/1	U33/1	U33/1	U33/1	U33/1	U33/1
SiO ₂	63.4	63.3	37.6	37.2	51.5	62.1	60.2	49.1	57.6
Al ₂ O ₃	18.3	18.7	31.1	31.0	14.5	19.5	18.2	16.2	18.6
TiO ₂	<0.03	<0.03	-	-	0.33	<0.03	0.06	0.73	0.60
Cr ₂ O ₃	<0.03	0.03	-	-	<0.03	<0.03	<0.03	0.03	<0.03
MgO	<0.03	0.11	-	-	8.79	1.47	0.90	4.67	1.75
CaO	0.08	0.16	0.16	0.32	6.71	0.42	7.30	3.23	2.51
MnO	<0.03	<0.03	-	-	0.18	0.04	0.12	0.22	0.13
FeO*	0.56	0.12	0.18	0.24	4.68	0.72	1.03	11.5	7.01
Na ₂ O	0.14	0.62	24.2	24.4	0.86	0.78	0.09	1.08	0.92
K ₂ O	16.9	15.63	0.14	0.08	6.16	6.32	4.24	5.30	4.66
Cl	-	-	6.64	6.64	-	-	-	-	-
Total	99.38	98.67	100.02	99.88	93.71	91.35	92.14	92.06	93.78

FeO* = total Fe as FeO

Table 5 Average compositions in wt% (with standard deviation) of sulfide minerals in eclogite xenoliths U33/1 and UX/1

Mineral	Djerfisherite	Pyrrhotite		Pentlandite	
	U33/1	U33/1	UX/1	U33/1	UX/1
N	18	12	5	7	4
Fe	40.2 (8)	62.6 (2)	62.6 (1)	36.2 (3)	36.1 (6)
Ni	5.33 (66)	0.16 (15)	0.14 (18)	26.6 (10)	26.3 (2)
Co	0.03 (2)	0.02 (2)	0.01 (2)	1.90 (9)	4.11 (54)
Cu	9.95 (96)	0.02 (2)	0.02 (3)	1.00 (88)	0.07 (7)
Na	0.02 (2)	-	-	-	-
K	8.94 (18)	-	-	-	-
S	32.0 (3)	36.1 (3)	36.5 (2)	31.8 (3)	33.1 (6)
Cl	1.36 (5)	-	-	-	-
Total	97.83	98.90	99.27	97.50	99.71

(Fig. 6). The garnets in UX/1 show an apparent bimodal compositional pattern, but this probably is an artifact of relatively small number of analyses.

The Na content of the U33/1 and UX/1 garnets (0.1 to 0.2 wt% Na₂O) is in accord with the published data on Yakutian diamondiferous eclogites (Reid et al. 1976;

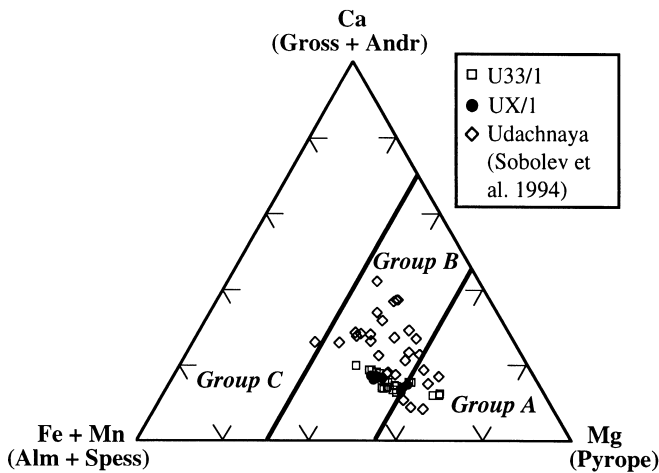


Fig. 5 Ca–(Fe+Mn)–Mg plot of garnets in U33/1 and UX/1, indicating that they are *Group B* eclogites. The three points falling in the *Group A* eclogite field represent one small garnet crystal at the edge of a kelyphitic rim. The garnets are clearly a subset of the eclogite xenoliths recovered from the Udachnaya kimberlite (Sobolev et al. 1994). The boundaries for the three groups of eclogites (*A*, *B*, and *C*), at 30 and 55 mol% pyrope, are from Coleman et al. (1965)

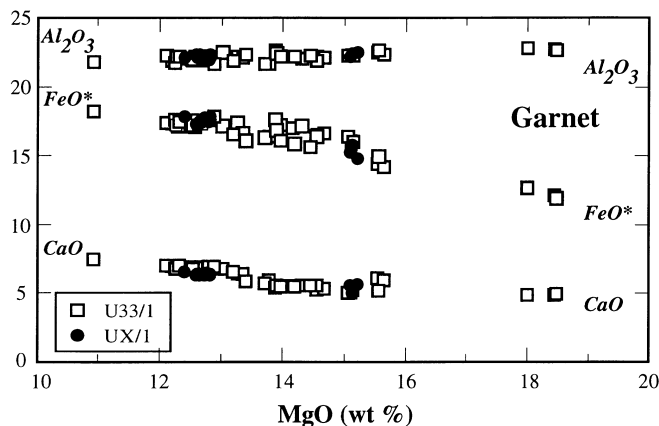


Fig. 6 Variation of Al_2O_3 , FeO^* and CaO relative to MgO (all in wt%) in U33/1 and UX/1 primary garnets. FeO^* = total Fe as FeO

Sobolev et al. 1994; Sobolev et al. 1999) and is characteristic of Type I eclogites described from Bellsbank (MacGregor and Carter 1970; McCandless and Gurney 1986). The presence of low but significant Na content of diamondiferous eclogite garnets was attributed by Sobolev and Lavrentyev (1971) to the high pressure of garnet crystallization, a conclusion supported qualitatively by subsequent experimental studies (Thompson 1975; Irving and Frey 1976), but no experimental calibration of the Na content of garnet as a function of pressure is currently available.

Clinopyroxenes

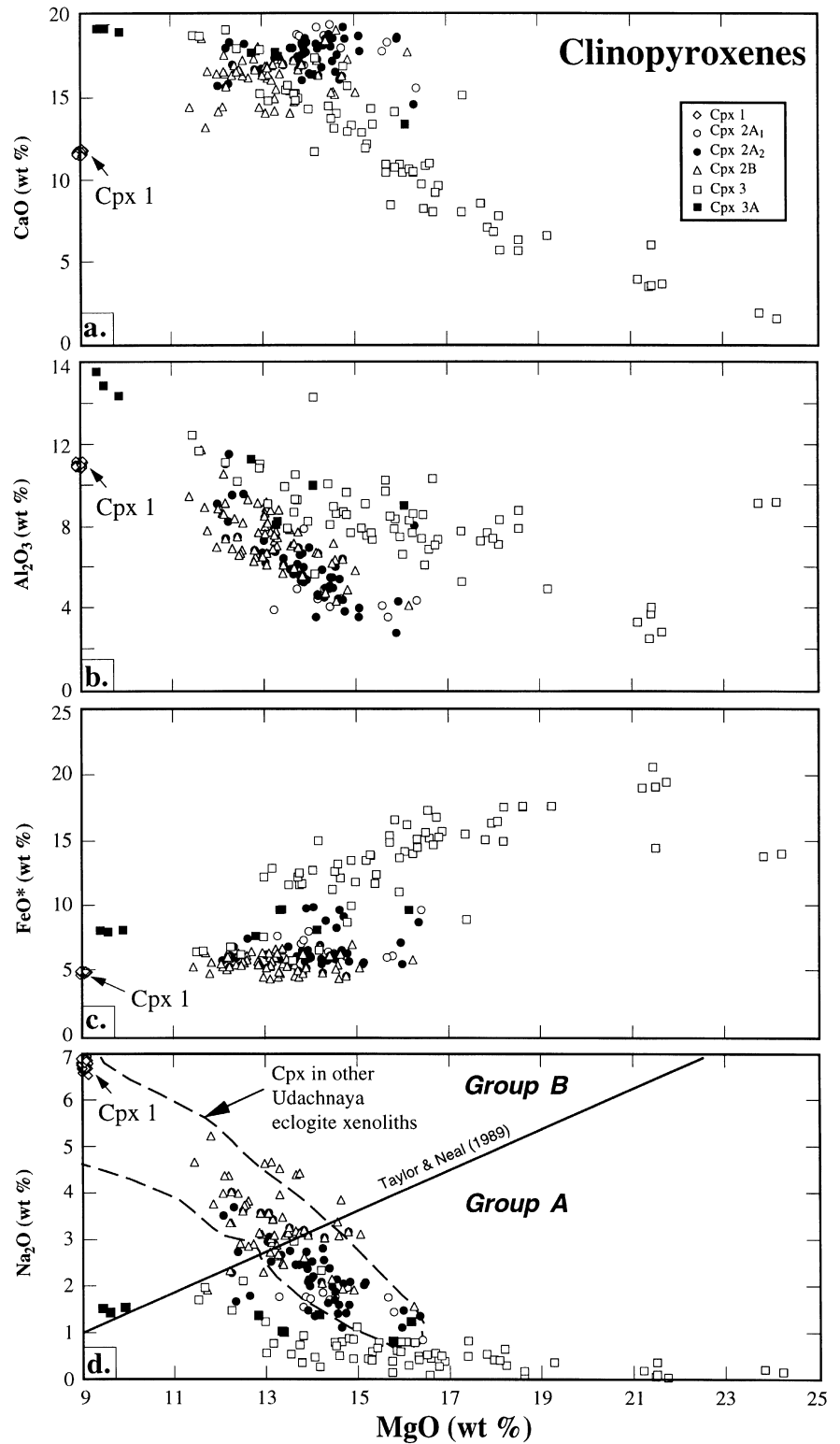
The primary clinopyroxene (Cpx 1) in the two xenoliths is omphacite. Its composition is remarkably uniform in

each xenolith and lies at the high-Na end of the field for clinopyroxenes in Udachnaya eclogites; the compositions of the secondary clinopyroxenes, in contrast, are quite variable, especially of Cpx 3 (Fig. 7). The TiO_2 , Cr_2O_3 , MnO, and K_2O contents of all clinopyroxenes are invariably low (Tables 1 and 2). The most apparent discrimination among the textural varieties of clinopyroxenes is provided by their wt% Na_2O contents (Fig. 7d): Cpx 1 – 6.5 to 7.0%; Cpx 2B – 2 to 5%; Cpx 2A₂ – 1 to 3.5%; Cpx 2A₁ – 1 to 2%; and Cpx 3 – <2% (but predominantly <1%). The decrease in Na_2O in Cpx 2A and Cpx 2B is accompanied by a corresponding increase in MgO and CaO, the former in turn showing a negative correlation with Al_2O_3 (Fig. 7b) and a positive correlation with CaO (Fig. 7a). The FeO^* content of the Cpx 1-associated secondary clinopyroxenes is relatively uniform at about 5 to 7 wt%, except for a few values up to about 10 wt% in UX/1 (Fig. 7c). There is no systematic compositional difference between Cpx 2A₁ and Cpx 2A₂, indicating that the two textural varieties of Cpx were cogenetic. The composition of Cpx 3, the secondary clinopyroxene associated with garnet alteration, is markedly different and much more variable. In addition to consistently lower Na_2O , it is characterized by generally higher Al_2O_3 and significantly higher FeO^* and lower CaO, all of which correlate systematically with MgO (Fig. 7). The CaO– Na_2O plot for the clinopyroxenes (Fig. 8b) confirms that Cpx 2 and Cpx 3 are distinctly different populations — the Na content of Cpx 2 increasing with decreasing Ca and an opposite trend for Cpx 3 — and support the textural observation of different precursors for the two. There is also a suggestion of a positive correlation between Ca and Na in the garnet (Fig. 8a), but the range of Na concentrations in the garnet is too low for a discernible trend.

Phlogopite

Phlogopite is a common metasomatic mineral in peridotite mantle xenoliths (Erlank et al. 1987) but not so in eclogite xenoliths, as it does not form readily by reaction of metasomatizing fluids with clinopyroxene or garnet (Kushiro and Aoki 1968). This is because clinopyroxene and garnet contain substantial amounts of Ca that cannot be accommodated in the phlogopite structure. Of the two xenoliths studied, only UX/1 contains phlogopite and that also as a minor phase. The phlogopite occurs as a few relatively large, platy crystals (up to $\sim 0.4 \times 0.1$ mm) in apparent textural equilibrium with primary garnet (Fig. 3f). The phlogopite has a mottled appearance and appears to be mildly deformed. We interpret the UX/1 phlogopite as “primary” (after Carswell 1975) or “modal metasomatic” (after Harte 1983), a product of subsolidus crystallization in equilibrium with the primary eclogite assemblage. The phlogopite has jagged margins embayed by later kelyphitic alteration (spinel + Cpx 3), but “secondary” phlogopite that occurs in many peridotite and eclogite xenoliths as

Fig. 7 Variation of CaO , Al_2O_3 , FeO^* and Na_2O relative to MgO (all in wt%) in primary clinopyroxene (*Cpx 1*) and different textural types of secondary clinopyroxenes (*Cpx 2A₁*, *Cpx 2A₂*, *Cpx 2B*, *Cpx 3*) in U33/1 and UX/1. FeO^* = total Fe as FeO. Sources of data for *Cpx* in other Udachnaya eclogite xenoliths (Fig. 7d): Sobolev et al (1994), Sobolev et al. (1999), and Taylor et al. (2000). Note that the composition of *Cpx 3* islands in garnet-associated chlorite, designated as *Cpx 3A*, has been significantly modified during chloritic alteration

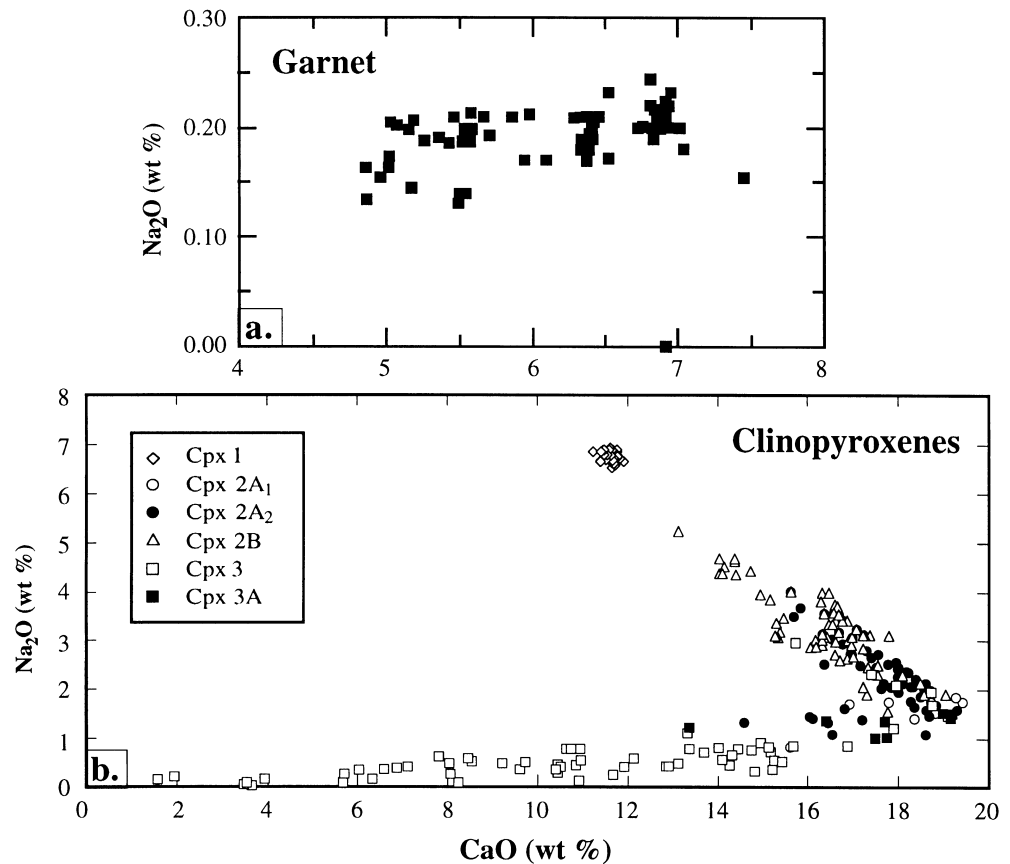


masses of small and irregular crystals produced by alteration of the primary assemblage was not observed in either U33/1 or UX/1.

The chemical composition of the UX/1 phlogopite (Table 3), with a K_2O content of about 10 wt%, is similar to that reported for phlogopites in eclogite

xenoliths from Udachnaya (Sobolev et al. 1999) and Bellsbank (Taylor and Neal 1989; McCormick et al. 1994), all characterized by very low Cr_2O_3 (<0.20 wt%). Phlogopites in these eclogite xenoliths, however, are of the secondary type that occurs in alteration rims around either garnet crystals

Fig. 8 Variation of Na_2O relative to CaO in clinopyroxenes and garnet of U33/1 and UX/1. Note the negative correlation for secondary clinopyroxenes (*Cpx 2A₁*, *Cpx 2A₂*, *Cpx 2B*) related to the alteration of *Cpx 1* in contrast to the positive correlation for *Cpx 3* related to the alteration of garnet. FeO^* = total Fe as FeO



(Udachnaya) or garnet and clinopyroxene crystals (Bellsbank). Apparently, the chemical discrimination between primary and secondary phlogopite in peridotite xenoliths based on wt% Cr_2O_3 content — 0.5 to 1.1 for primary phlogopite and > 1.1 for secondary phlogopite (Dawson and Smith 1975) — does not apply to eclogite xenoliths.

Amphibole

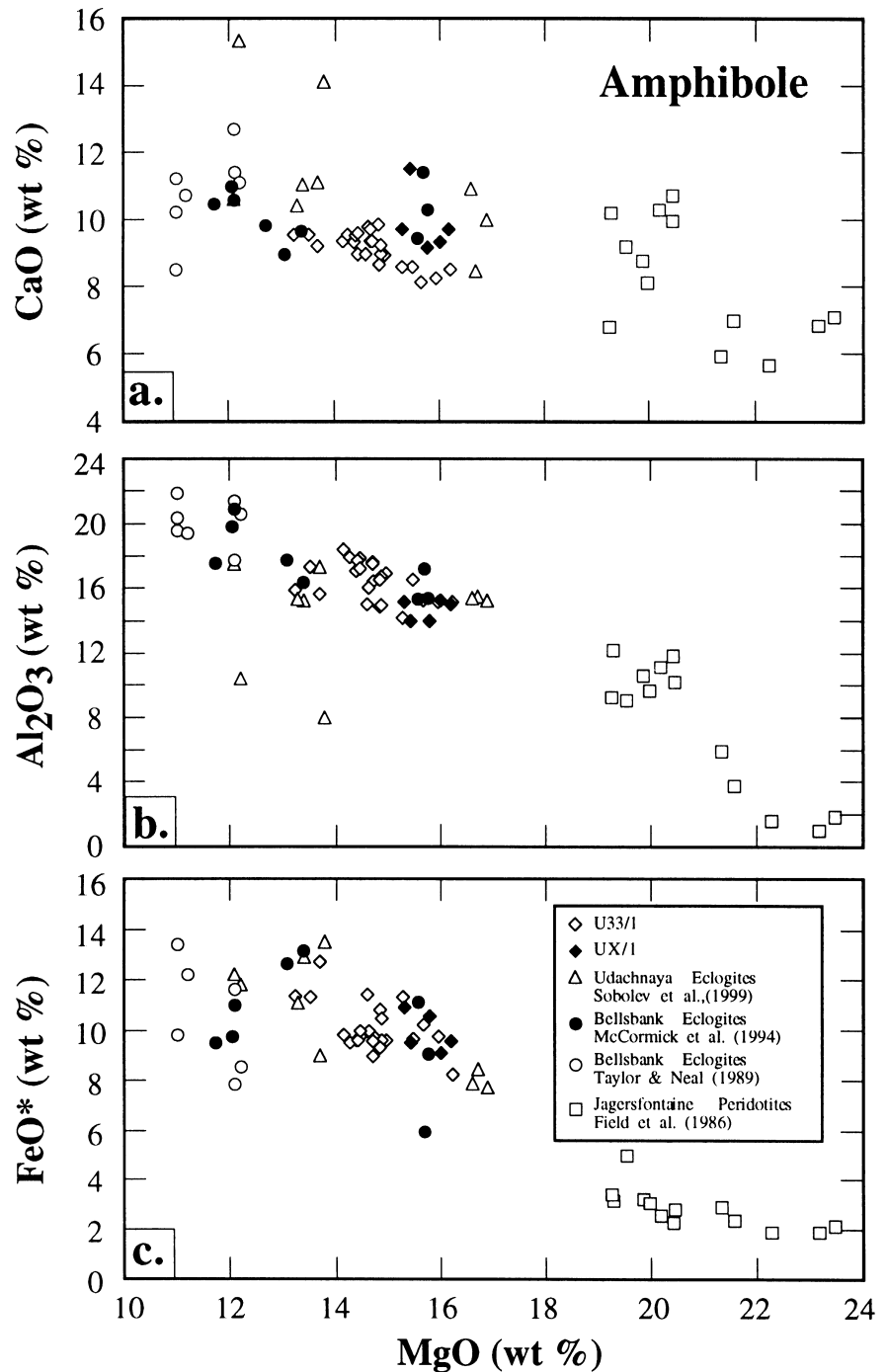
The amphibole in U33/1 and UX/1 is pargasitic in composition with < 2 wt% TiO_2 , about 3 wt% Na_2O , and a characteristic K_2O content of about 0.8 wt% (Tables 1 and 2) that serves as a useful criterion for distinguishing it from *Cpx 2B* with which it is commonly associated. The MgO content of amphibole varies from about 13 to 16 wt%, and the increase in MgO is compensated largely by a corresponding decrease in FeO^* and Al_2O_3 , as is the case with Bellsbank and other Udachnaya eclogite xenoliths (Fig. 9). Note that the compositions of amphiboles from Jagersfontein (South Africa) peridotite xenoliths are quite different and, according to the compilation of Field et al. (1986), plot within the field of upper mantle amphiboles from other intrusives. Most of the eclogite amphiboles have lower MgO but higher FeO^* and Al_2O_3 , compared with the upper mantle amphiboles considered by Field et al. (1986). This compositional

difference is compatible with, but not an evidence of, an origin of the eclogite by subduction of oceanic crust.

Spinel

The spinel, which occurs as easily recognizable euhedral crystals in both the xenoliths, is a Fe-Mg-Al spinel (pleonaste) that contains only minor amounts of Ti (0.3–0.6 wt% TiO_2), Cr (< 0.3 wt% Cr_2O_3), V (< 0.1 wt% V_2O_5), Mn (\leq 0.2 wt% MnO), and Ca (< 0.1 wt% CaO) (Tables 1 and 2; Fig. 10). In U33/1, most of the spinel crystals are zoned from a core with lower Fe to a rim with higher Fe, which is compensated by lower Mg and lower Al. Similar compositional zoning is present also in UX/1 spinel, but in most crystals the rims are too thin (< 10 μm) for reliable EMP analysis. Such a core-to-rim Fe-enrichment trend appears to be characteristic of garnet kelyphites and is the opposite of that observed in all other petrogenetic types of spinels in kimberlites (Haggerty 1975). The spinel composition is similar to that of two other eclogite xenoliths analyzed by Sobolev et al. (1999), except for much higher Fe enrichment (35.3 wt% FeO^*) in one of the samples, but is markedly different compared to the zoned spinels in kimberlites reported by Pasteris (1983). The spinel zoning is likely due to exsolution from a higher temperature pleonaste solid solution.

Fig. 9a–c Variation of CaO (a), Al_2O_3 (b), and FeO^* (c) relative to MgO (all in wt%) for U33/1 and UX/1 amphiboles. Note that there is no systematic difference between the amphiboles of Udachnaya and Bellsbank kimberlites, but amphiboles from the Jagersfontaine peridotite nodules constitute a separate population characterized by higher MgO and lower FeO



K-feldspar and Glass

K-feldspar is quite common in U33/1 and UX/1, and it is interstitial to Cpx 2A₁ and Cpx 2A₂ (Fig. 3b); no K-feldspar was observed associated with Cpx 2B or Cpx 3. The composition of the K-feldspar — K₂O mostly in the range of 14.5 to 16.5 wt%; Na₂O < 1 wt% and CaO < 1 wt% — is similar to that reported for other eclogite xenoliths from Udachnaya (Sobolev et al. 1999) and Roberts Victor (Reid et al. 1976). The K-Ca-Mg-Fe glass in the two xenoliths is easily distinguished from K-feldspar by its composition — much lower K₂O (4 to

7 wt%) but much higher MgO (up to ~ 9 wt%), FeO* (up to ~ 11%), and CaO (up to ~ 7 wt%) (Table 4; Fig. 11). The glass composition is much more variable, without any apparent difference in terms of its association with Cpx or Gt.

Sulfides

The pyrrhotite is invariably close to troilite (FeS) in composition (atomic metal:sulfur ratio = 0.98 to 1.01) with very little Co, Ni, or Cu (Table 5). The associated pentlandite, a product of exsolution from an Fe-Ni-Co-

Fig. 10a,b MgO vs. Al_2O_3 (a) and FeO^* (b) plots for U33/1 and UX/1 spinels. The *spinel* (pleonaste) is compositionally zoned with relatively Fe-rich rim

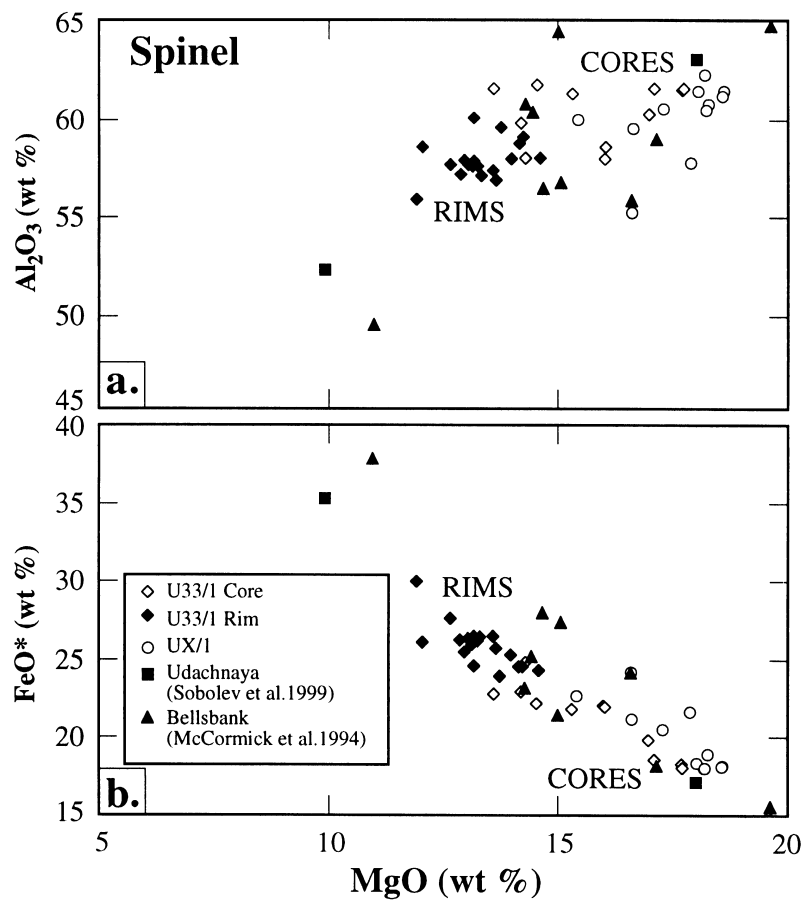


Fig. 11a,b Compositions of K-feldspar and glass in U33/1 and UX/1 compared with those in other eclogite xenoliths

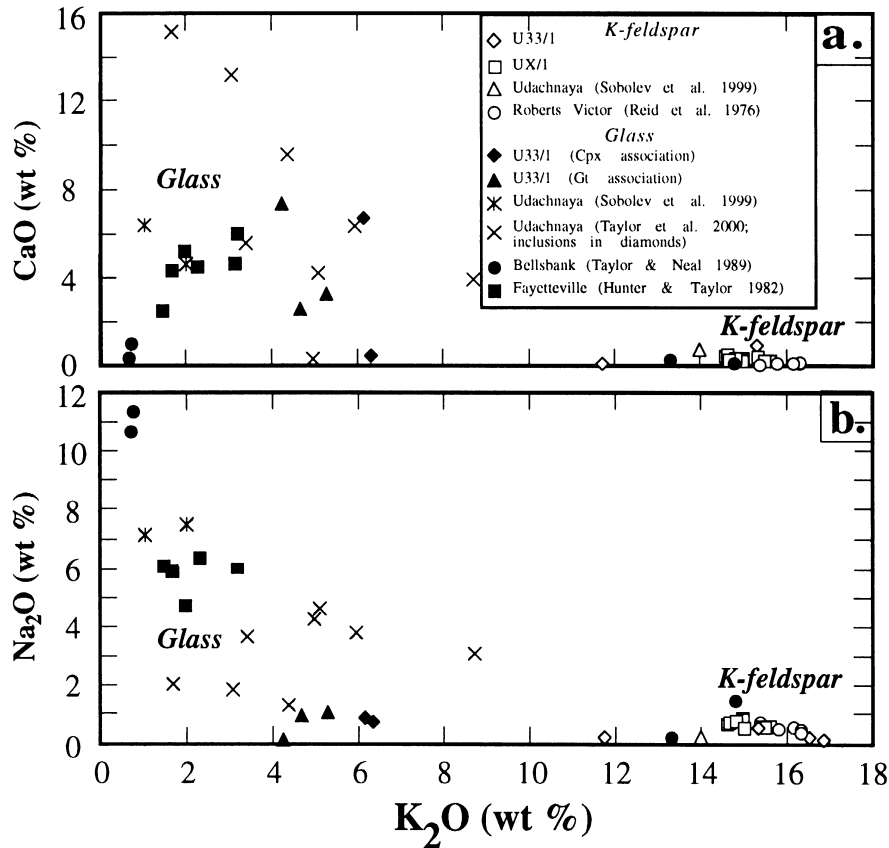
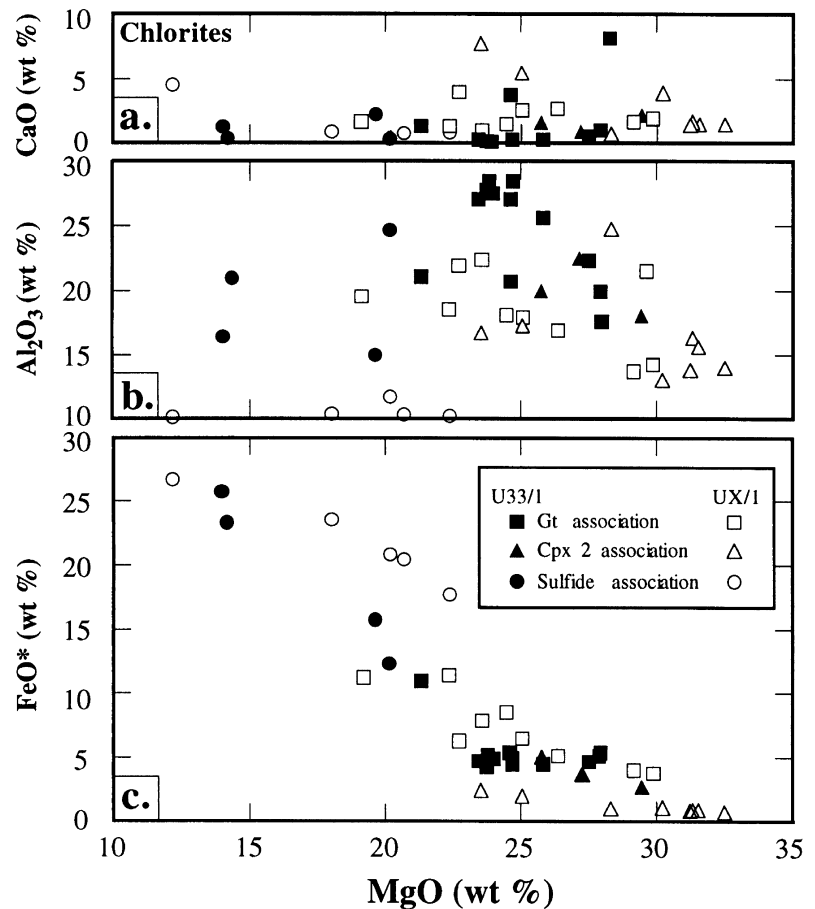


Fig. 12a–c Compositional variation of chlorites associated with *Gt*, *Cpx 2*, and *Sulfides* in U33/1 and UX/1



Cu monosulfide solid solution (mss), contains variable amounts of Cu (up to 6.2 wt%) and Co (up to 4.7 wt%), and is approximately stoichiometric in composition (atomic metal:sulfur ratio = 1.10 to 1.17). The compositions of the coexisting pyrrhotite and pentlandite are consistent with relatively low temperature of equilibration (less than 300 °C) of the two sulfide phases (Misra and Fleet 1973).

Almost all of the sulfide grains in U33/1 and UX/1, whether they are interstitial to or included in the primary silicate minerals, are mantled by a discontinuous rim of djerfisherite, which we interpret as a metasomatically altered product of Fe-Ni-Co sulfides. Djerfisherite, a cubic mineral with a unit cell edge of $10.34 \pm 0.01 \text{ \AA}$, was identified as a possible new mineral in two enstatite chondrites by Fuchs (1966). He determined the idealized composition as $\text{K}_3(\text{Na,Cu})(\text{Fe,Ni})_{12}\text{S}_{14}$. EMP analyses of the mineral consistently showed about 1 wt% Cl, but the Cl was assumed to represent contamination from traces of lawrencite, although no lawrencite was actually observed. Considering Cl to be part of the sulfide structure, Bulanov et al (1982, quoted in Sobolev et al. 1999) proposed $\text{K}_6\text{Fe}_{26-x}\text{S}_{26}\text{Cl}$ as the ideal formula of djerfisherite. The formula, based on the average djerfisherite composition in U33/1 (Table 5), works out to be $\text{K}_{5.95}\text{Na}_{0.02}\text{Fe}_{18.72}\text{Ni}_{2.36}\text{Co}_{0.01}\text{Cu}_{4.08}\text{S}_{26}\text{Cl}$, close to the composition of djerfisherite in Udachnaya eclogite

xenoliths reported by Spetsius et al (1985) and Sobolev et al (1999). Currently available data indicate that significant amounts of Ni and Cu are characteristic of djerfisherite in eclogite xenoliths.

Chlorite

The chlorites may be described as clinoclinoles with highly variable composition (MgO – 12 to 33 wt%; FeO* – less than 1 to 27 wt%), but with a strong negative correlation between MgO and FeO* (Table 3; Fig. 12). There is also a discernible correlation between the chlorite composition and its association, the chlorite associated with the Cpx 2A being characterized by higher Mg/Fe ratios than the chlorite associated with Gt; the chlorite associated with sulfides has the lowest Mg/Fe ratios. The chloritic alteration has significantly affected the composition of enclosed islands of Cpx 3 (see Fig. 7) and Cpx 2A (see Fig. 4b). The aegirine-augite islands in chloritic alteration contain up to about 22 wt% Fe_2O_3 and 9 wt% Na_2O .

Geothermometry

We have used the Gt-Cpx geothermometer to estimate the equilibration temperature of the primary eclogite

assemblage at an assumed pressure that is reasonable for the mantle underlying the Yakutia region. The contacts between garnet and Cpx 1 in U33/1 and UX/1 are invariably marked by a zone of secondary minerals. However, considering the small compositional variation in both the garnet and Cpx 1 (Tables 1 and 2), it is reasonable to assume that they were in equilibrium at the time of crystallization and to calculate the equilibration temperature from their average compositions. The mineral chemistry of the eclogites does not permit a direct estimation of the equilibration pressure. So, a pressure of 6.5 GPa, corresponding to a depth of 180 km in the mantle and well within the stability field of diamond, was assumed. This was the pressure estimated by Taylor et al. (2000) for a Yakutian diamondiferous eclogite based on the geotherm for the Siberian craton.

Calculated equilibration temperatures for the primary eclogite assemblage, using average garnet and clinopyroxene compositions and a pressure of 6.5 GPa, range from about 1,250–1,270 °C based on the calibrations by Ellis and Green (1979) and Krogh (1988) to more than 1,400 °C based on the empirical formulation of Ai (1994) (Table 6). Using the calibration of Ellis and Green (1979), Taylor et al. (2000) had obtained a temperature of 1,260 °C for a Yakutian diamondiferous eclogite. The similar temperature for both U33/1 and UX/1 indicates these two xenoliths were derived from eclogite lenses at about the same depth, possibly from the same region of the mantle.

Interpretation

Eclogite type

Coleman et al. (1965) classified eclogites into groups A, B, and C on the basis of geologically similar occurrences, but they also recognized consistent differences in mineralogy and mineral chemistry (garnets and clinopyroxenes) among the three groups, which they attributed to different *P-T* conditions of crustal metamorphism of basaltic rocks. Additional oxygen, strontium, and neodymium isotopic data have shown that the three-fold classification is a valid one (e.g., Shervais et al. 1988; Taylor and Neal 1989; Snyder et al. 1997). However, the origin of each of the eclogite groups — whether through subduction and high-pressure melting of oceanic crust

(Helmstaedt and Doig 1975; Jagoutz et al. 1984; MacGregor and Manton 1986; Shervais et al. 1988; Neal et al. 1990), or by crystallization of juvenile mantle melts (MacGregor and Carter 1970; Smyth and Caporuscio 1984; Smyth et al. 1989), or both — may not be unique. For example, in the Yakutia region of Russia, the diamond-bearing eclogite xenoliths from the Mir kimberlite pipe (predominantly Group B and Group C eclogites) are interpreted to have been derived from a subducted ophiolite complex (Beard et al. 1996), whereas those from the Udachnaya kimberlite pipe (predominantly Group B eclogites) lack crustal signatures and may be mantle-derived (Sobolev et al. 1994; Snyder et al. 1997, 1998). In terms of bulk compositions of the garnets, U33/1 and UX/1, along with most of the other Udachnaya eclogite xenoliths (Sobolev et al. 1994), plot within the field of Group B eclogites (Fig. 5). The Udachnaya eclogites do not show any evidence for the involvement of a crustal component and may, at least in part, represent a mafic mantle-derived protolith (Snyder et al. 1993, 1995; Taylor et al. 2000) rather than recycled altered oceanic crust as proposed by Jacob et al. (1994, 1998).

Mantle metasomatic events

The common occurrence of K-bearing hydrous minerals (e.g., amphibole, phlogopite), with textures strongly indicative of alteration, in both peridotite and eclogite mantle xenoliths from all cratonic areas in the world provides strong evidence for widespread metasomatism in the upper mantle (e.g., Reid et al. 1975; Gurney and Harte 1980; Bailey 1984; Dawson 1984; Nixon and Davies 1987; Nielson and Noeller 1987; Wilshire 1987). Metasomatism in the mantle has been classified into two main types (Dawson 1984): (a) “patent” metasomatism (largely equivalent to “modal” metasomatism of Harte 1983, 1987), recognized by the presence of secondary alkali-bearing hydrous minerals such as phlogopite and amphibole; and (b) “cryptic” metasomatism, recognized by enrichment in incompatible trace elements, especially of clinopyroxene in LREE relative to HREE.

The textures, despite pervasive alteration, clearly indicate that the original assemblage in U33/1 and UX/1 consisted essentially of garnet (pyropic) and clinopyroxene (omphacite), with a small amount of Fe-Ni-Cu-Co monosulfide solid solution (mss). The various

Table 6 Garnet – Clinopyroxene (Cpx 1) geothermometry (*P* = 6.5 GPa)

Eclogite xenolith	Garnet (wt%)				Cpx 1 (wt%)		$K_d^{Gt-Cpx 1}$	Ellis and Green (1979) (°C)	Krogh (1988) (°C)	Ai (1994) (°C)
	FeO*	MgO	MnO	CaO	FeO*	MgO				
U33/1 ^a	16.5	13.7	0.36	6.14	4.74	9.05	2.304	1,273	1,275	1,447
UX/1 ^b	17.1	13.2	0.35	6.18	4.84	9.02	2.410	1,250	1,248	1,415

^aNo. of analyses: Gt = 52, Cpx 1 = 19;

^bNo. of analyses: Gt = 12, Cpx 1 = 31; FeO* = total Fe as FeO

components of metasomatic alteration are: (a) platy phlogopite associated with garnet; (b) spongy-textured, fine- to medium-grained clinopyroxene (Cpx 2A₁ and Cpx 2A₂) + K-feldspar ± glass; (c) relatively coarse-grained secondary clinopyroxene (Cpx 2B); (d) kelyphitic alteration of garnet, characterized by intergrown low-Na clinopyroxene (Cpx 3) + zoned spinel; (e) pargasitic amphibole (f) alteration rims of djerfisherite around polyphase sulfide grains; (g) other secondary minerals such as sodalite, calcite, glass, K-feldspar, and Ba-Sr sulfate; and (h) chloritic alteration that overprints all earlier assemblages. It is our interpretation that the alteration assemblages observed in U33/1 and UX/1 (excluding that resulting from chloritic alteration) are a composite of two distinct metasomatic events (I and II) imposed on the primary eclogite assemblage, and that each event was the result of fluid infiltration along cracks and grain boundaries, accompanied by local-scale diffusion of metasomes across grain boundaries.

Metasomatic Event I: Formation of Phlogopite

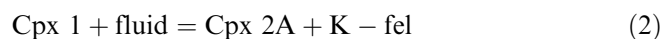
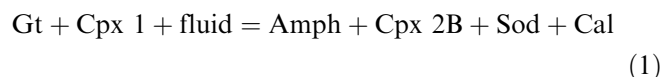
The small amount of phlogopite in UX/1 is considered to be metasomatic, resulting from infiltration of K- and H₂O-bearing fluids. Garnet and clinopyroxene contain no more than about 1,000 ppm of water at most (Wilkins and Sabina 1973; Skogby et al. 1990). The present K₂O contents of garnet or Cpx 1 is in the order of 0.1 wt% or less, and the lack of phlogopite exsolution lamellae in either suggests that the K₂O content was not significantly higher when the eclogites formed in the upper mantle. Thus, an external source of K and H₂O would be necessary for the formation of phlogopite. At high pressures (> about 3 GPa), where carbonate is stable to provide a repository for CO₂ but amphibole is not to provide a repository for H₂O, the fluid in the mantle should be H₂O-rich (Watson et al. 1990). The apparent textural equilibrium of the phlogopite with the primary garnet and its mild deformation indicate that this metasomatic event probably occurred in situ (i.e., prior to the incorporation of the xenoliths in the kimberlite) within the stability field of phlogopite in mantle rocks, which may extend to pressures in excess of 6 GPa (Kushiro and Aoki 1968).

Metasomatic Event II: Formation of Secondary Pyroxenes, Amphibole, Spinel, Sodalite

The bulk of the secondary mineral assemblage observed in U33/1 and UX/1 is believed to have formed in several stages after the incorporation of the xenoliths into the kimberlite, in course of its upward transport toward the surface. The main reason for this interpretation is that the pressure estimated for the source region of the eclogite xenoliths (in the range of 6.5 GPa) is well above the stability fields of two main components of the secondary mineral assemblage, amphibole and spinel. The interpretation is also compatible with a lack of

deformation in the secondary minerals and a lack of apparent metamorphic equilibration textures between the primary and secondary minerals.

The alteration assemblage formed by the second metasomatic event is interpreted to have resulted from four sets of complementary reactions involving garnet, Cpx 1, and a K-rich fluid containing H₂O, CO₂, and Cl. These reactions may be represented as:



The fluid also probably contained minor amounts of Ti to account for the enrichment of Ti in the amphibole relative to all other associated phases, and of Ba, Sr, and SO₂ to account for the small amount of Ba-Sr sulfate in the metasomatic assemblage. This metasomatic event occurred in the spinel lherzolite zone of the upper mantle (1–2 GPa) where both spinel and amphibole are stable phases. The fluid may have been the vapor phase associated with the kimberlite melt. Many authors have ascribed mantle metasomatism to volatile-rich fluids of mafic melts (Griffin et al. 1984; Menzies et al. 1985; Nielson and Noller 1987).

Amphibole, where present, occurs exclusively in the original contact zones between garnet and Cpx 1 and is always associated with Cpx 2B, toward the Cpx 1 side of the contact. The bulk of the sodalite occurs adjacent to Cpx 2B and amphibole, and is commonly accompanied by granular calcite (first generation) (Fig. 3e). The texture, in combination with the significant amount of K in amphibole (up to about 0.8 wt% K₂O), suggests that garnet and Cpx 1 reacted in the presence of a K–CO₂–H₂O fluid to produce amphibole, Cpx 2B, sodalite, and calcite. The additional Na and Al needed to satisfy the stoichiometry of this reaction was provided by the conversion of Cpx 1 to Na- and Al-depleted Cpx 2 in the interior portions of the original clinopyroxene crystals and by the alteration of garnet into Cpx 3 and spinel.

The development of the Na- and Al-depleted, spongy-textured clinopyroxene (Cpx 2A₁ and 2A₂) with interstitial K-feldspar probably was the combined effect of decreased pressure with the upward movement of the host kimberlite and partial melting of the omphacite due to fluid influx. Na and Al depletion in “cloudy porous” clinopyroxene rims around clear primary clinopyroxene cores in garnet lherzolite xenoliths from South African kimberlites was attributed by Carswell (1975) to a pressure decrease during kimberlite emplacement. In the eclogite xenoliths we have investigated, partial melting of the omphacite due to fluid influx, as advocated in other studies of xenoliths (Donaldson 1978; Taylor and Neal 1989; Taylor et al. 2000; Spetsius and Taylor 2002),

probably played a more important role in the conversion of jadeite-rich Cpx to relatively jadeite-poor, optically continuous spongy-textured clinopyroxene. The effect of various fluids on the melting behavior of omphacite has not been experimentally investigated, but it is expected to be similar to that of diopside (Eggler 1973; Rosenhauer and Eggler 1975), a significant depression of the solidus temperature in the presence of H₂O-rich fluid. Experimental studies by Ryabchikov et al. (1982) have also shown that hydrous fluids coexisting with omphacitic clinopyroxenes leach sodium silicate component from the solid leaving less jadeitic pyroxenes behind, the amount of Na leached at constant temperature increasing with decreasing pressure. Without an apparent source of K in the eclogites, the invading fluid must have had a high activity of K to form the interstitial K-feldspar, utilizing the Al released from the Cpx 1 alteration. The grain size difference between Cpx 2A₁ and Cpx 2A₂ was probably a consequence of local thermal gradients set up within the relatively large Cpx 1 crystals during fluid circulation.

The formation of djerfisherite rims around sulfide grains is attributed to the interaction of the K- and Cl-bearing fluid with Fe-Ni-Co sulfides, the sulfides serving as a source of Fe, Co, and Ni. A metasomatic origin of djerfisherite was also proposed by Bulanova et al. (1982) and Spetsius et al. (1985). The thin tentacles of sulfide ± djerfisherite extending from interstitial sulfide grains into the adjacent silicates (Fig. 4a) appear to be related to this metasomatism. The small amount of glass in the xenoliths formed at this stage was probably due to extremely localized partial melting induced by the hot K-rich fluid, as noted by Taylor et al. (2000) in the case of U51 eclogite xenolith. Evidence of more widespread partial melting — veinlets and stringers of glass containing small crystals of spinel, microlites of plagioclase, and augite- and analcime-filled vesicles — documented in eclogite xenoliths from the Roberts Victor mine (Reid and Dawson 1972) were not observed in U33/1 or UX/1.

Kelyphitic alteration (Cpx 3 + Sp) is confined to garnet and has no consistent spatial relationship to any of the other metasomatic minerals. The Na content of Cpx 3 (up to about 2 wt% Na₂O), however, precludes the formation of kelyphite by an isochemical breakdown of garnet. The kelyphite, therefore, is interpreted as a metasomatic product of reaction between garnet and the fluid, the Na being supplied by the alteration of Cpx 1 to Cpx 2. The fluid penetrated the garnet crystals along fractures that are now represented by kelyphite veins, some of which at the margins contain small amounts of K-feldspar, sodalite, and calcite (Fig. 3d). The small amount of glass in kelyphite, as in the case of Cpx 2, may be attributed to local partial melting of the garnet, or it may represent the residual product of kelyphitic reaction.

Chloritic alteration

Not much information is available in the literature on chloritic alteration in eclogite xenoliths. Smith (1979)

reported chlorite as one of the hydrous minerals in the peridotite inclusions from the Green Knobs and Buell Park diatremes (Colorado Plateau). He interpreted the hydrous mineral suite, which shows apparent equilibrium metamorphic textures, as “primary” in the sense that it was formed in peridotite at depth before the peridotite was disaggregated and incorporated in the erupting diatreme. In contrast, chloritic alteration in U33/1 and UX/1 clearly replaces garnet and secondary clinopyroxenes, and, as discussed earlier, the chlorite composition has been controlled by the mineral it replaces (Fig. 12). Thus, chloritic alteration appears to be the last pervasive alteration event experienced by these xenoliths. Considering that chlorite is a common product of hydrothermal alteration in low- and medium-grade metamorphic rocks, we speculate that the chloritic alteration occurred in the upper crustal environment.

Relationship between alteration and diamond formation

An important feature of U33/1 and UX/1, as was reported earlier for the Udachnaya eclogite xenolith U51 (Taylor et al. 2000), is that the diamond crystals are always surrounded by secondary clinopyroxene or chlorite (Fig. 4b), and are never in contact with garnet or its kelyphitic alteration assemblage. This spatial relationship raises the possibility that the diamond formation was genetically related to at least some part of the metasomatic alteration.

We have no direct data for the age of the two eclogite xenoliths we have studied or of their diamonds, and age data available in published literature are limited. The age of the xenoliths, however, should be comparable to the ages reported for other diamond-bearing eclogites from the Udachnaya kimberlite pipe. These include a whole rock Pb-Pb age of 2.76 Ga (Jacob et al. 1994), a whole-rock Re-Os age of 2.9 ± 0.4 Ga (Pearson et al. 1995), and a sulfide Re-Os age of 2.6 ± 0.6 Ga (Taylor et al. 2000). Burgess et al. (1992) determined a ⁴⁰Ar-³⁹Ar age of 1149 ± 37 Ma for a clinopyroxene inclusion in Udachnaya diamond. This age is significantly younger than the ages determined for the eclogites, but still considerably older than the 360–390 Ma age of Udachnaya kimberlite (Davis 1978; Jagoutz 1986; Snyder et al. 1993; Kinny et al. 1997). Thus, it is reasonable to conclude that the diamonds in U33/1 and UX/1 formed long before the xenoliths were entrained in the kimberlite. This conclusion is consistent with the non-fibrous nature of the diamonds in U33/1 and UX/1, as the high degree of nitrogen aggregation characteristically associated with such diamonds is indicative of their long residence time in the mantle (Taylor et al. 1996).

As discussed earlier, the Event II alteration assemblage includes amphibole and spinel, which must have formed at a significantly lower pressure (shallower depth) compared to the source region of the eclogite xenoliths (estimated pressure in the range of 6.5 GPa). That this metasomatic alteration of the primary eclogite

assemblage occurred after diamond formation is also supported by the presence of spongy-textured alteration of Cpx inclusions in diamonds from other eclogite xenoliths in the Udachnaya pipe (Taylor et al. 2000). They found the spongy-textured alteration to be Na-depleted secondary Cpx, similar in composition to the spongy-textured secondary Cpx in the host eclogites, and attributed the alteration to fluid penetration along numerous cracks in the diamonds.

The formation of eclogitic diamonds from C-rich metasomatic fluids has been advocated by many authors (e.g., Spetsius 1999; Navon 1999; Taylor et al. 2000, 2001; Spetsius and Taylor 2002). However, the observed metasomatic alterations in U33/1 and UX/1 appear to have taken place much later than the emplacement of diamonds in the eclogite xenoliths. The concentration of secondary pyroxenes and chlorite around the diamond crystals in U33/1 and UX/1 appears to be an artifact of impediment to the flow of metasomatizing fluids because of already existing diamond crystals.

Summary and conclusions

The primary mineralogy of the two diamondiferous xenoliths, U33/1 and UX/1, from the Udachnaya kimberlite pipe was essentially a two-phase assemblage of pyrope-almandine garnet and omphacitic clinopyroxene (Cpx 1, 6.5–7 wt% Na₂O), with small amounts (<3%) of interstitial and included Fe-Ni-Cu-Co sulfides.

Metasomatic alteration products in the two xenoliths consist of the following: (a) platy phlogopite (~10 wt% K₂O) associated with garnet; (b) spongy-textured, fine- to medium-grained, Na-depleted clinopyroxene (Cpx 2A, 1–3 wt% Na₂O) + K-feldspar ± K-Ca-Fe-Mg glass (<1%); (c), relatively coarser grained, Na-depleted clinopyroxene (Cpx 2B, 2–5 wt% Na₂O), (d) kelyphite characterized by low-Na clinopyroxene (Cpx 3, mostly <1 wt% Na₂O) intergrown with zoned, Mg-Fe-Al spinel (pleonaste) characterized by Fe-enriched rims; (e) relatively K-enriched, pargasitic amphibole (~0.8 wt% K₂O; 3–3.5 wt% Na₂O); (f) alteration rims of djerfisherite (K_{5.95}Na_{0.02}Fe_{18.72}Ni_{2.36}Co_{0.01}Cu_{4.08}S₂₆Cl) around pyrrhotite-pentlandite sulfide grains; and (g) other secondary minerals such as sodalite, calcite, K-feldspar, and Ba-Sr sulfate. This alteration assemblage is overprinted by a pervasive chloritic alteration, represented by clinocllore + magnetite ± apatite.

The observed alterations in U33/1 and UX/1 (excluding that pertaining to chloritic alteration) appear to be the result of two distinct metasomatic events caused by fluid infiltration in the upper mantle. The first event (Event I) was responsible for the formation of phlogopite and occurred before the xenoliths were incorporated in the kimberlite. The rest of the alteration assemblage, except that due to chloritic alteration, is interpreted to have formed during the second event (Event II) through a series of complementary reactions

involving garnet, Cpx 1, and a K-rich fluid containing H₂O, CO₂, Cl, Ti, Ba, Sr, and SO₄. This event occurred after the xenoliths were incorporated in the kimberlite and transported to a level where spinel and amphibole would be stable. The chloritic alteration probably was an upper crustal phenomenon.

The diamond crystals in U33/1 and UX/1 are always surrounded by secondary clinopyroxene (Cpx 2) and chlorite, but the diamonds formed before the entrainment of the xenoliths in kimberlite, whereas the observed metasomatic alterations occurred at lower pressures after entrainment.

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