

Trace elements in diamond inclusions from eclogites reveal link to Archean granites

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Abstract

We report trace element data for rare garnet and clinopyroxene inclusions trapped within diamonds occurring in eclogite xenoliths from the Siberian craton. These inclusions are more depleted in incompatible trace elements and have lower Mg# than the eclogite host minerals, reflecting metasomatic enrichment of the eclogites after diamond formation by high Mg# melts that are enriched in incompatible trace elements (such as kimberlites). A reconstructed whole rock composition (using inclusion data) is severely depleted in light rare earth elements and niobium but shows a marked strontium enrichment. The melt in equilibrium with this eclogite is calculated to have had very high La/Yb and Sr/Nd and is Nb depleted (if rutile is present), characteristics similar to those of some convergent margin magmas but most especially Archean tonalitic rocks. Experimental petrologic studies demonstrate that eclogites of the type described here are in equilibrium with silicic melts such as tonalites or trondhjemites. Thus, both our trace element data and petrological considerations are consistent with the eclogites forming in equilibrium with Archean tonalitic or trondhjemitic magmas. Our data may therefore comprise the first evidence for the fate of these voluminous residues. A corollary of our findings is that trace element and isotopic data from eclogite minerals must be interpreted with caution because of the eclogite's complex evolutionary history. Specifically, models of early Earth differentiation based on isotopic data from Siberian eclogites [1,2] require re-evaluation.

1. Introduction

Granites of the trondhjemite–tonalite–granodiorite (TTG) suite are volumetrically dominant in Archean cratons and are believed to have formed by 15–30% melting of a mafic, garnet-bearing precursor [3–5], either in the lowermost

crust or the upper mantle. A consequence of this model is the production of large volumes of complementary residual eclogite, which have not yet been identified in either the deep crust or the lithospheric roots of Archean cratons.

Eclogites occur as xenoliths in kimberlitic magmas that penetrate the Archean cratons and their origins are not well understood. This is, in part, due to the fact that these xenoliths are pervasively altered by kimberlite-related fluids, making whole rock geochemistry of limited value in deciphering their origins. Ringwood and Green [6]

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first recognized that basaltic crust subducted into the upper mantle will undergo phase transitions that ultimately lead to an eclogite mineralogy. Helmstaedt and Doig [7] later proposed that some eclogite xenoliths are subducted and metamorphosed ocean floor basalts. In contrast, others have argued that they are high-pressure cumulates from basaltic magmas [8,9]. Recently, trace element and isotopic data for clean mineral separates from eclogite xenoliths have been used to infer their origin and geologic history (e.g. [1,2,10–13]). An underlying assumption in such studies has been that the measured mineral compositions can be recombined to yield the original rock composition.

We report here major and trace element compositions of two rare silicate inclusions in diamonds from eclogite xenoliths and compare these to the compositions of the corresponding phases in the host rocks. The differences in compositions between these two eclogitic assemblages allow an unprecedented glimpse into the evolutionary history of the eclogite and the reconstruction of the original eclogite composition. By examining this inferred original composition, we propose a link between these eclogites, which currently reside in the lithospheric keel beneath the Siberian craton, and Archean granites found in that craton (e.g. [14,15]).

2. Samples and regional geology

The eclogites come from the Devonian Udachnaya pipe in the Daldyn–Alakit kimberlite field of Siberia [16]. This kimberlite field lies near the middle of the Siberian platform, surrounded by Paleozoic sediments and Triassic volcanics of the Siberian traps. The nearest basement outcrops lie 200 and 1000 km north and southeast, in the Anabar and Aldan shields, respectively. Both shields contain 2–3 Ga TTG, metabasites and metasediments, all metamorphosed under granulite facies conditions [14,17,18]. Tonalites and trondhjemites in both shields have the strongly LREE (light rare earth) enriched, H (heavy) REE depleted patterns that are so typical of Archean TTGs [14,15].

Both xenoliths are coarse-grained diamondiferous eclogites with significant alteration along cracks and grain boundaries. Sulfides occur in both samples and rutile is absent. The samples contain 3 and 6 octahedral diamonds, respectively, ranging from 1 to 3 mm in diameter. In one sample (Ud94) a 400 μm garnet inclusion occurs within one of the diamonds and in the second sample (Ud146) a 300 μm omphacite inclusion is found within diamond.

3. Analytical techniques

Both host rock and diamond inclusion (DI) minerals were analyzed by electron probe for major elements, and the sensitive, high resolution ion microprobe (SHRIMP) for trace element compositions. The SHRIMP I ion probe at the Australian National University was operated using a modified energy filtering technique [19] to discriminate against complex molecular interferences. While high mass resolution can be used to exclude most of the isobaric interferences around the REE mass spectrum, the actual ionic intensities are a strong function of the matrix composition. Thus, while high mass resolution offers much more intense secondary ion signals than energy filtering, the benefits in counting statistics are compromised by the requirement of analyzing compositionally similar standards. At sufficiently high energy offsets, the energy filtering technique reduces the matrix effect to negligible levels for different compositions of the same mineral and often between minerals. This is particularly so for silicate mineral systems where it has been found that a silicate glass can be used as a suitable standard for zircon [20], silicate glass [21] and clinopyroxene and garnet (this study).

The energy filtering technique used on SHRIMP I is similar to that used on the Cameca ion microprobes but utilizes an energy offset in the electrostatic analyzer rather than in the secondary extraction voltage. In this case the mass calibration of the secondary ion mass spectrum must be modified to account for the change in energy of the selected ions. The secondary ion intensities from $^{30}\text{Si}^+$ to $^{238}\text{U}^+$ were monitored

Table 1
Major (wt%) and trace element (ppm) contents of minerals from eclogites and diamond inclusions

Method	Sample Ud146											
	GARNET-Rock			CPX-Rock			GT-DI			CPX-DI		
	SHRIMP ±	SSMS ±	Calc. WR* ±	SHRIMP ±	SSMS ±	Calc. WR* ±	SHRIMP ±	SSMS ±	Calc. WR* ±	SHRIMP ±	SSMS ±	Calc. WR* ±
SiO ₂	41.10		48.2	41.45		99.33	99.92		99.99	100.06		99.82
TiO ₂	0.40		0.45	0.32		74.0	67.4		75.2	79.6		74.3
Al ₂ O ₃	22.59		15.7	22.75		221	—		2240	415	17	750
FeO	13.03		9.00	14.66		28.2	45.0	1.4	13.3	0.6	14.4	24.2
MnO	17.26		0.19	0.30		170	70	14	317	28	254	195
MgO	4.69		14.3	16.99		440	315	19	493	25	433	394
CaO	0.17		8.79	3.30		0.02	—	0.16	0.02	—	—	0.24
Na ₂ O			2.85	0.15		0.10	0.16	0.1	0.109	0.08	0.10	0.13
Total	99.55		99.33	99.92		99.33	99.92		99.99	100.06		99.82
Mg#	70.3		74.0	67.4		74.0	67.4		75.2	79.6		74.3
K	1.9	0.8	—	—	—	221	—	—	2240	415	17	750
Sc	45.0	5.0	—	—	—	28.2	45.0	1.4	13.3	0.6	14.4	24.2
V	74	7	—	—	—	170	70	14	317	28	254	195
Cr	370	14	—	—	—	440	315	19	493	25	433	394
Rb	—	0.17	0.06	—	—	0.08	0.02	0.08	0.03	0.08	0.10	0.07
Sr	0.44	0.04	0.1	1.12	0.08	0.11	0.27	0.46	0.02	0.02	0.02	0.03
Y	34.8	6.0	42.0	9.0	37.2	0.7	3.8	0.4	19	35.1	2.7	44.1
Zr	42.6	4.0	50.0	6.0	14.7	2.8	41.0	4.0	39	25.1	1.0	29.8
Nb	0.39	0.06	0.46	0.05	0.056	0.08	0.78	0.11	0.61	0.13	0.21	0.21
Ba	—	0.30	0.05	—	—	0.41	0.04	0.03	—	—	—	0.80
La	0.035	0.020	0.022	0.022	0.018	0.14	1.53	0.24	0.78	0.03	0.02	0.02
Ce	0.170	0.048	0.36	0.04	0.096	0.70	5.37	0.71	2.77	0.13	0.04	0.32
Pr	0.056	0.026	0.08	0.01	0.051	0.25	1.03	0.14	0.54	0.06	0.03	0.07
Nd	0.590	0.140	0.72	0.1	0.499	0.40	4.83	0.52	2.78	0.50	0.14	0.63
Sm	0.57	0.14	0.62	0.09	0.91	0.14	1.12	0.18	1.22	0.10	0.13	0.55
Eu	0.39	0.06	0.37	0.04	0.50	0.06	0.39	0.03	0.38	0.28	0.06	0.32
Gd	1.87	0.40	1.98	0.18	2.86	0.60	1.39	0.83	1.58	1.83	0.40	1.65
Tb	0.57	0.10	0.53	0.05	0.57	0.12	0.18	0.04	0.16	0.02	0.35	0.54
Dy	3.85	0.28	4.38	0.26	4.90	0.40	0.72	0.10	0.76	0.04	0.26	0.46
Ho	0.94	0.24	1.22	0.07	1.33	0.26	0.09	0.04	0.12	0.01	0.14	0.26
Er	3.31	0.30	4.04	0.27	4.53	0.56	0.22	0.06	0.23	0.01	0.11	0.26
Tm	0.38	0.10	0.44	0.07	0.67	0.18	0.05	0.02	0.02	0.02	0.02	0.03
Yb	3.44	0.22	4.08	0.27	4.63	0.64	0.15	0.04	0.12	0.02	0.10	0.20
Lu	0.62	0.10	0.68	0.17	0.94	0.14	0.02	0.02	0.12	0.01	0.02	0.07
Hf			0.40	1.63	0.16	1.16	—	—	0.33	0.02	—	0.8

Gt = garnet; cpx = clinopyroxene; ± = 1σ error; Mg# = 100 × (Mg/(Mg + ΣFe)); — = below detection limit, see text for discussion of detection limit.

Major elements by electron probe. ¹³⁹La peak in SSMS analysis is inferred from Ca–Al molecular species.

* Whole rocks (WR) calculated using the observed modal mineral proportions (Ud94: 50% gt, 50% cpx; Ud146: 32% gt, 68% cpx) and the following data: major elements electron probe, K–Ba SHRIMP, Nd–Yb and Hf SSMS. Cpx: La–Pr SSMS, Gt: La–Pr SHRIMP

** Whole rock calculated using cpx DI and groundmass garnet.

and the mass spectrum from ^{138}Ba to ^{180}Hf was deconvolved for the contributions of monoxide species whose intensities are typically around 5% of the atomic species. The concentration of each element can be determined by normalizing the intensity of a given isotope (or several isotopes) to the secondary ion signal of a major element (in this case $^{30}\text{Si}^+$) and multiplying by sensitivity factors determined through the analysis of suitable standards. Therefore, the concentration of a given element A is given by:

$$[A] = F_A(^1A^+ / ^{30}\text{Si}^+)[\text{SiO}_2]$$

where F_A is the sensitivity factor for isotope $^1A^+$ relative to $^{30}\text{Si}^+$ and the concentration of SiO_2 can be determined by electron probe.

The primary standard used in this work is a fused sample of Hawaiian basalt, BHVO, whose geochemical characteristics have been well determined by a wide variety of analytical techniques. Repeated analyses of this standard between measurements of the eclogite minerals were used to obtain sensitivity factors. The reproducibility of the measurements of BHVO was better than 5% for all elements other than the heavy REE, Hf, U and Th, whose precision was limited by counting statistics to around 10–15%. For these elements the sensitivity factors were also checked by analyzing a zircon standard and this showed good agreement with the sensitivity factors obtained from BHVO. In addition, we have analyzed a variety of other glasses created from USGS rock standards to check the accuracy of our technique. In all cases for elements with a concentration above 5 ppm, the concentration of elements differed from the expected values by less than 10%, where counting statistics allowed sufficient precision for a comparison.

The detection limits for these analyses are a function of the counting times, the ionization yield of a given species and the presence or absence of isobaric interferences. For Ba and the LREE the detection limit is around 10 ppb (at the counting times employed for garnet analyses). Shorter count times were used for the clinopyroxene analyses, resulting in higher detection limits.

The HREE detection limits are dependent on the REE pattern, since LREE monoxides interfere with the HREE atomic species and an error is propagated during the peak stripping. Detection limits are markedly higher (30–50 ppb) for a phase enriched in LREE, such as clinopyroxene; in a phase depleted in LREE, such as garnet, the detection limits approach the counting statistics limit at around 20 ppb. Shorter counting times were employed for garnet because it is HREE enriched. The detection limit for Hf is high (around 200 ppb) for both clinopyroxene and garnet because of errors associated with estimating the Dy abundance and, consequently, the DyO contribution to the Hf peaks. Detection limits for Sr, Y, Zr and Nb are also somewhat higher (around 30–50 ppb) because, due to their often higher abundances, shorter counting times were employed compared to LREE.

The absence of matrix effects in our analyses is supported by a comparison of SHRIMP analyses of host rock garnet and clinopyroxene with trace element abundances determined on clean, acid leached mineral separates measured by spark source mass spectrometry (SSMS)[22]. SSMS and SHRIMP data are generally within error; except that Ba, Ce and Sr are consistently higher in the SSMS garnets, and Ba is higher in SSMS cpx (well beyond 2σ uncertainties) compared with SHRIMP data (Table 1). Kimberlite-borne xenoliths are typically hydrothermally altered due to invasion of fluids derived from the kimberlite. This alteration enhances Ba, Sr and LREE contents of the minerals (our unpublished results), and we believe it is responsible for the higher Ba and Sr abundances determined by SSMS. Note that inclusion of a very small amount of altered mineral into a bulk separate will only have a noticeable effect on elements with intrinsically low abundances in the minerals (e.g., Ba, Ce and Sr in garnet and Ba (but not Sr or Ce) in clinopyroxene).

Minerals were examined by both electron probe (traverses across garnet and cpx in both samples) and SHRIMP (4 analyses of cpx in Ud146) for evidence of zoning; none was found. The SHRIMP data reported here are therefore the means of 2–4 spot analyses for each mineral.

4. Results

The major element compositions of minerals from both the eclogite and from within the diamond (Table 1) are similar to those for bi-mineralic eclogite xenoliths and eclogitic DI from a number of kimberlite occurrences described in the literature [11,23–27]: omphacites contain 36–44% jadeite and the garnets are almandine–pyrope–grossular solid solutions ($\text{Alm}_{26-62}\text{-Py}_{30-62}\text{-Gr}_{8-16}$) with low Cr_2O_3 . Fewer trace element analyses of eclogite minerals are available for comparison. Our host rock results are comparable to the REE data for other Siberian diamondiferous eclogites ([28], as described below) and Roberts Victor eclogites [29]. Our data show significantly greater LREE depletion than INAA data obtained for mineral separates from other South African eclogites [12,13].

Only a limited number of trace element data exist for eclogitic DI. Eclogitic garnet DI from the Monastery mine, South Africa, display an incredibly large range in Y and Zr abundances [30], which overlap our data (we refer here to Moore et al.'s 'Group A' garnets — those that do not contain pyroxene in solid solution). The single Monastery garnet for which REE data are reported has an unusual major element composition (2.4% TiO_2) and has the highest REE abundances yet reported for an eclogitic garnet (i.e., 7.4 ppm Ce, 36 ppm Yb).

Rather large differences exist between the major and trace element contents of our Siberian samples and eclogitic DI from Western Australia [31,32]. The Siberian garnet DI has generally lower Na_2O , TiO_2 and grossular contents, an order of magnitude less Sr and 2–12 times lower Zr contents than the Western Australian samples, at comparable Y values. Our clinopyroxene DI has a Sr content which is a factor of 2–20 lower than the Western Australian samples and no detectable U (i.e., < 30 ppb). Overall, this comparison suggests that the eclogitic protoliths for the Western Australian diamonds are far more enriched in incompatible elements than their Siberian counterparts. Note, however, that we have also examined the same samples measured by Griffin et al. [32] using SHRIMP in high mass

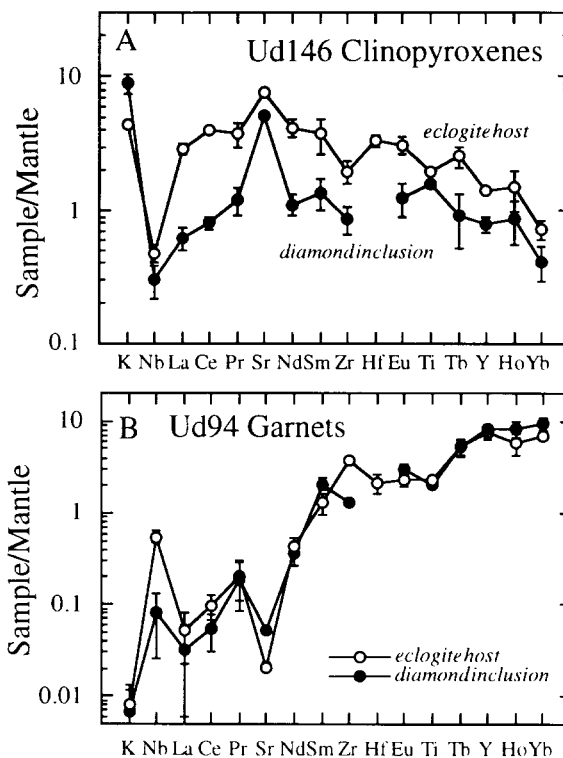


Fig. 1. Comparison of trace element compositions of minerals contained within diamond and in eclogite host (normalizing values in this and other diagrams from [39]). Ti data are from electron probe analyses, Hf data for host rock phases are from SSMS, the remainder of the data are from SHRIMP. Error bars represent 1σ of the mean.

resolution mode (in which Pb and U are well determined) and found that the Pb count rates were low and decreased exponentially with time (suggesting Pb is present predominantly as surface contamination) and no detectable U (cf. 6–17 ppm reported in Griffin et al.).

Significant compositional differences exist between the phases trapped in the diamonds and their host rock counterparts. Compared to garnet in the eclogite host, the garnet DI in Ud94 has lower Mg#, Ti, Nb and Zr, but higher CaO and Sr (Table 1). The clinopyroxene DI in Ud146 has lower Mg#, Ti, Nb, Sr, REE, Zr and Y but higher K, Ba and jadeite ($\text{NaAlSi}_2\text{O}_6$) component than the host rock clinopyroxene. These comparisons are illustrated in Fig. 1.

5. Discussion

5.1. Causes of chemical differences

Chemical differences between minerals in the host eclogite and in the diamonds may reflect re-equilibration of the former due to changes in P or T and/or open system exchange of these minerals with a passing fluid or melt. The DI minerals are isolated from both re-equilibration and exchange and, thus, provide the best evidence for the original composition of the eclogite. In the following discussion we assume: (1) the diamonds are not xenocrystic within their host rocks and (2) the diamond and its silicate inclusion crystallized at the same time, when the eclogite (re)crystallized in the diamond stability field (e.g., [33]).

Pressure decrease after diamond formation can account for the lower K and jadeite component in the host rock clinopyroxene of Ud146 compared to the DI clinopyroxene, since both these components are pressure sensitive [23,34]. (Ba is the only other incompatible trace element that is preferentially enriched in the DI compared to the host rock clinopyroxene and we speculate that its partitioning into clinopyroxene may also be enhanced by pressure.) Likewise, the higher Mg# of the host rock clinopyroxene is consistent with a temperature decrease [35], although this difference may also have resulted from metasomatism, as discussed below. The marked enrichments of incompatible trace elements in the host rock clinopyroxene are unlikely to be due to changing P and T conditions. We suggest that these enrichments (with a factor ≤ 5) have been caused by metasomatism of the eclogite by passing melts.

Enhanced abundances of the high field strength elements (Nb, Zr and Hf) in the host rock garnet in Ud94 compared to the DI garnet may also be due to metasomatic enrichment of the rock by passing melt. The higher Mg# of the host rock garnet in Ud94 compared with the DI garnet would require a temperature increase in the rock after the diamond grew. While this is possible, we consider a more likely explanation for the Mg# increase (in both Ud94 and Ud146) is that it, too, was caused by metasomatism. Im-

portantly, Sobolev et al. [36] reported both clinopyroxene and garnet DI from a Siberian eclogite that show lower Mg# than their corresponding host phases, indicating that, in this case, the Mg# variations cannot be explained by changes in temperature and require an Mg# enrichment of the eclogites after diamond growth. We believe our data also reflect an increase in Mg# in the whole rock eclogites after diamond growth.

From the data presented above we conclude that the eclogites were metasomatized after diamond growth, which enhanced the incompatible trace element content of the rocks while at the same time increasing its Mg#. In contrast to peridotites, where metasomatism generally decreases Mg#, eclogites have relatively evolved, basaltic compositions. For example, average MORB has a Mg# = 56 [37] and average Archean basalt/picrite has a Mg# = 66 [R. Rudnick, unpublished data]. Thus, interaction of these compositions with a primitive, peridotite-derived melt, having high Mg# (~ 74 , based on a pyrolitic mantle having olivine of Fo₈₉), would increase the Mg# of the eclogite. A likely candidate for the metasomatic agent is a kimberlite melt, which has high Mg# (88–89) and is strongly LREE enriched [38].

We attribute the lower K content of the clinopyroxene that remained outside the diamond as being due to a pressure drop after diamond growth, since partitioning of K into clinopyroxene is highly pressure sensitive (increasing by a factor of 2 over a 1 GPa pressure increase; [34]). Using the experimentally determined D values of Edgar and Vukadinovic [34] for clinopyroxene at 5–6 GPa and 1200–1400°C in equilibrium with a lamproitic melt, the K₂O content of the metasomatizing melt was between 0.65 and 3.25wt%, which reproduces the range of K₂O contents in group I kimberlites [38] remarkably well.

5.2. Reconstructed whole rock compositions

Eclogite whole rock compositions can be reconstructed from their mineral compositions and modal proportions. The uncertainty in this calculation lies in the accurate determination of modal

proportions because of the small sizes of the xenoliths (2–3 cm diameter) and their coarse-grained character (each grain is several millimeters in length). Reasonable limits can be placed on the garnet:clinopyroxene proportions by comparing the calculated major element composition with those of other eclogite xenoliths that have been determined by measurement of whole rock powders (Fig. 2) and assuming that our samples should lie within this range. Both calculated compositions fall within the major element range displayed by eclogite xenoliths; lying at the high SiO_2 and Na_2O end and low CaO end of the eclogite field. Because SiO_2 , Na_2O and CaO contents are uniformly higher in clinopyroxene than in garnet, these observations suggest that the observed modal mineralogies are approximately correct. That is, if the clinopyroxene abundances are increased in order to elevate the whole rock CaO content, then the SiO_2 and Na_2O content of the whole rocks would be significantly higher than that observed in other eclogites. Likewise, if the garnet abundances are increased in order to decrease the whole rock SiO_2 and

Na_2O content, the CaO contents would be lower than observed in other eclogites. We conclude from these observations that the observed modal proportions are correct to within 10%, as illustrated in Fig. 2.

The resulting major element compositions have $\text{CaO}/\text{Al}_2\text{O}_3$ (~ 0.6) which overlap only a small percentage of Archean basalts ($\text{CaO}/\text{Al}_2\text{O}_3 = 0.55 - > 2$), MORB ($\text{CaO}/\text{Al}_2\text{O}_3 = 0.35 - > 1$) and other bi-mineralic eclogites ($\text{CaO}/\text{Al}_2\text{O}_3 = 0.4 - > 1$). These observation suggests either: (1) an unusually low CaO protolith for these particular eclogites or (2) CaO was lost from the host rock garnet in Ud146 during the metasomatism (as is the case for garnet in Ud94, Table 1).

REE patterns of reconstructed eclogite whole rocks are compared with data for other Udachnaya eclogites [28] in Fig. 3. These eclogites are light REE depleted, but show a curious 'double-hump' pattern (Fig. 3a). In contrast, most Udachnaya eclogites are more LREE depleted than those shown in Fig. 3a, with similar HREE abundances to the samples investigated here (Fig. 3b).

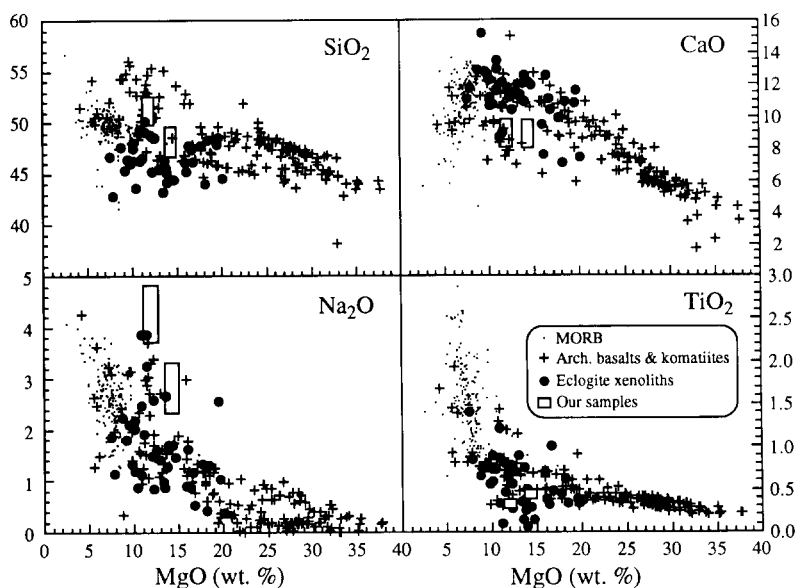


Fig. 2. MgO versus SiO_2 , TiO_2 , CaO and Na_2O for MORB, Archean basalts and komatiites and eclogite xenoliths (data compiled from the literature). The two Siberian samples described here are shown as large boxes—the size of the box represents the estimated error based on the uncertainties in modal proportions. Ud146 whole rock was calculated using the diamond inclusion clinopyroxene and rock garnet compositions, whereas Ud94 was calculated using the compositions of the rock phases.

Fig. 4a shows the REE pattern of Ud146 reconstructed using the clinopyroxene DI and host rock garnet composition. (We have not reconstructed the pre-metasomatic whole rock composition for Ud94 due to uncertainties in the original clinopyroxene composition; garnet compositions are not sensitive indicators of the LREE abundances—see Table 1.) This pattern represents our best estimate of the original (pre-metasomatic) whole rock composition, although uncertainties remain regarding the original garnet composition. For example, if the pre-metasomatic garnet was similar in composition to Ud94 DI, then the reconstructed whole rock for Ud146 (Fig. 4b) may have too much Nb, Zr and Hf and its CaO and Sr contents may be too low. The original eclogite was extremely LREE depleted, comparable to the most LREE depleted eclogite measured from Udachnaya [28] (Fig. 3).

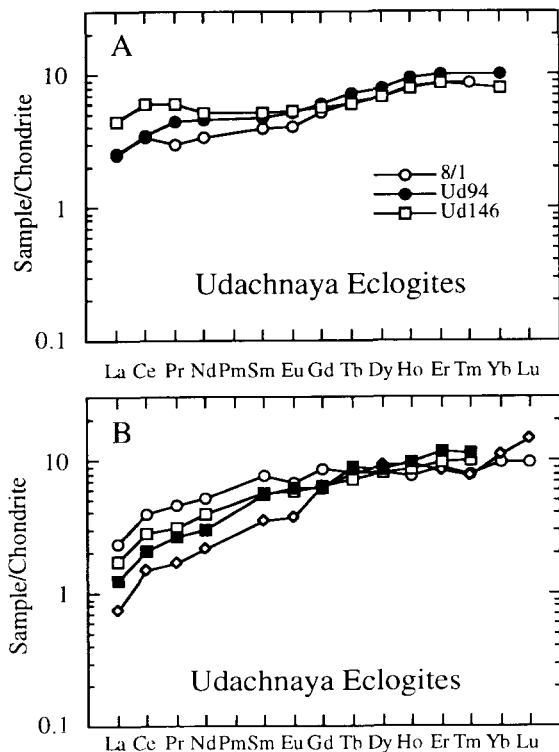


Fig. 3. Reconstructed whole rock REE patterns of Udachnaya eclogites. (a) Data from [28] and this paper, modes given in Table 1. (b) Data from [28] (assuming 50% clinopyroxene, 50% garnet).

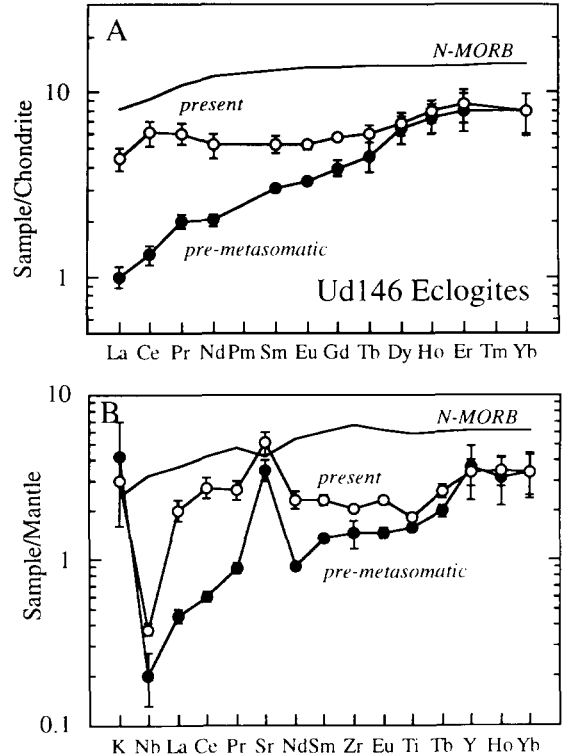


Fig. 4. Reconstructed, pre-metasomatic whole rock for Ud146. (a) REE (typical N-MORB is shown for comparison [39]) and (b) multi-element diagram. Error bars represent 10% uncertainty in modal proportions.

This suggests that many of the Udachnaya eclogites may have experienced metasomatic enrichment of incompatible trace elements (and probably increased Mg#).

Several papers report Sr and Nd isotopic compositions of Siberian eclogites proposing evidence for early Earth differentiation events (ca. ≥ 4 Ga) beneath Siberia [1,2]. The data presented above, however, provide compelling evidence that Siberian eclogites have experienced complex, multistage histories and, thus, their present compositions are unlikely to reflect those at the time of their formation. Major uncertainties surround: (1) the timing of the metasomatism; (2) the isotopic composition of the metasomatic agent(s); and (3) the change in parent/daughter ratio associated with the metasomatism (for the majority of eclogites where DI are not available). Given these uncertainties, the present incompatible trace ele-

ment and Sr, Nd and Pb isotopic ratios of eclogite minerals cannot be easily interpreted in terms of the petrogenesis of these rocks and no confidence can be placed in suggestions of early Earth differentiation events.

5.3. Origin of the eclogites

The major element compositions of these and other eclogites do not match those of MORB but are similar to those of Archean basalts (Fig. 2). However, the REE abundances of the pre-metasomatic eclogite are unlike those of common melts: the LREE are severely depleted, much more so than typical N-MORB ($(\text{La}/\text{Yb})_n = 0.13$ cf. $(\text{La}/\text{Yb})_n$ N-MORB = 0.55–0.68 [37,39], Fig. 4a) or Archean basalts [40–42]. These features are consistent with eclogite formation at high pressure, as a garnet-bearing cumulate or residue in equilibrium with a melt.

Insights into the nature of a melt phase in equilibrium with eclogite can be obtained from both melting and crystallization experiments. Melting of a basaltic protolith at 3 GPa produces melts of tonalitic to trondhjemitic composition that are in equilibrium with an eclogite residue having mineral compositions similar to many biminerals eclogites (e.g., 30–38 mol% jadeite in clinopyroxene and Cr-poor garnets [43]). In contrast, crystallization of basalts at these pressures produces clinopyroxene having a low jadeite component (8–10 mol% jadeite) and garnet that contains a significant Cr_2O_3 component [44–46]. From a petrological point of view, therefore, tonalite or trondhjemite is the melt in equilibrium with eclogite of the type described here.

More detailed knowledge of the major element composition of the equilibrium melt is not possible without experimental melting studies of a protolith with the appropriate composition (for these samples this would be an Archean basalt having low TiO_2 and relatively high Na_2O and SiO_2 —Fig. 2). The composition of the protolith is more apparent. If the tonalite/trondhjemite formed by relatively small degrees of melting (10–15%) we would not see a dramatic change in major element composition between the protolith and the residue, except, perhaps, for a decrease

in SiO_2 , since the silica-bearing phase is the first to melt in an eclogite [44]. In addition, Na_2O becomes compatible in clinopyroxene at pressures above ~ 4 GPa [47], suggesting that partial melting may have little effect on Na_2O . The protolith composition was, therefore, similar to that of a high SiO_2 and Na_2O , low CaO Archean basalt; the high Na_2O content may reflect sea floor alteration.

Trace element characteristics of the equilibrium melt can be estimated from the pre-metasomatic eclogite composition (Table 1, Fig. 4b) and the partitioning behavior of trace elements between garnet, clinopyroxene and melt [48–51]. Because of the very large variations in mineral D values as a function of melt and mineral composition, uncertainties in modal proportions and how D values change with P and T , these calculations are necessarily imprecise. Nevertheless, there are robust features of the coexisting melt that are distinctive and allow some constraints to be placed on the composition of the equilibrium melt. This melt had lower HREE abundances and higher LREE abundances than those of the eclogite, and a strongly fractionated REE pattern, due to the effects of residual garnet. The most striking feature of the eclogite trace element composition is the strong enrichment of Sr over the LREE. This feature is also present in the equilibrium melt, as shown in Fig. 5 (see appendix for details of the calculation).

High Sr/Nd is also seen in the eclogite whole rock reconstructed from clean garnet and clinopyroxene, demonstrating that the metasomatism has not obliterated these original features. In fact, high Sr/Nd appears to be a common feature amongst Siberian eclogites (average Sr/Nd = 27, range = 10–55, data from this study, [2] and our unpublished results), suggesting that our results for Ud146 are generally applicable. The trace element features of melts in equilibrium with these eclogites are distinct from any modern magmas but (with the exception of the higher Nb contents) closely resemble those of Archean granitoids of the trondhjemite-tonalite-granodiorite (TTG) suite (Fig. 5).

The lack of Nb depletion in the calculated equilibrium melts compared to the dramatic Nb

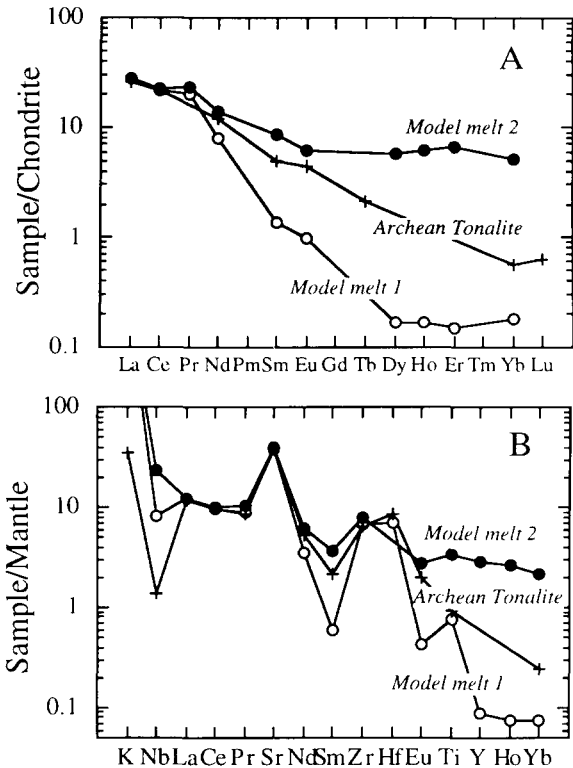


Fig. 5. (a) REE and (b) multi-element plots comparing the calculated equilibrium melt composition for original Udachnaya eclogite Ud146, with two Archean tonalites from the Superior province, Canada (samples JN-17 and JN-32 from [70]). Phase proportions used in the calculation correspond to the observed modal mineralogy: 68% clinopyroxene and 32% garnet. See appendix for calculation details.

depletion of Archean TTG (Fig. 5) warrants discussion. Neither eclogite investigated here contains rutile, yet rutile is a common accessory phase in many eclogite xenoliths. The small sample size of our eclogites makes it difficult to conclude that they are, indeed, rutile free. The D value for Nb in rutile is large (e.g., [52]), making even small amounts of refractory rutile of major importance in determining the degree of Nb depletion in the coexisting melt. Experimental studies have demonstrated that Ti phase solubility decreases strongly with increasing SiO_2 of melt, decreasing temperature and increasing pressure [5,53,54]. Thus, if a tonalite forms by melting at very high pressure (4–6 GPa), as envisaged here, then rutile may be a residual phase even in low

TiO_2 bulk compositions (such as Archean basalts, Fig. 2). This could account for the pervasive Nb depletion observed in Archean TTG.

We envisage that the following sequence of events have created the eclogites as we sample them today:

- (1) Formation (in the Archean) of basaltic or picritic oceanic crust with attendant hydrothermal alteration and deposition of carbonates, causing enhancement of Sr concentration and introduction of carbon.
- (2) Subduction of carbonated mafic crust to upper mantle depths; transformation to eclogite mineralogy.
- (3) Redox melting (e.g. [55]) of eclogite in the diamond stability field (depths > 150 km) to produce tonalite or trondhjemite melts that rise, leaving behind residual diamond-bearing eclogite. The eclogite remains in the lithospheric mantle and carbon acts as a refractory component, consistent with recent experimental investigations on melting of subducted carbonated oceanic crust [56].
- (4) Later metasomatism of the eclogites by passing kimberlitic melts, causing an increase in the most incompatible trace element concentrations and an increase in Mg#.
- (5) Entrainment of the eclogites into the host kimberlite in the Devonian.

5.4. Implications for TTG genesis and the composition of cratonic mantle lithosphere

Numerous experimental and geochemical studies of Archean TTG have demonstrated that these rocks form by 15–30% melting of a mafic, garnet-bearing source (e.g. [3,5]). The depth of melting remains uncertain; it may have occurred in the deeper portions of a thickened crust [57], leaving residual mafic granulite, or may have occurred within basaltic crust that was subducted into the upper mantle, leaving residual eclogite [4,58]. Seismic studies of cratonic regions show that the lower third of the crust typically has high P wave velocities that are indicative of mafic granulite composition [59,60]. However, a simple volumetric calculation shows that in a 10×10 km section of 45 km thick Archean crust, in which

the upper 30 km contains 70% TTG, 7000–10,500 km³ of mafic residue would be produced during the production of the TTG. This is 1.5–3 times the volume of the entire crust and 5–7 times the volume of mafic lower crust currently present in Archean cratons.

Could these residues be in the underlying lithospheric mantle? If so, they would constitute 35–68% of the mantle lithosphere, depending upon whether any are contained within the crust and assuming that the lithosphere is 200 km thick [61]. Estimates of the relative proportions of eclogite to peridotite in cratonic mantle may be derived from statistical treatments of xenolithic materials and from geophysical investigations.

Eclogite xenoliths are not randomly distributed in craton-penetrating kimberlite pipes — they tend to dominate the xenolith populations at some pipes (e.g., Roberts Victor) and be absent from others. Schulze [62] has calculated the amount of eclogite likely to exist in the lithospheric mantle underlying the craton in South Africa and northernmost Siberia, based upon a statistical examination of heavy mineral separates from several eclogite-rich kimberlites. He concluded that 3–15% of the mantle (by volume) is eclogite, as sampled by these pipes, and that, overall, < 1% of the lithospheric mantle is eclogite.

Distinguishing eclogite from peridotite on the basis of their seismic properties is difficult. An 'average' eclogite with 50% garnet and 50% clinopyroxene and average mineral compositions (as determined from a compilation of mineral compositions from the literature) would have a V_p of 8.5 km/sec (at room temperature and pressure, using elastic properties of [63,64]), but V_p in eclogites may realistically range from 8.25 to 8.84 km/sec, depending upon modal mineralogy. Calculated V_p in garnet peridotites of primitive to refractory compositions range between 8.30 and 8.36 km/sec. Thus, although eclogites may have, on average, higher V_p than garnet peridotite, they may not be distinguishable in terms of V_p at the limits of resolution common in seismic profiling.

In addition to V_p differences, seismic anisotropy is expected in peridotite and not in eclogite [65,66]. However, the absence of

anisotropy does not establish the presence of eclogite and few regions have been sufficiently well studied to determine the degree of upper mantle anisotropy. In studies where anisotropy is present, it is not clear what proportions of eclogite may still be permissible. Thus, although anisotropy reflects the presence of peridotite, it provides few constraints on the absolute abundance of eclogite in the upper mantle.

Recent seismic investigations of the upper mantle beneath the Siberian platform have revealed an anomalously high P_n velocity of 8.6–8.9 km/sec underlying the Malo–Botuobiya and Daldyn–Alakit kimberlite fields [67]. These data, in conjunction with the temperature- and pressure-corrected ($\sim 200^\circ\text{C}$ at 1.5 GPa, based on the very low heat flow in Siberia of $\sim 20 \text{ mW/m}^2$ [68]) P wave velocities for eclogite and peridotite cited above, are suggestive of an eclogitic (with 50–80% garnet) uppermost mantle in these regions. The surrounding regions have more typical upper mantle velocities in the range 8.0–8.2 km/sec and may be composed primarily of peridotite. Thus, seismic studies are consistent with an eclogite-dominated upper mantle in some regions of the subcontinental lithosphere but it is highly unlikely that the comparatively large amounts of residual eclogite required as the complement to the TTGs are present within the Siberian cratonic mantle.

In summary, the large amounts of mafic residue that are complementary to the voluminous Archean TTG are not present in the lower crust of Archean cratons. Our data suggest that some eclogite xenoliths derived from the lithospheric mantle may represent this complementary residue and seismic studies of the Siberian lithospheric mantle are in accord with a high proportion of eclogite in some regions. However, statistical studies of minerals from kimberlites suggest that the overall abundance of eclogite is low and, if so, we must conclude that much of the TTG residue has escaped the lithosphere. The latter is consistent with TTG genesis linked to subduction of oceanic lithosphere, since only in rare circumstances is subducted lithosphere trapped within the continental lithosphere. If, indeed, most TTG residues are subducted beyond the lithosphere,

Table 2
Calculated melt compositions

ref.	Ud146 WR using DI (table 1)	Melt 1: Rhyolite D values				Melt 2: Basalt D values			
		Gt D [49]	Cpx D [71] ¹	Bulk D	Melt 1	Gt D [51]	Cpx D [48]	Bulk D	Melt 2
Ti	1998	5.6	0.9	2.4	831	0.6	0.384	0.5	4408
V	248	7	14	11.8	21		3.1	2.1	118
Cr	420	4	56	39.4	11		3.8	2.6	163
K	1500	10 ⁻⁵ †	0.12†	0.1	18382	10 ⁻⁵	0.12†	0.1	18382
Sr	74	0.02	0.17	0.1	610	0.006*	0.1283	0.1	835
Y	17	130	5.5	45.3	0.36	3	0.467	1.3	12.9
Zr	16	0.4	0.2	0.26	61	0.3	0.1234	0.18	89.2
Nb	0.14	0.06		0.02	7.42	0.01	0.0077	0.01	16.9
La	0.31	0.001	0.49	0.33	0.94	0.001	0.0536	0.04	8.48
Ce	1.07	0.01	1.1	0.75	1.42	0.004	0.0858	0.06	17.9
Pr	0.25	0.06	1.5	1.04	0.24	0.018	0.12	0.09	2.82
Nd	1.22	0.4	2.7	1.96	0.62	0.057	0.1873	0.15	8.37
Sm	0.59	6.4	5.5	5.79	0.10	0.5	0.291	0.36	1.65
Eu	0.24	10	3.6	5.65	0.04	1	0.32	0.54	0.46
Gd	1.02					2			
Tb	0.21								
Dy	2.04	116	7.1	41.9	0.05	2.5	0.442	1.1	1.86
Ho	0.52	130	5.9	45.6	0.01	2.75	0.467	1.2	0.44
Er	1.68	170	4.7	57.6	0.03	3	0.387	1.2	1.37
Tm									
Yb	1.67	140	2.1	46.2	0.04	4	0.43	1.6	1.06
Lu	0.01								
Hf	0.38	0.07	0.41	0.30	1.26	0.1	0.256	0.2	1.84

¹ Values for the highest Mg# clinopyroxene (sample 15814-28, Mg# = 66). † Potassium *D* values for clinopyroxene from [34], 1300°C, 6 GPa data; garnet *D* values from [51]. * Sr *D* values for garnet/basalt are from [52]. *D* values in italics are interpolated.[71]

then they may constitute a discrete refractory eclogite reservoir deep within the mantle, which has been postulated to exist on the basis of chemical mass balance between crust and depleted mantle reservoirs [69].

6. Conclusions

Significant chemical differences between garnet and omphacite inclusions in diamonds from eclogite xenoliths and these same phases in the host eclogite reveal metasomatic enrichment of the eclogite by passing melts. The composition of the original eclogite has been reconstructed from clinopyroxene encapsulated in diamond and is severely depleted in LREE, is HREE enriched and has a high Sr abundance compared to the

REE. These features, coupled with petrological constraints, are consistent with the eclogite forming in equilibrium with a tonalitic melt that is strongly LREE enriched and has a high Sr/Nd ratio — characteristics of the voluminous tonalites–trondhjemites–granodiorites found in Archean cratons.

The data presented here suggest a link between eclogites, derived from the deep lithosphere of an Archean craton (> 150 km deep, within the diamond stability field), and the crustal rocks of that craton. If our interpretations are correct, they imply an even deeper origin for TTG than previously suspected. Further experimental studies of eclogite melting in the 4–6 GPa range would go far towards testing this hypothesis.

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Appendix 1: Calculation of trace element composition of equilibrium melt

Trace element compositions of the melt in equilibrium with eclogite Ud146 have been calculated by using:

$$C_1 = C_s/D$$

where C_1 = the concentration of an element in the melt; D = the bulk distribution coefficient calculated using the observed modal proportions of garnet and omphacite in the rock and literature D values (Table 2); and C_s = the trace element concentration in the solid, as calculated from the modal proportions and measured concentrations in the diamond inclusion omphacite and the host rock garnet. This calculation is independent of degree of melting.

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