# Archean mantle heterogeneity and the origin of diamondiferous eclogites, Siberia: Evidence from stable isotopes and hydroxyl in garnet

### **GREGORY A. SNYDER, LAWRENCE A. TAYLOR, ERIC A. JERDE**

Planetary Geosciences Institute, Department of Geological Sciences, University of Tennessee, Knoxville, Tennessee 37996, U.S.A.

# **ROBERT N. CLAYTON, TOSHIKO K. MAYEDA**

Enrico Fermi Institute, University of Chicago, Chicago, Illinois 60637, U.S.A.

#### PETER DEINES

Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

### GEORGE R. ROSSMAN

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.

## NIKOLAI V. SOBOLEV

Institute of Mineralogy and Petrography, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

#### ABSTRACT

Data are presented for the O isotopic composition of clinopyroxene and garnet, the C isotopic composition of diamond, and the OH<sup>-</sup> content of garnet from eclogite xenoliths brought to the surface by the Udachnaya kimberlite pipe, Yakutia, Siberia. Radiogenic isotopic data suggest that the eclogites could have been derived from an ultradepleted mantle at approximately 2.9 Ga (Pearson et al., 1995; Snyder et al., in preparation). O isotopic compositions generally show equilibration between the eclogitic minerals ( $\Delta_{Cpx-Grt} = 0.11-0.41\%$ ) and have  $\delta^{18}O_{SMOW}$  for both garnet and clinopyroxene that lie near the range of accepted mantle values of 5.7 ± 0.7‰. However, several eclogites indicate significant deviations from this range, at higher values of 6.8–7.0‰. Also, two eclogites lie at the lower end of the mantle range, at values of 4.8 and 5.0‰ (all in clinopyroxene). C isotopic compositions of diamonds all have  $\delta^{13}C_{PDB}$  in the range of -1 to -7% and are centered at approximately -5%, also within the range of accepted mantle values. The OH<sup>-</sup> contents of the garnet are generally between 0 and 22 ppm (as H<sub>2</sub>O), although two samples exceed 70 ppm. This range of OH<sup>-</sup> is similar to eclogitic garnet from the Kaapvaal craton of southern Africa.

The mantle C isotopic values of associated diamonds, the majority of O isotopic data, and the low OH<sup>-</sup> content of the minerals, although suggesting a general lack of crustal participation in the formation of the Udachnaya eclogites, do not rule out the participation of some ancient crustal material. That these eclogites include both <sup>18</sup>O-enriched and <sup>18</sup>Odepleted types suggests that the protoliths may have been overprinted by both low- and high-temperature hydrothermal events (cf. Jacob et al., 1994). A positive correlation between  $\delta^{18}$ O and <sup>87</sup>Sr/<sup>86</sup>Sr allows the interpretation of these eclogites as representing a cross section of an Archean ophiolite. However, the lack of a single coherent grouping on a plot of  $\delta^{18}$ O vs. <sup>87</sup>Sr/<sup>86</sup>Sr suggests that, if the Udachnaya eclogites were derived from oceanic crust, they cannot be cogenetic and must represent at least two separate ophiolite sequences. Conversely, if the eclogites are found to be cogenetic, then a totally different process affected their formation and a probable metasomatic mechanism was operative. Because of the total lack of correlation of  $\delta^{18}$ O with other geochemical parameters, we find no compelling evidence that all eclogites are derived ultimately from oceanic crust.

## INTRODUCTION

The origin of kimberlitic eclogite xenoliths has remained an area of intense research and debate for over a decade. Eclogite xenoliths are of roughly basaltic composition and consist of mostly garnet and clinopyroxene. The diamondiferous eclogites are hosted exclusively by kimberlites where they generally comprise <10% of the xenolith population of any given locality. However, because of the presence of diamonds, these rare xenoliths have received more than their fair share of attention.

Three major, contrasting models have been proposed

for the origin of eclogite xenoliths. The first model involves the precipitation of garnet and clinopyroxene as high-pressure igneous cumulates that formed within the upper mantle (e.g., O'Hara and Yoder, 1967; MacGregor and Carter, 1970; Hatton, 1978; Smyth and Caporuscio, 1984; Taylor and Neal, 1989; Snyder et al., 1993). Evidence for a mantle origin for at least some of the eclogites (classified as Group A by Shervais et al., 1988) includes the following: (1) Mg-rich and Cr-rich garnet and clinopyroxene combined with moderate- to low-jadeite component in some grains of clinopyroxene; (2) high wholerock Mg'; (3) uniformly low <sup>87</sup>Sr/<sup>86</sup>Sr in clinopyroxene; and (4)  $\delta^{18}$ O values within the mantle range. The second model asserts that eclogite xenoliths are the metamorphosed products of subducted oceanic-crustal protoliths for both basalt and feldspathic cumulates (e.g., Helmstaedt and Doig, 1975; Jagoutz et al., 1984; Haggerty, 1986; MacGregor and Manton, 1986: Shervais et al., 1988: Taylor and Neal, 1989; Neal et al., 1990; Jacob et al., 1994; Ireland et al., 1995). Evidence in favor of such an origin for some eclogites (classified as Groups B and C by Shervais et al., 1988) includes the following: (1) high Na<sub>2</sub>O contents in clinopyroxene from some eclogites (experimental data suggest that pyroxene crystallized from basaltic compositions at high pressure should have a lowjadeite component; Thompson, 1974); (2) positive Eu anomalies and Al-rich whole-rock reconstructions, which point to a low-P. anorthositic precursor (Taylor and Neal. 1989); (3) Sr and O isotopic ratios consistent with hydrothermal seawater alteration (MacGregor and Manton, 1986; Neal et al., 1990); and (4) positive correlations in FeO, Sm/Nd, <sup>87</sup>Sr/<sup>86</sup>Sr, and <sup>143</sup>Nd/<sup>144</sup>Nd, and negative correlations in CaO, vs.  $\delta^{18}$ O (Jacob et al., 1994). The third hypothesis allows that eclogites are the remnants of the early accretion of the Earth (Anderson, 1981, 1989; McCulloch, 1989). Because oceanic crust is derived ultimately from the mantle, it is often difficult to differentiate between the first two models. In practice, the evidence for a mantle precursor is based on the absence of signatures that indicate crustal involvement. Therefore, a crustal signature (such as O isotopic values outside of the mantle range) for a few samples is often used as evidence that many samples of a suite are from oceanic crust. It still appears that eclogite xenoliths predominantly show evidence of the first two models, although all three may be feasible.

Radiogenic isotopic studies of eclogite xenoliths have indicated their antiquity. Although it is often not possible to determine igneous crystallization ages, metamorphic ages give minimum estimates. Manton and Tatsumoto (1971) and Kramers (1979) presented U-Th-Pb data for southern African eclogites that indicated ages of 2.2–2.7 Ga. Sm-Nd and Rb-Sr systematics of southern African eclogites hint at model ages in excess of 3 Ga and give a well-defined whole-rock age of 2.7 Ga (Jagoutz, 1984). Siberian eclogites suggest a variety of ages, from mid-Proterozoic (1.7 Ga Sm-Nd mineral isochron: Mc-Culloch, 1989) to mid-Archean. A Pb-Pb age of 2.7 Ga is reported by Jacob et al. (1994) for the Udachnaya eclogites. Re-Os model ages cluster between 2.7 and 3.3 Ga and yield a whole-rock isochron consistent with an age of 2.9 Ga (Pearson et al., 1995). Snyder et al. (in preparation) also suggested an age of 2.9 Ga on the basis of a Sm-Nd clinopyroxene isochron. These mainly Archean ages indicate that the study of eclogites yields important information on the early magmatic and tectonic evolution of the Earth.

Until the last few years, most of the information and all of our models of eclogite genesis were based on xenoliths from the Kaapvaal craton, southern Africa. The Archean Siberian craton appears to represent a tectonic setting similar to that of the Kaapvaal craton. However, unlike the kimberlites of southern Africa, the Siberian mantle samples have received little attention in the western world (e.g., Sobolev et al., 1968; Sobolev, 1977; Sobolev and Nixon, 1987: Pokhilenko and Sobolev, 1986: Ustinov et al., 1988), largely because suitable suites of Yakutian samples have not been readily available. An earlier study by our group (Jerde et al., 1993b) described the major- and trace-element geochemistry of 14 eclogites from the Udachnaya kimberlite, and subsequent work (Sobolev et al., 1994; Snyder et al., 1993, and in preparation) has dealt with 19 other samples and radiogenic isotopes on all of the xenoliths. This paper discusses results from the study of C and O isotopes and OHcontents of eclogite xenoliths from the Udachnava kimberlite pipe. We will attempt to contrast and compare eclogite xenoliths from the Siberian and Kaapvaal cratons to place them within a global context and allow a critical evaluation of various models for the origin of eclogite xenoliths.

### **OCCURRENCE**

The Siberian Platform occupies a large area, extending from Lake Baikal on the south to well beyond the Arctic Circle. Diamond-bearing kimberlites are located mainly in the central portions of the ancient Archean-Proterozoic basement. These pipes contain many exotic eclogites, some of which are diamondiferous. Other eclogites are kyanite- or corundum-bearing, including grospydites [grossular + pyroxene + disthene (kyanite) with >50%grossular component in the garnet]. The diamond-bearing xenoliths from Udachnaya are diverse, including pyroxenites, some that are nearly garnetites, as well as eclogites containing kyanite or coesite. Both microdiamonds  $(<500 \ \mu m)$  and larger diamonds up to 1.5 cm across are present (Ponomarenko et al., 1976, 1980; Pokhilenko et al., 1982; Sobolev et al., 1991a, 1991b). All 37 samples discussed herein are from the Udachnaya pipe.

The suite of eclogites from Udachnaya used in this study is part of an extensive collection of diamondiferous eclogites sampled over an extended period of time, mainly at the processing plant where xenoliths with exposed diamonds are sorted (Sobolev, 1991a, 1991b). Most xenoliths are bimineralic, containing garnet and clinopyroxene (a few contain kyanite), which vary from 2 to 10 cm in longest dimension. Rounded, orange-colored garnet grains make up 30-40% of most samples but occasionally reach ~80%. Clinopyroxene is green and interstitial. Traces of oxide and sulfide phases are common but not ubiquitous. When present, such phases are blebby and generally 0.5 mm or less across. The eclogites are medium- to coarse-grained, with garnet grains 0.2-1 cm across. Occasionally, smaller grains are seen as glomerocrysts or, rarely, as layers over 1 cm thick. The garnet grains are generally extensively fractured, and although kelyphitic rims are common, the majority of grains are fresh. Pyroxene is commonly fresh but is more likely than garnet to be altered, generally to greenish phlogopite and other secondary phases. The pyroxene grains are interstitial, 0.5 mm to over 1 cm across and, like garnet, occasionally appear as glomerocrysts or layers >1 cm thick. There are rare examples of orthopyroxene exsolution lamellae in the clinopyroxene. No garnet lamellae were observed.

#### **ANALYTICAL METHODS**

C isotopic compositions were determined in the Department of Geosciences at Pennsylvania State University, using the methods described by Deines et al. (1984, 1987, 1991). O isotopic compositions were determined on whole rocks and mineral separates at the Enrico Fermi Institute, University of Chicago, utilizing the BrF, method of Clayton and Mayeda (1963). Garnet reacts slowly with BrF<sub>5</sub>; O yields of 80–100% were obtained in 2 d reactions at 700 °C. For the determination of  $\delta^{18}$ O, samples were analyzed as CO<sub>2</sub>.

Infrared spectra of the hydroxyl (OH<sup>-</sup>) contents of garnet were obtained using methods described by Bell and Rossman (1992b). Thicknesses of doubly polished grains varied from 0.3 to 0.4 mm. Two hundred and fifty-six scans were averaged for each analysis point to yield the desired signal-to-noise ratio. Backgrounds (from Fe<sup>2+</sup>) were visually estimated and subtracted and OH contents were determined from integrated absorbances using the calibration data of Bell et al. (1995), where ppm  $H_2O =$ 0.719 times integrated absorbance per centimeter sample thickness.

#### GEOCHEMISTRY

#### Major- and trace-element compositions

The compositional ranges of major elements in clinopyroxene and garnet from 33 xenoliths from Udachnaya have been presented (Jerde et al., 1993b; Sobolev et al., 1994; Snyder et al., in preparation) and are similar to those of eclogites from southern Africa (e.g., Smyth and Caporuscio, 1984; Taylor and Neal, 1989). However, compositional systematics between the two minerals (such as Cr-rich garnet associated with Mg-rich clinopyroxene) observed in xenoliths from the Kaapvaal craton (e.g., Shervais et al., 1988; Taylor and Neal, 1989) are not as commonly observed in the Siberian eclogites, indicating heterogeneity of mantle composition and processes.

Mineral compositions for Udachnaya eclogites (14 from Jerde et al., 1993b, plus 19 additional samples: Sobolev



Fig. 1. Compositions of garnet (A) and clinopyroxene (B) in eclogites from the Udachnaya kimberlite. The data for "all eclogites" are from the literature (references in Jerde et al., 1993a, 1993b).

et al., 1994) are consistent with data obtained previously (Sobolev, 1977) for eclogite xenoliths from Siberia (Fig. 1). However, a narrower range of garnet compositions is present in the Udachnaya kimberlite (Fig. 1A), reflecting a paucity of grospydites in this particular pipe (Ponomarenko et al., 1976). The garnet compositions extending toward the grossular apex of Figure 1 are from grospydites obtained at the Zagadochnaya kimberlite. Clinopyroxene has a range of compositions similar to Siberian eclogites in general (Fig. 1B), although with fewer MgOor Na<sub>2</sub>O-rich varieties.

The HREE abundances in both garnet and clinopyroxene are typical for eclogites in general, although some of the pattern slopes are unusual (Fig. 2). Several grains of Udachnaya garnet have chondrite-normalized HREE abundances that show a pronounced negative slope [(Sm/ Yb)n > 1; Fig. 2A]. Other garnet grains (e.g., U-5 and U-73) reach high points at Eu, then drop down to lower,



Fig. 2. Plots of (La/Nd)n (degree of LREE enrichment relative to chondritic abundances) vs. (Sm/Yb)n (degree of HREE depletion relative to chondritic abundances) for Udachnaya eclogite minerals: (A) garnet, (B) clinopyroxene. Chondrite normalization factors are from Anders and Grevesse (1989).

uniform abundances for the HREE, lending the appearance of a hump in the REE pattern (Jerde et al., 1993b; Snyder et al., in preparation), which one could interpret as a positive Eu anomaly.

The trace elements, particularly the rare earth elements (REE), serve to separate the Siberian eclogites from their counterparts from southern Africa (Fig. 3). In the pyroxene profiles, the high point in the REE abundance generally occurs at Nd but occasionally is at Pr or Sm (Fig. 2B). Furthermore, several clinopyroxene profiles exhibit both HREE-depleted and extremely LREE-depleted signatures, atypical of clinopyroxene from other mantle xenoliths and suggestive of complex, multistage histories. Unlike clinopyroxene from southern Africa, most clinopyroxene grains from Udachnaya are LREE-depleted (Fig.



Fig. 3. Plot of REE abundances (as ppm Nd) vs. degree of LREE enrichment [(La/Nd)n] for Siberian (Udachnaya and Mir pipes; Jerde et al., 1993b; Snyder et al., unpublished manuscript) and South African (Taylor and Neal, 1989; Jerde et al., 1993a) eclogitic pyroxenes.

3). This may be a result in large part of the lower REE abundances that make grains of Southern African clinopyroxene (Fig. 3) more susceptible to alteration by REEenriched components. In that case, the systematically higher REE abundances of Udachnaya eclogites must be explained.

Eu anomalies are present in a few of the eclogite minerals; these are always positive and are subdued (Jerde et al., 1993b). The presence of Eu anomalies has been cited as evidence for a crustal affinity (i.e., plagioclase) among some of the eclogites from Bellsbank, South Africa (Taylor and Neal, 1989). Similarly, these anomalies may suggest such an affinity for a few Siberian samples as well (four of the Udachnaya eclogites; Jerde et al., 1993b).

## C isotopes

C isotopic compositions ( $\delta^{13}C_{PDB}$ ) were obtained for diamonds from 37 of the xenoliths (including a duplicate), and the results are given in Table 1 and shown in Figure 4. All the values lie between -1 and  $-7\infty \delta^{13}C_{PDB}$ . This range is similar to that of one of the modes in the bimodal distribution of eclogitic diamonds from Orapa, Botswana, seen by Deines et al. (1991). This range is also similar to that of peridotitic diamonds (Fig. 4A) and suggests that the C in the Udachnaya eclogites is of mantle origin rather than crustal, which would tend to lower values of  $\delta^{13}C$ . Another possibility is suggested by the work of Galimov (1984), who stated that diamonds of higher *P* and *T* origin are likely to have more positive, less variable  $\delta^{13}C$ .

### **O** isotopes

O isotopic compositions ( $\delta^{18}O_{SMOW}$ ) have been determined for 19 whole-rock splits, 19 clinopyroxene sepa-

δ<sup>13</sup>C Sample  $\delta^{13}C$ Sample U-7/1 -4 24 U-59/2 -5.86 $U_{-8/1}$ -6.21U-73/2 -3.86U-8/1 -6.1 U-75/2 -5.39U-10/1 U-76/2 -5.26 -7.0 U-25/2 5.18 U-80/3 -4.6 U-27a/1 -4.91 U-81/2 -5.4 U-33/1 -5.14 U-82 -6.5 U-35/1  $U_{-85/3}$ -40-5.3U-37/11 -4.43 U-97/2 -5.4U-44/3 -5.5 U-100/2 -5.35U-48/2 -5.9 U-102 -3.9 U-49/3 -6.2 U-103/2 -3.67 U-50/2 -3.15 U-107/2 -4.95 U-51/3 -6.78 U-108/3 -4.27 U-52 -38 U-113/3 -4.9 U-53/3 -5.83  $U_{-}119/3$ -472 U-56/2 4.8 Zh-9/3 -3.72U-57/3 -1.32Zh-25/3 -4.22U-58/2 -5.58 Zh-26/3 -4.5 Note: all values are in parts per mil relative to PDB.

TABLE 1. C isotope composition of Udachnaya diamonds

rates, five garnet separates, and one kvanite separate from the Udachnaya eclogites and are given in Table 2. The majority of these fall within the range of  $5.7 \pm 0.7\%$  (the range found for 90% of mantle xenoliths; Deines, 1989). Four of the eclogites (U-1, U-35, U-51, and U-75) have higher  $\delta^{18}$ O values (Table 2). A couple (U-6 and U-86) lie at the lower end of the mantle range. This is in contrast to the O results of Neal et al. (1990) for Bellsbank, South Africa, where the deviations from mantle values were all to lower  $\delta^{18}$ O values, and those of Garlick et al. (1971), MacGregor and Manton (1986), and Ongley et al. (1987) for the Roberts Victor pipe, South Africa, which show both higher and lower  $\delta^{18}$ O values (Fig. 5). These large variations have been interpreted as evidence for the involvement of ancient oceanic crustal material in the formation of the eclogites.

#### Hydrous components

The OH- contents of garnet were determined to compare them with mantle garnet from other localities and to assess the role of H<sub>2</sub>O in the formation of these samples. Most of the garnet studied has low intensity OHabsorptions in the infrared spectrum (Fig. 6). The features in the spectra resemble those of the eclogitic garnet from the Roberts Victor Mine presented by Bell and Rossman (1992b; their Fig. 2g), consisting of dominant absorptions near 3650 and 3590 cm<sup>-1</sup>. The absolute concentrations generally cluster in the range from near 0 to 22 ppm  $(H_2O)$ . although samples U-237 and U-281 have concentrations exceeding 70 ppm (Table 3). Eclogitic garnet from both Udachnaya and southern Africa (Bell and Rossman, 1992b) appears to contain, on average, less OH- than their counterparts from the Colorado Plateau of North America (Aines and Rossman, 1984) and diamond-bearing crustal rocks from Kazakhstan (Langer et al., 1993).



Fig. 4. Histograms showing the distribution of  $\delta^{13}$ C in diamonds from Udachnaya (C; this study) and, for comparison, from diamonds in Yakutian peridotites (A) and other eclogites (B; Deines, unpublished data).

### DISCUSSION

The origin of eclogite xenoliths continues to be the subject of intense debate. Models for the formation of eclogite xenoliths have been largely dependent on material from kimberlites in southern Africa. It is widely held that many of the African eclogites have their origin in recycled oceanic crust (e.g., Jagoutz et al., 1984; MacGregor and Manton, 1986; Ongley et al., 1987; Shervais et al., 1988; Taylor and Neal, 1989; Neal et al., 1990). Evidence includes low and high  $\delta^{18}$ O values (+2.2 to +8.0‰) relative to average mantle values, high <sup>87</sup>Sr/<sup>86</sup>Sr, positive Eu anomalies, and Al-rich (anorthositic?) protolith reconstructions (Taylor and Neal, 1989, 1993). However, Sny-

Sample	Whole rock	Срх	Garnet	Kyanite
U-1	9.13		6.80	
U-6	6.15	4.98		
U-8	6.42	5.87		
U-25	5.95	5.42		
U-35	7.74	6.93		
U-37	5.34	5.30		
U-41	6.41	5.83		
U-51	7.26	7.02		
U-73	6.11	5.35		
U-75	6.95	6.92		
U-79	6.21	5.95	5.80	
U-86		4.81	4.61	
U-102	5.86	5.43		
U-108	6.06	5.44		
U-112	5.77	5.23		5.75
U-119	4.77	5.06		
U-236	5.42	5.25		
U-237	5.60	5.44	5.03	
U-281	6.05	5.15	5.04	
O-160*	5.99	5.90		
	es are δ <sup>18</sup> O <sub>smov</sub> sample from th			

TABLE 2. O isotopic composition of Udachnaya eclogites

der et al. (1993) presented Nd and Sr isotopic evidence consistent with a mantle derivation for Udachnaya eclogites. Jacob et al. (1994) and Ireland et al. (1995) presented other types of elemental and isotopic data on Udachnaya eclogites that they interpreted as evidence of subducted oceanic crust. Although an oceanic crustal component cannot be ruled out for some eclogites, we believe it is premature to attribute all eclogites to such a process. In particular, Udachnaya eclogites are unlike their counterparts worldwide, yielding, at best, only sketchy evidence of a crustal component.

A case in point is the narrow range of C isotopic values in Udachnaya diamonds in comparison with other eclo-



Fig. 5. A histogram of  $\delta^{18}$ O in clinopyroxene from South African (Neal et al., 1990; MacGregor and Manton, 1986; Garlick et al., 1971; Ongley et al., 1987) and Siberian (this study; Snyder et al., unpublished manuscript; Jacob et al., 1994) eclogites.



Fig. 6. Typical infrared absorption spectra of Udachnaya eclogite garnet. Note the low intensity of the OH<sup>-</sup> absorption bands in the 3550–3650 cm<sup>-1</sup> region. Sample U-236 has a  $H_2O$  content of ~10 ppm.

gitic diamonds. Past work (e.g., Deines et al., 1984, 1987, 1991), has shown that diamond-bearing eclogites from Orapa possess two main populations of <sup>13</sup>C, one centered at  $\delta^{13}C \approx -5.5\%$  and another at approximately -15.5%. There is also a tail of  $\delta^{13}C$  to lower values (Fig. 4B). Deines et al. (1987) suggested that the two groups reflect two different mantle source regions. In this model, the eclogites with lighter C are believed to have originated at deeper levels in the mantle. The C-isotope compositions of the Udachnaya diamonds are all within the population centered at  $\delta^{13}C \approx -5.5\%$ , corresponding to the shallow mantle source of Deines et al. (1987).

If the protoliths for these eclogites are Archean in age then this could pose a further problem in the identification of crustal involvement. At such an early period in Earth history, it is likely (indeed, probably inevitable) that oceanic crustal material was a great deal different from what we see at present. The Sr isotopic composition of seawater was much lower than at present, and crustal and mantle reservoirs may not have had sufficient time to diverge in terms of their radiogenic isotopic compositions. Furthermore, many C reservoirs that would have contained fractionated isotopic compositions (relative to the mantle), such as sedimentary organic material, were more restricted in abundance and distribution than they are today. As a result, the subduction of such crust might not leave a characteristic signature in any resulting eclogites. This limits the use of C isotopes, as well as Sr iso-

TABLE 3. Hydroxyl contents of garnet from Udachnaya

Sample	H₂O (ppm)	Description	
U-1	6	clear, pale orange	
U-5	4	clear, pale orange	
U-6	14	nearly clear, med. orange	
U-51	0	clear, med. orange	
U-75	0	clear, med. orange	
U-79	2	clear, light orange	
U-112	14	clear, pale orange	
U-119	22	clear, med. orange	
U-236	10	clear, light orange	
U-237	72	clear, pale orange	
U-281	71	some inclusions, dark orange	

topes, as an effective tool for the discrimination between crustal and noncrustal progenitors. In any event, it appears that a definitive crustal signature is lacking in these Udachnaya samples.

The measured H<sub>2</sub>O content of eclogitic garnet is also equivocal. OH- contents in garnet from mantle samples vary over a wide range (e.g., Bell and Rossman, 1992a, 1992b), even for materials from a single kimberlite, although eclogitic garnet tends to be among the least hydrous garnet from southern African localities. The Udachnaya eclogitic garnet likewise varies over a considerable range but tends to have predominantly low OHcontents. The relatively low OH- content of eclogitic garnet may mean that components from subducted oceanic crust (with its entrained water) are comparatively unimportant in the formation of these eclogites. Conversely, the low OH<sup>-</sup> contents of Udachnaya garnet may indicate that the down-going crustal slab, from which some of these eclogites could have been derived, was efficiently dehydrated through melting, prior to transition to eclogite. As such, OH- contents in garnet cannot be used as definitive indicators of either crustal or mantle protoliths. In contrast to the OH<sup>-</sup> contents of garnet and the C isotopic compositions of diamonds, the O isotopic variations of eclogitic minerals are relatively well understood and display enough variation to allow a critical evaluation of the involvement of oceanic crust in eclogite genesis.

### O isotopic heterogeneity of the Earth's mantle

Variations in  $\delta^{18}$ O of minerals and rocks from the mantle may be subdivided into those intrinsic to mantle processes and those influenced by crustal processes. Intrinsic mantle variations are caused by the equilibrium fractionation among mineral phases and the fractionation between minerals and melts or other fluids. Among the major minerals in the upper mantle, the largest fractionation is between plagioclase and olivine, which has a value of 0.95‰ at a representative temperature of 1200 °C (for An<sub>60</sub>-Fo, from Clayton and Kieffer, 1991). The fractionation between a melt and olivine is estimated to be 0.6-0.7% on the basis of the assumption that the isotopic properties of the melt are intermediate between those of plagioclase and pyroxene. Fractionations between orthopyroxene and clinopyroxene and between pyroxene and garnet are probably <0.2‰ at 1200 °C (Chiba et al., 1989;



Fig. 7. A histogram of  $\delta^{18}$ O for igneous clinopyroxene from the Earth and Moon. All data are from the laboratory of R.N. Clayton.

Rosenbaum et al., 1994), although larger values are expected with increasing jadeite components (Matthews et al., 1983). For a given mineral, the intrinsic mantle variations are probably on the order of 0.5<sup>∞</sup>. This behavior is illustrated in Figure 7 for pyroxene in lunar rocks. Whole-rock variations of about 1‰ are expected because of variations in modal abundances of minerals. Figure 7 also shows data for terrestrial pyroxene from eclogite nodules. All data in Figure 7 are taken from the same laboratory to eliminate interlaboratory bias and small differences in the definition of the SMOW standard. The dispersion of the terrestrial data is about eight times that of the lunar data, indicating the involvement of processes other than anhydrous melting and crystallization in the upper mantle. It is noteworthy that the terrestrial data peak at the same compositions as the lunar data, which suggests that broadening of the terrestrial range occurs in both directions, i.e., both increases and decreases relative to mean mantle composition. It has been pointed out that the aqueous alteration of the oceanic crust has just this property: <sup>18</sup>O enrichment in the upper levels and <sup>18</sup>O depletion at deeper levels as a consequence of the temperature gradient (Gregory and Taylor, 1981; Muehlenbachs, 1986). The range of O isotopic compositions seen in ophiolites (e.g., Stern et al., 1976; Gregory and Taylor, 1981; Cocker et al., 1982) is very similar to that seen in eclogites (Fig. 8). This coincidence has led to the proposal that most eclogites are derived from subducted oceanic crust (MacGregor and Manton, 1986; Ongley et al., 1987; Jacob et al., 1994).

Pyroxene from the Udachnaya eclogites has a range of about 2‰ in  $\delta^{18}$ O (Table 2 and Jacob et al., 1994), with values both enriched and depleted in <sup>18</sup>O relative to the mean mantle composition. Very low values (less than +4‰), which occur in some of the African samples, have not been observed in the Udachnaya samples. Neverthe-



Fig. 8. Plots of  ${}^{87}$ Sr/ ${}^{86}$ Sr vs.  $\delta^{18}O_{SMOW}$  for Udachnaya clinopyroxene (Sr data from Snyder et al., 1993, and in preparation). Plot A compares the Udachnaya data to that for South Africa (Neal et al., 1990). In **B**, a line is shown for the average mantle values for O (5.7 ± 0.7‰-90% of values from mantle xenoliths; Deines, 1989). Also shown is a schematic representation of the curved trend in  ${}^{87}$ Sr/ ${}^{86}$ Sr vs.  $\delta^{18}O_{SMOW}$  for the Samail Ophiolite, Oman (McCulloch et al., 1981) along with dark, shaded boxes indicating the ophiolite stratigraphy. The lightly shaded box in the schematic would be the modern location of our data set (i.e., in **A**) in this schematic section. However, because the hypothesized oceanic crust precursor for the Udachnaya would have been Archean in age, the  ${}^{87}$ Sr/ ${}^{86}$ Sr values of the entire section would likely be substantially lower (as seen).

less, the O isotope data are consistent with a crustal precursor for some of the Udachnaya eclogites.

### The ophiolite analogue for eclogites

In their study of Udachnaya eclogites, Jacob et al. (1994) looked for correlations between O isotopic compositions and various chemical parameters that might reflect seafloor alteration processes. For instance, trends between  $\delta^{18}$ O and other chemical parameters, such as  ${}^{87}$ Sr/ ${}^{86}$ Sr,  ${}^{143}$ Nd/ ${}^{144}$ Nd, Sm/Nd, Fe, and Ca, may be indicative of oceanic crustal involvement (Jacob et al., 1994). Many samples from throughout a complete section of a modern ophiolite would exhibit  $\delta^{18}$ O values within the mantle range (see Fig. 8). However, the trends of decreasing and then increasing  $\delta^{18}$ O with increasing  ${}^{87}$ Sr/ ${}^{86}$ Sr, Fe, and Ca from the bottom of the section to the top of the section (e.g., McCulloch et al., 1981; Jacob et al., 1994) are what is most important and demand an explanation.

With a limited data set (six samples), Jacob et al. (1994) found correlations that are masked, if not contraindicated, when our additional 15 samples are considered (Jerde et al., 1993b; Snyder et al., 1993, and in preparation). Eclogites from Udachnaya display at least two separate trends of increasing  $\delta^{18}$ O with increasing  ${}^{87}$ Sr/ ${}^{86}$ Sr values (Fig. 9). It is possible to explain these trends for Udachnaya eclogites by appealing to an ancient ophiolite ana-



Fig. 9. Plots of  $\delta^{18}O_{SMOW}$  vs. oxides, elemental ratios, and radiogenic isotopic compositions of Siberian and South African eclogitic clinopyroxene. Shaded fields in all three plots are for the data presented by Jacob et al. (1994) on six Udachnaya eclogites. Data labeled as Udachnaya are from this study. (A) FeO (wt%), (B) Sm/Nd abundance ratio, (C) <sup>143</sup>Nd/<sup>144</sup>Nd (calculated at the eruption age = 390 Ma for Udachnaya eclogites; Snyder et al., 1993). Bellsbank data are from Neal et al. (1990).

logue. In this model, eclogites with lower  $\delta^{18}$ O and  ${}^{87}$ Sr/ <sup>86</sup>Sr would have come from lower in the ophiolite sequence (possibly in the cumulate gabbro section), and those eclogites with higher  $\delta^{18}$ O and  ${}^{87}$ Sr/<sup>86</sup>Sr would have come from the upper portions of the ophiolite sequence (possibly in the sheeted dike to pillow-lava section). This ancient ophiolite was then subducted during the Archean and converted to eclogite and finally returned in pieces to the surface by alkalic magmas (approximately 389 Ma; Snyder et al., 1993). Whereas only the low- $\delta^{18}$ O component of such a sequence was seen in South African Bellsbank eclogites (Neal et al., 1990), Udachnaya eclogites may afford the first look at an intact Archean ophiolite sequence from cumulate gabbros to sheeted dikes and pillow lavas (as per McCulloch et al., 1981).

Further support for the subducted-crust hypothesis for the Udachnaya eclogites includes sympathetic trends of  $\delta^{18}$ O with <sup>87</sup>Sr/<sup>86</sup>Sr, Fe, Sm/Nd, and <sup>143</sup>Nd/<sup>144</sup>Nd and a negative trend for Ca vs.  $\delta^{18}$ O. Again, trends indicated by the six clinopyroxene samples of Jacob et al. (1994) are not supported when all data are considered (Fig. 9). Instead, eclogites tend to plot in a cluster about the average mantle O value with several other samples plotting in diffuse fields. Although there appears to be no correlation between FeO in clinopyroxene and O isotopic composition, at least two separate trends are indicated by plots with Sm/Nd and <sup>143</sup>Nd/<sup>144</sup>Nd (Fig. 9).

It is important to note that these two distinct trends on a plot  $\delta^{18}$ O vs.  ${}^{87}$ Sr/ ${}^{86}$ Sr indicate that not all Udachnaya eclogites are cogenetic. If the ophiolite analogue is considered plausible, then eclogites from Udachnaya must have sampled at least two separate ophiolite sequences. Conversely, if these eclogites are cogenetic as interpreted by Jacob et al. (1994), then another model must be proposed to explain the data.

#### An alternative model

Snyder et al. (in preparation) proposed an alternative to the subducted ophiolite model for eclogite xenoliths on the basis of (1) low Rb/Sr and high Sr/Nd abundance ratios, (2) MREE enrichment (indicative of earlier LREE enrichment that has been masked by LREE depletion during eclogite formation; Snyder et al., 1993), and (3) both nonradiogenic <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd of some Udachnava clinopyroxene. In this model, most of the eclogites are determined to be melts of an ancient ( $\sim 2.9$ Ga), ultra depleted mantle. This melting event was then followed by carbonatitic metasomatism, which affected the protoliths to varying degrees. Several samples, including especially U-5, which has a Sr/Nd of 100, show abundant evidence of this metasomatism, which also could have been the source for diamond in these rocks. This scenario is highly speculative but could explain the mantle nature of the C isotopes in diamond. It is also interesting to note that a recent study of fluid inclusions in six Yakutian diamonds (Schrauder et al., 1994) found five that yielded evidence of high CaO and MgO (>15 wt% each) and low SiO<sub>2</sub> ( $\leq$ 12 wt%), K<sub>2</sub>O (<8 wt%), and  $Al_2O_3$  (<2 wt%) fluids, at least consistent with a carbonatitic origin.

#### SUMMARY

The principal conclusion to be drawn from the above data is that crustal progenitors can explain the stable isotopic data for the Udachnaya eclogites, although they are not necessarily required by the data. Nor do the data strongly indicate a subducted oceanic crust protolith for these eclogites. This conclusion is at least consistent with the radiogenic isotope results of Snyder et al. (1993), who attributed the Nd isotopic systematics to the formation, through melting, of both depleted and enriched mantle sources, the latter of which could be in excess of 4 Ga in age. Other isotopic data have yielded depleted-mantle ages from 2.76 to in excess of 3 Ga.

That these eclogites represent a differentiation event in the Earth's mantle during the mid- to late-Archean is without dispute. However, the processes that determined this differentiation are intensely debated. Many workers postulate that eclogites are end-products of mantle melting and extrusion onto the ocean floor in a fashion similar to modern ophiolites, followed by subduction of the ophiolite sequence deep into the mantle. Ireland et al. (1995) also presented evidence that indicates eclogites are possible residues of melting of this crust to form tonalites. Portions of this highly modified crust were then returned to the surface as nodules in kimberlites.

O isotopic compositions of coexisting garnet and clinopyroxene in Udachnava eclogites indicate heterogeneity in the Archean mantle. This heterogeneity could have been produced by recycling of oceanic crust into the mantle. However, trends in O isotopic data compared with other chemical parameters indicate that the Udachnaya eclogites are not cogenetic. Therefore, these eclogite xenoliths must represent separate ophiolite sequences, different portions of the subducting slab, or both. Conversely, if these eclogites are thought to be cogenetic, then a totally different process for their formation must be postulated. A mantle origin cannot be precluded. As an alternative to a crustal derivation, we speculate that these eclogites could be the products of melting of ultradepleted mantle at  $\sim 2.9$  Ga followed by selective carbonatitic metasomatism. This hypothesis can explain the uniform C isotopic compositions, low Rb/Sr, high Sr/Nd, and both nonradiogenic Sr and Nd in some samples.

The Udachnaya eclogites continue to provide contrasts with their southern African counterparts, underlining the difficulties inherent in utilizing eclogitic xenoliths to draw global conclusions about the mantle. Instead, it appears likely that eclogite xenoliths may better serve in mantle characterization only on regional and temporal scales.

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