DIAMOND ECLOGITES: COMPARISON WITH CARBONACEOUS CHONDRITES, CARBONACEOUS SHALES, AND MICROBIAL CARBON-ENRICHED MORB

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The ~ 0 to -30% carbon isotopic range of eclogitic diamond has been attributed to derivation from carbonaceous chondritic mantle, or to mixing continental carbon with MORB through subduction. Primordial differentiation of carbonaceous chondritic mantle is required to produce ¹³C-depleted diamond and maintain the basaltic composition of diamond eclogite, whereas continental carbonaceous shales could account for some diamond eclogite when mixed with MORB, but carbonaceous shales are not readily subducted. Seafloor-ridge hydrothermal vents contain abundant ¹³C-depleted carbon from microbial activity, as sediments and within MORB itself. Subducting MORB with sediments enriched in ¹³C-depleted microbial carbon can account for both the ¹³C-depleted nature of some eclogitic diamonds and the basaltic composition of diamond eclogite. The -11 to +14%o variation in $\delta^{34}S$ for sulphide inclusions in eclogitic diamonds can also be explained by subduction of a bacterially-fractionated seawater or igneous sulfur reservoir in the vicinity of seafloor-ridge hydrothermal vents. Microbial organic carbon and bacterially fractionated sulfur is preserved in Proterozoic vent settings and can survive subduction without significant fractionation. Seafloor hydrothermal vents (and associated biota) were more prevalent in the Proterozoic and may explain why most eclogitic diamonds are Proterozoic or younger in age, whereas eclogites of Archaean age have diamonds nearer to the mantle value of -6%. Some ¹³C-depleted eclogitic diamond formation may thus be linked with the evolution, and eventual subduction, of the seafloor-ridge vent biosphere. Diamond, eclogite, organic, carbon, sulfur, isotopes

INTRODUCTION

The significance of diamond eclogite has been debated since the first xenolith in kimberlite was discovered nearly a century ago. The xenoliths were first proposed to be concretions of the enclosing kimberlite magma [1, 2], or as the parent rock of diamond but kimberlite itself was questioned as to having an igneous origin [3]. It was also correctly proposed that most diamonds originate in deep-seated peridotite or eclogite regions of the mantle that are sampled by the kimberlite magma on its ascent to the surface [4]. Modern-day radiometric dating confirms that most diamonds and diamond eclogites are much older than the igneous host rocks in which they are found [5-10]. Diamond-bearing xenoliths in kimberlite are rare; most of what is known about the original host rock is derived from analyzing the inclusions within diamond [11]. Olivine, chromite, enstatite and pyrope garnet are diagnostic of peridotitic diamonds because these are the major phases in peridotite. Omphacitic pyroxene and pyrope-almandine are the most common inclusions of eclogitic diamonds although kyanite, corundum, coesite, and rutile inclusions also occur in diamond. Although the chemistry of the eclogitic minerals can vary slightly between those included in diamond and their xenolith host [12], the mineralogy itself is diagnostic of eclogite when these inclusions are detected in single diamonds. Thus in the ensuing discussion, 'diamond eclogite' and 'eclogitic diamond' are treated as analogous. In contrast to peridotitic diamonds with a narrow carbon isotopic range of -1 to -10%, eclogitic diamonds have δ^{13} C values from ~0 to -30% (where δ^{13} C is the difference in the 13 C/ 12 C ratio of the sample relative to a standard, divided by the standard and

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Fig. 1. Carbon concentration and isotopic fields for MORB, carbonaceous chondrites, carbonates, and continental carbonaceous shales (CCS) (data from [21, 22, 49, 54, 73]). Arrows indicate extensions beneath adjacent fields or beyond the limits of the diagram. MORB values include light carbon liberated at low temperature [49]. The field for diamond eclogites is obtained by combining isotopic data from single eclogitic diamonds (open bars on histogram; [13]) and diamonds in eclogites (solid bars on histogram; [38, 46]) with estimated total carbon for diamond eclogites from Table 1. The carbon isotopic range for methanogenic bacteria is a range expected for chemosynthetic microorganisms at seafloor hydrothermal vent settings [42, 74].

multiplied by 1000; Fig. 1; [13, 14]). The sulfur isotopic compositions of sulfide inclusions in peridotitic and eclogitic diamonds behave similarly, sulfide inclusions in peridotitic diamonds have primordial sulfur isotopic compositions with δ^{34} S $\approx 0\%$ (similar notation for the 34 S/ 32 S ratio) whereas eclogitic sulfide δ^{34} S varies from -11 to +14\% [15–17].

Determining the protolith of diamond eclogite is the major controversy in diamond eclogite research, which at present is divided into the 'primordial' and 'subduction' schools of thought (reviewed in [13]). (Rayleigh fractionation, also proposed to explain the range of δ^{13} C in eclogitic diamonds, does not account for extremely light values; see [13]) The primordial carbon model maintains that ¹³C-depleted eclogitic diamonds reflect primordial carbon isotopic heterogeneities in the mantle [14, 18, 19]. For example, δ^{13} C values as light as -25 are observed in some carbonaceous chondrites (Fig. 1; [20-22]). The subduction model suggests that diamond eclogite is derived from subducted mid-ocean ridge basalt (MORB) and related rocks [13, 23-26]. Because carbon is a minor component in fresh MORB and has an average $\delta^{13}C$ around -6% ([18, 27], subduction proponents argue that ¹³C-depleted organic carbon is introduced into MORB via subducted marine rocks such as carbonates and continental carbonaceous shales (CCS; Fig. 1; [13, 16, 28]). However most Proterozoic CCS reside in shelf or intracratonic basin settings that are not prone to subduction, a problem that subduction opponents are quick to point out [18]. Recent observations of abundant microbial activity in present-day seafloor hydrothermal vent settings [29, 30] suggest that microbial organic carbon could provide ¹³C-depleted carbon necessary to produce eclogitic diamond; a new and as yet untested concept [31]. In this study, diamond-bearing eclogite bulk compositions, including carbon content, are calculated and compared with carbonaceous chondrites and continental carbonaceous shales. The results suggest that neither could produce ¹³C-depleted eclogitic diamond by isochemical processes. To evaluate the possibility that ¹³C-depleted carbon is decoupled from CCS and added to MORB during subduction, a quantitative mixing model is used and demonstrates that CCS, subducted with MORB, cannot account for the compositional and carbon isotopic characteristics of diamond eclogite. A new model is presented that demonstrates that microbial carbon from ophiolitic carbonaceous shales, which are intimately juxtaposed with MORB, can account for the carbon isotope and compositional aspects of diamond eclogite. Only diamond eclogite is considered in the following model, though the results may also apply to some diamond-absent mantle eclogites.

METHODS AND RESULTS

Mantle eclogite is often compared to MORB with respect to trace element and isotopic characteristics, but simple bulk composition comparisons are rare. Whole rock analyses of eclogite are often compromised by the presence of secondary phases due to reaction of the primary minerals with metasomatising fluids. This problem may be overcome by analysing the primary minerals and combining the results with modal abundance determinations to reconstruct a bulk composition [32, 33]. Modal analyses are limited by the grain size of the primary minerals present relative to the total mass of the xenolith, and can be difficult for diamond eclogites of only a few grams that are dominated by coarse mineral grains [26, 34]. For this reason, the bulk composition determinations presented here are for diamond eclogites mostly >10 g in mass for which microprobe and modal data were available. Carbon abundance is seldom accurately determined in diamond eclogite, and diamond eclogites with carbon abundance data determined by weight were included when possible [35]. Recent studies suggest that diamond eclogites with carbon estimates based on surface examination alone may be low by factor of ~ 3 [36]. However, more accurate carbon estimates are unlikely to change the general conclusions of this study, which demonstrate a broad and significant range of carbon concentration in diamond eclogite (Table 1).

Although major and minor elements may vary due to uncertainties in modal estimations, diamond eclogites from Siberia, southern Africa, and North America are clearly similar to MORB, and are dramatically different from carbonaceous chondrite (Fig. 2). Primordial differentiation of chondritic mantle has been previously proposed for some diamond eclogites based on REE and radiogenic isotope studies [34], but the carbon isotopic values of -1 to -7% for diamonds in the xenoliths are not ¹³C-depleted [37, 38]. Continental carbonaceous shales (CCS) are also different from diamond eclogite in bulk composition and could not produce diamond eclogite by isochemical melting or metamorphism (Fig. 2). Subductionists would argue that the MORB composition of diamond eclogite is maintained while biogenic carbon from CCS is introduced via partial melting or a fluid phase that does not greatly affect the bulk chemistry of MORB [13]. In this instance the

Diamond Eclogite Bulk Compositions and Weight										
Oxide	XRV22 d/g	HRV247 d/g	PJL18 d/g	JJG531 d/g	TP121 d/g	AK1/9 d	AK1/10 d	AK1/25 d/g	Uv-6/79 d	Uv-9/79 d
SiO ₂	51.3	44.9	52.3	53.0	51.1	49.5	49.6	48.4	47.7	47.8
TiO ₂ *	0.38	0.37	0.30	0.30	0.36	0.52	0.15	0.43	0.37	0.35
Al_2O_3	11.5	18.6	17.1	10.7	14.2	15.5	14.86	16.1	14.6	14.7
Cr ₂ O ₃	0.13	0.10	0.07	0.16	0.06	0.01	0.10	0.08	0.05	0.06
FeO	5.73	9.16	4.27	7.42	7.02	6.12	4.14	6.69	12.1	12.1
MnO	0.19	0.17	0.07	0.17	0.15	1.39	0.12	0.17	0.17	0.23
MgO	15.3	13.1	9.43	12.6	12.1	12.1	13.6	12.1	10.1	9.91
CaO	12.6	12.0	11.0	11.0	11.2	12.3	15.3	13.8	13.1	13.1
Na ₂ O	2.69	1.30	5.08	4.41	3.77	2.70	2.47	2.48	2.23	2.30
K ₂ O**	0.03	0.02	0.14	0.08	0.07	0.03	0.08	0.06	0.14	0.13
C***	0.03	0.35	0.002	0.45	3.40 [±]	0.36^{\pm}	0.003 [±]	0.03	< 0.0001	0.0005
Total, g	248	943	116	13	32	7	15	12	600	100

Table 1									
hnome	Eclogite	Bulk Compositions	and	Waight					

Note. XRV22, HRV247, PJL18, Roberts Victor, South Africa; AK1/9, AK1/10, AK1/25, Orapa, Botswana; JJG531, Jagersfontein, South Africa; TP121, Sloan, USA; Uv6/79, Uv9/79, Udachnaya, Siberia. Compositions for North American and Southern African eclogites are calculated from [35, 70]. Siberian eclogite compositions are calculated from [71] assuming clinopyroxene and garnet are present in equal proportions.

 \pm — minimum concentration estimated from surface examination; d — diamond; d/g — diamond/graphite. *Minimum because rutile (TiO₂) comprises up to 1% of the South African eclogites. **K₂O may be under represented in diamond eclogites because clinopyroxene exsolves K₂O during ascent in the kimberlite magma, resulting in at least a two-fold K₂O reduction for clinopyroxene in eclogite [71, 72]. Diamond eclogite K₂O is doubled in Fig. 2 to account for this effect. ***For southern African eclogites, total carbon includes graphite and is estimated for data in [35], approximating all graphite to a disc shape with radius and height = 0.03 cm.

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Fig. 2. Log plot of major and minor element ranges in weight percent for diamond eclogite, continental carbonaceous shale (CCS), carbonaceous chondrite, and MORB including altered and Proterozoic examples (data from Table 1 and [22, 75-79]).

decoupling of C from other major elements is required, and can be modeled quantitatively. A fluid phase or partial melt that preferentially removes carbon is likely to mobilise other incompatible elements such as potassium, thus K₂O may be used to monitor the compositional effect of mixing CCS with MORB. Although the relative incompatibilities of K and C in the mantle are unknown, the approach is a reasonable first approximation because K₂O is abundant in mantle fluids associated with diamond formation [39]. Up to 5% CCS added to MORB can produce diamond with $\delta^{13}C = -30\%$, but the resultant mixture does not account for the high carbon content of some diamond eclogites before leaving the diamond eclogite field (Fig. 3). This suggests that, even when circumstances permit their subduction, CCS are an unlikely carbon reservoir for ¹³C-depleted eclogitic diamond. MORB is the best protolith for diamond eclogite, but the nearly three orders of magnitude carbon enrichment reflected in diamond eclogite must be accounted for without modifying MORB bulk composition.

THE SEAFLOOR-RIDGE HYDROTHERMAL VENT SYSTEM: "PROTOENVIRONMENT" OF DIAMOND ECLOGITE

Recent observations indicate that ¹³C-depleted carbon is intimately associated with MORB in the vicinity of seafloor-ridge hydrothermal vents, where upwelling, heated seawater circulates through oceanic lithosphere. Seafloor-ridge hydrothermal vents host a unique biosystem that depends directly or indirectly on chemosynthesis, deriving energy through chemical reactions with dissolved components in the hydrothermal fluids [40]. Although tube worms, clams, and crabs are the most visible life forms at the vents, new evidence suggests much of the biomass is microbial and lives beneath the seafloor in hydrothermal fluids that circulate through the basaltic rocks [29, 30]. Unusually high methane emissions from vents with δ^{13} C ratios of -55% support the existence of microbial activity in pore fluids beneath the seafloor [41]. Organisms in the vent effluent are hyperthermophilic methanogenic archaebacteria, similar to fossil archaebacteria found in seafloor hydrothermal vents associated with ophiolitic rocks as old as 2,000 Ma [30, 42, 43]. In the Outokumpu ophiolite in Finland, 2.0 Ga carbonaceous shales are interpreted as the remains of chemosynthetic microorganisms in the vicinity of seafloor hydrothermal vents and have δ^{13} C values of -15 to -30%. These ophiolitic carbonaceous shales (OCS) have 2-18 wt.% carbon, considerably more than the 1–5 wt.% carbon typical of Proterozoic CCS [44, 45]. Up to 10% OCS can be added to MORB to produce eclogitic diamond with δ^{13} C = -27%, raising



Fig. 3. Log-log plot of C and K₂O for MORB, shale and diamond eclogite. Mixing lines represent C and K₂O introduced into MORB via a partial melt or fluid phase. The dashed upper boundary for K₂O in diamond eclogite represents potentially higher concentrations as discussed in Table 1. Tick marks are additions of C and K₂O to MORB in weight percent, and the lowest δ^{13} C of diamond produced in per mil δ^{13} C. Continental carbonaceous shale (CCS); K₂O = 4.0 wt.%, C = 2.5 wt.%, δ^{13} C = -32‰. Ophiolitic carbonaceous shale (OCS); K₂O = 1.7 wt.%, C = 13.4 wt.%, δ^{13} C = -27‰. Carbonrich ophiolitic shale (CRS); K₂O = 0.5 wt.%, C = 28.4 wt.%, δ^{13} C = -27‰ [80]. MORB; K₂O = 0.05 wt.%; C = 0.01 wt.%; δ^{13} C = -6‰.

carbon concentration two orders of magnitude while remaining in the diamond eclogite field (Fig. 3). Diamond eclogites with higher carbon concentrations may be explained by mixing of MORB with carbon-rich ophiolitic shales (CRS; Fig. 3). Ophiolitic carbonaceous shales are also enriched in Fe and Cr, obviating arguments that the formation of ¹³C-depleted diamonds containing high Cr-Fe inclusions cannot be achieved using subducted organic carbon [46]. OCS are ¹³C-depleted, metal-enriched, and have been intimately juxtaposed with MORB since the Proterozoic. OCS provide the most obvious means of producing both the MORB bulk compositions of diamond eclogite and the ¹³C-depleted compositions of eclogitic diamonds.

Although OCS provide an unlimited reservoir for ¹³C-depleted carbon, some ¹³C-depleted eclogitic diamond can also be produced by introducing ¹³C-depleted microbial carbon directly into permeable MORB via hydrothermal fluids. This process has been confirmed by recent observations that prolific microbial activity begins shortly after seafloor volcanism [47, 48]. Organic carbon from microbial activity may account for the small amounts of ¹³C-depleted carbon in otherwise unaltered MORB [49]. This ¹³C-depleted carbon is routinely excluded for MORB igneous δ^{13} C determinations, but it is clearly present and available for subduction. When this ¹³C-depleted component is included, the bulk δ^{13} C composition of MORB ranges from -6 to -14‰ and could account for nearly 75% of the eclogitic diamond compositions shown in Fig. 1. Mixing of carbon from other rock types in the seafloor hydrothermal vent environment with MORB can explain eclogitic diamonds with δ^{13} C > -6‰, such as metalliferous carbonates with δ^{13} C = 0‰ that precipitate when vent fluids mix with cold seawater [50, 51]. Thus, every carbon reservoir required to account for the δ^{13} C range of eclogitic diamond can be found in the present-day seafloor hydrothermal vent environment.

Sulfur isotope variations in diamond eclogites may also be accounted for in the seafloor hydrothermal vent setting. Sulfur is abundant at ridge crests in base metal sulfides that precipitate from the hydrothermal fluid when it contacts cold seawater, forming chimney structures up to 60 meters high. Sulfur isotope ratios from 0 to +5% for sulfides comprising these structures reflect mixing of seawater and mantle sources [52, 53] and if subducted would account for the high δ^{34} S values of some eclogitic sulfides [16, 17]. Isotopically lighter sulfur is provided by the biomass, with hydrothermal vent sulfides, seawater sulfate with δ^{34} S = +20% and primary igneous sulfur in MORB with δ^{34} S = 0% serving as reservoirs for sulfur-metabolising bacteria. Bacterial sulfate reduction can produce sulfides with δ^{34} S from +15 to -45% for a seawater sulfate reservoir (+20%), or +5 to -45% from a hydrothermal or igneous sulfate reservoir (0%; Fig. 4, [54]). In contrast, sulfide-oxidizing bacteria will produce δ^{34} S values from -2 to +18% from chemosynthetic oxidation of a



Fig. 4. The carbon isotopic range for eclogitic diamond and the sulfur isotopic range for sulfide inclusions in diamond (shaded box), with the trends for fractionation of seawater and igneous carbon and sulfur by chemosynthetic bacteria (arrows). Reduction of igneous sulfate with $\delta^{34}S = 0\%$ (cross) or seawater sulfate with $\delta^{34}S = +20\%$ (circle) produces sulfur with $\delta^{34}S$ extending to -45% as indicated by the left-pointing arrows. Chemosynthetic oxidation of sulfur produces positive $\delta^{34}S$ values to +18% as indicated by the right-pointing arrow. Methanogenic bacterial reduction of a CO₂ source with $\delta^{13}C = -7\%$ leads to carbon isotope fractionations from +7 to -38% (vertical arrows). Data from [15–17, 54].

sulfide reservoir with $\delta^{34}S = 0\%$ (Fig. 4; [54–56]). The products of bacterial activity cover the entire carbon and sulfur isotopic range of diamond eclogite. It is clearly unnecessary to subduct CCS with MORB to explain the sulfur and carbon isotopic variations and the carbon concentrations observed in diamond eclogite; these reservoirs are readily available at seafloor hydrothermal vent settings.

PRESERVATION OF ¹³C-DEPLETED ORGANIC CARBON DURING SUBDUCTION

The final requirement for microbial organic carbon to account for ¹³C-depleted eclogitic diamond is that it does not break down as a consequence of subduction. Past studies suggested that organic carbon would break down to methane and graphite through disproportionation reactions that go to completion by 200 °C and ~2 kbar, preferentially breaking ¹²C-¹³C bonds over ¹²C-¹²C bonds and leaving the δ^{13} C of the graphite residue at around -10%o [57-59]. Eclogitic diamonds produced by subducted organic carbon would thus be limited to δ^{13} C values of -10%o [28]. However, new experimental and theoretical studies indicate that organic compounds resist disproportionation under increasing pressure and temperature due to kinetic barriers and may survive to at least 500 °C and 10 kbar [60–62]. Ophiolitic rocks from the eclogite facies with graphite $\delta^{13}C = -25\%o$ support the possibility that ¹³C-depleted carbon can survive high grade metamorphism without significant fractionation [63]. Products of disproportionation can also remain locked in source rocks in the absence of fracturing, so the bulk carbon isotopic composition of the material remains the same [64]. If permeability is limited during metamorphism, incomplete mixing of microbial organic carbon (-55%o) with individual diamonds [13, 65]. The process may be similar to limited fluid mobility in granulite facies rocks in which 30‰ differences exist between veins and host-rock graphite only centimeters apart [66].

DISCUSSION

Some predictions may be put forth if microbial organic carbon is the source for ¹³C-depleted carbon in eclogitic diamond. A diamond eclogite grade of 500 carats per tonne (1 carat = 0.2 grams) is much higher than kimberlite with 0.3–1.0 carats per tonne, and its disaggregation in kimberlite could easily account for all the diamonds present [34, 67]. Yet this xenolith 'grade' converts to only 0.01 wt.% C, the upper range of igneous carbon in MORB (Figs. 1, 2). Diamond eclogite with a carbon content typical of MORB may therefore have δ^{13} C values closer to the mantle value of -6%. Diamond eclogite with a higher carbon content may deviate either way as ¹³C-depleted organic carbon or carbonate with δ^{13} C = 0‰ may contribute to the MORB

protolith. No combined carbon isotope and carbon abundance data are presently available for diamond cclogites, but graphite eclogite xenoliths from Orapa with carbon concentrations near 0.01 wt.% C also have δ^{13} C near -5% (compare data [35, 67]). Obtaining reliable carbon estimates is difficult without destroying the xenolith; computer-assisted tomography X-ray scanning is at present the most promising non-destructive technique [36].

Although microbial organic carbon in MORB is emphasized here as the source for ¹³C-depleted eclogitic diamond, hydrothermal fluids also circulate through the gabbros and lherzolites that underlie MORB, and the depths in the oceanic crust at which chemosynthetic bacteria may exist is presently unknown. It is possible that the rare occurrence of ¹³C-depleted peridotitic diamonds [65] may be explained by microbial organic carbon that has penetrated to these depths in the seafloor.

CONCLUSIONS

Diamond eclogite major element compositions differ drastically from chondritic mantle and cannot be derived from this reservoir by isochemical processes. Differentiation of chondritic mantle to produce diamond eclogite, based on REE and radiogenic isotope studies, also does not account for the occurrence of ¹³C-depleted eclogitic diamond [34, 37]. Continental carbonaceous shales (assuming they can be subducted) also cannot be mixed with MORB in sufficient quantities to produce ¹³C-depleted eclogitic diamond without shifting the product away from a basaltic composition. MORB is the best protolith for diamond eclogite, and can account for both the occurrence of ¹³C-depleted eclogitic diamond and the carbon abundance of diamond eclogite when mixed with microbial organic carbon found near seafloor-ridge hydrothermal vents. The seafloor-ridge hydrothermal vent setting is proposed as the protoenvironment of diamond eclogite.

Large eclogitic diamonds that have been dated are mostly Proterozoic or younger in age [5-9]. Present-day seafloor-ridge systems exist because pressure and temperature conditions are near the critical endpoint of water, where its ability to fracture rock and advect chemical components is optimized [68]. The Archaean seafloor had more ridges, but shallower ocean depths prevented seawater from reaching the supercritical conditions necessary to form extensive hydrothermal vent systems [69]. Ocean depth increased in the late Proterozoic, enabling supercritical seawater to develop extensive hydrothermal systems [69], and vent biota flourished. Isotopically light eclogitic diamonds may have formed more readily in Proterozoic and Phanerozoic time because, prior to 2.5 Ga, large amounts of biogenic carbon were not available for subduction. In contrast, diamonds from several Siberian eclogites are also not ${}^{13}C$ -depleted ($\delta^{13}C = -1$ to -7%;

[37, 38]). Trace element and radiogenic isotopic studies indicate Archean ages and derivation from primordial mantle [34], or from subduction of oceanic lithosphere [25, 26]. This oceanic lithosphere was subducted in the Archean [10] which in our scenario was before significant amounts of biogenic carbon was subducted into the mantle. Thus, biogenic carbon did not contribute significantly in the formation of diamond eclogite prior to the Proterozoic.

Could the appearance of ¹³C-depleted eclogitic diamonds be linked with the evolution and eventual subduction, of the seafloor ridge vent biosphere? Only by further study of diamond eclogites, and the diamonds within them, will we find an answer.

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REFERENCES

[1] G. V. Corstorphine, The occurrence in kimberlite of garnet-pyroxene nodules carrying diamonds, Trans. Geol. Soc. S. Afr., vol. 10, p. 65, 1907.

[2] F. W. Voit, The origin of diamonds, Trans. Geol. Soc. S. Afr., vol. 10, p. 75, 1907.

[3] T. G. Bonney, On the supposed kimberlite magma and eclogite concretions, Trans. Geol. Soc. S. Afr., vol. 10, p. 95, 1907.

[4] J. P. Johnson, Note on Iherzolite and eclogite boulders from the Roberts Victor Mine, Trans. Geol. Soc. S. Afr., vol. 10, p. 112, 1907.

[5] S. H. Richardson, Latter-day origin of diamonds of eclogitic paragenesis, *Nature*, vol. 322, p. 623, 1986.

[6] S. H. Richardson, A. J. Erlank, J. W. Harris, and S. R. Hart, Eclogitic diamonds of Proterozoic age from Cretaceous Kimberlites, *Nature*, vol. 346, p. 54, 1990.

[7] C. B. Smith, J. J. Gurney, W. Harris, D. N. Robinson, S. R. Shee, and E. Jagoutz, Sr and Nd isotopic systematics of diamond-bearing eclogite xenoliths and eclogitic inclusions in diamond from southern Africa, in: J. M. Ross (ed.) Kimberlite and Related Rocks, Vol. 2: Their Mantle/Crust Setting, Diamonds and Diamond Exploration, Blackwell Scientific, Victoria, Australia, p. 853, 1989.

[8] C. B. Smith, J. J. Gurney, W. Harris, M. L. Otter, M. B. Kirkley, and E. Jagoutz, Neodymium and strontium isotope systematics of eclogite and websterite paragenesis inclusions for single diamonds, Finsch and Kimberley Pool, RSA, *Geochim. Cosmochim. Acta*, vol. 55, p. 2579, 1991.

[9] P. D. Kinney, and H. O. A. Meyer, Zircon from the mantle: a new way to date old diamonds, J. Geol., vol. 102, p. 475, 1994.

[10] D. G. Pearson, G. A. Snyder, S. B. Shirey, L. A. Taylor, R. W. Carlson, and N. V. Sobolev, Archaean Re-Os age for Siberian eclogites and constraints on Archaean tectonics, *Nature*, vol. 374, p. 711, 1984.

[11] H. O. A. Meyer, Inclusions in diamond, in: P. H. Nixon (ed.), *Mantle Xenoliths*, Wiley Interscience, New York, p. 478, 1987.

[12] L. A. Taylor, G. A. Snyder, G. Crozaz, V. Sobolev, E. S. Yefimova, and N. V. Sobolev, Eclogitic inclusions in diamonds: evidence of complex mantle processes over time, *Earth Planet. Sci. Lett.*, (1996, in press).

[13] M. B. Kirkley, J. J. Gurney, M. L. Otter, S. J. Hill, and L. R. Daniels, The application of C isotope measurements to the identification of the sources of C in diamonds: a review, *Appl. Geoch.*, vol. 6, p. 477, 1991.

[14] P. Deines, J. J. Gurney, and J. W. Harris, Associated chemical and carbon isotopic composition variations in diamonds from Finsch and Premier kimberlite, South Africa, *Geochim. Cosmochim. Acta*, vol. 48, p. 325, 1984.

[15] M. Chaussidon, F. Albarède, and S. M. F. Sheppard, Sulphur isotope variation in the mantle from ion microprobe analyses of micro-sulphide inclusions in diamond, *Nature*, vol. 330, p. 242, 1987.

[16] C. S. Eldridge, W. Compston, I. S. Williams, J. W. Harris, and J. W. Bristow, Isotope evidence for the involvement of recycled sediments in diamond formation, *Nature*, vol. 353, p. 649, 1991.

[17] R. L. Rudnick, C. S. Eldridge, and G. P. Bulanova, Diamond growth history from in situ measurement of Pb and S isotopic compositions of sulfide inclusions, *Geology*, vol. 21, p. 13, 1993.

[18] P. Deines, Mantle carbon: concentration, mode of occurrence, and isotopic composition, in:
 M. Schidlowski et al. (eds.), *Early Organic Evolution*, Springer-Verlag, Berlin, p. 133, 1992.

[19] S. E. Haggerty, Superkimberlites: a geodynamic window to the Earth's core, *Earth Planet. Sci. Lett.*, vol. 122, p. 57, 1994.

[20] P. Deines and F. E. Wickman, Stable carbon isotopes in enstatite chondrites and Cumberland Falls, Geochim. Cosmochim. Acta, vol. 49, p. 89, 1985.

[21] J. F. Kerridge, Carbon, hydrogen and nitrogen in carbonaceous chondrites: abundances and isotopic compositions in bulk samples, *Geochim. Cosmochim. Acta*, vol. 49, p. 1707, 1985.

[22] B. Mason, Handbook of Elemental Abundances in Meteorites, Gordon and Breach Publishers, New York, 1971.

[23] E. M. Galimov, I. N. Ivanovskaya, F. V. Kaminsky, N. V. Sobolev, V. V. Gritsik, R. B. Zezin, M. V. Lukyanovic, and Yu. A. Klyuev, New data on the isotope composition of carbon in diamonds from various regions of the Soviet Union [in Russian], in: *Trudy – Tsentral'nyy Nauchno-Issledovatel'skiy Geologorazvedochnyy Institut*, vol. 153, p. 19, 1980.

[24] H. H. Helmstaedt and D. J. Schulze, Southern African kimberlites and their mantle sample: implications for Archean tectonics and lithosphere evolution, in: J. M. Ross (ed.), *Kimberlite and Related Rocks, Vol. 2: Their Mantle/Crust Setting, Diamonds and Diamond Exploration*, Blackwell Scientific, Victoria, Australia, p. 358, 1989.

[25] D. Jacob, E. Jagoutz, D. Lowry, D. Mattey, and G. Kudrjavtseva, Diamondiferous eclogites from Siberia: remants of Archean ocean crust, *Geochim. Cosmochim. Acta*, vol. 58, p. 5191, 1994.

[26] E. A. Jerde, L. A. Taylor, G. Crozaz, N. V. Sobolev, and V. N. Sobolev, Diamondiferous eclogites from Yakutia, Siberia: evidence for a diversity of protoliths, *Contrib. Mineral. Petrol.*, vol. 114, p. 189, 1993.

[27] D. J. Des Marais and J. G. Moore, Carbon and its isotopes in mid-oceanic basaltic glasses, Earth Planet. Sci. Lett., vol. 69, p. 43, 1984.

[28] M. B. Kirkley and J. J. Gurney, Carbon isotope modelling of biogenic origins for carbon in eclogitic diamonds, in: F. R. Boyd, H. O. A. Meyer and N. V. Sobolev (eds.), *Extended Abstracts, Workshop on Diamonds*, 28th International Geological Congress, Washington, D.C., p. 40, 1989

[29] J. W. Deming and J. A. Baross, Deep-sea smokers: windows to a subsurface biosphere?, Geochim. Cosmochim. Acta, vol. 57, 3219, 1993.

[30] J. R. Delaney, J. A. Baross, M. D. Lilley, D. S. Kelley, and R. W. Embley, Is the quantum event of crustal accretion a window into a deep hot biosphere?, EOS, vol. 75, p. 617, 1994.

[31] E. G. Nisbet, D. P. Mattey, and D. Lowry, Can diamonds be dead bacteria?, Nature, vol. 367, p. 694, 1994.

[32] L. A. Taylor and C. R. Neal, Eclogites with oceanic crustal and mantle signatures from the Bellsbank kimberlite, South Africa. Part 1: mineralogy, petrography, and whole rock chemistry, J. Geol., vol. 97, p. 551, 1989.

[33] C. R. Neal, L. A. Taylor, J. P. Davidson, P. Holden, A. N. Halliday, P. H. Nixon, J. B. Paces, R.N. Clayton, and T. K. Mayeda, Eclogites with oceanic crustal and mantle signatures from the Bellsbank kimberlite, South Africa, part 2: Sr, Nd, and O isotope geochemistry, *Earth Planet. Sci. Lett.*, vol. 99, p. 362, 1990.

[34] G. A. Snyder, E. A. Jerder, L. A. Taylor, A. N. Halliday, V. N. Sobolev, and N. V. Sobolev, Nd and Sr isotopes from diamondiferous eclogites, Udachnaya kimberlite pipe, Yakutia, Siberia: evidence of differentiation in the early Earth?, *Earth Planet. Sci. Lett.*, vol. 118, p. 91, 1993.

[35] D. N. Robinson, Diamond and graphite in eclogite xenoliths from kimberlite, in: F. R. Boyd and H.O. A. Meyer (eds.), *The Mantle Sample: Inclusions in Kimberlites and Other Volcanics*, American Geophysical Union, Washington, D.C., p. 50, 1979.

[36] D. J. Schulze, D. Wiese, and J. Steude, Abundance and distribution in eclogite revealed by volume visualization of CT X-ray scans, J. Geology, vol. 104, p. 109, 1996.

[37] V. N. Sobolev, L. A. Taylor, and G. A. Snyder, Diamondiferous eclogites from the Udachnaya kimberlite pipe, Yakutia, Int. Geol. Rev., vol. 36, p. 42, 1994.

[38] G. A. Snyder, L. A. Taylor, E. A. Jerde, R. N. Clayton, T. K. Mayeda, P. Deines, G. R. Rossman, and N. V. Sobolev, Archean mantle heterogeneity and origin of diamondiferous eclogites, Siberia: evidence from stable isotopes and hydroxyl in garnet, *American Mineralogist*, vol. 80, p. 799, 1995.

[39] O. Navon, I. D. Hutcheon, G. R. Rossman, and G. J. Wasserburg, Mantle-derived fluids in diamond micro-inclusions, *Nature*, vol. 335, p. 784, 1988.

[40] H. W. Jannasch, Chemosynthetically sustained ecosystems in the deep sea, in: H.G. Schlegel and B. Bowien (eds.), Autotrophic Bacteria, Springer-Verlag, Berlin, p. 147, 1989.

[41] M. D. Lilley, D. A. Butterfield, E. J. Olson, J. E. Lupton, S. A. Macko, and R. E. McDuff, Anomalous CH_4 and NH_4^+ concentraions at an unsedimented mid-ocean-ridge hydrothermal system, *Nature*, vol. 364, p. 45, 1993.

[42] J. A. Baross and S. E. Hoffman, Submarine hydrothermal vents and associated gradient environments as sites for the origin and evolution of life, Orig. Life, vol. 15, p. 327, 1985.

[43] E. Oudin and G. Constantinou, Black smoker chimney fragments in Cyprus sulphide deposits, Nature, vol. 308, p. 349, 1984.

[44] K. Loukola-Russkeeniemi, Geochemical evidence for the hydrothermal origin of sulphur, base metals and gold in Proterozoic metamorphosed black shales, Kainuu and Outokumpu areas, Finland, *Mineral. Dep.*, vol. 26, p. 152, 1991.

[45] K. Loukola-Russkeeniemi, T. Heino, J. Talvitie, and J. Vanne, Base-metal-rich metamorphosed black shales associated with Proterozoic ophiolites in the Kainuu schist belt, Finland: a genetic link with Outokumpu rock assemblage, *Mineral. Dep.*, vol. 26, p. 143, 1991.

[46] P. Deines, J. W. Harris, D. N. Robinson, J. J. Gurney, and S. R. Shee, Carbon and oxygen isotope variations in diamond and graphite eclogites from Orapa, Botswana, and the nitrogen content of their diamonds, *Geochim. Cosmochim. Acta*, vol. 55, p. 515, 1993.

[47] R. M. Haymon, D. J. Fornari, K. L. Von Damm, M. D. Lilley, M. R. Perfit, J. M. Edmond, W.C. Shanks III, R. A. Lutz, J. M. Grebmeier, S. Carbotte, D. Wright, E. McLaughlin, M. Smith, N. Beddle, and E. Olson, Volcanic eruption of the mid-ocean ridge along the East Pacific Rise crest at 9945-52,N: direct submersible observations of seafloor phenomena associated with an eruption event in April, 1991, *Earth Planet. Sci. Lett.*, vol. 119, p. 85, 1993.

[48] M. R. Fisk, S. J. Giovanonni, and T. D. Mullins, Microbial alteration of ocean ridge basalt glass, EOS, 75, 706, 1994.

[49] J. G. Blank, J. R. Delaney, and D. J. Des Marais, The concentration and isotopic composition of carbon in basaltic glasses from the Juan de Fuca Ridge, Pacific Ocean, *Geochim. Cosmochim. Acta*, vol. 57, p. 875, 1993.

[50] V. Marchig and J. Erzinger, Chemical composition of Pacific sediments near 209S: changes with increasing distance from the East Pacific Rise, Init. Rep. DSDP, 1986.

[51] T. J. Barrett, P. N. Taylor, and J. Lugoski, Metalliferous sediments from DSDP Leg 92: The East Pacific Rise, Geochim. Cosmochim. Acta, vol. 51, p. 2241, 1987.

[52] R. A. Zierenberg, R. A. Koski, J. L. Morton, R. M. Bouse, and W. C. Shanks III, Genesis of massive sulfide deposits on a sediment-covered spreading center, Escanaba Trough, southern Gorda Ridge, *Econ. Geol.*, vol. 88, p. 2069, 1993.

[53] W. D. Goodfellow and J. M. Franklin, Geology, mineralogy, and chemistry of sediment-hosted clastic massive sulfides in shallow cores, Middle Valley, northern Juan de Fuca Ridge, *Econ. Geol.*, vol. 88, p. 2037, 1993.

[54] M. Schidlowski, J. M. Hayes, and I. R. Kaplan, Isotopic inferences of ancient biochemistries: carbon, sulfur, hydrogen and nitrogen, in: J. W. Schopf (ed.), *Earth's Earliest Biosphere*, Princeton University Press, New Jersey, p. 149, 1983.

[55] T. M. McCollom and E. L. Shock, Energetics of biological sulfate reduction within chimney walls at mid-ocean ridges, EOS, vol. 75, p. 707, 1994.

[56] T. H. Donnelly and I. H. Crick, Biological and abiological sulfate reduction in two northern Australian Proterozoic basins, in: M. Schidlowski et al. (eds.), *Early Organic Evolution*, Springer-Verlag, London, p. 398, 1992.

[57] J. M. Hunt, Petroleum Geochemistry and Geology, W.H. Freeman, New York, 1979.

[58] D. M. McKirdy and T. G. Powell, Metamorphic alteration of carbon isotopic composition in ancient sedimentary organic matter: new evidence from Australia and South Africa, *Geology*, vol. 2, p. 591, 1974.

[59] J. Hoefs and M. Frey, The isotopic composition of carbonaceous matter in a metamorphic profile from the Swiss Alps, *Geochim. Cosmochim. Acta*, vol. 40, p. 945, 1976.

[60] E. L. Shock and H. C. Helgeson, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partial molal properties of organic species, *Geochim. Cosmochim. Acta*, vol. 54, p. 915, 1990.

[61] R. Eggen, A. Geerling, J. Watts, and W. M. de Vos, Characterization of pyrolysin, a hyperthermoactive serine protease from the archaebacterium Pyrococcus furiosus, *FEMS Microbiol. Lett.*, vol. 71, p. 17, 1990.

[62] E. L. Shock, Geochemical constraints on the origin of organic compounds in hydrothermal systems, Orig. Life Evol. Bios., vol. 20, p. 331, 1990.

[63] S. Nadeau, P. Philippot, and F. Pineau, Fluid inclusion and mineral isotopic compositions (H-C-O) in eclogite rocks as tracers of local fluid migration during high-pressure metamorphism, *Earth Planet. Sci. Lett.*, vol. 114, p. 431, 1993.

[64] L. C. Price, Thermal stability of hydrocarbons in nature: limits evidence, characteristics, and possible controls, *Geochim. Cosmochim. Acta*, vol. 57, p. 3261, 1993.

[65] M. L. Otter, J. J. Gurney, M. B. Kirkley, B. Harte, and T. E. McCandless, The carbon isotope composition of Sloan diamonds: evidence of a subducted ophiolite sequence?, *Geochim. Cosmochim. Acta*, submitted.

[66] M. Santosh and H. Wada, Microscale isotopic zonation in graphite crystals: evidence for channelled CO influx in granulites, *Earth Planet. Sci. Lett.*, vol. 119, p. 19, 1993.

[67] P. Deines, J. W. Harris, D. N. Robinson, J. J. Gurney, and S. R. Shee, Geochim. Cosmochim. Acta, vol. 57, p. 2781, 1993.

[68] D. Norton, A theory of hydrothermal systems, Annu. Rev. Earth Planet. Sci., vol. 12, p. 155, 1984.
[69] J. F. Kasting and N. G. Holm, What determines the volume of oceans?, Earth Planet. Sci. Lett., vol. 109, p. 507, 1992.

[70] T. E. McCandless and J. J. Gurney, Sodium in garnet and potassium in clinopyroxene: criteria for classifying mantle eclogites, *Data Appendix Kimberlite Res. Grp. Int. Rep. 10*, Dept. Geol. Sci. Univ. Cape Town, South Africa, 1986.

[71] V. N. Sobolev, I. T. Bakumenko, E. S. Yefimova, and N. P. Pokhilenko, Morphological characterisitics of microscopic diamonds of two eclogite xenoliths from the Udachnaya kimberlite pipe (Yakutia) containing

traces of sodium in garnets and of potassium in pyroxenes, Trans. Russ. Acad. Sci. Earth Sci. Sect., vol. 322, p. 138, 1994.

[72] T. E. McCandless and D. S. Collins, A diamond-graphite eclogite from the Sloan 2 kimberlite, Colorado, USA, in: J. M. Ross (ed.), *Kimberlite and Related Rocks, Vol. 2: Their Mantle/Crust Setting, Diamonds and Diamond Exploration*, Blackwell Scientific, Victoria, Australia, p. 1063, 1989.

[73] H. Strauss, D. J. Des Marais, J. M. Hayes, and R. E. Summons, Proterozoic organic carbon – its preservation and isotopic record, in: M. Schidlowski et al. (eds.), *Early Organic Evolution*, Springer-Verlag, Berlin, p. 203, 1992.

[74] M. Schidlowski and P. Aharon, Carbon cycle and isotope record: geochemical impact of life over 3.8 Ga of Earth history, in: M. Schidlowski et al. (eds.), *Early Organic Evolution*, Springer-Verlag, 1992, Berlin, p. 147, 1992.

[75] E. M. Cameron and R. M. Garrels, Geochemical compositions of some Precambrian shales from the Canadian Shield, *Chem. Geol.*, vol. 28, p. 181, 1980.

[76] K. M. Gillis and G. Thompson, Metabasalts from the Mid-Atlantic Ridge: new insights into hydrothermal systems in slow spreading crust, *Contri. Miner. Petrol.*, vol. 113, p. 502, 1993.

[77] Basaltic Volcanism Study Project Basaltic Volcanism on the Terrestrial Planets, Pergamon Press, New York, 1981.

[78] J. H. Breitkopf and K. J. Maiden, Tectonic setting of the Matchless Belt pyritic copper deposits, Namibia, *Econ. Geol.*, vol. 83, p. 710, 1988.

[79] A. Kontinen, An early Proterozoic ophiolite - Jormua mafic-ultramafic complex, northeastern Finland, Prec. Res., vol. 35, p. 313, 1987.

[80] E. Peltola, On the black schists in the Outokumpu region in eastern Finland, Bull. Comm. Geol. Finl., vol. 192, 1960.

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