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Notes

Anticorrelation between low $\delta^{13}\text{C}$ of eclogitic diamonds and high $\delta^{18}\text{O}$ of their coesite and garnet inclusions requires a subduction origin

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ABSTRACT

Diamond is essentially impermeable and unreactive under many conditions, and tiny mineral inclusions within natural diamonds can faithfully preserve information on the chemical and physical conditions during diamond growth. The stable isotope ratios of carbon, nitrogen, oxygen, and sulfur in diamonds and their mineral inclusions have been used to constrain models of diamond formation, but interpretations of the data have differed dramatically. The crux of the controversy lies in the interpretation of the carbon isotope ratios of eclogite-suite diamonds, which range well outside those expected for typical mantle materials such as peridotites, basalts, and carbonatites. Proposed explanations for these anomalous carbon isotope ratios include derivation from primordial mantle inhomogeneities, fractionated mantle fluids, and subducted biogenic carbon. Working with samples from three continents, we have analyzed the carbon isotope compositions of eclogite-suite diamonds and the oxygen isotope composition of their mineral inclusions, primarily by ion microprobe methods. We have discovered a previously unrecognized, remarkably consistent anticorrelation between these two isotopic systems, in that virtually all diamonds with anomalously low carbon isotope ratios have silicate inclusions with anomalously high oxygen isotope ratios. This is a fundamental observation that can only be explained by formation of eclogite-suite diamonds through subduction of sea-floor altered basalt, admixed with marine biogenic carbon, into the field of diamond stability.

INTRODUCTION

From the study of diamonds that contain syngenetic inclusions, and of diamond-bearing mantle xenoliths, it is clear that most natural diamonds belong to one of two suites, peridotitic and eclogitic. Diamonds of the peridotite (P) paragenesis appear to be more common than eclogitic (E) diamonds, and most geochemical features of P-suite diamonds and associated minerals seem to indicate origin of the great majority of P-suite diamonds entirely within the upper mantle (Cartigny, 2005). In contrast, many diamonds of the E suite have geochemical features that some workers have ascribed to inheritance from a crustal protolith (e.g., Sobolev et al., 1979; Kirkley et al., 1991; Eldridge et al., 1991; Schulze et al., 2003).

The $\delta^{13}\text{C}$ values of E-suite diamonds range from approximately -39‰ to $+5\text{‰}$ VPDB (Vienna Pee Dee belemnite carbon isotope standard), as recently reviewed by Cartigny (2005). This wide range contrasts

with that of the vast majority of peridotitic diamonds that have $\delta^{13}\text{C}$ values in the range -8‰ to -2‰ , typical of carbon isotope compositions of most mantle-derived materials, such as basalts and carbonatites (e.g., Cartigny, 2005). The unusually wide range of $\delta^{13}\text{C}$ values and the large number below -8‰ in diamonds of the eclogite suite have been variably attributed to mantle fractionation effects, the persistence of primordial inhomogeneities in the mantle, and crustal carbon subducted into the mantle. Supporting evidence for the fractionation and subduction hypotheses has been cited from nitrogen isotope studies of diamonds (Cartigny et al., 1998) and sulfur and oxygen isotope studies of phases included in diamonds (Eldridge et al., 1991; Lowry et al., 1999; Schulze et al., 2003), respectively, but the origin of E-suite diamonds remains contentious (Haggerty, 1999; Cartigny, 2005; Griffin and O'Reilly, 2007).

In this paper, we present stable isotope data for eclogitic diamonds and their coesite and garnet inclusions, primarily measured with ion microprobe/secondary ion mass spectrometry (SIMS) methods. We use the results to constrain competing models for the origin of low- $\delta^{13}\text{C}$ eclogitic diamonds.

SAMPLES AND METHODS

Coesite, a high-pressure silica polymorph, and Cr-poor Ca-Mg-Fe garnet are well-known members of the eclogite suite of minerals included in diamonds (Meyer, 1987; Sobolev, 2006). We have studied diamonds with coesite inclusions from the Quebrada Grande placer deposits in the Guaniamo region of Venezuela, the Argyle lamproite in Western Australia, and the Orapa kimberlite in Botswana, and garnet-bearing diamonds from Argyle. The Guaniamo and Orapa samples were analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in polished sections of diamonds using a CAMECA 4f ion microprobe at the University of Edinburgh, Scotland (Schulze et al., 2003, 2004, and references therein). The Guaniamo and Orapa diamonds show distinct zoning in cathodoluminescence images (e.g., Fig. 1) and are typically zoned in $\delta^{13}\text{C}$ (e.g., Schulze et al., 2004). The carbon isotope compositions reported here are for analytical points adjacent to the coesite grains. The $\delta^{18}\text{O}$ values for coesite and garnet inclusions in the Argyle diamonds were measured on grains extracted from diamonds by breakage (Jaques et al., 1989), mounted in epoxy, and analyzed by SIMS methods using a CAMECA 1280 ion microprobe at the University of Wisconsin (United States) with methods described by Kelly et al. (2007), Kita et al. (2009), and Page et al. (2010). Carbon isotope compositions of the Argyle stones were determined by combustion methods using fragments of the diamonds (Jaques et al., 1989; Table 1).

RESULTS

Carbon isotope ratios of all but one of the diamonds are anomalously low ($\delta^{13}\text{C} < -8\text{‰}$) relative to typical upper-mantle values. The Guaniamo stones have $\delta^{13}\text{C}$ in the range -22.3‰ to -11.3‰ , those from Argyle have

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Figure 1. Cathodoluminescence image of diamond 13-127-16 from Guaniamo, Venezuela. Intensity of luminescence differs primarily due to nitrogen content of different growth zones. Silicate inclusions (two coesites, two omphacites, and one kyanite) appear as nonluminescent (black) regions. Locations of the two coesites analyzed in this study are indicated by arrows, and locations of the spots analyzed for carbon isotopes are indicated by x. Diamond is ~2 mm across.

$\delta^{13}\text{C}$ in the range -15.9‰ to -9.0‰ (and one stone with $\delta^{13}\text{C} = -5.9\text{‰}$), and the Orapa diamond has a $\delta^{13}\text{C}$ value of -9.0‰ . For each suite, the data are within, and typical of, the published carbon isotope compositions of eclogitic diamonds from that locality (Jaques et al., 1989; Kaminsky et al., 2000; Deines et al., 1993).

The oxygen isotope compositions of the coesite inclusions are anomalously high ($\delta^{18}\text{O} > +6.0\text{‰}$), and mostly well outside the range of typical mantle values. The $\delta^{18}\text{O}$ ratios of Guaniamo coesites are in the range $+10.2\text{‰}$ to $+16.1\text{‰}$, those from Argyle in the range $+6.7\text{‰}$ to $+16.0\text{‰}$, and the Orapa coesite has $\delta^{18}\text{O} = +8.5\text{‰}$. The $\delta^{18}\text{O}$ ratios of the Argyle garnets are in the range $+6.0\text{‰}$ to $+8.3\text{‰}$, with the exception of the garnet from the diamond with the highest carbon isotope value (-5.9‰), which has a $\delta^{18}\text{O}$ ratio of $+5.7\text{‰}$. The carbon and oxygen isotope data are summarized in Table 1 and illustrated in Figure 2.

COMPARISON WITH DIAMOND ECLOGITES

In addition to data from single diamonds, Figure 2 also contains data from diamondiferous eclogite xenoliths and polycrystalline diamond aggregates (framesite) from several kimberlites (Deines et al., 1991; Snyder et al., 1995; Jacob et al., 2000). For reference, a field labeled “common mantle” is illustrated, with boundaries of $\delta^{13}\text{C} = -8\text{‰}$ to -2‰ and $\delta^{18}\text{O}(\text{whole rock}) = +5\text{‰}$ to $+6\text{‰}$, which would enclose the vast majority of data for fresh mantle-derived materials such as basalts and carbonatites (e.g., Cartigny, 2005) that have not had crustal material play a role in their genesis. Approximately two-thirds of the diamond-bearing eclogites and diamond aggregates (Deines et al., 1991; Snyder et al., 1995; Jacob et al., 2000) have silicates (garnet or clinopyroxene) with $\delta^{18}\text{O}$ values outside

the “common mantle” range of $+5\text{‰}$ to $+6\text{‰}$, and all but two of these are above $+6\text{‰}$. Furthermore, all eclogite xenoliths in which diamond has $\delta^{13}\text{C}$ values below -8‰ have garnet and/or clinopyroxene with anomalously high oxygen isotope compositions ($\delta^{18}\text{O} > 6\text{‰}$).

The carbon isotope values of diamonds from both suites (those from this study and those from the diamond-bearing xenoliths) range to very low values ($\delta^{13}\text{C}$ of $\sim -23\text{‰}$). The $\delta^{18}\text{O}$ values of the silicates (garnet and clinopyroxene) from the low- $\delta^{13}\text{C}$ diamondiferous xenoliths, however, though higher than typical mantle, are much more restricted in their oxygen isotope values ($\delta^{18}\text{O} = +6.5\text{‰}$ to $+9.2\text{‰}$) than are the coesite and garnet diamond inclusions in our study ($\delta^{18}\text{O} = +5.9\text{‰}$ to $+16.1\text{‰}$). Indeed, the coesite data range to much higher $\delta^{18}\text{O}$ values than are known from the entire population of mantle eclogite xenoliths in kimberlite or any other mantle rock type. We view the correlation of low $\delta^{13}\text{C}$ in diamond with high to extremely high $\delta^{18}\text{O}$ of included coesite or garnet, not previously noted, to be of fundamental importance in understanding the relationship between the sources of oxygen and carbon in the eclogitic diamond paragenesis. This relationship suggests that information critical in deciphering the origin of eclogitic diamonds may be preserved only inside the impermeable diamonds, and has been lost or modified in the unencapsulated minerals of the diamond-bearing eclogites in the open system of the upper mantle in the billions of years following diamond formation.

DISCUSSION

Initial interpretations of anomalously high (and low) oxygen isotope values in mantle eclogites as the result of fractionation effects in mantle magmas (Garlick et al., 1971) are inconsistent with experimental data

TABLE 1. ISOTOPIC COMPOSITIONS OF COESITES, GARNETS, AND HOST DIAMONDS IN THIS STUDY

Location	Mineral inclusion	Diamond no.	$\delta^{18}\text{O}$ (‰)	2 sd*	$\delta^{13}\text{C}$ (‰)	2 sd*
Orapa	Coeseite	OR-1	+8.5 (1) [†]	2.1	-9.0 (3)	-
Venezuela	Coeseite	13-127-16	+16.1 (3) [§]	2	-11.5 (6)	1.2
Venezuela	Coeseite	13-127-34B	+13.2 (2)	2.1	-22.3 (2)	1.3
Venezuela	Coeseite	13-127-67	+15.6 (2)	2.1	-16.9 (1)	1.3
Venezuela	Coeseite	13-127-x	+10.2 (1) [§]	2	-18.3 (1)	1.2
Argyle	Coeseite	39	+8.0 (3)	0.1	-13.4 (1)	<0.2
Argyle	Coeseite	54	+14.2 (4)	0.3	-11.9 (1)	<0.2
Argyle	Coeseite	63	+8.5 (4)	0.4	-14.1 (1)	<0.2
Argyle	Coeseite	87	+16.0 (2)	0.4	-11.2 (2) [#]	<0.2
Argyle	Coeseite	124	+6.7 (3)	0.4	-10.3 (1)	<0.2
Argyle	Garnet	17	+6.9 (3)	0.4	-	-
Argyle	Garnet	18	+6.8 (4)	0.3	-	-
Argyle	Garnet	34	+7.3 (2)	0.4	-13.4 (1)	<0.2
Argyle	Garnet	52	+8.3 (3)	0.5	-9.1 (1)	<0.2
Argyle	Garnet	54	+7.2 (2)	0.6	-11.9 (1)	<0.2
Argyle	Garnet	59	+7.1 (2)	0.3	-11.7 (1)	<0.2
Argyle	Garnet	68	+7.4 (2)	0.6	-12.0 (1)	<0.2
Argyle	Garnet	69	+7.7 (2)	0.3	-12.9 (2)	<0.2
Argyle	Garnet	75	+7.3 (2)	0.5	-12.3 (1)	<0.2
Argyle	Garnet	77	+7.5 (3)	0.7	-12.1 (1)	<0.2
Argyle	Garnet	78	+7.4 (2)	0.1	-10.9 (1)	<0.2
Argyle	Garnet	111	+6.0 (6)	0.5	-9.0 (2)	<0.2
Argyle	Garnet	116	+7.8 (3)	0.3	-8.9 (2)	<0.2
Argyle	Garnet	121	+7.5 (2)	0	-11.0 (1)	<0.2
Argyle	Garnet	134	+7.9 (2)	0.1	-9.2 (2)	<0.2
Argyle	Garnet	136	+7.0 (2)	0.1	-15.9 (2)	<0.2
Argyle	Garnet	145	+5.7 (2)	0	-5.9 (2)	<0.2

*Standard deviations (sd) calculated using multiple drift-corrected values of standard analyses bracketing the unknowns.

[†]Values in parentheses indicate number of analyses.

[§]Coeseite data from Schulze et al. (2003). The value for sample 13-127-16 represents the average of three analyses of two inclusions.

[#]Two chips of diamond 87 were analyzed by combustion at the University of Wisconsin, yielding $\delta^{13}\text{C}$ values of -11.48‰ and -10.80‰, a difference greater than the analytical error on each analysis (<0.1‰). Other carbon isotope analyses as described in the text.

(Chacko et al., 2001). Anomalous oxygen isotope values in mantle eclogite assemblages (eclogite xenoliths and E-suite inclusions in diamonds) are now generally thought to be inherited from seafloor weathered and/or hydrothermally altered crustal basalts and gabbros (e.g., Jagoutz et al., 1984; Jacob, 2004; Schulze et al., 2004; Cartigny, 2005). The seafloor hypothesis is supported by the fact that throughout the process of subduction of altered basic rocks and prograde metamorphism to eclogite facies, the characteristic oxygen isotope signature of seafloor alteration is largely preserved, as is evident from the anomalous $\delta^{18}\text{O}$ values of subduction-zone eclogites (e.g., Leech and Ernst, 1998). The origin of the anomalously low carbon isotope values of eclogitic diamonds associated with the subducted ocean-floor material, however, has remained a point of contention (Cartigny, 2005; Griffin and O'Reilly, 2007).

The "primordial inhomogeneity" model for the wide range of $\delta^{13}\text{C}$ in eclogitic diamonds (Deines, 1980; Haggerty, 1999) has been generally discounted as it is "not supported by data from other fields of mantle isotope geochemistry" (Cartigny, 2005, p. 81). Agreement has not been reached, however, on the other two competing hypotheses. Is the carbon in eclogitic diamonds completely mantle derived, and low carbon isotope ratios the result of Rayleigh fractionation of mantle fluids (Deines, 1980; Cartigny et al., 1998; Griffin and O'Reilly, 2007), or are the low carbon isotope ratios inherited from biogenic carbon subducted into the mantle (Sobolev et al., 1979; Kirkley et al., 1991)?

It has been argued that because many low $\delta^{13}\text{C}$ eclogitic diamonds have nitrogen isotope ratios that appear to indicate a mantle source for the nitrogen, the carbon in these diamonds must also be mantle derived

Figure 2. Anticorrelation of $\delta^{13}\text{C}$ of diamond and $\delta^{18}\text{O}$ of coesite inclusions in diamond (Table 1; solid squares from Venezuela, solid circles from Argyle [Australia], and solid cross from Orapa [Botswana]), and garnet inclusions from Argyle diamonds (Table 1; solid diamonds) from this study. Gray shading highlights the region of values for diamond coesite. Also shown, as open circles, are the $\delta^{13}\text{C}$ of diamond and $\delta^{18}\text{O}$ of coexisting garnet or clinopyroxene in eclogite xenoliths (Deines et al., 1991; Snyder et al., 1995) and diamond-silicate intergrowths (Jacob et al., 2000), and, as open diamonds, the $\delta^{13}\text{C}$ of diamond and $\delta^{18}\text{O}$ of eclogite-suite garnet inclusions from Finsch mine (South Africa) (Lowry et al., 1999). As described in the text, the field labeled OFO-BIC (ocean floor oxygen-biogenic carbon, defined by dotted line) indicates the correlation between $\delta^{13}\text{C}$ values below "common mantle" that could represent biogenic carbon and $\delta^{18}\text{O}$ values above those of "common mantle" that among basic rocks are the result of ocean-floor weathering and low-temperature hydrothermal alteration. VSMOW—Vienna standard mean ocean water; VPDB—Vienna Pee Dee belemnite.

(Cartigny et al., 1998; Cartigny, 2005). In this model, the low $\delta^{13}\text{C}$ of the diamonds is the result of Rayleigh fractionation effects, and the model has been applied to both E-suite and P-suite diamonds (Cartigny et al., 1998). This interpretation of the data, however, requires a common source for both carbon and nitrogen in the diamonds, but such a common origin has not been demonstrated. Furthermore, Argyle eclogitic diamonds, with low $\delta^{13}\text{C}$ values, have been shown to have a wide range in $\delta^{15}\text{N}$, spanning a range from -4.6‰ to +13.6‰ (Van Heerden et al., 1995), encompassing values expected for crustal and mantle nitrogen, and showing little correlation with carbon isotope ratios. Values $\delta^{15}\text{N}$ for some other diamond suites span equally large ranges (e.g., $\delta^{15}\text{N} = -24.2\text{‰}$ to -0.3‰ at Pipe 50, China; Cartigny et al., 1997), demonstrating that the nitrogen isotope composition of the mantle is not homogeneous, and is not well known.

We suggest that the correlation between low $\delta^{13}\text{C}$ values of diamonds and the high to extremely high $\delta^{18}\text{O}$ values of their silicate inclusions is compelling evidence in support of a subduction origin for the low $\delta^{13}\text{C}$ in the diamonds. Although clearly anticorrelated (Fig. 2), the data do not follow linear or smoothly curving trends as envisioned by Griffin and O'Reilly (2007), for example, that might be interpreted as the result of fractionation of mantle fluids. The anticorrelation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (ocean floor oxygen-biogenic carbon, OFO-BIC in Figure 2) is that to be expected for protoliths from an ocean-floor setting. There, biogenic carbon (with low $\delta^{13}\text{C}$) is associated with seafloor weathered, or near-surface low-temperature hydrothermally altered, basalts (with elevated $\delta^{18}\text{O}$). The carbon and oxygen isotopic systems are decoupled, but the anomalous $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are linked by formation in a common geologic environment by unrelated processes.

Although many mantle eclogites have anomalously low $\delta^{18}\text{O}$ values ($<+5\text{‰}$), representing subducted eclogite-facies metabasites that acquired their $\delta^{18}\text{O}$ signatures through high-temperature hydrothermal sub-seafloor alteration of lower oceanic crust (e.g., Jacob, 2004), the rare examples of these that contain diamonds (Snyder et al., 1995) have $\delta^{13}\text{C}$ values within the range of “common mantle” carbon (Fig. 2). This is consistent with our model, in which little biogenic carbon would be present at the high temperatures ($>350^\circ\text{C}$) and depths at which hydrothermal exchange with heated seawater could create a mafic (e.g., metagabbro) protolith with low $\delta^{18}\text{O}$ values (e.g., Gregory and Taylor, 1981). The “common mantle” $\delta^{13}\text{C}$ values of rare diamonds associated with the low $\delta^{18}\text{O}$ eclogites are those to be expected if the carbon itself is derived from mantle carbon contained within the mantle-derived mafic rock.

The alternative model for the preferential association of low- $\delta^{13}\text{C}$ diamond with eclogites is based on experimental evidence that decarbonation reactions in the mantle, capable of producing low- $\delta^{13}\text{C}$ fluids that could precipitate low- $\delta^{13}\text{C}$ diamond, are restricted to eclogite (not peridotite) mineral assemblages (Luth, 1993). In this model, however, low- $\delta^{13}\text{C}$ diamonds should occur in eclogite assemblages with any $\delta^{18}\text{O}$ value (above, below, or within those of the “common mantle”). The data in Figure 2 do not support this hypothesis. There is no known process that could operate at mantle temperatures to fractionate oxygen isotope ratios and form the high $\delta^{18}\text{O}$ shown in Figure 2 starting with a mantle-like value of 5.5‰ . Therefore, the high $\delta^{18}\text{O}$ values must have been acquired at low temperatures. In diamonds with eclogitic inclusions and in diamond-bearing eclogitic rocks, diamonds with low $\delta^{13}\text{C}$ are consistently associated with silicate minerals with high $\delta^{18}\text{O}$. We conclude, therefore, that this anticorrelation of oxygen and carbon isotopes provides strong new evidence demonstrating that the original source of carbon in these eclogitic diamonds is from subducted biogenic material.

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