Australian Journal of Earth Sciences (2012) **59**, (1135–1142)

Noble gas and carbon isotope ratios in Argyle diamonds, Western Australia: Evidence for a deeply subducted volatile component

M. HONDA[1], D. PHILLIPS[2], M. A. KENDRICK[2], M. K. GAGAN[1] AND W. R. TAYLOR[3]

[1]*Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia.*
[2]*School of Earth Sciences, The University of Melbourne, Parkville, Victoria 3010, Australia.*
[3]*Energy Metals Limited, West Perth, Western Australia 6005, Australia.*

The Argyle lamproite pipe of Western Australia contains diamonds formed at depths exceeding 150 km. We undertook noble gas and carbon isotope ratio ($\delta^{13}C$) analyses of three diamonds (likely of eclogitic paragenesis) from the Argyle lamproite to test for the possible presence of deeply subducted volatile components, and to further constrain the noble gas evolution of the Earth's mantle. The Argyle diamonds are characterised by mantle ^3He (with $^3He/^4He$ ratios of 0.79 R_A to 0.25 R_A, where R_A is the atmospheric $^3He/^4He$ ratio of 1.4×10^{-6}), small excess Ar and Xe isotope anomalies relative to atmospheric components, and $\delta^{13}C$ values of –11.6 to –10.2‰ VPDB. These observations indicate that noble gas and carbon isotopic compositions of the mantle where the Argyle diamonds formed, represent mixtures of an intrinsic mantle component with sedimentary and atmospheric components that may have been introduced through subduction processes.

KEY WORDS: diamond, noble gas, carbon, mantle evolution, continental lithosphere, subduction.

INTRODUCTION

One of the key research goals in noble gas geochemistry is to understand the structure of the Earth's mantle and to generate a coherent model of its evolution. In this regard, noble gas compositions of mid-ocean-ridge basalts (MORBs) and ocean island basalts (OIBs) have provided valuable information on the mantle (e.g. McDougall & Honda 1998). However, virtually all these data are from samples that are effectively of zero-age; therefore, they only provide information about the present composition of mantle noble gases. If noble gas measurements can be conducted on mantle-derived samples of different ages, this approach would allow further refinement of models concerning the structure of the mantle and mass transport within the mantle.

Diamonds have unique characteristics which make them potentially very useful time capsules of noble gases from the mantle: (1) most diamonds appear to be derived from 150 km to 200 km depth in the Earth, (2) diamonds cover a wide range of crystallisation ages (based on mineral inclusion data) of between 3.5 and 1.0 Ga (e.g. Richardson *et al.* 2004; Stachel & Harris 2008), and (3) diamonds are inert and are largely unaffected by the transporting kimberlite magma or subsequent interactions with the crust or atmosphere. Thus, diamonds provide a direct window into the ancient mantle. As part of a broader investigation into the evolution of the noble gases through time, Honda *et al.* (2004, 2011) studied the noble gas compositions of polycrystalline and framesite diamonds from the *ca* 235 Ma Jwaneng kimberlite pipe, Botswana. These studies showed that Jwaneng framesites are characterised by 'crustal' noble gases, whereas Jwaneng polycrystalline diamonds appear to contain noble gas isotopic compositions similar to the mantle source for MORBs. These data (particularly He, Ne and Ar isotopic results) also indicate that the Jwaneng polycrystalline diamonds may have formed in recent times, possibly close to the time of kimberlite emplacement at *ca* 235 Ma. In contrast, the Jwaneng framesites could be as old as gem diamonds dated previously (mineral inclusion ages of *ca* 2.9 Ga; Shirey *et al.* 2001). Furthermore, the data imply that the sub-continental mantle lithosphere in the region is characterised by heterogeneous noble gas isotopic compositions, and/or that these compositions evolved over time.

To complement the studies of Honda *et al.* (2004, 2011) on *ca* 235 Ma and 2.9 Ga Jwaneng diamonds, this paper presents new noble gas and carbon isotope ratio ($\delta^{13}C$) data for three single diamonds from the *ca* 1.2 Ga Argyle lamproite pipe, Western Australia. These new results are integrated with previous noble gas and $\delta^{13}C$ data available on diamonds from worldwide sources, to demonstrate a correlation between the noble gas and carbon isotopic compositions. Such a correlation has

*Corresponding author: masahiko.honda@anu.edu.au

ISSN 0812-0099 print/ISSN 1440-0952 online
http://dx.doi.org/10.1080/08120099.2012.741076

not been noted previously and provides new insight into the role of subduction-related processes in the genesis of diamonds.

ARGYLE DIAMONDS

The highly diamondiferous Argyle olivine lamproite pipe occurs within the East Kimberley region of Western Australia and represents the richest diamond pipe in the world. The pipe intrudes Paleo- to Mesoproterozoic meta-sediments (Atkinson *et al.* 1984) and comprises a series of volcaniclastic tuffs cut by olivine ± phlogopite dykes (Jaques *et al.* 1986). The lamproite has been dated by the Rb–Sr phlogopite method at 1178 ± 47 Ma (Pidgeon *et al.* 1989), which provides a minimum age for the entrained diamonds. The Argyle diamonds contain variable abundances of mineral inclusions, with eclogite-related minerals (e.g. orange garnet, pale green omphacite and colourless coesite) comprising more than 90% of the inclusion suite (Jaques *et al.* 1989a). Richardson (1986) reported a Sm–Nd age of 1580 ± 80 Ma for eclogite-related inclusions extracted from Argyle diamonds; this result provides the only current constraint on the timing of Argyle diamond formation.

Three single Argyle diamond samples were selected for noble gas analysis in this study. The diamonds are all approximately 5 mm in diameter and mainly amber–brown in colour. The diamond surfaces were characterised by the presence of hexagonal and trigonal resorption pits. The three Argyle diamonds contained numerous black inclusions, which are likely to be graphite and/or sulfides, but no diagnostic eclogite-related minerals were identified. The morphology of the diamonds is similar to that of the bulk of the commercial diamond population reported previously (Hall & Smith 1984; Jaques *et al.* 1989a). As more than 90% of Argyle diamonds are in eclogitic paragenesis (Hall & Smith 1984) and the carbon isotope values observed in the Argyle diamonds (in this study) are typical of eclogitic diamonds, we assume the Argyle diamonds investigated have an eclogitic paragenesis.

EXPERIMENTAL PROCEDURES

Noble gas analysis

The diamond samples were initially coarsely crushed into millimetre-size fragments. Clean diamond fragments were then hand-picked under a binocular microscope in preparation for noble gas analyses. These fragments were then leached with 7% HF, and ultrasonically cleaned in distilled water and analytical grade acetone and ethanol. Thereafter, the samples were wrapped in tin foil and loaded into a metal sample holder attached to the noble gas handling system for bake-out at 200°C for at least 12 h. After the bake-out, the tantalum crucible and molybdenum liner were outgassed at 2100°C for at least 3 h, to further reduce procedural hot blanks. The diamond samples were dropped into the molybdenum liner and graphitised at 2000°C to extract noble gases for analysis. The procedures for noble gas extraction, purification and mass spectrometric analysis are essentially the same as those described in Honda *et al.* (2004, 2011). Typical procedural hot blanks at 2000°C were $^{4}He = 2–6 \times 10^{-11}$, $^{20}Ne = 1–4 \times 10^{-12}$, $^{40}Ar = 4–9 \times 10^{-9}$, $^{84}Kr = 1 \times 10^{-13}$, and $^{132}Xe = 1 \times 10^{-13}$ cm^3 STP. Within uncertainties, noble gas isotopic ratios in blank runs were atmospheric.

Carbon isotopic analysis

After the noble gas analyses, the graphitised Argyle diamonds were retrieved from the molybdenum liner and analysed for carbon isotopes in the Earth Environment Stable Isotope Laboratory at RSES, ANU. It is assumed that carbon isotopes in the graphite residues are identical to those in original diamonds. This assumption is reasonable because under the reduced conditions of an UHV furnace, diamonds are quantitatively converted to graphite, and carbon is not lost as carbon dioxide. For each analysis, about 3 mg of graphite was combusted with excess CuO and Ag wire in a sealed and evacuated quartz tube for 6 h at 900°C (Sofer 1980; Engel & Maynard 1989). After cooling, water was removed from the evolved H_2O–CO_2 gas by freezing and then vapourising CO_2 in a double trap system using liquid nitrogen. The pure CO_2 was then analysed for carbon isotopes using a Multiport inlet coupled to a Finnigan MAT-251 stable-isotope ratio mass spectrometer. The isotopic data are reported in delta (δ) notation as per mil (‰) deviations relative to the Vienna Peedee Belemnite (V-PDB) standard, based on in-run measurements of the IAEA-CH6 standard ($\delta^{13}C = -10.45$‰) and NBS 21 graphite standard ($\delta^{13}C = -28.16$‰). Analytical precision for replicate measurements ($n = 4$) of $\delta^{13}C$ on the IAEA-CH6 standard was ± 0.04‰ (1σ).

RESULTS

Noble gases

Table 1 lists the noble gas elemental abundances of He, Ar, Kr, Xe and the $^{3}He/^{4}He$ and $^{40}Ar/^{36}Ar$ isotope ratios obtained from the three Argyle diamonds. The helium concentrations range from 3.8 to 8.7×10^{-6} cm^3 STP/g, which are slightly higher than those found in African polycrystalline diamonds, where He concentrations are in the range 10^{-7}–10^{-6} cm^3 STP/g (Burgess *et al.* 1998). There were detectable amounts of mantle ^{3}He in the Argyle diamonds. However, their $^{3}He/^{4}He$ ratios are less than the atmospheric value of 1.4×10^{-6} and range from 0.79 R_A to 0.25 R_A (where R_A is the atmospheric $^{3}He/^{4}He$ ratio). Thus, these samples do not contain significant amounts of primordial mantle-derived He, as observed in diamonds from some other localities (Ozima & Zashu 1988, 1991). The apparent enrichment of radiogenic helium, with respect to mantle He, in the Argyle diamonds will be discussed below. Neon yields from the Argyle diamonds were at or below the levels of the procedural hot blanks (1–4 × 10^{-12} cm^3 STP), and are not reported in Table 1. $^{38}Ar/^{36}Ar$ ratios of the Argyle diamonds are atmospheric within the uncertainties.

The $^{40}Ar/^{36}Ar$ ratios vary between 310 and 1147, slightly higher than the atmospheric value of 296, but significantly lower than $^{40}Ar/^{36}Ar$ ratios observed in MORB glasses, which exceed 20,000 in some cases (e.g. Graham 2002). As no potassium-bearing mineral inclusions were found in the Argyle diamonds of the present study, the $^{40}Ar/^{36}Ar$ ratios observed in the samples are interpreted as gases trapped when the diamonds were formed. Thus, the low $^{40}Ar/^{36}Ar$ ratios observed in the Argyle diamonds could be interpreted as an indication that atmospheric Ar has been transported into the diamond-forming region of the sub-continental mantle (see Discussion). Krypton isotopic ratios measured in the Argyle diamonds are atmospheric at the one sigma uncertainty level, and are not listed in Table 1. The xenon isotopic compositions of the three diamonds are characterised by slight xenon isotopic anomalies relative to atmospheric compositions (Table 2). Samples Argyle0 and Argyle1 show small levels of excess ^{129}Xe, relative to atmospheric Xe. The ^{129}Xe isotope anomalies observed in mantle-derived samples, including MORBs and some OIBs, are generally attributed to radioactive decay of an extinct nuclide ^{129}I (half-life of 16 Ma), once present in the Earth (e.g. Ozima & Podosek 2002). There are also small excesses in $^{131–136}Xe$, relative to atmospheric xenon in the Argyle diamonds. These excesses are attributed to spontaneous fission-derived xenon either from ^{238}U (half-life of 4468 Ma) or an extinct nuclide, ^{244}Pu (half-life of 82 Ma). Because the differences in the fission xenon spectrum produced from ^{238}U and ^{244}Pu are small, it is not possible to resolve whether the parent element was ^{238}U or ^{244}Pu (e.g. Graham 2002).

Carbon isotopes

Carbon isotopic values obtained from the three graphitised Argyle diamonds are listed in Table 3. The diamonds exhibit a narrow range in $\delta^{13}C$ values, ranging from –11.6 to –10.2‰. The $\delta^{13}C$ values for approximately 300 Argyle diamonds, for both eclogitic and peridotitic parageneses, are available in the literature (Jaques *et al.* 1989a; van Heerden *et al.* 1995). The majority of Argyle diamonds contain eclogite paragenesis inclusions, and show lower $\delta^{13}C$ values, mostly in the range –13 to –9‰, with a peak at –11 to –10‰, which is identical to the values reported for the current samples. In contrast, the $\delta^{13}C$ values for Argyle diamonds of peridotitic paragenesis are mostly –6 to –5‰ but range from –9 to –4‰ (Jaques *et al.* 1989a; van Heerden *et al.* 1995).

DISCUSSION

$^{40}Ar^*/^4He$ ratios

In Figure 1, $^{40}Ar^*/^4He$ ratios for three Argyle diamonds analysed in this study are plotted against R_A values, where $^{40}Ar^*$ is calculated using the following equation:

$$^{40}Ar^* = {}^{36}Ar_{observed} \times \left\{ \left(^{40}Ar/^{36}Ar\right)_{observed} - \left(^{40}Ar/^{36}Ar\right)_{atmospheric} (= 296) \right\} \quad (1)$$

In addition, we compiled $^{40}Ar^*/^4He$ ratios and R_A values from 63 diamond samples (including framesites

Table 1 Noble gas abundances and He and Ar isotopic compositions of Argyle single diamond stones[a].

Sample	^4He	$^3He/^4He$	R/R_a	^{36}Ar	$^{40}Ar/^{36}Ar$	^{84}Kr	^{132}Xe
Argyle0	3.78E–06	7.87E–07	0.56	1.95E–10	923.6	5.21E–12	2.00E–13
(0.267 g)	[7.6E–08]	[2.8E–08]	[0.02]	[5.0E–12]	[17.0]	[3.4E–13]	[1.0E–14]
Argyle1	8.66E–06	3.47E–07	0.25	5.40E–11	1,147.4	7.52E–13	2.22E–13
(0.164 g)	[1.8E–07]	[2.7E–08]	[0.02]	[3.6E–12]	[72.7]	[7.5E–13]	[3.4E–14]
Argyle2	5.93E–06	1.11E–06	0.79	3.96E–11	310.6	b.b.	6.28E–14
(0.222 g)	[1.2E–07]	[2.3E–08]	[0.02]	[6.8E–12]	[42.8]		[2.0E–14]
Air		1.40E–06	1.00		296		

[a] Noble gas contents are in cm^3 STP/g. Quoted errors, shown inside square brackets, are one standard deviation.
Ne abundances were below blank level of $^{20}Ne = 1–4 \times 10^{-12}$ cm^3 STP. $^{38}Ar/^{36}Ar$ and Kr isotopic ratios in the samples are atmospheric within uncertainties.
b.b., below procedural blank ($^{84}Kr = 10^{-13}$ cm^3 STP).
$R/R_a = (^3He/^4He)_{measured}/(^3He/^4He = 1.4 \times 10^{-6})_{air}$.

Table 2 Xe isotopic compositions of Argyle single diamond stones[a].

Sample	$^{129}Xe/^{132}Xe$	$^{130}Xe/^{132}Xe$	$^{131}Xe/^{132}Xe$	$^{134}Xe/^{132}Xe$	$^{136}Xe/^{132}Xe$
Argyle0	1.03	0.156	0.853	0.383	0.318
(0.267 g)	[0.02]	[0.005]	[0.02]	[0.011]	[0.005]
Argyle1	1.02	0.169	0.863	0.431	0.418
(0.164 g)	[0.036]	[0.019]	[0.037]	[0.025]	[0.048]
Argyle2	0.925	0.160	0.793	0.435	0.422
(0.222 g)	[0.107]	[0.037]	[0.062]	[0.079]	[0.089]
Air	0.983	0.151	0.789	0.388	0.329

[a] See footnotes for Table 1.

Table 3 Carbon isotopic values of graphitised Argyle diamonds.

Sample	δ^{13}C ‰ VPDB
Argyle0	−10.5
Argyle1	−10.2
Argyle2	−11.6

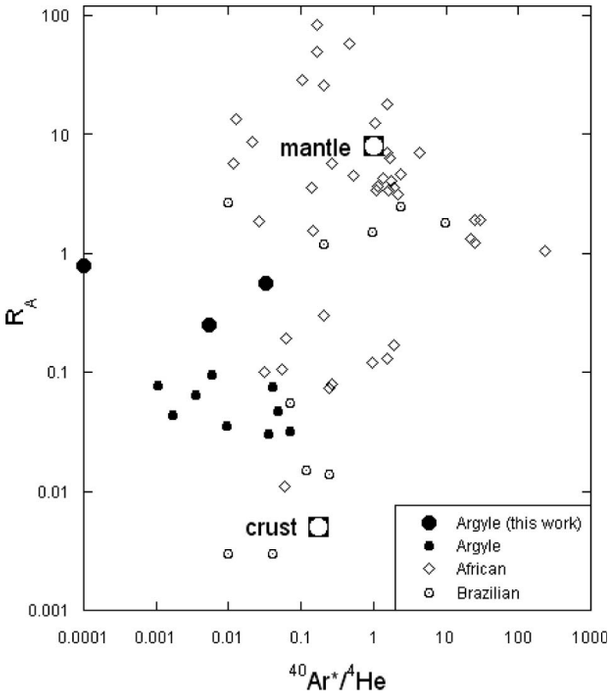

Figure 1 $^3He/^4He$ *vs* $^{40}Ar^*/^4He$ for 63 Argyle, African and Brazilian diamonds. The data sources are as follows: African diamonds (43) [De Beers Pool (1), Finsch (1), Jwaneng (10), Orapa (6), Zaire (3), Premier (4), Central African Republic (3), and unknown (15) (Ozima *et al.* 1983, 1985; Burgess *et al.* 1998)], Argyle diamonds (12) [(Ozima *et al.* 1985; Honda *et al.* 1987; McConville *et al.* 1991; this work)] and Brazilian diamonds (10) [Sao Luiz (5) and unknown (5) (Burgess *et al.* 1998)]. The average $^{40}Ar^*/^4He$ values for the mantle (=1.0) and the crust (=0.175) are from Ballentine & Burnard (2002).

and carbonados), from previous studies. These include 43 African diamonds (De Beers Pool (1), Finsch (1), Jwaneng (10), Orapa (6), Zaire (3), Premier (4), Central African Republic (3), and unknown (15); Ozima *et al.* 1983, 1985; Burgess *et al.* 1998), 12 Argyle diamonds (Ozima *et al.* 1985; Honda *et al.* 1987; McConville *et al.* 1991; this work) and 8 Brazilian diamonds (3 Sao Luiz and 5 unknown; Burgess *et al.* 1998). Because the diamonds in these studies are generally considered to be devoid of potassium and uranium-bearing mineral inclusions, $^{40}Ar^*$ and ^4He in the diamonds are interpreted as representing trapped components that formed by decay of ^{40}K, U and Th in the mantle and were incorporated into the diamonds when they crystallised. The average $^{40}Ar^*/^4He^*$ values for the present-day mantle (=1.0) and the crust (=0.18) are taken from Ballentine & Burnard (2002). The majority of the $^{40}Ar^*/^4He$ data for African and Brazilian diamonds scatter around the mantle and crustal values, regardless of their R_A compositions (Figure 1). However, the scatter from the mantle and crustal reference values could reflect the variable K/(Th+U) composition of the lithospheric mantle or imply that some of the diamonds contain radiogenic ^{40}Ar and ^4He produced from *in situ* decay of ^{40}K and U and Th in fluid/melt/mineral inclusions in the diamonds.

In the case of the Argyle diamonds (Ozima *et al.* 1985; Honda *et al.* 1987; McConville *et al.* 1991; this work), the observed $^{40}Ar^*/^4He$ ratios are systematically lower than the mantle and crustal values (Figure 1). Thus, the $^{40}Ar^*/^4He$ systematics indicate an enrichment in $^4He^*$ relative to $^{40}Ar^*$, for the Argyle diamonds; in the following section we examine possible causes for this enrichment.

Enrichment of $^4He^*$ in Argyle diamonds

The apparent enrichment of $^4He^*$ relative to $^{40}Ar^*$ in the Argyle diamonds has three possible explanations: (i) the source region was enriched in U and Th and had an anomalously low K/U ratio for the mantle; in this scenario $^4He^*$ observed in the Argyle diamonds represents a trapped component; (ii) helium atoms (α-particles) produced from decay of U and Th, in the lamproite matrix were implanted into the diamond outer surfaces, during the prolonged crustal residence (*ca* 1.2 Ga) in the Argyle lamproite pipe; or (iii) radiogenic $^4He^*$ was produced within the diamonds by *in situ* decay of U and Th.

We now consider each of these suggestions in turn. A trapped radiogenic ^4He component in the Argyle diamonds should be accompanied by nucleogenic ^{21}Ne, which is produced in the mantle via the nuclear reaction $^{18}O(\alpha,n)^{21}Ne$, with α-particles derived from decay of uranium and thorium. The production ratio of nucleogenic $^{21}Ne^*$ relative to radiogenic $^4He^*$ in the Earth's mantle is well constrained, at $\sim 4.5 \times 10^{-8}$ (Yatsevich & Honda 1997). As diamonds are essentially oxygen-free, any nucleogenic ^{21}Ne observed in diamonds would be attributed to a trapped component that accumulated in the mantle. For example, the amount of ^4He released from sample Argyle1 (0.164 g) is 1.4×10^{-6} cm^3 STP; if all the ^4He is assumed to represent a trapped component, the corresponding nucleogenic $^{21}Ne^*$ expected in the sample is 6.3×10^{-14} cm^3 STP. The amount of ^{21}Ne measured in hot (2000°C) blanks run was calculated to be 3×10^{-15} cm^3 STP, on the basis of the quantity of ^{20}Ne ($=1 \times 10^{-12}$ cm^3 STP) observed in the blank run prior to analysis of sample Argyle1 (Table 1). The noise level of the Daly detector on the VG5400 noble gas mass spectrometer used for the present study is equivalent to 1×10^{-14} cm^3 STP. Therefore, if trapped nucleogenic ^{21}Ne existed in sample Argyle1, it should have been detected during the mass spectrometric analyses. The lack of detectable nucleogenic ^{21}Ne in the sample strongly suggests that the ^4He observed in the Argyle diamonds does not represent a trapped mantle component.

The high abundances of $^4He^*$ could also be explained by alpha-implantation from external U and Th sources

(e.g. the sandy tuff volcaniclastic lithologies in the Argyle lamproite (Jaques *et al.* 1986, 1989b)). McConville *et al.* (1991) calculated implanted ^{4}He contents as high as 1×10^{-5} cm^3 STP/g for a 1 mm diameter diamond contained in the Argyle lamproite (which has average U and Th contents of 12 and 2.8 ppm, respectively) for 1178 Ma (Jaques *et al.* 1989b). Thus, small (<1 mm) diamonds could contain an abundance of implanted ^{4}He that is comparable to the ^{4}He concentrations measured in the current Argyle diamonds (3.8–8.7 $\times 10^{-6}$ cm^3 STP/g; see Table 1). However, ^{4}He implantation only affects the outer 30 μm of diamonds (Shelkov *et al.* 1998); thus the amount of implanted ^{4}He is strongly dependent on sample size or surface:volume ratio. The relatively large size of the current Argyle samples (i.e. ~5 mm in diameter) together with the lack of surficial green coats or spots (indicative of significant α-particle damage and hence ^{4}He implantation) suggests very limited contributions from implantation. Furthermore, Sumino *et al.* (2011) observed implanted recoiling nucleogenic Ne (produced in the mantle) in micro diamonds from the Kokchetav massif in northern Kazakhstan. The ratio of the recoiling nucleogenic ^{21}Ne to implanted radiogenic ^{4}He in the Kokchetav diamonds was found to be similar to the ^{21}Ne/^{4}He production ratio in the mantle. This observation implies that a significant fraction of nucleogenic ^{21}Ne could be implanted onto diamond surfaces. The lack of detectable nucleogenic ^{21}Ne in the Argyle diamonds, as noted in the previous paragraph, suggests that the majority of ^{4}He is not due to implantation processes.

In order to evaluate the third alternative (*in situ* radiogenic ^{4}He*), we first calculate the upper limit for ^{4}He amounts trapped in the diamonds when they formed, based on the detection limit of ^{21}Ne ($= 1 \times 10^{-14}$ cm^3 STP) of the mass spectrometer and the nucleogenic ^{21}Ne*/^{4}He* production ratio in the Earth's mantle ($= 4.5 \times 10^{-8}$). The expected amount of ^{4}He corresponds to 2.2×10^{-7} cm^3 STP, and this amount is subtracted from the total ^{4}He amounts observed in the samples. On this basis, 78, 84 and 83% of the total ^{4}He observed in samples Argyle0, Argyle1 and Argyle2, respectively (Table 1), are estimated to be *in situ* products. Furthermore, based on the amounts of ^{3}He amounts observed, the lower limits of trapped (mantle) ^{3}He/^{4}He ratios are calculated to be 2.6, 1.6 and 4.7 R_A, respectively. The *in situ* produced radiogenic ^{4}He contents of the Argyle diamonds (average: 5.1×10^{-6} cm^3 STP/g) could be generated from decay of 17 ppb U, over a period of 1178 Ma (based on the emplacement age of the Argyle lamproite; Pidgeon *et al.* 1989) and a U/Th ratio of 4. Alternatively, the *in situ* produced radiogenic ^{4}He could have been produced from a U concentration of 12 ppb if the diamonds are 1580 Ma in age (Sm–Nd data for Argyle eclogitic diamonds; Richardson 1986). There are few constraints on the concentration of U in Argyle (and other) diamonds. Fardy & Farrar (1992) were unable to detect U in six Argyle diamonds using the neutron activation technique, which has a detection limit of ~30 ppb U. However, Rege *et al.* (2008) measured concentrations of 10 to 480 ppb U and 20 to 1020 ppb Th in 11 polycrystalline diamond samples from southern Africa, utilising a LAM-ICPMS. The range of U contents in diamonds indicates that a significant fraction of the ^{4}He in the Argyle diamonds could be radiogenic ^{4}He*, produced from *in situ* decay of U and Th. Furthermore, these calculations illustrate that in the future, combined analyses of U–Th and He/Ne on the same diamonds have the potential to constrain minimum formation ages for Argyle (and other) diamonds via the U–Th/He dating technique.

In conclusion, the apparent enrichment of ^{4}He* in the three Argyle diamonds is most likely due to the addition of radiogenic ^{4}He produced from the *in situ* decay of U and Th within the diamonds. Thus, the ^{3}He/^{4}He ratios observed in Argyle diamonds (Ozima *et al.* 1985; Honda *et al.* 1987; McConville *et al.* 1991; this work) are interpreted as lower limits for the trapped helium isotope components.

He *vs* C in diamonds

In Figure 2, ^{3}He/^{4}He ratios are plotted against δ^{13}C values observed in the three Argyle diamonds (Argyle0, Argyle1 and Argyle2) analysed in this study. In addition, we compiled ^{3}He/^{4}He ratio and δ^{13}C data from 63 diamond samples (including framesites and carbonados), from previous studies. The Argyle diamonds are characterised by similar δ^{13}C values of approximately –11‰, and R_A values ranging between 0.8 and 0.03. Thus, it appears that the Argyle diamonds are more enriched in radiogenic ^{4}He (^{4}He*) for the same δ^{13}C values, compared with diamonds from other localities. As discussed above, we attribute the enrichment of ^{4}He* in the Argyle diamonds to the addition of *in situ* radiogenic ^{4}He produced within the diamonds. Calculated lower limits for (trapped) ^{3}He/^{4}He ratios in samples Argyle0, Argyle1 and Argyle2 are also plotted in Figure 2.

For comparison, the ^{3}He/^{4}He (R_A) and δ^{13}C values representative of the upper mantle at different times in Earth history (26.6 and 8.1 R_A; $\delta^{13}C = -6$‰), sediments (0.005 R_A; $\delta^{13}C = -26$‰) and altered oceanic crust (0.005 R_A; $\delta^{13}C = 0$‰) are added to Figure 2. The He isotopic ratio of 8.1 R_A is an average value for MORBs (Burnard *et al.* 2002), and thus represents a present-day value for the upper mantle. The R_A value of 26.6 at 1.6 Ga (eclogitic inclusion age for Argyle diamonds; Richardson 1986) was calculated for open system evolution within the MORB environment, based on the model developed by Seta *et al.* (2001). In this model, the noble gases and their parent elements (K, U and Th) are assumed to have been transferred continuously from mantle reservoirs to the crust and atmosphere, with mass flows decreasing exponentially with time to simulate vigorous degassing at an early stage of Earth history. The R_A value of 0.005 used for crustal components (sediments or altered oceanic crust) is an average value suggested by Ballentine & Burnard (2002). The δ^{13}C value of –6‰ given for the mantle is based on an average value for MORB samples (Deines 2002). In contrast, subducted crust has variable C isotope values ranging from δ^{13}C of –26‰ for organic-rich sediments (Schidlowski 1988) to 0‰ for altered ocean crust or marine carbonate (Schidlowski 1988).

As previously recognised by Honda *et al.* (1987) and Burgess *et al.* (1998), there is a crude positive correlation between $^3He/^4He$ (R_A) and $\delta^{13}C$ in many diamonds. In Figure 2, we plot binary mixing curves between helium and carbon isotope end-members: mantle (27 R_A; $\delta^{13}C = -6‰$) and subducted sediment (0.005 R_A; $\delta^{13}C = -26‰$), with variable '*r*' values, where $r = (^{12}C/^4He)_{mantle}/(^{12}C/^4He)_{sediment}$. The helium and carbon isotopic data from African and Brazilian diamonds cover the entire range between the two end-members (intrinsic mantle and subducted sediment). Provided that the He represents a trapped component (discussed more fully above), the carbon and helium isotopic results from African and Brazilian diamonds can be explained by variable mixing between (upper) mantle and subducted sedimentary components. This observation implies that the low $^3He/^4He$ ratios (R_A) and ^{13}C depleted $\delta^{13}C$ values (relative to mantle values) observed in diamonds from Africa, Brazil and Argyle (this study) result from the addition of subducted sedimentary material that was transported into the diamond-forming region of the subcontinental mantle lithosphere (e.g. Navon 1991; Wyllie 1995). It should be noted that the He results from the previous studies plotted in Figure 2, have not been examined in detail for the existence of *in situ* produced radiogenic ^4He. Thus, the previous He isotope data can also be interpreted as minimum trapped $^3He/^4He$ ratios. Therefore, if *in situ* produced radiogenic ^4He is subtracted from each datum, the mixing trends between helium and carbon isotopes in the figure would be better defined. In this interpretation, subducted sedimentary helium (enriched in radiogenic ^4He produced from U and Th) and subducted carbon must have mixed into the fluids responsible for diamond crystallisation in many parts of the Earth's mantle (Figure 2). In the most extreme cases, such as some of Brazilian diamonds, the subducted C and He totally overwhelmed the mantle signatures, and lead to the formation of diamonds with C and He isotope compositions similar to organic-rich sediments (Figure 2).

However, if subduction of marine carbonate with $\delta^{13}C$ values of ~0‰ (Schidlowski 1988) played a significant role in supplying carbon for diamond formation (e.g. van Heerden *et al.* 1995; Stachel *et al.* 2009), the end-member for subducted carbon would be more enriched in ^{13}C than –26‰, the value for organic-rich sediments. The potentially variable carbon isotope values of subducted carbon (between –26 and 0‰) means that the relative proportions of mantle and crustal carbon are poorly constrained in these diamonds. In the most extreme scenario, the $\delta^{13}C$ values of ~–11‰, observed in Argyle eclogitic diamonds, could be explained by mixing subducted marine carbonate ($\delta^{13}C = 0‰$) and organic carbon ($\delta^{13}C = -26‰$), with no input of mantle carbon required.

The helium isotope data provide additional constraints on the origin of diamond forming volatiles, because the diamonds have $^3He/^4He$ ratios intermediate between that of sediments (average $^3He/^4He$ value of ~0.005 R_A) and the Proterozoic mantle ($^3He/^4He$ ~ 27 R_A; Figure 2). Thus, although there are significant uncertainties in defining the carbon isotope values of the subducted end-member, the combined He and C isotope systematics provide strong evidence that both mantle and subducted carbon components are present in all diamonds (Figure 2).

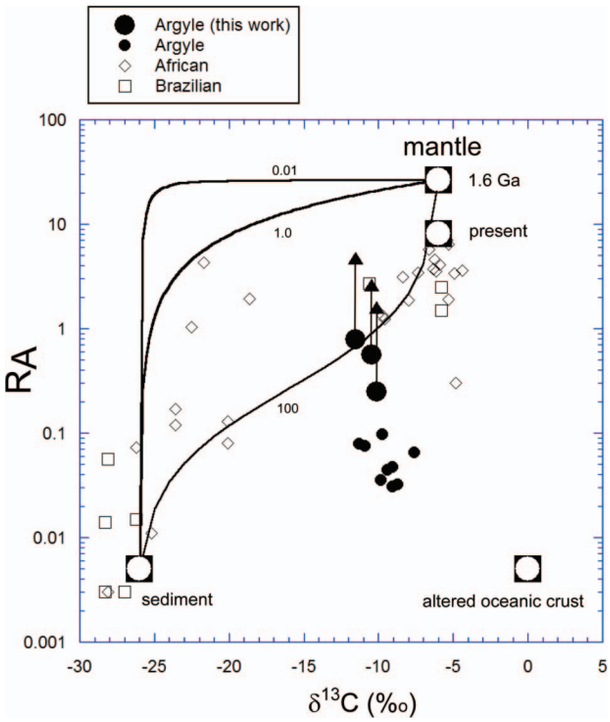

Figure 2 $^3He/^4He$ *vs* $\delta^{13}C$ for Argyle, African and Brazilian diamonds. The data sources are as described in Figure 1 caption. For Argyle diamonds from the present study, inferred lower limits of mantle $^3He/^4He$ ratios are plotted, in addition to the observed ratios. Mixing curves are calculated for two end-members: mantle at 1.6 Ga (26.6 R_A; $\delta^{13}C = -6‰$) and sedimentary material (0.005 R_A; $\delta^{13}C = -26‰$), with variable '*r*' values, where $r = (^{12}C/^4He)_{mantle}/(^{12}C/^4He)_{sedimentary}$, as indicated in the diagram. The majority of data from African and Brazilian diamonds, as well as those from the Argyle diamonds (with inferred lower limits of mantle He ratios), are located between the mantle and *organic-rich* sedimentary components, implying mixing. For comparison purposes, an end-member for altered oceanic crust (0.005 R_A; $\delta^{13}C = 0‰$) is also plotted.

Noble gas abundances in Argyle diamonds – subduction of atmospheric gases

As discussed above, it is possible that significant quantities of recycled sedimentary carbon were transported into the Argyle diamond-forming region in subcontinental mantle, by subduction-related processes. In this regard, it is important to note that marine sediments can contain high abundances of atmospheric noble gases (e.g. Matsuda & Nagao 1986; Staudacher & Allègre 1988). Atmospheric noble gases have variable elemental abundance ratios in sedimentary rocks, probably reflecting fractionation of noble gases between sedimentary minerals and fluid phases in the depositional and diagenetic environments. Kendrick *et al.* (2011) recently demonstrated that noble gases are incorporated into hydrous minerals, like serpentine,

and follow a similar subduction pathway as other volatiles. Furthermore, this study suggested that, because noble gases are lost from the slab by advection in slab-derived fluids (not diffusion), noble gas abundance ratios are not strongly fractionated during subduction. Therefore, it may be significant that the atmospheric noble gases in the Argyle diamonds have a similar abundance pattern to that reported for marine sediments (Figure 3).

In Figure 3, the noble gas elemental abundances observed in the Argyle diamonds are plotted as F values, where

$$F = \left(\mathrm{X}/^{36}\mathrm{Ar}\right)_{\mathrm{observed}} / \left(\mathrm{X}/^{36}\mathrm{Ar}\right)_{\mathrm{atmospheric}} \quad (2)$$

and X = ^{22}Ne, ^{84}Kr or ^{132}Xe. This diagram demonstrates that the noble gases observed in the Argyle diamonds are enriched in the heavier noble gases (Xe and to lesser extent Kr), and depleted in Ne (shown as upper limits), relative to atmospheric composition. This pattern is similar to that observed in marine sediments (e.g., Matsuda & Nagao 1986; Staudacher & Allègre 1988). It is also noteworthy that the current Argyle diamonds do not show clear evidence of mantle-like noble gas isotopic signatures, such as the high ^{40}Ar/^{36}Ar ratios and large ^{129}Xe/^{132}Xe isotope anomalies observed in MORB glasses (e.g. Graham 2002). This implies that the mantle noble gas signatures of the Argyle eclogitic diamonds were significantly diluted by subducted atmospheric and crustal noble gases.

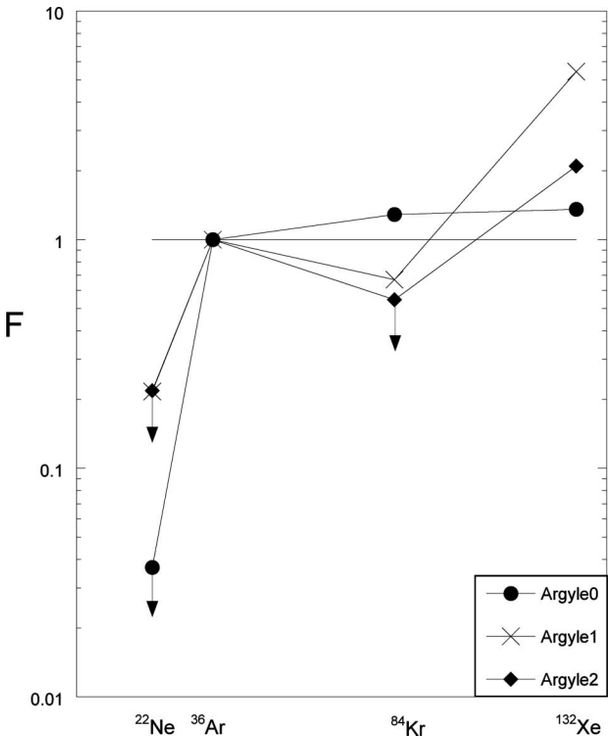

Figure 3 F plots for the three Argyle diamonds from this study, where $F = (\mathrm{X_i}/^{36}\mathrm{Ar})_{\mathrm{sample}}/(\mathrm{X_i}/^{36}\mathrm{Ar})_{\mathrm{atmospheric}}$. Upper limits were calculated for Ne in all samples and Kr in sample Argyle2, where gases released were below blank levels; calculations were based on blank amounts divided by sample weights (see Table 1). Uncertainties for F_{Kr} and F_{Xe} are 7 and 15–50%, respectively. Noble gas elemental abundances, relative to ^{36}Ar and normalised to atmospheric values, in the Argyle diamonds, show depletion of Ne and enrichment of Xe. This implies that elementally fractionated atmospheric noble gases may have been subducted into the mantle where the diamonds formed. Elemental fractionation could be caused by the mechanisms responsible for noble gas subduction (e.g. breakdown of serpentinites; Kendrick *et al.* 2011).

CONCLUSIONS

(1) Noble gas elemental and isotope abundances and carbon isotope ratios have been measured on three diamonds from the Argyle lamproite, Western Australia. The analyses show that the Argyle diamonds contain mantle ^{3}He, but only slightly elevated ^{40}Ar/^{36}Ar ratios and xenon isotopic anomalies, relative to atmospheric compositions. These observations indicate that the mantle noble gases have been diluted by atmospheric and crustal noble gases in the region where the Argyle diamonds formed.

(2) Carbon isotope ratios measured on the graphitised Argyle diamonds range from –11.6 to –10.2‰, and are within the range found for most Argyle diamonds of eclogitic paragenesis (Jaques *et al.* 1989a; van Heerden *et al.* 1995).

(3) The apparent ^{4}He enrichment in the Argyle diamonds is attributed to *in situ* radiogenic ^{4}He produced from U and Th within the diamonds.

(4) Helium (after correction for *in situ* produced radiogenic ^{4}He) and carbon isotope values observed in the Argyle diamonds are compared with those from African (De Beers Pool, Finsch, Jwaneng, Orapa, Zaire, Premier, Central African Republic, and unknown) and Brazilian (Sao Luiz and unknown) diamonds. Helium and carbon isotope data form general mixing trends between mantle and subducted sedimentary end-member components (Figure 2) that are variably altered by *in situ* production of radiogenic ^{4}He.

(5) These data support recent results from analyses of subducted serpentinites, and imply that in addition to subduction of atmospheric noble gases, sedimentary helium may be subducted to the mantle depths of at least 150–200 km in the region where the Argyle diamonds formed. These subducted noble gases were mixed with mantle noble gases, to produce the noble gas systematics observed in the Argyle diamonds.

ACKNOWLEDGEMENTS

Rong Shi participated in the project in its early stage. Igor Yatsevich and Joan Cowley are thanked for technical assistance. This work was partially supported by the ARC Discovery Program and also by the donation made by Ms Lai Ho Seet. Constructive comments from

Lynton Jaques and official reviews by Fred Jourdan and an anonymous reviewer are appreciated for improving the manuscript.

REFERENCES

ATKINSON W. J., HUGHES F. E. & SMITH C. B. 1984. Kimberlites I: kimberlites and related rocks. *In*: Kornprobst J. ed. *Kimberlites I: Kimberlites and related rocks,* pp. 195–224. Amsterdam: Elsevier.

BALLENTINE C. J. & BURNARD P. G. 2002. Production, release and transport of noble gases in the continental crust. *In*: Porcelli D. P., Ballentine C. J. & Wieler R. eds. *Noble gases in geochemistry and cosmochemistry,* pp. 481–538. Mineralogical Society of America, Washington, DC.

BURGESS R., JOHNSON L. H., MATTEY D. P., HARRIS J. W. & TURNER G. 1998. He, Ar and C isotopes in coated and polycrystalline diamonds. *Chemical Geology* **146**, 205–217.

BURNARD P. G., GRAHAM D. W. & FARLEY K. A. 2002. Mechanisms of magmatic gas loss along the Southeast Indian Ridge and the Amsterdam–St. Paul Plateau, *Earth Planetary Science Letters* **203**, 131–148.

DEINES P. 2002. The carbon isotope geochemistry of mantle xenoliths. *Earth-Science Reviews* **58**, 247–278.

ENGEL M. H. & MAYNARD R. J. 1989. Preparation of organic matter for stable carbon isotope determination by sealed tube combustion: a cautionary note. *Analytical Chemistry* **61**, 1996–1998.

FARDY J. J. & FARRAR Y. J. 1992. Trace-element analysis of Argyle diamonds using instrumental neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry* **164**, 337–345.

GRAHAM D. W. 2002. Noble gas isotope geochemistry of mid-ocean ridge and ocean island basalts: Characterization of mantle source reservoirs. *In*: Porcelli D. P., Ballentine C. J. & Wieler R. eds. *Noble gases in geochemistry and cosmochemistry,* pp. 247–317. Mineralogical Society of America, Washington, D. C.

HALL A. E. & SMITH C. B. 1984. Lamproite Diamonds: Are They Different? *In*: Glover J. E. & Harris P. G. eds. *Kimberlite occurrence and origin: a basis for conceptual models in exploration,* pp. 167–212. Geology Department and University Extension, University of Western Australia.

HONDA M., PHILLIPS D., HARRIS J. W. & MATSUMOTO T. 2011. He, Ne and Ar in peridotitic and eclogitic paragenesis diamonds from the Jwaneng kimberlite, Botswana – Implications for mantle evolution and diamond formation ages. *Earth and Planetary Science Letters* **301**, 43–51.

HONDA M., PHILLIPS D., HARRIS J. W. & YATSEVICH I. 2004. Unusual noble gas compositions in polycrystalline diamonds: preliminary results from the Jwaneng kimberlite, Botswana. *Chemical Geology* **203**, 347–358.

HONDA M., REYNOLDS J. H., ROEDDER E. & EPSTEIN S. 1987. Noble gases in diamonds: occurrences of solarlike helium and neon. *Journal of Geophysical Research* **92**, 12507–12521.

JAQUES A. L., HAGGERTY S. E., LUCAS H. & BOXER G. L. 1989a. Composition of crystalline inclusions and C-isotopic composition of Argyle and Ellendale diamonds. *Geological Society of Australia Special Publication* **14**, 966–989.

JAQUES A. L., LEWIS J. D. & SMITH C. B. 1986. The kimberlites and lamproites of Western Australia. *Geological Survey of Western Australia Bulletin* **132**, 268 pp.

JAQUES A. L., SUN S-S. & CHAPPELL B. W. 1989b. Geochemistry of the Argyle (AK1) lamproite pipe, Western Australia. *Geological Society of Australia Special Publication* **14**, 170–188.

KENDRICK M. A., SCAMBELLURI M., HONDA M. & PHILLIPS D. 2011. High abundances of noble gas and chlorine delivered to the mantle by serpentinite subduction. *Nature Geoscience* **4**, 807–812.

MATSUDA J. & NAGAO K. 1986. Noble gas abundances in a deep-sea sediment core from eastern equatorial Pacific. *Geochemistry Journal* **20**, 71–80.

MCCONVILLE P., REYNOLDS J. H., EPSTEIN S. & ROEDDER E. 1991. Implanted ^{3}He, ^{4}He, and Xe in further studies of diamonds from Western Australia, *Geochimica et Cosmochimica Acta* **55**, 1977–1989.

MCDOUGALL I. & HONDA M. 1998. Primordial solar noble-gas component in the Earth: consequences for the origin and evolution of the Earth and its atmosphere. *In*: Jackson I. ed. *The Earth's mantle: composition, structure, and evolution,* pp. 159–187. Cambridge: Cambridge University Press.

NAVON O. 1991. High internal pressures in diamond fluid inclusions determined by infrared absorption. *Nature* **353**, 746–748.

OZIMA M. & PODOSEK F. A. 2002. *Noble gas geochemistry*. Cambridge: Cambridge University Press.

OZIMA M. & ZASHU S. 1988. Solar-type Ne in Zaire cubic diamonds. *Geochimica Cosmochimica Acta* **52**, 19–25.

OZIMA M. & ZASHU S. 1991. Noble gas state of the ancient mantle as deduced from noble gases in coated diamonds. *Earth Planetary Science Letters* **105**, pp. 13–27.

OZIMA M., ZASHU S., MATTEY D. P. & PILLINGER C. T. 1985 Helium, argon and carbon isotopic composition in diamonds and their implications in mantle evolution. *Geochemical Journal* **19**, 127–134.

OZIMA M., ZASHU S. & NITOH O. 1983. ^{3}He/^{4}He ratio, noble gas abundance and K–Ar dating of diamonds—An attempt to search for the records of early terrestrial history. *Geochemica Cosmochimica Acta* **37**, 2217–2214.

PIDGEON R. T., SMITH C. B. & FANNING M. C. 1989. Kimberlite and lamproite emplacement ages in Western Australia. *Geological Society Australia Special Publication* **14**, 369–381.

REGE S., GRIFFIN W. L., KURAT G., JACKSON S. E., PEARSON N. J. & O'REILLY S. Y. 2008. Trace-element geochemistry of diamondite: Crystallisation of diamond from kimberlite–carbonatite melts. *Lithos* **106**, 39–54.

RICHARDSON S. H. 1986. Latter-day origin of diamonds of eclogitic paragenesis. *Nature* **322**, 623–626.

RICHARDSON S. H., SHIREY S. B. & HARRIS J. W. 2004. Episodic diamond genesis at Jwaneng, Botswana, and implications for Kaapvaal craton evolution. *Lithos* **77**, 143–154.

SCHIDLOWSKI M. 1988. A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature* **333**, 313–318.

SETA A., MATSUMOTO T. & MATSUDA J. 2001. Concurrent evolution of He-3/He-4 ratio in the Earth's mantle reservoirs for the first 2 Ga. *Earth and Planetary Science Letters* **188**, 211–219.

SHELKOV D. A., VERCHOVSKY A. B., MILLEDGE H. J. & PILLINGER C. T. 1998. The radial distribution of implanted and trapped ^{4}He in single diamond crystals and implications for the origin of carbonado. *Chemical Geology* **149**, 109–116.

SHIREY S. B., CARLSON R. W., RICHARDSON S. H., MENZIES A. H., GURNEY J. J., PEARSON D. G., HARRIS J. W. & WIECHERT U. 2001. Archean emplacement of eclogitic components into the lithospheric mantle during formation of the Kaapvaal Craton. *Geophysical Research Letters* **28**, 2509–2512.

SOFER Z. 1980. Preparation of carbon dioxide for stable carbon isotope analysis of petroleum fractions. *Analytical Chemistry* **52**, 1389–1391.

STACHEL T. & HARRIS J. W. 2008. The origin of cratonic diamonds—Constraints from mineral inclusions. *Ore Geology Reviews* **34**, 5–32.

STACHEL T., HARRIS J. W. & MUEHLENBACHS K. 2009. Sources of carbon in inclusion bearing diamonds. *Lithos* **112**, Supplement 2, 625–637.

STAUDACHER T. & ALLÈGRE C. J. 1988 Recycling of oceanic crust and sediments: the noble gas subduction barrier. *Earth and Planetary Science Letters* **89**, 173–183.

SUMINO H., DOBRZHINETSKAYA L. F., BURGESS R. & KAGI H. 2011. Deep-mantle-derived noble gases in metamorphic diamonds from the Kokchetav massif, Kazakhstan. *Earth and Planetary Science Letters* **307**, 439–449.

VAN HEERDEN L. A., BOYD S. R., MILLEDGE H. J., PILLINGER C. T. 1995. The carbon and nitrogen-isotope characteristics of the Argyle and Ellendale Diamonds, Western Australia. *International Geology Review* **37**, 39–50.

WYLLIE P. J. 1995. Experimental petrology of upper mantle materials, processes and products. *Journal of Geodynamics* **20**, 429–468.

YATSEVICH I. & HONDA M. 1997. Production of nucleogenic neon in the Earth from natural radioactive decay. *Journal of Geophysical Research* **102**, 10291–10298.

Received 5 December 2011; accepted 19 September 2012