Abstract

In order to better investigate the compositions and the origins of fluids associated with diamond growth, we have carried-out combined noble gas (He and Ar), C and N isotope, K, Ca and halogen (Cl, Br, I) determinations on fragments of individual microinclusion-bearing diamonds from the Panda kimberlite, North West Territories, Canada. The fluid concentrations of halogens and noble gases in Panda diamonds are enriched by several orders of magnitude over typical upper mantle abundances. However, noble gas, C and N isotopic ratios (\(3^4\text{He}/4^4\text{He} = 4–6\, \text{Ra}, \, 4^0\text{Ar}/3^6\text{Ar} = 20,000–30,000, \, \delta^{13}\text{C} = -4.5\%_{oo}\) to \(-6.9\%_{oo}\) and \(\delta^{15}\text{N} = -1.2\%_{oo}\) to \(-8.8\%_{oo}\)) are within the worldwide range determined for fibrous diamonds and similar to the mid ocean ridge basalt (MORB) source value. The high \(3^6\text{Ar}\) content of the diamonds (>\(1 \times 10^{-9}\, \text{cm}^3/\text{g}\)) is at least an order of magnitude higher than any previously reported mantle sample and enables the \(3^6\text{Ar}\) content of the subcontinental lithospheric mantle to be estimated at \(<0.6 \times 10^{-12}\, \text{cm}^3/\text{g}\), again similar to estimates for the MORB source. Three fluid types distinguished on the basis of Ca–K–Cl compositions are consistent with carbonatitic, silicic and saline end-members identified in previous studies of diamonds from worldwide sources. These fluid end-members also have distinct halogen ratios (Br/Cl and I/Cl). The role of subducted seawater-derived halogens, originally invoked to explain some of the halogen ratio variations in diamonds, is not considered an essential component in the formation of the fluids. In contrast, it is considered that large halogen fractionation of a primitive mantle ratio occurs during fluid–melt partitioning in forming silicic fluids, and during separation of an immiscible saline fluid.

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1. INTRODUCTION

Microinclusions in fibrous diamonds provide unique samples of deep fluids from the mantle. Investigation of the isotopic and chemical composition of these fluids is useful for several reasons. First, they improve our understanding of the processes of diamond growth and help elucidate the composition of the upper mantle environment in which diamonds originate (Navon et al., 1988; Navon, 1999; Schrauder and Navon, 1994; Izraeli et al., 2001; Klein-BenDavid et al., 2004, 2006, 2007; Zedgenizov et al., 2004, 2007; Tomlinson et al., 2006). Secondly, detailed investigation of the microinclusion fluid compositions in diamonds that formed during different epochs and in different geographical regions of the world, provides an opportunity to trace the time-resolved, global evolution of volatile elements in the mantle (Johnson et al., 2000; Burgess et al., 2002; Klein-BenDavid et al., 2007). Finally, fluids trapped in diamonds are potentially the best samples to assess to what extent mantle processes (e.g. metasomatism) are able to
produce large chemical (and time-integrated isotopic) variations and to test whether volatiles derived from the subducted crust are able to penetrate to the base of continental cratons (e.g. Richardson et al., 2001; Cartigny, 2005).

Previous investigations have revealed that the isotopic composition of volatile elements such as C, N, He and Ar, in microinclusion-bearing diamonds from Africa (Jwaneng mine, Botswana and from the Democratic Republic of Congo), Siberia (Alkhal mine, Yakutia, Russia) and Canada (Ekati mine, Lac de Gras, North West Territories, Canada) are similar to present-day upper mantle values (Boyd et al., 1992; Cartigny et al., 2003; Johnson et al., 2000; Burgess et al., 2002; Wada and Matsuda, 1998). In contrast, the chemical composition of the fluids in diamonds are highly variable with three end-members identified (summarised in Klein-BenDavid et al., 2007) as follows: (1) carbonatitic fluid rich in carbonate, K, Ca, Fe and Mg; (2) silicic fluid containing water, Al and K; and (3) saline fluid containing high concentrations of Cl and K. Mixtures of carbonatitic and silicic fluids have been found in microinclusions in diamonds from southern Africa, Brazil and Siberia (Navon et al., 1988; Schrauder and Navon, 1994; Shiryaev et al., 2005), and in Canadian diamonds from the Diavik (Klein-BenDavid et al., 2006, 2007) and Panda mines (Tomlinson et al., 2006). Saline fluids containing high concentrations of Cl (up to 40 wt.% and K were first documented in cloudy diamonds from Koffiefontein, South Africa (Izraeli et al., 2001). Subsequently, Klein-BenDavid et al. (2004, 2006, 2007) and Tomlinson et al. (2006) have shown that saline fluids are present in microinclusion-bearing diamonds from Diavik and Panda, Canada, where they occur mixed with carbonatitic fluids. The absence of co-existing saline and silicic fluid microinclusions suggests that these two fluid types may be immiscible during diamond growth (Perchuk et al., 2002; Navon et al., 2003; Klein-BenDavid et al., 2004, 2006, 2007), which is supported by recent experimental work (Safonov et al., 2007). The saline fluid is associated with both peridotitic and eclogitic mineral inclusions in diamonds from Koffiefontein (Izraeli et al., 2001) and Panda (Tomlinson et al., 2006), and with peridotitic minerals in Diavik diamonds (Klein-BenDavid et al., 2004, 2007). Izraeli et al. (2001) suggested the brine in Koffiefontein diamonds may have formed by separation of immiscible fluid, or possibly was derived from subducted seawater.

Previously, we have reported high halogen abundances and variable halogen ratios (Br/Cl and I/Cl) in coated diamonds from four kimberlites from the Ekati property, North West Territories, Canada (Fox, Grizzly, Koala and Leslie kimberlites: Johnson et al., 2000; Burgess et al., 2002). The highest Br/Cl and I/Cl values measured in some of these diamonds are well above values for other mantle samples, including Siberian and African diamonds, and are similar to the highest values reported for crustal fluids (Johnson et al., 2000). The origin of the halogen fractionation is uncertain, and may be related to crystallisation of a Cl-bearing phase such as apatite leaving a fluid enriched in Br and I, recycling of crustal halogens having high Br/Cl and I/Cl values, or melt–fluid partitioning with halogen fractionation controlled by differences in the ionic radii of halide ions (Johnson et al., 2000).

In this study we combine analyses of K, Ca and halogens (Cl, Br and I) determined using the Ar–Ar technique, noble gas (He and Ar), C and N isotopes, and infra-red spectroscopy, to understand the relationships between different fluid types in diamonds from the Panda kimberlite, Canada. This enables better constraints to be placed on likely scenarios for generating the large range of halogen ratios observed for different fluid compositions.

2. EXPERIMENTAL METHODS

2.1. Panda diamond samples

Twelve diamond samples from the Panda kimberlite have been studied. Panda is a group I kimberlite, and is one of several diamondiferous kimberlites forming the Ekati property, North West Territories. The Panda kimberlite has a phlogopite Rb–Sr eruption age of 53.2 ± 0.3 Ma (2σ; Creaser et al., 2004). An overview of Panda kimberlite geology is given by Nowicki et al. (2004).

The diamond samples analysed in this study were either whole samples or fragments weighing between 0.02 and 0.05 g of light or dark grey coated diamonds (fibrous “coats” overgrowing clear octahedral cores) with coat thicknesses between 0.2 and 0.7 mm (Fig. 1). Only one sample, PEK013/9 differs in having a frosted appearance on the surface possibly resulting from partial resorption by the host kimberlite magma (Robinson et al., 1989). The coats contain fluid-bearing microinclusions ≤1 μm in size (Schrauder and Navon, 1994; Tomlinson et al., 2006), that are too small to analyse by conventional fluid inclusion techniques, and even using micro-scale techniques (e.g. electron and ion probes) it is difficult to avoid the complicating effects of overlapping the analysing beam with host diamond matrix or nearby inclusions. Tomlinson et al. (2006) have reported the chemical compositions of co-existing silicate macroinclusions and fluid microinclusions in the fibrous coats of eight coated diamonds from the Panda kimberlite. Their study revealed that fibrous diamonds with either eclogitic or peridotitic mineral inclusions also contain fluid microinclusions dominated by H2O, carbonate and KCl. They conclude that fibrous diamonds grow in the same paragenetic environments as octahedral diamonds and that the fluid components, possibly originally derived from a subducted slab, were chemically modified during mantle metamorphism. The mineral parageneses of the Panda diamonds in this study were not determined.

Westerlund et al. (2006) obtained a Re–Os isochron age of 3.52 ± 0.17 Ga for eleven sulfide inclusions in peridotitic octahedral diamonds from the Panda kimberlite. The age of the diamond coat growth is unknown but must have occurred after the octahedral diamonds formed. Insight into the relative timing of coat growth can be obtained from the aggregation state of nitrogen in diamond. During diamond growth, nitrogen is trapped by substitution for carbon atoms (Type Ib diamond). The nitrogen then migrates to form pairs of atoms (Type IaA) and eventually,
clusters of four atoms and a vacancy (Type IaB) and platelets. The aggregation process is diffusion controlled and the percentage of the nitrogen B-centres (i.e. clusters) depends upon initial nitrogen concentration and the integrated time–temperature history of the diamond (Taylor et al., 1996). Nitrogen aggregation states are expressed as the proportion of the B-defect relative to the total nitrogen content (%B). Available data have shown that fibrous diamonds are characterised by moderately aggregated nitrogen without any development of B-centers (Boyd et al., 1987; Navon et al., 1988). Tomlinson et al. (2006) found only nitrogen in A centres in Panda coats, compared with up to 33% B nitrogen (absorptions at 1332 and 1175 cm\(^{-1}\)) in the cores as well as some platelets (~1370 cm\(^{-1}\)). The low aggregation state of nitrogen is a global feature of coated diamond and is usually interpreted to indicate either unusually low temperature storage in the mantle, or a relatively short mantle residence time (e.g. Taylor et al. 1996).

Prior to experimental work, Panda diamonds were cleaned in 10% HF acid at room temperature for 48 h to remove any adhering silicate material, followed by ultrasonic cleaning in acetone and deionised water. A visual inspection under a binocular microscope was made to ensure complete removal of any silicates. Each diamond was then broken into a number of fragments, each weighing a few milligrams, for use in different experiments. Between 2 and 10 fragments from each diamond were analysed for noble gases (Ar and He), or irradiated for Ar–Ar isotopic (Ar, K, Ca, Cl, Br, I, U) experiments. Infra-red (IR) spectra were obtained on broken (i.e. unpolished) diamond fragments of moderate size (<2/3 mm\(^3\)), and because of the irregular shape and small sample size, it was not possible to investigate the spatial variation of nitrogen content or fluid characteristics within each sample. Sample thickness was estimated assuming an 11.94 absorbance at 1992 cm\(^{-1}\). Nitrogen contents were measured from the baseline-corrected absorbance at 1282 cm\(^{-1}\) using coefficients of 16.5 and 79.4 at. ppm cm\(^{-1}\) for A- and B-centres (Boyd et al., 1994, 1995a). Water and carbonate were determined from the baseline-corrected absorbance of the O–H stretching (\(\varepsilon_{3420} = 80 \text{ L/mol cm}^{-1}\)) and the v3 stretching band of carbonate using an absorption coefficient (following subtraction for diamond absorption) of 235 L/mol cm\(^{-1}\), respectively (see details in Navon et al., 1988; Tomlinson et al., 2006). The presence and nature of silicates can be investigated from absorption bands at 1000 cm\(^{-1}\) (Tomlinson et al., 2006). Errors in the nitrogen content and aggregation state, water and carbonate contents are estimated to be better than 20% and 5% (Boyd et al., 1987), ±25 and ±40 ppm (Navon et al., 1988), respectively.

Nitrogen isotopes, nitrogen contents and carbon isotope determinations were subsequently made using procedures described in Boyd et al. (1995b). After online diamond combustion in an oxygen atmosphere at a temperature of

![Fig. 1. Photographs of Panda coated diamond analysed in this study. The examples shown are the most intact diamonds investigated, other samples were broken fragments containing mixed core and coat material.](image)
1100 °C, nitrogen was separated from carbon dioxide and any nitrogen oxides reduced to N₂ using a CaO/Cu mixture at 600 °C. Nitrogen concentrations were measured with a capacitance manometer with a precision better than 5% and the nitrogen isotopic composition was analyzed with a home-made triple collector static vacuum mass spectrometer directly connected to the extraction line. Carbon dioxide produced by the combustion was analyzed with a conventional dual-inlet gas source mass spectrometer. Isotopic compositions are expressed using delta notation, defined as δ₁₅N = [(¹⁵N/¹⁴N_sample)/(¹⁵N/¹⁴N_air) - 1] × 1000 and δ₁³C = [(¹³C/¹²C_sample)/(¹³C/¹²C_air) - 1] × 1000. In addition to blank determination, ⁴⁰Ar (m/z = 40) was also monitored in the mass spectrometer as an indicator of potential atmospheric contamination for both sample and blank. For all samples, the blank contribution was below 3.5 × 10⁻⁸ g N with a corresponding δ¹⁵N value between −10‰ and 0‰. The accuracy of the measurement, established on the basis of standard analyses, is better than ±0.1‰ and ±0.5‰ (2σ) for δ¹³C and δ¹⁵N, respectively (Boyd et al., 1995b). However, the errors reported in Table 1 can be larger and take into account a maximum blank contribution with ¹⁵N = [(¹⁵N/¹⁴N_sample)/(¹⁵N/¹⁴N_air) - 1] × 1000. Noble gas analyses

Argon isotopic analysis of neutron-irradiated diamonds was used to determine Ar, K (via ³⁹ArK), Cl (³⁸ArCl), Ca (³⁷ArCa), Br (⁸⁰KrBr), I (¹²⁸XeI) and U (¹³⁴Xe) isotopic compositions in each fragment. Neutron irradiation of samples was carried out in position B2W of the SAFARI-1 reactor, NECSA, Pelindaba, South Africa with a fast neutron flux of 1 × 10¹⁸ n/cm² as determined from Pb³⁵Br flux monitors included in the irradiation. Experimental procedures were similar to those described previously in Johnson et al. (2000) and Burgess et al. (2002). Argon was extracted in a resistance furnace using two temperature steps each of 30 min duration. A low temperature step at 800 °C was used to remove adsorbed atmospheric noble gases from the samples, followed by a high temperature step at 2150 °C to graphitise the diamond and liberate noble gases from microinclusions.

Isotopic measurements were made using the MS1 mass spectrometer which is equipped with a Faraday detector for Ar isotope measurements and a channel electron multiplier for lower abundance Kr and Xe isotope detection. Average furnace blanks at 2150 °C were approximately 1.5 × 10⁻⁹ cm³ STP ⁴⁰Ar, 0.2 × 10⁻¹² cm³ STP ⁸⁰Kr and 0.4 × 10⁻¹² cm³ STP ¹²⁸Xe. Blank corrections are minor for most noble gas isotopes, the exception is ³⁶Ar where samples released between 2 and 8 times blank levels. Argon isotopic measurements were corrected for blanks, mass discrimination, ³⁷Ar decay and neutron interferences. The latter were determined from CaF₂ and K₂SO₄ to give the following values: (⁴⁰Ar/³⁹Ar)K = 0.044 ± 0.023; (³⁸Ar/³⁹Ar)K = 0.01243 ± 0.00002; (³⁸Ar/³⁷Ar)Ca = 0.000745 ± 0.000003; and (³⁶Ar/³⁵Ar)Ca = 0.000269 ± 0.000007.

Bromine and iodine concentrations were calculated from ⁸⁰KrBr, ¹²⁸XeI, respectively (Johnson et al., 2000). A combined blank and air correction has been applied to ⁸⁰Kr and ¹²⁸Xe from measured ⁸⁴Kr and ¹³⁴Xe, respectively, and assuming air ratios. ⁸⁴Kr was initially corrected for a small (<1%) contribution from neutron-induced fission of U based upon ¹³⁴Xe release and assuming ¹³⁴Xe/¹³²Xe = 0.02356. With the exception of PEK013/9, blank corrections amounted to <1% and 2–5% for ⁸⁰Kr and ¹²⁸Xe, respectively. For PEK013/9 the blank corrections were higher at 1–3% and 13–44% for ⁴⁰Kr and ¹²⁸Xe, respectively. Thermal and resonant neutron production of ¹²⁸Xe (and ⁸⁰Kr) was monitored using the Shallowater meteorite which has an initial ¹²⁷I/¹²⁹I ratio of 1.125 × 10⁻⁴. The main uncertainties in Br and I contents derive from the measurement precision of m/z 80 and 128 ion beams in the mass spectrometer.

It was not possible to determine Ca (via ³⁷ArCa, t₁/₂ = 35 days) contents of three Panda diamonds (samples PEK013/5, PEK013/10 and PEK013/11) because they were analysed more than 6 months following irradiation, after which ³⁷ArCa had decayed to negligible levels.

Helium and Ar isotopes were extracted from unirradiated diamond fragments using a low blank filament furnace

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (mg)</th>
<th>δ¹³C (%)</th>
<th>δ¹⁵N (%)</th>
<th>±δ¹⁵N (%)</th>
<th>N (ppm)</th>
<th>FTIR</th>
<th>H₂O (ppm)</th>
<th>CO₂ (ppm)</th>
<th>100 H₂O/H₂O (molar)</th>
<th>Other main absorptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEK013/1</td>
<td>0.4249</td>
<td>-6.93</td>
<td>-3.1</td>
<td>+0.6</td>
<td>1136</td>
<td>1193</td>
<td>0</td>
<td>1854</td>
<td>802</td>
<td>85</td>
</tr>
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<td>PEK013/2</td>
<td>0.6506</td>
<td>-5.34</td>
<td>-8.8</td>
<td>+0.5</td>
<td>1352</td>
<td>n.d.</td>
<td>n.d.</td>
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<td></td>
</tr>
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<td>PEK013/4</td>
<td>0.3548</td>
<td>-5.10</td>
<td>-2.3</td>
<td>+0.5</td>
<td>1899</td>
<td>808</td>
<td>13.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEK013/5</td>
<td>0.2348</td>
<td>-5.20</td>
<td>-2.3</td>
<td>+0.6</td>
<td>775</td>
<td>712</td>
<td>27.8</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>PEK013/9</td>
<td>0.5226</td>
<td>-5.52</td>
<td>-4.1</td>
<td>+0.6</td>
<td>418</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
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<tr>
<td>PEK013/10</td>
<td>0.5682</td>
<td>-6.15</td>
<td>-1.2</td>
<td>+0.5</td>
<td>1872</td>
<td>1347</td>
<td>0</td>
<td>959</td>
<td>621</td>
<td>79</td>
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<tr>
<td>PEK013/11</td>
<td>0.3961</td>
<td>-4.53</td>
<td>-1.7</td>
<td>+0.6</td>
<td>1222</td>
<td>1283</td>
<td>0</td>
<td>1886</td>
<td>1262</td>
<td>78</td>
</tr>
</tbody>
</table>
system. This consisted of five tungsten ribbon filaments each welded to a pair of wires mounted on an 11-pin electrical feedthrough flange. Prior to sample loading a current was passed through each filament, heating it to high temperature (>1800 °C) in order to degas any adsorbed atmospheric He and Ar. Diamond fragments were loaded on to the filaments by inserting them into a “V” shape formed in the filament and enclosed by heat shields. Samples were heated in single steps of 5 min duration in order to release noble gases. Purification was achieved using a hot (450 °C) Zr–Al getter (SAES GP50) for 10 min. Argon was then separated from He at liquid nitrogen temperature (−196 °C) on activated charcoal. He and Ar isotopes were analysed in a MAP 215 mass spectrometer using procedures described in Harrison et al. (2003). High temperature blanks were determined on an unloaded filament to be \((3.6 ± 0.7) \times 10^{-13} \text{ cm}^3 \text{ STP} \) \(^{4}\text{He}\) and \((1.4 ± 0.6) \times 10^{-10} \text{ cm}^3 \text{ STP} \) \(^{40}\text{Ar}\). These amounts correspond to <0.1% of the amount of He and Ar released from a diamond sample, thus only a minor blank correction has been applied to the data.

All noble gas and Ar–Ar data are reported at a one standard deviation level of uncertainty unless otherwise stated. Concentrations of He, Ar and halogens were obtained by combining the amounts released from fragments of each diamond and are reported relative to the bulk diamond. Noble gas/halogen and halogen ratios are given as molar values.

3. RESULTS AND DISCUSSION

3.1. Nitrogen aggregation, FTIR spectra and carbon and nitrogen isotopes

Five of the seven investigated samples have type IaA aggregation states which, together with high levels of nitrogen (average ~1360 ppm), are typical of fibrous diamonds (Table 1: Boyd et al., 1987, 1992; Cartigny et al., 2003; Tomlinson et al., 2006). However, two samples (PEK013/4 and PEK013/5) show significant B-percentage values (up to 28%, Table 1) from which we infer that despite the results of our visual inspection some core material was present (e.g. Boyd et al., 1987; Navon et al., 1988; Tomlinson et al., 2006).

Sufficient material was available from three Panda diamonds for FTIR spectroscopy (Table 1). These diamonds have water contents of between 78% and 85%, higher than the range of 55–68% reported previously by Tomlinson et al. (2006). Significant peaks in the FTIR spectra of PEK013/1 and PEK013/11 are from silicate-related absorptions. The saline fluid composition described by Klein-Ben-David et al. (2007) is strongly depleted in silica. Thus, the significant silicate peak identified in the course of the present FTIR investigation are likely to relate to silicate inclusions, as reported previously by Tomlinson et al. (2006), and also inferred later in Section 3.3 from their apparent Ca-enrichment. Samples are characterised by additional absorptions bands (see Table 1) and we did not make any attempt to determine possible phases. Residual internal diamond pressure results in a shift of characteristic absorption bands relative to 1 bar reference spectra and, given that high pressure spectral data are still lacking, the identification of any phase would be speculative.

Carbon and nitrogen isotope compositions show rather restricted ranges, with \(\delta^{13}\text{C}\) and \(\delta^{15}\text{N}\) between −6.9‰ to −4.5‰, and −8.8‰ to −1.2‰, respectively (Fig. 2). Carbon and nitrogen isotopic compositions do not appear to correlate with fluid composition, or any halogen and noble gas isotopic variations. \(\delta^{13}\text{C}\)-\(\delta^{15}\text{N}\) values are similar to the global range for fibrous diamond: \(\delta^{13}\text{C} = −8\text{‰} \) to −5‰ and \(\delta^{15}\text{N} = −12\text{‰} \) to −0‰ (Cartigny, 2005). The two samples analysed that were inferred to contain some non-fibrous diamond cores (PEK013/4 and PEK013/5) have carbon and nitrogen isotope ratios well within the range for Panda diamonds (Table 1) indicating that the core material does not have a highly unusual composition. In detail however,

Fig. 2. Carbon and N isotope composition Panda diamonds. Most samples lie within the range determined for fibrous and cubic diamonds from worldwide localities (Cartigny, 2005).
it is clear that most (6 out of 7) δ¹⁵N values fall on the enriched δ¹⁵N-side of the fibrous diamond range (Fig. 2). It is possible that the higher δ¹⁵N content reflects slight differences in their mantle source compared with Siberian and African cratonic lithospheres, although confirmation of this will require further detailed study.

A comparison between the N content determined by FTIR and bulk combustion (n = 5) shows good agreement (within 10%) for three analyses (Table 1). However, a comparison of these two techniques for the remaining two samples shows differences in N concentrations of up to a factor 2.4 (PEK013/4). Large differences in nitrogen contents of gem quality diamonds are commonly found when comparing bulk and FTIR (which is more spatially resolved) techniques (e.g. Cartigny et al., 2001), while the cause is unknown (Koffiefontein) diamonds, and a Ca-rich component (Fig. 4). PEK013/9 is the only diamond in this study to lie along the carbonatitic–silicic fluid trend, as defined by two other diamonds from Canada (Diavik), and diamonds from African (Jwaneng) and Siberian (Aikhal) sources.

3.2. Ar–Kr–Xe analysis of irradiated diamonds

Argon, halogens, K, Ca and U data, as determined by noble gas analyses of neutron-irradiated diamonds, are presented in Table 2. Halogen data are discussed separately in Section 3.4. Results for Panda diamonds are similar to those obtained previously from diamonds at the nearby Fox, Grizzly, Koala and Leslie kimberlites (Johnson et al., 2000; Burgess et al., 2002). ⁴⁰Ar and K are poorly correlated in Panda diamonds with all apparent ages >4.5 Ga indicating the ubiquitous presence of excess ⁴⁰Ar* (⁴⁰Ar* = ⁴⁰Ar – 295.5 × ³⁷Ar). In situ contributions of radiogenic ⁴⁰Ar based upon K concentrations are insignificant (<0.1%) assuming a minimum age for coat growth of 53 Ma. Even using an upper limit for coat growth given by the Re–Os age for peridotitic diamonds of 3.52 Ga, gives a maximum of only 5% radiogenic ⁴⁰Ar in PEK013/9 and <1‰ in all other diamonds.

⁴⁰Ar*/Cl values are between 444 and 887 × 10⁻⁶ (Fig. 3; Table 2) which is about a factor of two lower than obtained previously for Canadian diamonds, but is similar to coated diamonds from Siberian and African sources (Johnson et al., 2000; Burgess et al., 2002). The ⁴⁰Ar–Cl correlation indicates the presence of a hydrous fluid-bearing phase containing noble gases and halogens. The range of K/Cl values determined for Panda diamonds is between 0.5 and 1.5 which is comparable to the range of 0.14–1.44 for inclusions analysed by electron microprobe (Tomlinson et al., 2006). The relatively limited variation in K/Cl of Panda diamonds means that it is not possible to use ⁴⁰Ar/Cl correlations to constrain the age of coat growth as was done previously for Siberian diamonds (Burgess et al., 2002).

3.3. Relationship to previously identified fluid types in diamonds

Determination of Ca, K and Cl (Table 2) means it is possible to relate fluid compositions of Panda diamonds to the carbonatitic, silicic and saline fluid end-members previously identified in Canadian, African, Brazilian and Siberian diamonds (Schrauder and Navon, 1994; Izraeli et al., 2001; Klein-BenDavid et al., 2004; Shiryaev et al., 2005; Klein-BenDavid et al., 2007). Fig. 4 shows K–Ca–Cl data for individual fragments and the weighted average for each Panda diamond analysed in this study, as well as published data for other Canadian, African and Siberian diamonds. With the exception of sample PEK013/9, the data from Panda diamonds form an array between the saline fluid composition found in most Canadian and some African (Koffiefontein) diamonds, and a Ca-rich component (Fig. 4). PEK013/9 is the only diamond in this study to lie along the carbonatitic–silicic fluid trend, as defined by two other diamonds from Canada (Diavik), and diamonds from African (Jwaneng) and Siberian (Aikhal) sources.

Fragments of individual Panda diamonds show considerable chemical variation in Fig. 4. Some of the intra-sample variation may result from chemical zoning as proposed for some other elements in Panda and Diavik diamonds (Klein-BenDavid et al., 2004, 2007; Tomlinson et al., 2006). However, it is also likely that some variation is related to Ca-rich silicate mineral inclusions whose presence is indicated by FTIR. Previously, Tomlinson et al. (2006) reported abundant silicate inclusions (2–20 µm size) of garnet, olivine, clinopyroxene and orthopyroxene in the coats of Panda diamonds. Using the high spatial resolution of the electron microprobe employed during their study, these mineral inclusions could be analysed separately from fluid microinclusions. However, the method used here of stepped heating is a bulk extraction method that releases noble gases simultaneously from all types of inclusions in the diamond.

Chlorine contents of silicate inclusions have not been reported, however they are expected to be low. Potassium is a minor element in pyroxene (clinopyroxene K<sub>2</sub>O ≤0.5 wt.%) and orthopyroxene <0.3 wt.%; Tomlinson et al., 2006). Therefore, the K and Cl concentrations of diamonds will be dominated by fluid microinclusions (Tomlinson et al., 2006). In contrast, the Ca contents of clinopyroxene and garnet are relatively high between 5 and 22 wt.% CaO (Tomlinson et al., 2006), hence these minerals will have high Ca/Cl and Ca/K ratios. Fig. 4 shows the range of compositions of silicate inclusions based upon data from Tomlinson et al. (2006).

During stepped heating of diamonds, the release of Ca-derived ³⁷Ar from any silicate mineral inclusions will skew data towards the Ca apex in Fig. 4. The extent to which individual fragments are displaced toward the Ca apex will be determined mainly by the composition and proportions of silicate inclusions. The trend toward high Ca/K shown by the majority of Panda diamonds (Fig. 4) suggests that garnet and clinopyroxene are the main source of calcium. This is consistent with the results of Tomlinson et al. (2006) who reported only four orthopyroxene inclusions that were present in a single Panda diamond. Although stepped heating is a bulk analysis technique, it does not enable partial resolution of the fluid end-member chemical composition. Thus, it is reasonable to conclude that saline fluids are present in all of the Panda diamonds analysed except PEK013/9. In the latter diamond, it is more likely that a mixture of carbonatitic and silicic fluids is present.
Table 2
Panda diamond Ar–Ar data. Errors are 1σ; nd = not determinable i.e error >30%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt (mg)</th>
<th>Cl (ppm)</th>
<th>Br (ppb)</th>
<th>I (ppb)</th>
<th>K (ppm)</th>
<th>Ca (ppm)</th>
<th>U (ppb)</th>
<th>Br/Cl</th>
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<td>Total 1</td>
<td>7.0</td>
<td>662 ± 4</td>
<td>70 ± 0.5</td>
<td>193 ± 14</td>
<td>680 ± 137</td>
<td>122 ± 5</td>
<td>1.36 ± 0.03</td>
<td>31.6 ± 0.3</td>
</tr>
<tr>
<td>Total 2</td>
<td>6.9</td>
<td>367 ± 2</td>
<td>9.0 ± 0.2</td>
<td>99 ± 4</td>
<td>220 ± 43</td>
<td>94 ± 6</td>
<td>1.63 ± 0.02</td>
<td>25.6 ± 0.6</td>
</tr>
<tr>
<td>Total 3</td>
<td>7.5</td>
<td>662 ± 4</td>
<td>70 ± 0.5</td>
<td>174 ± 4</td>
<td>279 ± 8</td>
<td>537 ± 189</td>
<td>431 ± 22</td>
<td>4.27 ± 0.16</td>
</tr>
<tr>
<td>Total 4</td>
<td>10.1</td>
<td>1092 ± 12</td>
<td>28.9 ± 1.5</td>
<td>680 ± 137</td>
<td>122 ± 5</td>
<td>1.36 ± 0.03</td>
<td>31.6 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Total 5</td>
<td>10.6</td>
<td>1380 ± 12</td>
<td>28.9 ± 1.5</td>
<td>680 ± 137</td>
<td>122 ± 5</td>
<td>1.36 ± 0.03</td>
<td>31.6 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Total 6</td>
<td>7.0</td>
<td>662 ± 4</td>
<td>70 ± 0.5</td>
<td>193 ± 14</td>
<td>680 ± 137</td>
<td>122 ± 5</td>
<td>1.36 ± 0.03</td>
<td>31.6 ± 0.3</td>
</tr>
</tbody>
</table>

Italicics were used to distinguish "totals" from sub-samples (fragments).
Fig. 3. $^{40}$Ar/$^{36}$Ar versus Cl/$^{36}$Ar correlation for Panda diamonds (open triangles – fragments, solid symbols – bulk compositions), errors are 1σ. The correlation indicates that $^{40}$Ar and Cl are present within fluid microinclusions in the diamonds, with variation of $^{40}$Ar/Cl in the fluid being within the range of approximately 500-1500 x 10^{-6} obtained from fluid microinclusions in diamonds from worldwide localities.

Fig. 4. Chemical composition of mantle fluids in Panda diamonds (open symbols – fragments; filled symbols – bulk values) and published data. Numbers (n) refer to sample numbers PEK013/n. The compositions of silicate macroinclusions (garnet, clinopyroxene [cpx] and orthopyroxene [opx]) are based upon data from Tomlinson et al., (2006). Data sources for diamonds: Diavik (14 samples) – Klein-BenDavid et al., 2004, 2006, 2007; Panda (7 samples) – Tomlinson et al., 2006; Jwaneng (10 samples) – Schrauder and Navon, 1994; Koffiefontein (10 samples) – Izraeli et al., 2001; Aikhal (5 samples) – Burgess et al., 2002.
3.4. Halogens

The fluids in Panda diamonds are enriched in halogens by a factor of 10–50 compared to values measured in coated diamonds from Africa and Siberia (Johnson et al., 2000; Burgess et al., 2002). This finding is consistent with electron microprobe measurements of fluid microinclusions by Tomlinson et al. (2006) who obtained high Cl contents, averaging 36.5 and 32.5 wt.% in Panda diamonds containing peridotitic and eclogitic mineral inclusions, respectively. Fig. 5a shows the halogen ratios of fragments and bulk samples of Panda diamonds, compared to some other diamonds, MORB and seawater. Panda diamonds show a range of Br/Cl = 1.4–4.3 × 10⁻³ and I/Cl = 9.4–37.2 × 10⁻⁶, they are distinct from seawater and extend significantly above the MORB value (Br/Cl = 1.03 ± 0.29 × 10⁻³ [Jambon et al., 1995]; I/Cl = 15–25 × 10⁻⁶ [see Johnson et al., 2000 for discussion]), however they are within the range previously determined for Canadian diamonds (Johnson et al., 2000). Some samples such as PEK013/3, show large halogen ratio variations between fragments (Fig. 5a) consistent with chemical zoning within the diamonds.

Fig. 5b shows a plot of Br/Cl versus I/Cl containing all published data for African, Canadian and Siberian dia-

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![Graph showing halogen ratios](image_url)

Fig. 5. (a) Br/Cl versus I/Cl of Panda diamonds (open symbols – fragments, filled symbols – bulk values) are shown enclosed by a solid line for each diamond. Number (n) refers to the sample number PEK013/n. Some samples show a large range in composition (e.g. PEK013/3) possibly indicative of chemical zoning. The seawater and MORB halogen compositions are shown for reference. (b) Br/Cl versus I/Cl for fluid-bearing diamonds from Panda, African (Jwaneng kimberlite, Botswana and Democratic Republic of Congo), other Canadian (Fox, Grizzly, Koala and Leslie, kimberlites) and Siberian (Aikhal kimberlite) sources (Johnson et al., 2000; Burgess et al., 2002). Halogen compositions from marine pore fluids (Martin et al., 1993; Mahn and Gieskes, 2001) and marine brines (Muramatsu et al., 2001) overlap with the range of composition in African diamonds, however the saline fluids in Canadian diamonds form a distinct array possibly reflecting fractionation during formation of an immiscible brine.
The majority of Canadian diamonds form a broad array in Fig. 5b, characterised by highly variable Br/CI and I/CI ratios extending from the MORB value to maximum Br/CI $\geqslant 63.0 \times 10^{-6}$ and I/CI $\geqslant 1703.5 \pm 10^{-6}$. Tomlinson et al. (2006) suggested that the diamond coats grew from an original carbonate-H$_2$O-KCl fluid that unmixed into carbonatitic and saline fluids, with silicic fluids possibly formed during metasomatic reactions with eclogitic minerals. This process appears to lead to the formation of saline fluid present with a wide variation of halogen ratios.

The halogen composition Aikhal (Siberia) diamonds is most similar to MORB, with Br/CI $= 1.74 \pm 0.18 \times 10^{-6}$ and I/CI $= 22.0 \pm 3.4 \times 10^{-6}$ (Burgess et al., 2002), and may represent the composition of carbonatitic fluid. Jwan-eng and Zaire (African) and a few Canadian diamonds form a sub-vertical array in Fig. 5b with a relatively wide range of I/Cl between 10 and $100 \times 10^{-6}$ but more restricted Br/CI of between 1 and $3 \times 10^{-3}$; this may reflect the composition of carbonatitic and silicic fluid components.

Several possible processes have been considered previously to explain the halogen variations in diamonds, including mixing, immiscibility and fractionation involving Cl-rich phases (Johnson et al., 2000; Izraeli et al., 2001; Burgess et al., 2002; Klein-Ben-David et al., 2007). Based on an expanded data-set of halogen determinations and our ability to establish their relationship to the three end-member fluid types (carbonatitic, silicic and saline fluids) we further consider the evidence for subducted halogens and mantle fractionation as the means to explain halogen variations.

3.4.1. Seawater-derived halogens

Upper crustal processes often lead to extreme chemical and isotopic fractionation so variations in mantle materials are often seemingly compatible with subduction recycling of crustal materials. The biologically-mediated enrichment of iodine in sediments means that modern marine pore fluids in sediment cores, and sediment-derived seafloor brines located adjacent to subduction zones, are highly enriched in iodine and Br relative to seawater (Martin et al., 1993; Mahn and Gieskes, 2001; Muramatsu et al., 2001). Data for modern marine pore fluids overlaps and extends beyond the range of I/CI and Br/CI of silicic fluids in African diamonds making it feasible that subducted halogens are present in fluid microinclusions in diamonds (Fig. 5b). The high enrichment of I in ocean sediments (15 ppm; Muramatsu and Wedepohl, 1998) and pore fluids (8–17 ppm; Martin et al., 1993; Mahn and Gieskes, 2001) compared to the subcontinental lithospheric mantle (SCLM; 0.4 ppb; Burgess et al., 2002) and MORB source (0.8 ppb; Deruelle et al., 1992), means that this element is potentially a sensitive indicator of crustal recycling. For example, the iodine abundance of the upper mantle of 0.8 ppb can be explained by 53 ppm of recycled marine sediment having an I concentration of 15 ppm and assuming no loss during subduction. This is notably similar to the 44 ppm of recycled seawater or marine pore fluid that has been proposed to explain the $^{36}$Ar concentration of the MORB mantle (Holland and Ballentine, 2006). To increase the mantle I/Cl value to the approximate range obtained for African diamonds of $10-100 \times 10^{-6}$, requires only 3–50 ppm of marine sediment with I/Cl of $150-1000 \times 10^{-6}$ a range that is typical for marine pore fluids.

If crustal recycling has influenced the halogen composition of the fluids sampled by diamonds, then it does not appear to have affected their N isotope compositions which retain upper mantle values. However, halogens and nitrogen are expected to be strongly fractionated during diamond formation because N content is controlled by its preferential substitution for carbon in the lattice, whereas halogens are present in trapped fluids in microinclusions (the fluid concentration of N is not known but may also be significant).

3.4.2. Mantle halogen fractionation

Fractionation of halogens may accompany the processes leading to the enrichment of halogens in mantle fluids. Mechanisms of halogen fractionation in the mantle are speculative, because the partition coefficients of halogens are unknown at the pressure, temperature and chemical conditions of diamond growth. However, partition coefficients are expected to be related to ionic radius with fluid/melt partitioning increasing in order of Cl $<$ Br $<$ I. Experimental halogen partitioning data are only available for albite and rhyolitic melts and hydrous fluids at significantly lower pressure than diamond formation (Bureau et al., 2000; Bureau and Métrich, 2003). These results indicate that Br/CI and I/CI of the fluid should be higher by factors of about 2 and 13, respectively, relative to their starting composition; this is similar to the level of enrichment found in hydrous silicic inclusions in African diamonds, but lower than in saline fluids in Canadian diamonds. Experiments on phase relations in the chloride-carbonate-silicate system support formation of an immiscible Cl-rich phase and show evidence for K/Cl variation with Si content (Safonov et al., 2007). The K/CI fractionation is considered to be controlled by complex exchange reactions with components in the melt (Safonov et al., 2007), however the effects of this process on halogen fractionation is unknown.

Further halogen fractionation may occur during crystallisation of Cl-rich phases (e.g. apatite and amphibole). Apatite may be stable in the diamond forming region of the SCLM, is a widespread accessory mineral in xenoliths from lithospheric mantle (O’Reilly and Griffin, 2000), and has been observed as a secondary phase in fluid microinclusions in diamonds (Tomlinson et al., 2006; Klein-Ben-David et al., 2007). The problem with invoking the crystallisation of Cl-rich phases to fractionate halogens is in explaining the relatively constant $^{36}$Ar/$^{40}$Ar ratios of the different fluid types which are all within about a factor of three and have a median value similar to the predicted MORB value (see Section 3.6). Similarly, any decrease in salinity of the residual fluids accompanying crystallisation of Cl and OH-rich phases such as apatite, may lead to a decrease in Br/CI and I/CI in the residual fluid, the opposite of what is observed in the most saline fluids. Other more complex diamond formation processes can also be envisaged including multiple or prolonged diamond growth events in the presence of an
unmixing metasomatic fluid, possibly during interaction with host mantle rocks, or from multiple fluid sources. These more dynamic interactions may help to account for the large halogen variability in saline fluids in diamonds.

3.5. Helium and argon isotopes

Helium and argon isotope data are presented in Table 3 and shown in Figs. 6–8. Sample PEK013/9 gave different results from other Panda diamonds, and is considered separately below. He isotope data (Fig. 6) show a narrow span of $^{3}$He/$^{4}$He values of 5.4–6.4 Ra (R/Ra = the $^{3}$He/$^{4}$He ratio normalized to the atmospheric value of $1.4 \times 10^{-6}$) however there is no apparent relationship between He isotope ratios and fluid composition. The $^{3}$He/$^{4}$He values are within the range of values reported previously for diamonds from African sources (Fig. 6; 3.7–7.0 Ra – Juweng, Burgess et al., 1998; 4.0–7.2 Ra – Democratic Republic of Congo, Wada and Matsuda, 1998). The majority also fall within the range obtained from many mantle xenoliths derived from the SCLM of 6 ± 1 Ra (Gautheron and Moreira, 2002; Dunai and Porcelli, 2002) and are generally lower than the MORB value of 8.75 ± 2.14 Ra (Graham, 2002). The $^{3}$He/$^{4}$He values of fluid-bearing diamonds are similar to the range of between 5.2 and 5.7 Ra obtained by in vacuo crushing release of melt inclusions in olivine from the Udachnaya kimberlite (Sumino et al., 2006) although they are much lower than fresh kimberlites from Greenland of up to 27 Ra (Tachibana et al., 2006) which may have preserved He from a deeper mantle source.

The concentration of He is exceptionally high at between 13 and $6 \times 10^{-6}$ cm$^3$/g and 1–2 orders of magnitude higher than diamonds containing carbonatitic or silicic fluids (Fig. 6). Helium concentration does not correlate with $^{3}$He/$^{4}$He ratio indicating that there has not been a significant post-entrapment contribution of He from in situ decay of U and Th, or by external x-implantation. In situ $^{4}$He contributions in diamonds where both $^{4}$He (Table 3) and U (Table 2) concentrations have been determined, and assuming 53 Ma as the age of coats growth, are estimated to be: 3% in PEK013/1; 2% in PEK013/2; and 1% in PEK013/4. Assuming an upper limit given by the Re–Os age of 3.52 Ga for peridotitic diamonds (Westerlund et al., 2006), although incompatible with N aggregation data, gives in situ produced $^{4}$He concentrations higher than those measured in all the samples except for PEK013/4 where it would account for 41% of the total $^{4}$He. At present it is not possible to determine whether the diamonds have quantitatively retained He (young coats) or experienced He loss by diffusion (ancient coats) although negligible He loss is most likely for diamond (Honda et al., 1987).

From hereon, it is assumed that no major addition or loss of He has occurred, and that the He abundances and isotope ratios are representative of the fluid trapped at the time of coat crystallisation.

Intra-sample helium concentrations vary by up to a factor of two (e.g. PEK013/1; Table 3; Fig. 6), which is attributed either to there being variable amounts of fluid-poor (diamond core) and fluid-rich (coat) material present in each fragment, or to variations of the inclusion population densities in fibrous diamonds (e.g. Klein-BenDavid et al., 2007). The He isotopic compositions of different fragments are all indistinguishable within two standard deviations suggesting there is no evidence for He isotope zoning within diamonds (Table 3).

Argon isotope ratios of Panda diamonds were measured by filament heating of unirradiated diamonds and resistance furnace stepped heating of irradiated samples during Ar–Ar analyses. Comparing results between the two methods indicates variations in Ar concentrations of up to a factor of 10 difference (PEK013/10) which may be attributed to the variable proportions of $^{40}$Ar*-poor core and $^{40}$Ar*-rich coat in the samples, or to differences in the numbers of microinclusions. Intra-sample $^{40}$Ar* variations reach a maximum of a factor of 5 in PEK013/9. From hereon, only the results from unirradiated diamonds are considered because they gave consistently higher $^{40}$Ar/$^{36}$Ar values due to the order of magnitude lower blank associated with filament heating.

Panda diamonds yielded $^{40}$Ar/$^{36}$Ar values in the range 17,000–36,000 (Fig. 7, Table 3) but like He, do not show any evidence for isotopic zonation. $^{40}$Ar* concentrations are high at between 26 and $95 \times 10^{-6}$ cm$^3$/g (Table 3) and are similar to the concentrations obtained previously for...
fibrous diamonds from nearby kimberlites of Fox, Grizzly, Koala and Leslie (Johnson et al., 2000). Panda diamonds also contain relatively high concentrations of $^{36}$Ar, however there is no obvious correlation with $^{40}$Ar/$^{36}$Ar ratio (Fig. 7). The origin and implications of the high $^{36}$Ar content of these diamonds is discussed in Section 3.6.

Most Panda diamonds have similar $^{40}$Ar*/$^{4}$He values in the range 1.1–2.6 (Fig. 8 and Table 3). This range is above the upper mantle $^{40}$Ar*/$^{4}$He production ratio of 0.6 (integrated over 4.5 Ga assuming K/U = 12,700), and also the present-day mantle production ratio of approximately 0.2 (e.g. Burnard, 2001). The $^{40}$Ar*/$^{4}$He value of diamonds are higher than the MORB popping rock (taken to be the least degassed basalt) value of ~0.7 (Moreira et al., 1998). Enhanced $^{40}$Ar*/$^{4}$He values in diamonds appears to be a widespread characteristic of fluid-bearing diamonds. Previously $^{40}$Ar*/$^{4}$He values of between 0.7–1.0 and 1.1–4.4 were obtained for diamonds from the Democratic Republic of Congo (Wada and Matsuda, 1998) and Jwaneng (Burgess et al., 1998), respectively (Fig. 8). It is possible that such high $^{40}$Ar*/$^{4}$He ratios are generated in a mantle region having an exceptionally high K/U of 50,000. However, K and
U concentrations of Panda diamonds determined by Ar–Ar analyses (Table 2), indicate that the mantle fluids have much lower K/U values that are mostly between 1000 and 2000. Lowering of \(^{40}\text{Ar}/^{36}\text{He}\) values in MORB samples has been related to the extent of magmatic degassing (e.g. Burnard, 2001), thus the higher values in diamonds may be characteristic of the mantle source where degassing processes are unlikely to be a major influence.

Sample PEK013/9 differs from other Panda samples in having much lower \(^{3}\text{He}/^{4}\text{He} = 3.0 \text{ Ra}, \quad ^{40}\text{Ar}/^{36}\text{Ar} \sim 500\) and \(^{40}\text{Ar}/^{36}\text{He} = 0.5–1\); the concentrations of He and Ar are also about an order of magnitude lower in this diamond (Figs. 6–8, Table 3). \(^{4}\text{He}\) produced by \textit{in situ} decay of U and Th (U = 46 ppb in Table 2, and assuming Th/U = 3.3) within the fluid inclusions since eruption 53 Ma ago, amounts to 11% of the total, giving an initial trapped \(^{3}\text{He}/^{4}\text{He}\) of only 3.4 Ra. The frosted surface appearance of this diamond suggests it has been partially resorbed in the host kimberlite, possibly removing a portion of an inclusion-rich outer layer. Some loss of noble gases may have occurred during the resorption process. However, the differences in noble gas isotope ratios are more likely to reflect a difference in the source of fluids trapped in PEK013/9.

### 3.6. \(^{36}\text{Ar}\) content of the subcontinental lithospheric mantle

The \(^{36}\text{Ar}\) content of the mantle is an important constraint for degassing models of the earth’s interior and formation of the atmosphere. It is commonly assumed that nearly all of the \(^{36}\text{Ar}\) present in MORB and OIB samples derives from atmospheric contamination and that measured \(^{40}\text{Ar}/^{36}\text{Ar}\) in basalts are therefore considered to be minimum estimates of their mantle source (e.g. Ballentine and Barfod, 2000). Using noble gas data from continental well gas samples it has recently been suggested that mantle \(^{36}\text{Ar}\) may be introduced as dissolved air in seawater by subduction processes (Holland and Ballentine, 2006). Because of their deep origin and low noble gas diffusivities, atmospheric contamination should be much less of a problem in diamonds.

The \(^{40}\text{Ar}/^{36}\text{Ar}\) values of diamonds are high, typically >3000 with some values in excess of 40,000 (Turner et al., 1990). However the \(^{36}\text{Ar}\) contents are usually low being of similar magnitude to the furnace blanks at temperatures above 2000 °C required for graphitisation. In contrast, heating experiments on Panda diamonds using a low blank filament furnace, show they contain unusually high concentrations of \(^{40}\text{Ar}\); making it possible to place some constraints on the \(^{36}\text{Ar}\) content of their mantle source. Fig. 7 is a plot of \(^{1}\text{He}/^{36}\text{Ar}\) versus \(^{40}\text{Ar}/^{36}\text{Ar}\) for Panda diamonds and published data for diamonds from the Democratic Republic of Congo (Wada and Matsuda, 1998) and popping rock sample 2nD43, the most noble gas-rich MORB glass sample yet analysed (Moreira et al., 1998; Trieloff et al., 2003). With the exception of Panda diamonds, all data form a broad trend between a component having a high \(^{36}\text{Ar}\) content and low \(^{40}\text{Ar}/^{36}\text{Ar}\) (\(^{36}\text{Ar} \sim 300\)) consistent with atmospheric Ar, and a mantle component having a low \(^{36}\text{Ar}\) content and high \(^{40}\text{Ar}/^{36}\text{Ar}\) (\(^{36}\text{Ar} < 0.1 \times 10^{-9} \text{ cm}^3/\text{g}\); \(^{40}\text{Ar}/^{36}\text{Ar} \gtrsim 30,000\), similar to MORB popping rock. It is not yet possible to determine whether the low \(^{40}\text{Ar}/^{36}\text{Ar}\) component is air contamination from furnace blank or an air-like component derived from the mantle source.

With the exception of sample PEK013/9, Panda diamonds have \(^{40}\text{Ar}/^{36}\text{Ar}\) of 17,000–36,000 and \(^{36}\text{Ar}\) concentrations of \(\gtrsim 1 \times 10^{-9} \text{ cm}^3/\text{g}\), which is at least an order of magnitude higher than any other diamond or mantle sam-
ples analysed (Fig. 7). The high 40Ar/36Ar of Panda diamonds is characteristic of the MORB value, indicating that the high 36Ar content is also derived from their mantle source. Similar concentrations of 36Ar to those found in Panda diamonds were reported previously in other Canadian diamonds (Johnson et al., 2000). The level of enrichment of 36Ar is at least a factor of 10 higher compared to African and Aikhal diamonds. This is of similar magnitude to the enrichment of major elements (e.g. K, Cl, Na) in the saline fluids (Klein-BenDavid et al., 2007), implying that the higher noble gas (He and Ar) contents are more likely to be related to evolution of the saline fluid rather than to differences in the population density of microinclusions. In Fig. 7, PEK013/9 lying along the array formed by African diamonds, again consistent with it having a fluid composition similar to these samples.

The mantle fluids are so Cl-rich that there is the possibility that some of the Ar in brines may have formed in situ from the neutron reactions: 39Cl(n,γ)39Ar and 37Cl(n,γ)37Ar, with the neutrons being supplied by radioactive decay of U and Th in the fluid and surrounding kimberlite. These reactions would generate a 38Ar/36Ar production ratio of 0.02, and lead to a gradual decrease over time of the original mantle 38Ar/36Ar value of 0.188. The measured 38Ar/36Ar ratios of Panda diamonds are all within error of 0.188 (Table 3) showing that neutron-produced 36Ar is only a minor component in the fluid and that the coasts are not exceptionally old. Using the measured U and Cl contents of the diamonds obtained from Ar–Ar analyses (Table 2), it is estimated that the proportion of Cl-derived 36Ar generated since the kimberlite was emplaced 53 Ma ago, is only of the order of 10−17 cm3/g. This is an approximate estimate because it neglects the fraction of thermal neutrons captured by other elements, and takes no account of the neutron flux from the surrounding kimberlite, however it is noted that the U concentration in the fluid is likely to be 100 times greater than in the kimberlite (Schrauder et al., 1996; Tomlinson et al., 2006; Zedgenizov et al., 2007). Despite these limitations, the contribution of nucleogenic 36Ar in the brines is likely to be negligible, and the 36Ar contents of Panda diamonds are, like the halogens, enriched by several orders of magnitude over typical upper mantle values.

The strong 40Ar/Cl correlation found in diamonds and mantle xenoliths during our previous studies is the evidence that 40Ar is dissolved in Cl-rich fluid (Turner et al., 1990; Johnson et al., 2000; Burgess et al., 2002). Furthermore, it has been argued that the relatively restricted range of 40Ar/Cl obtained in diamonds from global sources (currently 444–1347 × 10−6), is in good agreement with the value of 900 ± 400 × 10−6 estimated for MORB mantle based upon independent estimates of 40Ar and Cl concentrations of the upper mantle (Johnson et al., 2000). This suggests no significant fractionation of noble gases and chlorine during fluid evolution and justifies the use of Cl/36Ar values to estimate the 36Ar content in the region of the mantle where the diamonds formed.

The maximum Cl/36Ar of 30 × 106 is obtained during high temperature heating steps of Canadian diamonds (including Panda sample PEKO13/12). This value is assumed to be least affected by atmospheric contamination and therefore most representative of the mantle end-member. Combining this value with the average Cl content of 34.5 wt.% for microinclusions in Panda diamonds (Tomlinson et al., 2006) leads to a fluid 36Ar concentration of ~7 × 10−8 cm3/g. If it is further assumed that the SCLM has a Cl content of ~3 ppm (Burgess et al., 2002) with the same Cl/36Ar value as diamonds, then a 36Ar content of ~0.6 × 10−12 cm3/g (~1.7 × 106 atoms/g) is obtained for the mantle source. This is indistinguishable from estimates of the 36Ar content of the MORB mantle source based on He–Ar systematics of ~1.5 × 107 atoms/g (Holland and Ballentine, 2006).

It is suggested that the similar noble gas isotope composition (He and Ar) and abundance (36Ar) of SCLM and MORB mantle is not a coincidence and is evidence that these mantle regions have experienced similar levels of outgassing. Volatile components may be periodically concentrated within the SCLM during melting or metasomatising events, each perhaps marked by the growth of diamonds and formation of kimberlites.

4. CONCLUSIONS

Combined He, Ar, C, N isotope and K and halogens determinations have been carried-out on multiple splits of individual microinclusion-bearing diamonds from the Panda kimberlite, Slave Craton, Canada. The diamonds have high Br/Cl and I/Cl values within the range measured previously for Canadian diamonds from other kimberlites in this area. Despite the presence of silicate macroinclusions, Ca–Cl–K compositions enable the fluids in these diamonds to be reconciled with previously identified types viz carbonatitic, hydrous silicic and saline end-members. These fluids have distinctive Br/Cl and I/Cl values which, combined with their mantle-like C and N stable isotope compositions, enable source and mantle fractionation process to be elucidated. Carbonatitic fluids in Aikhal diamonds show least variation of halogen ratios and are most similar to present-day MORB values. Halogen ratios in African diamonds with silicic fluids trend toward and overlap with the lower end of the range of I/Cl values in marine sediments. The amount of marine pore fluid required to account for the halogen concentrations in the upper mantle is similar to that needed for 36Ar recycling. However, there are difficulties in understanding how large soluble ions like I are subducted, and the range of marine pore fluid I/Cl and Br/Cl does not explain the much larger halogen ratios in Canadian diamonds. Mantle fractionation processes involving, melt–hydrous fluid partitioning and separation of immiscible fluids are believed to play a major role in halogen fractionation, without the need to invoke crustal recycling.

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