## NOBLE GAS AND HALOGEN CONSTRAINTS ON THE ORIGIN OF VOLATILE-RICH FLUIDS IN CANADIAN DIAMONDS

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## INTRODUCTION

Diamond is an important mineral for investigating the storage of volatile elements in the mantle and their transport between the mantle and the Earth's surface. The mantle is the largest geochemical reservoir, so a knowledge of how the mantle has evolved through time, is an important requirement for understanding formation of the external reservoirs of crust, oceans and atmosphere. Noble gases and halogens are incompatible and conservative elements providing complementary information regarding the evolution of the atmosphere and oceans. Diamonds are inert, have high mechanical strength and low gas diffusivities, so unlike other mantle materials such as modern oceanic basalts, they are not prone to atmospheric contamination. In principle, diamonds be used to extend the noble gas and halogen record of the mantle through geological time. Here we report on an ongoing study to characterise the noble gases and halogens trapped in volatile-rich diamonds from Canadian diamonds.

## **EXPERIMENTAL METHODS**

Nine cubic diamonds from the Panda kimberlite, Slave Craton, Canada, weighing between 0.02 and 0.05 grams were selected for noble gas analysis. Each diamond was broken into a number of fragments (each weighing a few milligrams) for He, Ar-Ar and eventually carbon isotope analysis. Ar-Ar analysis of neutron-irradiated diamonds was used to measure Ar, K, Ca, U and halogens (Cl, Br and I) concentrations in each fragment. Noble gases were extracted from diamond fragments using a low blank microfurnace system. Each sample was heated to >2000C for 3 minutes to graphitise the diamond. Noble gas isotopes were analysed by mass spectrometry. Between two and nine fragments from each diamond were analysed using these techniques to check reproducibility and investigate possible chemical heterogeneities within each diamond.

## **RESULTS AND DISCUSSION**

#### HE AND AR ISOTOPES

Helium and argon isotope data are presented in Table 1. Data for PEK013/9 is distinctly different from other samples and is discussed separately below. The remaining diamonds show a narrow range of  ${}^{3}\text{He}/{}^{4}\text{He}$  between 5.4-6.5 Ra (Ra = atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$  = 1.4 x 10<sup>-6</sup>), slightly below the MORB value of 8 Ra, but within the range of values reported previously for cubic diamonds from Africa (Burgess et al., 1998) and for xenoliths derived from the subcontinetal lithosphere (Dunai and Porcelli, 2002).

# Table 1: He and Ar data for Panda diamonds

Sample	⁴He	<sup>3</sup> He/ <sup>4</sup> He	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>40</sup> Ar <sup>*</sup> / <sup>4</sup> He
		(Ra)		
4a	3.25	5.7	23,282	3.1
4b	2.92	5.4	28,280	3.0
1b	1.11	5.4	17,470	2.6
1a	2.37	6.5	27,680	2.0
2	1.66	6.4	26,830	2.3
5	4.84	5.7	36,000	1.8
11	5.58	5.6	26,120	1.9
10	5.54	5.6	31,370	1.9
9a	0.13	3.3	483	0.9
9b	0.24	2.8	500	0.5

The <sup>40</sup>Ar/<sup>36</sup>Ar values of 17,000-36,000 are typical of the range of MORB values. These diamonds have  $^{40}\text{Ar}^*/^4\text{He}$  in the range 2-3 that are significantly higher than the MORB mantle value of 0.5. The concentrations of He are relatively high at approximately  $10^{-5}$  cc/g. In contrast, PEK13/09 has a different noble gas composition, with much lower  ${}^{40}\text{Ar}/{}^{36}\text{Ar} = 1536$ ,  ${}^{3}\text{He}/{}^{4}\text{He} = 3.0 \text{ Ra and } {}^{40}\text{Ar}^{*}/{}^{4}\text{He} = 0.3$ ; the concentration of He is also about an order of magnitude lower in this diamond. On a diagram of <sup>40</sup>Ar<sup>\*</sup>/<sup>4</sup>He vs <sup>3</sup>He/<sup>4</sup>He data from all the diamonds show binary mixing between a fractionated mantle endmember  $(^{3}\text{He}/^{4}\text{He}\geq 6.5.$  $^{40}\text{Ar}^*/^4\text{He}\geq3$ ) and a component, defined by PEK013/9,

with low  ${}^{3}\text{He}/{}^{4}\text{He} \leq 3$  and a  ${}^{40}\text{Ar}*/{}^{4}\text{He}$  of  $\leq 0.2$ approaching the crustal production ratio. This sample also has a higher K (and U) content, and lower Cl content than other Panda diamonds (Table 2). The high  ${}^{40}\text{Ar}/{}^{4}\text{He}$  values could be explained by either fractionation of He from Ar, or a source region with a K/U ratio above the normal mantle value of  $10^{4}$ . Measured K/U ratios in Panda diamonds are between  $10^{3}$ - $10^{4}$ , lower than the mantle value and therefore unable to account for the high  ${}^{40}\text{Ar}*/{}^{4}\text{He}$  ratios. Since the inclusions are dominantly brine-bearing, then the Ar/He fractionation may be explained by the relatively higher solubility of Ar in water-rich fluids compared



Figure 1: He-Ar relationships in Panda cubic diamonds.

with He; the fluid should have higher  ${}^{40}\text{Ar}^*/{}^4\text{He}$  than the magma (where He has higher solubility).

#### AR-AR DATA - AR, K AND HALOGENS

Halogen and K data are presented in Table 2.  ${}^{40}$ Ar and K are poorly correlated in Panda diamonds with all apparent ages >4.5Ga indicating the presence of excess  ${}^{40}$ Ar. There is a good correlation between  ${}^{40}$ Ar<sup>\*</sup> and Cl ( ${}^{40}$ Ar<sup>\*</sup>/Cl = 5.8-7.8 x 10<sup>-4</sup> mol), indicating that excess  ${}^{40}$ Ar is dissolved in a water-rich phase in the microinclusions.

The halogen ratios of Panda diamonds are variable:  $Br/Cl = 1.8-8.8 \times 10^{-3}$  mol;  $I/Cl = 10.3-26.9 \times 10^{-6}$ ; but are within the range previously reported for Canadian diamonds (Johnson et al., 2000). They are in contrast to diamonds from Africa and Russia which have values close to the MORB ratio (Burgess et al., 2002) Previously, we have attributed high halogen ratios in Canadian diamonds to fractionation during crystallisation of Cl-rich phases in the diamond forming region of the mantle. However, a large variation in K/Cl is found both between and within diamonds. Nine fragments of PEK013/9 show the largest internal

variation of between 0.3-4.5, but other diamonds commonly have variations of about a factor of 2. A plot of K/Cl vs

### Table 1: <sup>40</sup>Ar, K and halogen data for Panda diamonds determined by Ar-Ar analysis

Sample	<sup>40</sup> Ar <sup>*</sup>	CI	K/CI	Br/Cl	I/CI
	(x10 <sup>-6</sup> cc/g)	(ppm)		$(x10^{-3}) (x10^{-6})$	
4	68.8	137	0.73	1.79	12.6
9	28.5	63	4.50	1.65	21.6
2	42.2	99	0.90	1.63	10.9
1	88.0	188	0.94	1.56	10.3
3	68.4	135	1.16	3.59	31.6
6	67.7	134	0.94	1.91	13.2
7	44.7	80	1.38	2.65	23.1
8	136.4	255	0.30	8.65	26.9
12	269.8	530	1.21	8.46	20.2

Br/Cl shows diamonds can be subdivided in a group containing a MORB-like Br/Cl but variable K/Cl defined by Africa, Russian and some Canadian diamonds; and a group formed only by some Canadian diamonds with high and variable Br/Cl and relatively constant K/Cl, the latter having a near chondritic ratio of 1. It is clear from Fig. 2 that the fractionation of K



**Figure 2.** Br/Cl vs K/Cl for volatile-rich diamonds from Russia, Africa and Canada (solid circles). Data are shown for different fragments of Panda diamonds.

and Br is decoupled and also that the variable Br/Cl ratios can not be simply attributed to loss of Cl in a crystallising phase, since this would also increase the K/Cl ratios. It may indicate the presence of at least two fluid types, one that is present only in African, Russian and some Canadian diamonds, and another that is unique to Canadian diamonds.

## REFERENCES

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