

HALOGEN COMPOSITION OF MANTLE FLUIDS IN DIAMOND

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Introduction: Application of the ^{40}Ar - ^{39}Ar method and noble gas studies to diamonds has increased our understanding of their age relationships to the host kimberlite or lamproite (Burgess et al., 1989, 1992; Phillips et al., 1989) and of the source and composition of volatile-rich fluids in the upper mantle (Turner et al., 1990). The properties of diamond (inert, high mechanical strength and low gas diffusivities) means they are especially useful samples for studying gases trapped deep within the earth (>150 km), because they are unlikely to have undergone loss or exchange of entrapped material since formation. Volatile-rich fluids (H_2O - CO_2 mixture) are important agents for metasomatic processes in the upper mantle and the noble gases and halogens preferentially partition into this phase leading to a strong geochemical coherence between these groups of elements.

The abundances of halogens in the major reservoirs of the earth shows a marked progression from chlorine, concentrated in the oceans, through to iodine which, through its affinity for organic material, is concentrated mainly in sediments. Although halogen abundances in the upper mantle are low, they are poorly constrained. This is particularly true for iodine, which is an element of special interest in view of its potential significance as an indicator of sediment recycling and by way of its link to ^{129}Xe anomalies in the mantle through the now extinct parent isotope ^{129}I .

Samples: Extensions of the ^{40}Ar - ^{39}Ar technique enable measurements of halogens (Cl, Br, I) and other elements (K, Ca, Ba, U) by production of noble gas isotopes from these species during neutron irradiation. Noble gases are extracted by stepped heating to diamonds in the temperature range 600 - 2100°C . Samples analysed include cubic (coated) and polycrystalline diamonds from southern Africa: 15 coated stones from an unknown source in Zaire, 3 coated stones from the Jwaneng kimberlite (Botswana) and 4 polycrystalline diamonds from the Orapa kimberlite (Botswana).

Results: Stepped heating gives a bimodal release of Ar with peaks at 1200°C and at the graphitisation temperature of 2000°C , both temperature intervals give high $^{40}\text{Ar}/^{36}\text{Ar}$ values of $20,000$ - $30,000$ typical of degassed upper mantle (MORB). Both types of diamonds contain excess ^{40}Ar (Ar^*) with most samples giving anomalously old apparent ages $>4.5\text{Ga}$. $^{40}\text{Ar}^*$ shows a good correlation with Cl and Br. $^{40}\text{Ar}^*/\text{Cl}$ for cubic diamonds is relatively constant at $8.5 \pm 0.9 \times 10^{-4}$ molar (M); this ratio is slightly higher and more variable in polycrystalline stones ($>10 \times 10^{-4}$).

Bromine and chlorine show good correlation in cubic and polycrystalline stones (Fig. 1). Br/Cl has a mean of $(1.4 \pm 0.3) \times 10^{-3}$ ($n=19$) which is, within error, equal to both the seawater and MORB ratios of 1.55×10^{-3} and 1.4×10^{-3} (Schilling et al., 1978). Figure 1 shows that I and Cl are not well-correlated, although coated diamonds show lower and less variable I/Cl (2 - 10) $\times 10^{-5}$ M than polycrystalline diamonds (30 - 300×10^{-5} M). Both types of diamond have I/Cl considerably higher than seawater ($\text{I}/\text{Cl} = 9.5 \times 10^{-5}$ M), but only the values from coated stones encompasses the MORB value 3×10^{-5} (Deruelle et al., 1992).

Discussion: The halogen content of the mantle fluid trapped in cubic diamonds are estimated to be 2-5 wt.% Cl, 60-120 ppm Br and 1-3 ppm I and the concentration of ^{40}Ar is $(1$ - $3) \times 10^{-2}\text{ml/g}$. This represents about a factor 5000 enrichment relative to present-day upper mantle values (MORB source). To achieve this level of enrichment the fluid phase must be present at a level of about 200 ppm.

The halogen abundances present in the mantle region from which the fluids derive can be estimated assuming an upper mantle ^{40}Ar concentration of 4×10^{-6} ml STP/g (Allegre et al., 1986) and using the measured $^{40}\text{Ar}^*/\text{Cl}$ value in diamond of 8.5×10^{-4} M. The estimated values are 7 ppm Cl, 25 ppb Br and 0.1-2.5 ppb I. In Table 1 these values are compared with abundances in the MORB source, crust and seawater. Table 1 shows that there is close correspondence between the halogen contents of the sub-continental mantle (from diamonds) and sub-oceanic mantle (MORB source). An important implication of this finding is that there is an apparent uniformity of halogen abundances and ratios throughout large regions of the upper mantle; a result which is consistent with observations made for other volatile elements (e.g., noble gases, C and N).

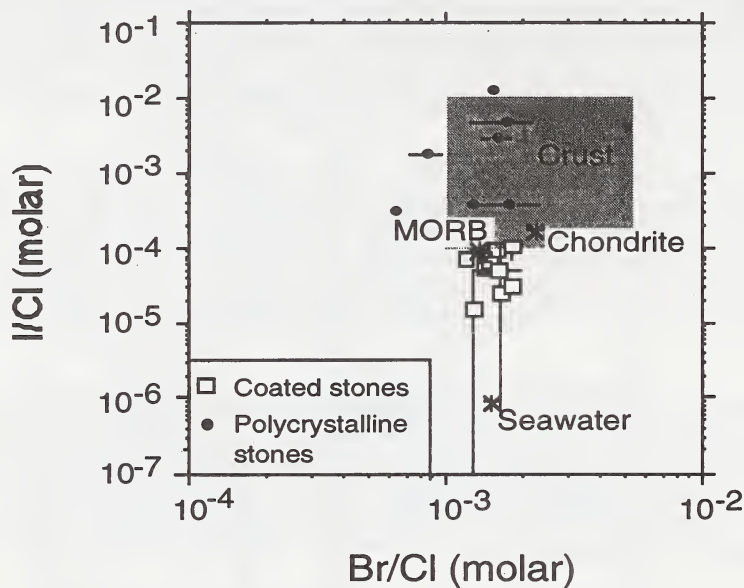


Figure 1. I/Cl versus Br/Cl for coated and polycrystalline stones. Each point represents the total release from an individual diamond. Shaded area is the range characteristic of crustal values.

	Cl (ppm)	Br (ppb)	I (ppb)
Diamond§	8	25	(0.1-2.5)
MORB¶	7	20	0.8
Crust	130	2700	820
Seawater	19000	67000	64

§Upper mantle [^{40}Ar] = 4×10^{-6} ml/g (Allegre et al., 1986); $^{40}\text{Ar}^*/\text{Cl}$ = 8.5×10^{-4} M.

¶MORB data: Cl - Schilling et al. 1980 and Br - Deruelle et al., 1980.

Table 1: Halogen abundances in the main terrestrial reservoirs

Figure 2 shows $\delta^{13}\text{C}$ versus I/Cl for coated and polycrystalline. The coated stones show a restricted range in $\delta^{13}\text{C}$ (-5 to -7 ‰) that are typical of mantle carbon values and relatively low I/Cl values that are similar to MORB. Two of the polycrystalline stones (one each from Orapa

and Jwaneng), give mantle $\delta^{13}\text{C}$ values and high I/Cl values. However, the remaining polycrystalline diamonds are more depleted in ^{13}C and have $\delta^{13}\text{C}$ values as low as -20‰. These diamonds have I/Cl values that are up to two orders of magnitude higher than those of coated diamonds. This indicates a separate diamond-forming event for polycrystalline diamond which may have involved subducted crustal material.

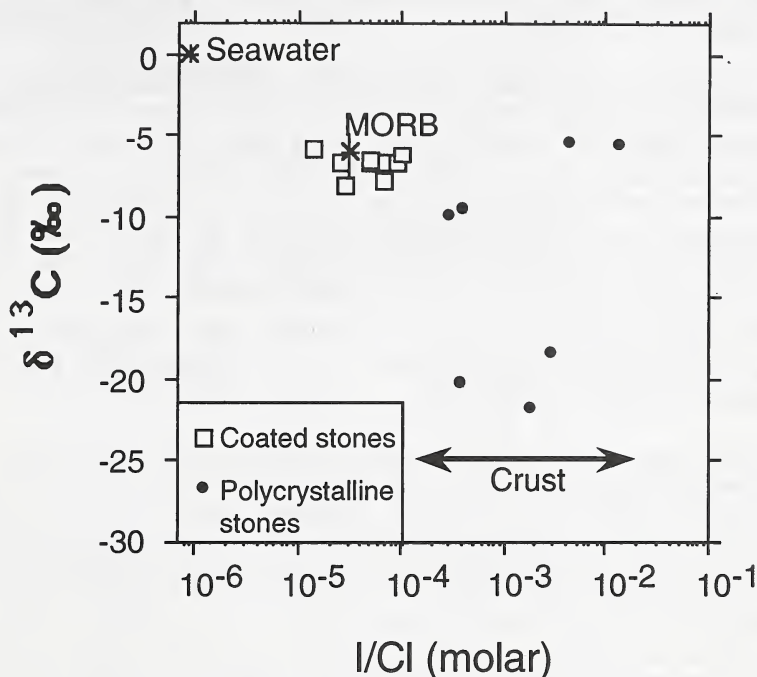


Figure 2. $\delta^{13}\text{C}$ versus I/Cl for polycrystalline and coated stones.

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