# CO$_2$-BEARING DIAMONDS FROM THE GEORGE CREEK K1 KIMBERLITE DYKE OF THE COLORADO-WYOMING STATE LINE DISTRICT.

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The nature of volatile phases present in the Earth's mantle is of great interest to geologists, but sampling these volatiles has proved problematic as most fluid inclusions in mantle rocks are of secondary origin (Pasteris, 1987). Diamond, due to its unrivalled tensile strength, is the most likely candidate to preserve primary fluid inclusions, and numerous mass spectrometric studies of encapsulated volatiles have been published. Nitrogen has been recognized as a significant impurity in Type Ia diamonds (Kaiser and Bond, 1959); in addition, the presence of $H_2O$, $CO_2$, $CH_4$, Ar and possible $H_2$ and CO has been reported by Melton *et al.*, (1972) following crushing experiments. However, experiments of this kind are extremely susceptible to gas contamination from the crushing apparatus. Further doubt is cast on these results by thermodynamic modelling which indicates that these species could not be stable in the proportions reported, at the temperatures and pressures required for diamond crystallization (Taylor, 1988).

Chrenko *et. al.* (1967) first reported the presence of $H_2O$ and carbonate in fibrous diamond coat. The presence of these phases in microscopic fluid inclusions has been confirmed by TEM studies (Guthrie *et al.*, 1991). The first conclusive evidence of $CO_2$ in an uncoated diamond of unknown origin has been presented by Schrauder and Navon (1993), who interpreted Infra-red (IR) absorption peaks at 3752, 3620, 2376, and 650 cm$^{-1}$ as being caused by $CO_2$ contained within sub-microscopic inclusions in the diamond lattice. The exact position of the $CO_2$ $\upsilon_3$ absorption peak is pressure-dependent (Hanson and Jones, 1981), and $\upsilon_3$ absorption at 2376 cm$^{-1}$ implies that the $CO_2$ is held at an internal pressure of 50 kb at room temperature (Schrauder and Navon, 1993).

Anomalous IR spectra, similar to those reported by Schrauder and Navon (1993), have been obtained for numerous uncoated diamonds from the George Creek K1 kimberlite dyke. Step-heating of selected diamonds with anomalous IR absorption spectra to 1200 °C in an Ar atmosphere had no effect on the anomalous peaks, but $CO_2$ and subordinate amounts of gas of unknown composition were released (A. Verchowsky, pers. comm., 1994). This may indicate that the $CO_2$ is now present in extremely stable sub-microscopic inclusions at lattice defect sites, rather than micron-sized fluid inclusions. SEM investigation failed to produce any evidence of fluid inclusions in the diamonds, furthermore the anomalous pink, brown or orange cathodoluminescence (CL) associated with $CO_2$-bearing diamond zones is consistent with the location of $CO_2$ in sub-microscopic fluid inclusions at lattice defect sites.

Schrauder and Navon (1993) reported a single $CO_2$ $\upsilon_3$ absorption peak at 2376 cm$^{-1}$, yet the George Creek specimens are more complex, with double or triple absorption peaks, occurring within the same specimen. Pressure estimates from the position of the $CO_2$ $\upsilon_3$ peak range from atmospheric pressure to unreasonable pressures in excess of 200 kb at room temperature which would correspond to even greater pressures in the hot mantle. This complexity may have resulted from high temperature annealing processes facilitated during prolonged residence of the diamonds in the mantle. Precipitation of negligible amounts of graphite on the walls of inclusion cavities may have decreased the volume (and hence increased the pressure) within the $CO_2$ inclusions, whereas the lower pressure estimates may be explained by decrepitation of $CO_2$ inclusions.

A correlation between the presence of $CO_2$ and yellow or orange UV luminescence, and yellow, brown or red body colour was noted. Cathodoluminescence photomicrographs of $CO_2$-bearing diamonds reveal complex intergrowth relationships between $CO_2$-bearing and $CO_2$-free diamond growth generations. In many instances the distribution of the $CO_2$-bearing generation suggests that it postdates the $CO_2$-free diamond growth generation(s), and that renewed diamond crystallization occurred from $CO_2$-bearing fluids which invaded fractures and etched embayments in the $CO_2$-free diamond growth generation(s).

Mineral inclusions recovered from George Creek diamonds are dominantly of the eclogitic paragenesis and no peridotitic inclusions were identified. Apart from black rosettes of graphite and sulphide, clinopyroxene and garnet are the most common eclogitic inclusions. Biminerallic garnet-clinopyroxene inclusions have been recovered, as have websteritic orthopyroxene-clinopyroxene and orthopyroxene-clinopyroxene-phlogopite inclusions from two diamonds. The phlogopite is unusual in its high titanium content of ± 10 wt %. Titanium is hosted in abundant orange-brown to dark brown rutile inclusions in diamonds of the eclogitic paragenesis. Ilmenite is commonly found as tiny (<10 - 40 micron in diameter) inclusions within eclogitic garnet inclusions. The nature of inclusions associated with the $CO_2$-bearing diamonds is mostly limited to black rosettes and rare rutile, although garnet and clinopyroxene inclusions have been recovered from the $CO_2$-free fractions of these diamonds. A single inclusion of pure silicon oxide (coesite/quartz) has also been recovered from a $CO_2$-bearing diamond. No evidence of high pressure inclusions (e.g. majoritic garnet) was found in $CO_2$-bearing or $CO_2$-free diamonds, but the accommodation of elevated contents of $K_2O$ in clinopyroxene inclusions, and $TiO_2$ and $Na_2O$ in garnet inclusions reflects not only the bulk composition of the diamond growth region, but also high pressures of crystallization.

The recognition of two compositionally distinct groups of eclogitic garnet and clinopyroxene inclusions attests to the heterogeneity of the diamondiferous mantle sampled by the George Creek K1 kimberlite. Group GC1 inclusions are more magnesian in composition than Group GC2 inclusions and generally contain detectable Cr. Group GC2 inclusions are characterized by higher K, Na, Al, Fe and Ti contents than Group GC1 inclusions. The compositional distinctions between Group GC1 and Group GC2 inclusions may reflect heterogeneity of possible oceanic protoliths recycled into the mantle by subduction processes.

Temperature estimates of 1071-1178 °C (mean = 1138 °C) for diamond formation were obtained by application of the Ellis and Green (1979) thermometer to coexisting non-touching garnet and clinopyroxene inclusions. Lower temperatures of 912-977 °C (using the Ellis and Green (1979) and Bertrand and Mercier (1985) thermometers) for touching garnet-clinopyroxene and ortho-pyroxene-clinopyroxene inclusions, correspond to mantle temperatures at the time of kimberlite eruption. This implies lithospheric cooling of ~200 °C between diamond formation and kimberlite eruption.

The thermal evolution of the Colorado-Wyoming lithospheric mantle may also be interpreted from quantitative IR assessment of the aggregation state of substitutional nitrogen defects within George Creek diamonds. The $CO_2$-bearing diamond growth generation lacks spectral evidence of nitrogen defects, whereas the $CO_2$-free generation is characterized by low contents of highly-aggregated nitrogen defects and variable platelet development. Infra-red spectra indicate that the nitrogen content varies from below the detection limit to ~1518 at. ppm in the $CO_2$-free diamonds studied. Significant variation in nitrogen content and aggregation state was detected within single diamonds. Quantitative analyses of the nitrogen aggregation states are consistent with equilibration of the George Creek diamonds at temperatures of ~1220 °C for an assumed mantle residence time of 1.25 Ga. The discrepancy between temperature estimates from non-touching diamond inclusions and nitrogen aggregation states may be caused by the relatively large uncertainties in the calculations used to calculate the time-averaged mantle residence temperatures ($T_{NA}$) from the IR spectra. If this discrepancy is not an artefact of the method used, a heating event subsequent to diamond formation and prior to lithospheric cooling is required.

The lack of brown colour in most plastically deformed diamonds from George Creek implies that deformation did not involve heating as this is believed to promote the development of brown colour by incipient graphitization. Heating may have been required to generate free $CO_2$ in the mantle as it may exist as a free phase only once carbonation of mantle assemblages is complete, or if the regional geotherm is unusually high to permit melting. The dominance of eclogitic material in the diamondiferous mantle sampled by the George Creek kimberlite may have favoured the stabilization of $CO_2$ fluid as total carbonation of eclogite requires addition of 20 wt. % less $CO_2$ than that required for total carbonation of peridotite (Schrauder and Navon, 1993).

Depletion of many eclogitic diamonds in $^{13}C$ has been ascribed to crystallization of these diamonds from isotopically light organic carbon subducted into the mantle (e.g. Kirkley *et al*., 1991). Evidence that subduction may have played an important role in the formation of diamonds in the Colorado-Wyoming is provided by the marked depletion in the lighter $^{13}C$ isotope of up to - 31 ‰ $\delta^{13}C$ detected in a number of diamonds from George Creek. The complex intergrowth relationships between $CO_2$-bearing and $CO_2$-free diamond growth generations in many George Creek diamonds necessitates considerable spatial resolution in the determination of carbon isotopic composition. Determination of the variation in carbon isotopic composition of polished diamond plates is currently being undertaken using the ion-probe at Edinburgh University.

Abundant yellow-green slip lines, which transect zones of $CO_2$-free diamond with blue CL, developed in response to plastic deformation during mantle residence time. The remarkable etch features present on the surfaces of both $CO_2$-bearing and $CO_2$-free diamonds from George Creek indicate that severe oxidation of the diamonds occurred, possibly in the hypabyssal dyke environment. Etching and resorption of $CO_2$-free diamonds also occurred prior to growth of the $CO_2$-bearing diamond generation. Conditions experienced by the George Creek diamonds thus show considerable fluctuation between conditions conducive to, and conditions detrimental to diamond growth and/or preservation.

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