

PRESSURE - TEMPERATURE - VOLUME PATH OF MICRO-INCLUSION-BEARING DIAMONDS.

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Bulk composition, mineralogy, and internal morphology of micro-inclusions in cubic and coated diamonds, suggest that they represent an $\text{H}_2\text{O}-\text{CO}_2-\text{SiO}_2-\text{K}_2\text{O}$ -rich fluid, trapped by the diamonds during their growth. However, the depth and temperature of their formation have remained unclear. Some authors suggested that micro-inclusion-bearing (MIB) diamonds grew as phenocrysts from their host kimberlite, or from a fluid phase that separated from it. Others preferred a more complex evolution at depth.

P-T conditions of diamond formation are commonly constrained using mineral equilibria between primary crystalline inclusions. Unfortunately, no such inclusions have been found in cubic diamonds, except for one report of a sanidine inclusion in the coat of a coated diamond (Novgorodov et al., 1990). The micro-inclusions themselves contain crystalline quartz, apatite, carbonates and phyllosilicates (Guthrie et al. 1989), but these are probably secondary phases that grew from the trapped fluid at a later stage.

Infrared spectroscopy of inclusion-rich zones in the diamonds did not reveal the characteristic quartz absorption bands at 779 and 798 cm^{-1} (Navon et al., 1988). Following the identification of quartz by TEM, the infrared spectra were re-examined and it is proposed here that the bands at ca. 784 and 811 cm^{-1} (Figure 1) are quartz absorption bands that were shifted to higher energies as the result of high internal pressure currently existing in the inclusions.

Using a diamond anvil cell, Velde and Couty (1987) calibrated the shift of the 779 and 798 cm^{-1} , and other bands of powdered quartz as a function of pressure. The MIB diamonds also contain small grains of quartz inside a diamond matrix and are a very close analog of the diamond cell experiment. The recorded positions of the quartz bands in 25 diamonds was recorded using the Nicolet SX60 FTIR in Prof. G.R. Rossman's laboratory at Caltech. Figure 1. presents the result together with the pressure calibration of Velde and Couty. The energy shift of both bands correspond to pressures of 1.6-2.1 GPa (16-21 kbar).

Such high internal pressures should effect other bands as well. The broader bands at ca. 475 and 525 cm^{-1} are consistent with about 2 GPa pressure shift of the 464 and 515 cm^{-1} bands of quartz (Velde and Couty, 1987). It must be noted, however, that many silicates absorb in this region and the bands may be related to the presence of other phases. Carbonates are also present in the micro-inclusions. EDS analyses by both TEM (Guthrie et al. 1989) and electron probe (Navon, this volume) show that they contain Ca, Mg, and Fe. Since no IR data exist for complex carbonates at high pressure, it is impossible to uniquely identify the carbonate phases, or to use them as a barometer. No high pressure IR data has been found for apatite.

The high pressure within the micro-inclusions is, to the best of my knowledge, the highest pressure ever recorded in any fluid inclusion. The preservation of this high internal pressure was probably enabled by the small sizes of the inclusions combined with the high strength of the diamond. Larger inclusions would probably lead to decrepitation of the diamond matrix (Taylor, 1985). Extrapolating Taylor's decrepitation model to sub-micrometer size inclusions, it seems likely that the stress applied by the micro-inclusions can be accommodated elastically by the diamond.

Guthrie et al. (1989) found euhedral crystals within the inclusions. In no case the crystals filled the entire volume of the inclusions. These observations and the detection of water by IR strongly suggest that the pressure within the inclusions is hydrostatic exerted by water. If so, and if the inclusion volume is conserved, a pressure - temperature path may be calculated along a water isochore. The isochore assumption is reasonable as diamond compressibility is small and its high Young's modulus ensures small elastic response to removal of confining pressure during eruption. Both are almost fully compensated by thermal expansion. Rough calculations predict volume changes of less than a few permilles. A less founded assumption is that precipitation of the crystalline phases do not introduce significant volume changes.

At 1.8 GPa, 23 C, water freezes to ice VI with specific volume of $0.71 \text{ cm}^3/\text{gr}$. The shape of the IR water band does not resemble that of ice VI. It looks similar to that of liquid water. This is probably because the large surface/volume ratio of the micro-inclusions and their high solute content prevent freezing. In that case a specific volume of $0.77 \text{ cm}^3/\text{gr}$ is estimated from the metastable extension of liquid water compression data (Liu, 1982). This volume may now be used with a suitable equation of state to predict pressures at high temperatures.

The MRK equation of Holloway (1981) cannot be extrapolated to such small volumes. That of Kerrick and Jacobs (1981) yields unreasonably high pressures. Both were fitted only to low-P data (<8 kbar). Taylor (1985) suggested a new modification for use at high pressures. Saxena and Fei (1987) used shock wave and low-P data to fit a virial equation of state. The resultant P-T paths are presented in Figure 2. When heated to reasonable temperatures (1000-1200 C) the internal pressure in the inclusions falls very close to pressure estimates for South-African diamonds (Boyd and Gurney, 1986, Meyer, 1987).

Based on the shift of the IR absorption of quartz, an internal pressure of 1.6-2.1 GPa is estimated for micro-inclusions in diamonds at room temperature. The inclusion volume is similar to their volume at high P and T. Neglecting volume changes due to precipitation of solid phases from the initial fluid, the water isochore intersects the geotherm at a pressure range that is typical of most diamonds. This is in agreement with additional observations that strongly suggest that MIB diamonds were formed within the diamond stability field in the upper mantle and not as a metastable phase. The high internal pressure is also a clear indication that most inclusions remained sealed, preserving the original, unaltered fluid from which the MIB diamonds grew.

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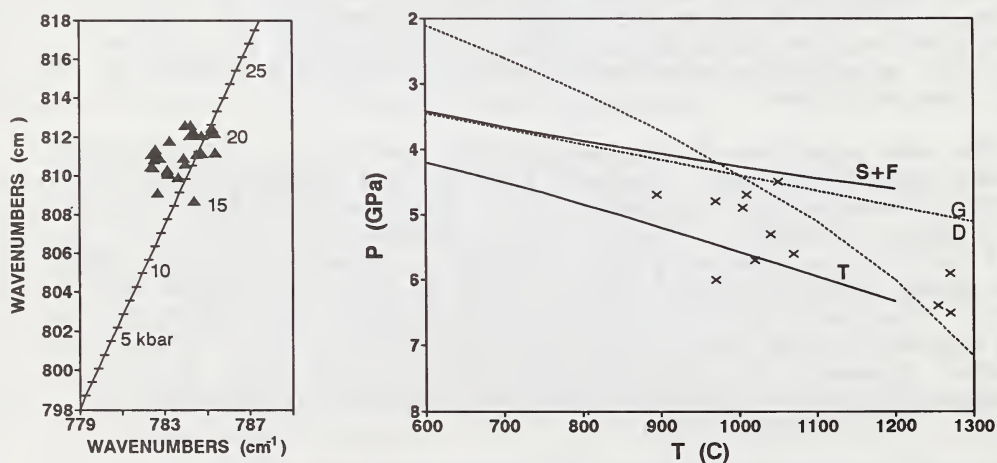


Figure 1. Peak wavenumbers of two IR absorption bands of quartz in micro-inclusions in diamonds. The scaled line indicates the pressure shift of the two bands, determined experimentally by Velde and Couty (1987). The quartz in the inclusions is under 15-21 kbar.

Figure 2. P-T path of MIB diamonds. Solid lines - isochores for water with specific volume of $0.77 \text{ cm}^3/\text{gr}$. S+F - Saxena and Fei, 1987; T - Taylor, 1985. Dotted line - Graphite-diamond transformation, dashed line - the 40 mW/m^2 geotherm. Crosses - P-T condition of diamonds with crystalline silicate inclusions (Meyer, 1987).