CARBONADO, CLATHRATE AND CAVITATION: A MODEL FOR THE ACOUSTIC INDUCTION OF DIAMOND.

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The most enigmatic of the diamond family is carbonado, which is loosely defined as sintered polycrystalline diamond. Carbonado is unusual because it is described as bonded, the material is porous and coke-like in appearance, is isotopically light (circa $-25^{0/00}\delta^{13}C$) contains low pressure crustal rather than upper mantle minerals, and occurs in Proterozoic alluvials (Brazil and central African Republic) without a recognized source in kimberlite or related rocks (Smith and Dawson 1985; Shibata et al., 1993, and refs. therein). These features have led to the proposition that carbonado may have formed by meteorite impact, which is unsupported because lonsdaleite (hexagonal diamond) is absent. Other interpretations for the origin of carbonado include ion-implantation by U and Th in coal deposits, crystal size modification of the P-T diagram for carbon (Kaminsky, 1994), or by a complex series of reactions in the upper mantle and subsequently in the crust (Kagi et al., 1994).

New observations show that carbonado ranges from clove brown thorough dark purple and to jet black. Carbonado has a patina implying melting and rapid quenching. Porosity varies from <1% to a maximum of 5% by volume, and permeability is extremely low. Microstructures are complex and highly variable. No mineral inclusions, apart from epigenetic vesicle-infilling at the surface of carbonado, has yet been observed.

The three largest "diamonds" ever reported from Brazil are carbonado, and Sergio is 61 cts heavier than the famous Cullinan. Given the restricted distribution of carbonado, at least in mineable concentrations in Brazil and the CAR, and the unusual properties of carbonado, it is possible that some exotic source and/or mechanisms are required for the synthesis of carbonado. The proposal made here may be described as the transformation of "ice to diamond," "acoustically-induced diamond," or CAROBS--"clathrates acoustically reduced on ballistic sonication". (carob = ceratonia siliqua; keration (GK) = little horn; qirat (Ab) = pod; hence, carat).

Acoustically generated hydrodynamic stresses have been shown to yield extraordinarily high temperatures (>5,000°C) and high pressures (exceeding 1 MBar) during transient (micro- to picosecond) cavitation of collapsing and imploding micro-bubbles (Moss et al., 1994); these physical and sonochemical (Suslick, 1990) conditions far exceed the minimum required for diamond formation (Fig. 1). Although cavitation has previously been suggested for the crystallization of diamond in kimberlite (Galimov, 1973) it is unlikely that the process is operative because bubble formation is a low confining pressure phenomenon which is at odds with the presence of high (5-6 GPa) to very high (10-15 GPa) pressure mineral inclusions in diamond.

The proposed starting material in the current model is a naturally occurring, three dimensional, molecular water ice framework (clathrate) that occurs in all oceans along continental margins. Clathrates contain cages of trapped gases (Kvenvolden, 1993). Type 1 and Type II clathrates are cubic, the latter has the structural symmetry of diamond and the versatility of hosting small and large diameter gas molecules (Fig. 2). Methane ($CH_4$) is present in naturally occurring clathrates and is the gas of choice in this diamond template. In the presence of water, high H:C ratios are achieved, providing protonation (i.e. hydrogen) and the required adhesion for diamond bonding. This is the heart of the carbon-vapor-deposition (CVD) process for the production of nanometer thin diamond films at low pressures and high plasma temperatures.

Ballistically accelerated cavitation would account for porosity, observed implanted rare gases (Xe, Ar, Kr from the clathrate), melt patinas, and bonding. The sonic source is unknown but several possibilities exist: intense seismic activity; sonic booms associated with explosive volcanism; shock and sono-transmitted irradiation by meteorite or comet impact; and less likely, sono-induced transmission from the spontaneous combustion of volatile hydrogen or hydrocarbon gases. Was the formation of carbonado a unique event in the Archaen in contiguous Brazil and the CAR? If the process is impact-related the K-T boundary Chicxulub crater in the Yucatan Peninsula would be a prime target for carbonado formation.

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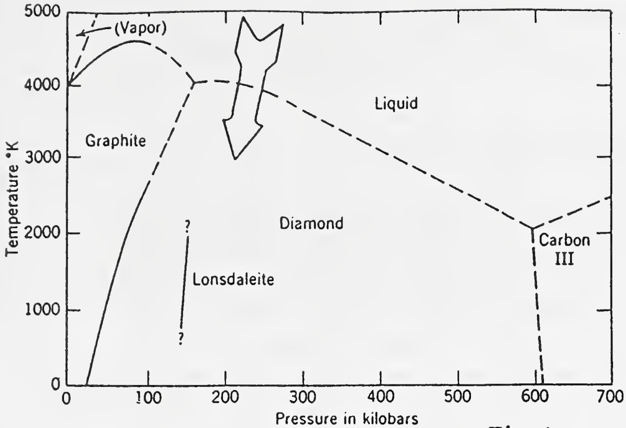
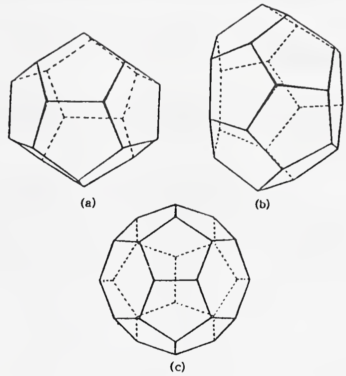
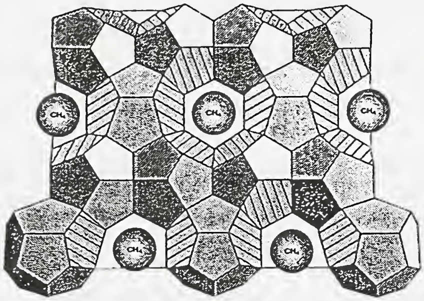



**Fig. 1**

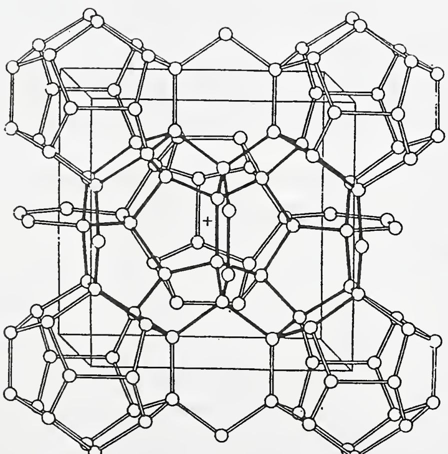



Gas cages in clathrates (see Fig. 3a-c) having 12 (in a), 14 (in b), and 16 (in c) faces in polyhedral coordination.

**Fig. 2**

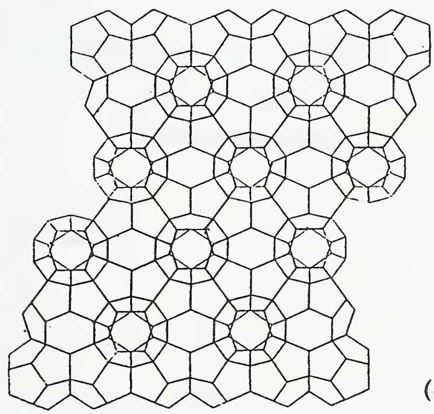


(a)



(b)

Type I clathrate structure. In (a) both the open and closed cages contain methane. The structure contains 12- and 14-hedra ·



(c)

Type II clathrate structure with 12- and 16-hedra cages, having the crystallographic and structural symmetry of diamond.

**Fig. 3**