

Diamond formation in the Earth's mantle

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Introduction. Despite the wealth of new and exciting information gathered in the past few years, a clear physical model of diamond formation has yet to emerge. A clear recipe for producing synthetic diamonds may be obtained, in principle, from a production engineer in a diamond factory. My feeling is that we are not yet at a stage where we, as diamond geologists, can give a clear recipe for what should be done for growing natural diamonds in the Earth's mantle. What are the sources of carbon for diamonds? What is the main carbon-bearing species during migration from the source and accumulation at the site of diamond formation? What are the physical conditions? What is the chemical reaction for diamond formation and how long does it take to grow? While good answers to some of the questions do exist, many are lacking. When were diamonds formed? More than a decade after we thought an answer was given by Richardson and co-workers, the question is open again, and the range of possible answers is from 3.3 Ga to just before emplacement at the surface.

Where is the Factory? Pressures and Temperatures of Diamond Formation.

Diamond formation in the mantle takes place under thermodynamically stable conditions. Thus, a first guess of the pressures and temperatures for diamond formation is given by a range of reasonable geotherms and the diamond-graphite phase boundary. Twenty years of thermobarometry has affirmed conditions within the diamond stability field. Most diamonds record formation along the 35-45 mW/m² geotherms and close to the diamond-graphite boundary (4.5-7.5 GPa, 950-1350°C). Some diamonds record higher temperatures, reflecting thermal disturbances. In addition to the classical thermobarometers, based on phase equilibria and major element chemistry, new thermometers and barometers, based on trace element partitioning among phases, were introduced. Although the exact calibration of the "Ni in garnet" thermometer is still debated, its strong temperature dependence is proved, and the ability to determine the temperature and pressure during trapping of individual peridotitic garnets is very useful. This is especially true in light of the recognition that inclusions trapped at different growth zones in a diamond record different conditions (commonly, falling temperature during growth). An important development is the identification of diamonds of very deep origin. In the 3rd IKC it was suggested that ferro-periclase (magnesiowüstite) and associated enstatites from Koffiefontein and Orroro are of possible lower mantle origin. Since then, new high pressure phases were added. Majoritic and khorringitic components in garnet inclusions and silicate spinel component in chromites suggest formation at depths in excess of 200 km. Solid CO₂ found in diamond may also originate at pressures of ~7 GPa. The recent finding of periclase, Ca-Si- and Mg-Si-perovskite, and a new tetragonal almandine-pyrope phase in diamonds from San Luiz, Brazil allowed confirmation of the ultra-deep source of this assemblage. These inclusions are, most probably, the only available natural samples of unaltered lower mantle minerals. One indication of the high pressure origin of the San Luiz inclusions was their expansion when released from their host diamonds. Determination of the internal pressure within mineral

inclusions provides an additional mean for diamond geobarometry. Garnets were shown to be under no pressure, but high internal pressures in olivine inclusions may allow barometry. The high internal pressure in fluid inclusions trapped in fibrous diamonds allowed determination of their depth of origin. The high temperature sensitivity of the rate of nitrogen aggregation in diamond makes it a useful thermometer. Even with the lack of precise age information, it can be used to assess the time-integrated temperature that the diamond experienced.

Where to get starting materials? Stable isotopes and the source of carbon. The only geochemical information recorded in the diamond crystal (and not in the inclusions) is the concentration and aggregation state of nitrogen impurities and the isotopic composition of C and N. Hydrogen is also present in the diamond lattice, but few studies examined its

concentration; its isotopic composition was never measured. The distinction between the carbon isotopic composition of peridotitic and eclogitic diamonds is well known. Peridotitic diamonds span a narrow range around -5‰, the eclogitic diamonds span a wide range (+3 to -30‰) with clustering at around -5, -10 and -20‰. This difference was interpreted as reflecting different sources for the carbon: mantle carbon for the peridotitic suite, subducted carbon for eclogitic diamonds. Studies of oxygen and sulfur isotopes of diamond inclusions are also compatible with this suggestion. However, the isotopic signature of nitrogen complicates the situation. Attention has been drawn recently to the negative values of $\delta^{15}\text{N}$ in most eclogitic diamonds. Subducted nitrogen is expected to be heavier and of positive values. An alternative source of carbon for eclogitic diamonds and the commonly quoted source for peridotitic diamond is "mantle carbon" or "astheno-spheric carbon". The physical picture of such a source is vague.

What does the factory look like? Diamond inclusions and source region mineralogy.

The rocks at the diamond source region are fairly well known: peridotites and eclogites. Diamond-bearing xenoliths supply information on the mineralogy just before the eruption time of the kimberlite. The minerals encapsulated in the diamonds preserve the information on the mineralogy at the time of diamond formation. If the two events are separated in time, compositional difference may evolve between the two suites. Some differences are documented in the major and trace element geochemistry. However, in general, the two suites present close similarity. In spite of expanding research, only a few new minerals or associations were documented in recent years. Most, like staurolite or magnesite belong to the eclogitic or the peridotitic suites. Only the "ultra-deep" inclusions may be considered as a new rock type. The focus of research was on integrated and more detailed studies. The relations between inclusion chemistry, the isotopic composition of the host diamond and its nitrogen content were studied in detail for specific mines. Attention was also given to the relation between inclusion chemistry and morphology and the growth history of their host diamond. Important observations include the identification of sulfides, wüstite, and native iron near the genetic center of some Siberian diamonds, the syngenetic relation between inclusion and host revealed by diamond growth zones that are cut by inclusions and are not wrapped around them, and the evolution of inclusion chemistry from core to rim. Using ion- and proton-probes it is now possible

to study the trace element chemistry of the inclusions along with the traditional major element composition. Such studies indicate a complex history for many inclusions. For example, harzburgitic garnets that are depleted in compatible major and trace elements are enriched in Sr and LREE. These *in-situ*, spot techniques now allow the examination of trace element zoning within individual inclusions. The recent finding of Sr zonation in garnet inclusions may indicate a young age of some peridotitic diamonds, or the presence of an enriched component encapsulated with the garnets in the inclusions.

What are the starting materials? Oxygen fugacity and volatiles in diamonds.

Carbon may be accumulated in some forms, including elemental carbon (graphite, amorphous carbon, or diamonds), carbon bearing minerals (e.g., carbonates or moissanite that are rarely found as inclusions in diamonds), and oxidized or reduced carbon bearing fluids. The morphology and growth pattern of diamonds suggest growth from fluid or melt, rather than a solid state growth. Fluids were found in diamonds, but it is interesting to note that in-situ determination of trapped fluids recorded only relatively oxidized species (C-CO₂-carbonate-H₂O). Trace element patterns of some mineral inclusions recorded enrichment in incompatible elements, commonly attributed to interaction with carbonatitic fluids. This is surprising, because oxygen fugacities indicated by mineral inclusions in diamonds span a wide range between the iron-wüstite (IW) and fayalite-magnetite-quartz buffers. Below the wüstite-magnetite buffer, CH₄ and other reduced species should dominate the volatile assemblage. Yet, they were never detected in-situ by IR measurements. Such reduced species were recorded in some analyses of gases released from crashed diamonds. Most studies of fluids in diamonds concentrated on the study of trapped fluids in fibrous diamonds. These diamonds appear as cubes of radiating diamond fibers, or as coats of similar material growing over octahedral diamonds. They carry varying amounts of microscopic inclusions rich in water, carbonates, silicates and phosphates. The uniformity of the chemical composition of inclusions found in individual diamonds and the presence of multi-phase assemblage in many individual inclusions suggest that they trapped a fluid (a volatile-rich melt or low density fluid) from which the present mineral phases crystallized during ascent, or at the surface. The finding of eclogitic inclusions within coated diamonds and of a coated diamond in an eclogitic xenolith attest to the close association of these fluids with the eclogitic environment. The major element compositions of the fluids span a wide range and vary between carbonate-rich endmember and silica-rich hydrous endmember. Most fluids are extremely rich in K and in other incompatible trace elements. The trace-element patterns of fluids in diamonds from Zaire and Botswana are highly fractionated and are roughly similar to those of kimberlites and lamproites. The fluids are also rich in Ar and halogens, and reveal relatively uniform, MORB-like ⁴⁰Ar/³⁹Ar, Br/Cl and I/Cl. Carbon isotope ratios of the fibrous diamonds are remarkably uniform. The $\delta^{13}\text{C}$ of coated and cubic fibrous diamonds from Zaire, Botswana, Sierra Leone and Siberia vary between -5 and -8‰. The $\delta^{15}\text{N}$ is also uniform (-2 to -9‰). The isotopic composition Sr in Zairian diamonds is similar to that of their host kimberlites. This, as well as the similarity in $\delta^{13}\text{C}$ and the low aggregation state of the nitrogen in fibrous diamonds led to suggestions of direct genetic relationship with the host kimberlites. In spite of the similarities, the difference in major element composition and the association with eclogitic inclusions and xenoliths preclude

direct genetic relationship. It was suggested that fibrous diamonds formed at the final stages of cooling and crystallization of kimberlite/lamproite-like melt at depth. Fluids were found in other diamonds as well. CO₂ was found in brown diamonds from the Colorado-Wyoming province and possibly Siberia. Cl-rich hydrous fluids were found in clouds of micro-inclusions in both eclogitic and peridotitic octahedral diamonds from South-Africa, Siberia and China. The clouds also host micro-inclusions of carbonate-rich fluids. Most important is the close association of these hydrous- and carbonate-rich fluids with micro-inclusions of garnet and clinopyroxene (in eclogitic diamonds) or olivine and phlogopite (in peridotitic diamonds) that are also found in these clouds. All the fluids described here were trapped in the diamonds during growth. They carry carbon and may precipitate diamonds in response to changes in P, T, or fO₂. They likely represent the solutions from which their host diamonds grew.

Are the competitors still around? The age of diamonds. The close similarity of diamond inclusions and minerals in diamondiferous xenoliths strongly suggests that diamonds were formed within such rocks and are not phenocrysts in the erupting kimberlite. Nd isotopes suggest that garnet and clinopyroxene inclusions in many diamonds were formed long before the kimberlitic eruption. For the decade following 1984 it was held that the majority of diamonds are old and reside in the mantle for long times. This convenient assumption is now shaken and the field is open for a new discussion. Following the Pb and Nd model ages it seemed that sulfides and harzburgitic garnets from Finsch and Kimberley are older than 2.5 Ga. Nd isochron dating of lherzolitic garnets and clinopyroxene from Premier and Udachnaya yielded ages of ~2 Ga for both, again, much older than the eruption age. In eclogitic diamonds, Nd isochron dating of inclusions in diamonds from Argyle, Orapa, and Finsch, fall in the range of 990-1580 Ma, 400-1400 Ma before the emplacement of their host kimberlites. Model ages of Finsch single eclogitic inclusions yielded similar, as well as older ages. In contrast, Nd, Pb and ⁴⁰Ar/³⁹Ar ages of inclusions in Premier diamonds are indistinguishable from the age of the kimberlite (~1180 Ma). Supporting evidence for the old formation age of most diamonds comes from study of N-aggregation in diamonds. Although there is a strong T-dependence of the aggregation rates, present calibrations combined with geothermometry suggest long residence times for diamonds rich in B-centers. In contrast, zoning of Sr concentrations in Siberian garnet inclusions calls for short residence times at mantle temperatures - if stored for more than 105 years, the concentration gradients must homogenize. When considered alongside the observations that Sr isotope compositions are decoupled from the Nd data, do not form isochrons, and are unsupported by Rb, these data suggest that the history of the diamonds and their inclusions may be more complex than that told by Nd isotopes alone. It is possible that the Nd ages are inherited from the garnet precursor, and that the crystallization of the garnet and its host diamond occurred shortly before eruption. Recent determination of a Re-Os model age for Koffiefontein P-type diamond close to that of kimberlite emplacement also indicates that the dating of diamond formation is still an open issue.

Acknowledgments. References to all the works mentioned here will be found in the Proceedings volume. I would like to thank Elad Izraeli for his help and the Israel Science Foundation for support.