CHAPTER 1

INTRODUCTION

1.1 General

Chemistry today has become deeply linked with all branches of natural sciences. One of the major emphasis of chemistry today is materials. With the current developments in instrumentation, with the power to see materials at smaller and smaller dimensions, a new branch called nanoscience has opened up. My research pertains to nanoscale materials embedded in bulk materials, especially gemstones which belong to the minerals of earth science. Earth’s interior is not a benign world but it stores the geological history of our planet.

Among the mineral kingdom, gemstones are traditionally classified as precious and semi-precious varieties in the west by ancient Greeks. In modern culture, the precious stones are diamond, ruby, sapphire, and emerald, while all other gemstones are relegated into the semi-precious varieties. Among them, diamond is the candidate of my research and is considered as the prince of solids in view of its highest hardness and relatively inert, unreactive nature.

1.2 Minerals / Determinative mineralogy

Minerals are products of earth science or sensu-stricto to geological science and distinctly embrace inorganic chemistry and materials. My research deals with inorganic minerals. Out of the more than 115 classified elements under the periodic table of D. I. Mendeleev, silicon and oxygen are by far the most abundant elements of the universe forming nearly 93% of all atoms representing 75% of all matter by weight. The other most common elements found in most of the natural or native minerals are Al, Fe, Ca, Na ,Mg, Na, and Ti, and these elements contribute to form more than 97% of the materials of the earth’s crust with oxygen being the most abundant (about 50%). Out of these, only a very small number of 12 play an important part of making up the crust of the earth and the water and air surrounding it. Yet, we
can find that only 4 of these elements are in abundance to constitute majority of earth and they are oxygen, silicon, iron and magnesium in the order of its abundance. The basic element of the commonest mineral of quartz is silica (SiO₂), a compound of silicon and oxygen.

By definition, mineral is a body produced by the processes of inorganic nature, having usually a definite chemical composition and, if formed under favourable conditions, a certain characteristic atomic structure which is expressed in its crystalline form and other physical properties. The definition further carries an explanation that a mineral must be a homogenous substance, even when minutely examined by the microscope. It must have a chemical composition which is commonly definite and expressed by a chemical formula. In some cases, minor variation of chemical composition will be there but within certain limits according to a definite law. Minerals are also found to occur in a native state in accordance with chemical laws without combining with other elements including the definite compounds of these elements, e.g. gold, silver, platinum, telluride and chalcopyrite–sphalerite, etc. A comprehensive study of physical mineralogy and chemical mineralogy is found to be the analytical approach for a thorough understanding of this branch of science.

Minerals such as quartz, feldspar, mica, pyroxene, amphibole and olivine are all to be considered as the building blocks of natural elements with an ordered atomic arrangement, and can be grouped into different silicate minerals by their chemical formulae. All minerals have a certain three-dimensional structure, which is based on the particular components of their atoms. For example, the basic structure of all silicates is a tetrahedron, a solid shape with four sides. The small silicon ion is at the centre, surrounded by four large oxygen ions in their corners. Such tetrahedrons combine with many types of similar structures to form rings, chains, streaks, etc. In the upper mantle, the greenish mineral olivine dominates, making up more than 70 percentage of the upper mantle’s mineral content. [1].
Hydrogen, nitrogen and carbon are the vital elements constituting the inorganic group of minerals which are also present in all the life forms of nature. An important study undertaken by Madison Berkeley [2] indicates that the International Mineralogical Association has recognized about 4,411 mineral species and out of them 2,523 of them contains hydrogen, representing 57% of this total figure. Hydrogen is by far the most abundant element in the universe: 93% of all atoms or 75% of all matter by weight. On earth, there are 91 known naturally occurring elements and, however, 94% of the earth is composed of only four elements as iron, oxygen, silicon and magnesium in the order of its abundance. Despite its lower relative abundance on earth, elemental hydrogen is found to be present in more than half of all minerals.

It is interesting to record that chemical signature of elements such as P, Ca, Zn, Mn, etc., are found preserved in the fossils of the first bird belonging to the 'Archaeopteryx' family which existed 150 million year old. This "dinosaur" fossil, long thought to contain nothing but fossilized bone and rock, has been hiding remnants of the animal's original chemistry. Using the bright X-ray beam of the Stanford Synchrotron Radiation Light source, located at the Department of Energy's SLAC National Accelerator Laboratory, an international team of palaeontologists, geochemists and physicists has revealed this transformative glimpse into one of the most important fossils ever discovered: the Archaeopteryx, a half-dinosaur/half-bird specie [3].

1.3 Inclusions in minerals

1.3.1 What is an inclusion?

Inclusions are considered as internal imperfections due to the rapid crystallization of magmatic fluids in the earth’s mantle environs. Hence, inclusions in minerals are viewed as their internal flaws which reduce the value of a gemstone. But to the mineralogist and gemmologist, they can reveal the gemstone's identity of how it formed and even the source of its origin. Most inclusions can be viewed using a hand
lens of suitable magnification (10x), but are best studied under the more powerful magnification of an optical polarizing microscope. Yet, inclusions in minerals are considered as the signature of God endowed with an exclusive aesthetics of nature and allured them as gemstones in our history from several thousands of years ago. We can appreciate the external beauty of minerals only through the internal exposition or its characteristics from which we can extrapolate the physical conditions in which they were formed such as temperature and pressure (barometrics) and the fluid contents such as O₂, CO₂ and juvenile H₂O prevailed in the mantle of earth. Fluid inclusions paved the way to report the isotopic analyses of carbon and oxygen in hydrothermal calcite of the Trostyanes volcanogenous complex (Ukranian Carpathians) [4] for the first time. The results of the isotopic analyses studies of carbon and oxygen showed homogeneous values of δ¹³C and δ¹⁸O, during the early stages of mineral formation and cooling. Thus, it is an established fact that the fluid inclusions capture and record the initial characteristics of the physical and chemical conditions during their growth within their natural surroundings. Inclusions throw light on the internal characteristics of its physical and chemical conditions during their growth in their natural surroundings. Inclusions are also termed as daughter products by Rossasco et al. and this was his first successful application of laser excited Raman spectroscopy of non-destructive identification of fluid inclusions [5]. The geological environments of the inclusions enable to relate them with their provenance also known as the native place of its genesis and its parent source rocks, including their geographical distributions. Hence, the studies of inclusions in nano and sub-micron dimensions of such elements or molecules are found very useful to probe into the origin and history of natural diamond, the candidate of my research.

1.3.2 Paragenesis

Besides, inclusions are the DNA-like evidences and considered as the treasure troves in tracing the origin of their sources and their mutual relationship with the host mineral in which they are found. The name inclusion is given to any foreign body enclosed within the crystal irrespective of its origin, phase and also of the period of its
inclusion as before, during or after the crystallization of the host mineral which are referred to as **protogenetic, syngenetic and epigenetic**, respectively [6]. Inclusions in minerals resemble an embedded time capsule of fossil time which reveals the **paragenesis** to mean the sequences of the host and the guest pair, their chemistry with its phases. In addition, inclusions throw light into the geological and chemical information. Among all available sample, syngenetic mineral inclusion in diamonds are significantly found suitable for the study of the mantle processes because they are well preserved from subsequent chemical modification by the host diamonds during their ascent to the surface.

### 1.3.3 Types of inclusions

Inclusions in minerals are found to be of homogeneous and heterogeneous nature.

#### 1.3.3.1 Homogeneous inclusions

In homogeneous inclusions, the host mineral and the inclusion mineral will have similar chemistry as graphite in diamond. Both graphite and diamond are constituted by a single element **carbon**. Graphite is $sp^2$ hybridized polymorph of carbon while diamond is $sp^3$ hybridized. The morphological or growth structures of carbon and diamond differ as carbon is in a hexagonal system while diamond in an isometric or cubic system of crystal habits, respectively.

#### 1.3.3.2 Heterogeneous inclusions

In heterogeneous inclusions, the host mineral and the inclusion minerals will have dissimilar chemistry due to different physicochemical conditions of crystallization. Magnetite ($Fe_3O_4$), rutile ($TiO_2$), and zircon ($ZrSiO_4$) are the common inclusions in many minerals though quartz ($SiO_2$) is found invariably with inclusions of rutile, tourmaline (B, Al, silicate), etc. Boron, nitrogen and fluorine including water molecule may also be found as inclusions in diamond depending upon their petrological and P-T conditions of the mantle environs. Some of the silicate minerals like garnet, pyroxene, a meta silicate of Mg, Fe and even carbonates like calcite ($CaCO_3$), magnesite ($MgCO_3$) are considered as important heterogeneous inclusions found as solid inclusions besides platinum, group elements (PGE) in diamonds. An
exhaustive coverage on these aspects is beyond the scope of this thesis. An inclusion of garnet in diamond is an exquisite example of heterogeneous inclusion of protogenetic origin as shown in Figure 1.

![Figure 1.1](image)

**Figure 1.1:** Red garnet inclusion in natural faceted diamond (Source: Christiane Woodward and Roger Harding, British Museum Natural History, Gemstones, Sterling Publishing Co, Inc. New York (1988)).

1.3.4 Nature of inclusions in minerals

Inclusions are found in **solid, liquid and gaseous** phases in most of the minerals and each is identifiable either by naked eyes when in macroscopic sizes and by an appropriate optical microscope, if they are found in microscopic sizes. In majority of cases, the observed liquid inclusion is simply water or it may be a salt solution if it is a saline environment. In the case of quartz, inclusion of liquid CO$_2$ was first proved by the Dutch pioneer, H. Vogelsang [7]. His findings of quartz, bearing trachyte inclusions are of historical importance and he was recognized as a fluid inclusion specialist since 1857. For example, the host mineral, the Columbian emerald, is found in a green matrix. Irregular shaped bubbles of inclusions in micrometre sizes are seen in the matrix of this host mineral. Among them, salt crystal is seen with high relief and gas bubble is seen with the least relief. Saline water is found with an intermediate relief.
Figure 1.2: Three phased inclusions in Columbian emerald; Emerald is the matrix in green colour. Salt crystal boundary is seen with a high relief, gas bubble shows a least relief and H₂O is seen with an intermediate relief. (Source: Christiane Woodward and Roger Harding, British Museum Natural History, Gemstones, Sterling Publishing Co, Inc. New York (1988).

1.3.5 Icon of inclusions of gemstones

The studies of inclusions in minerals or gemstones are incomplete without remembering Edward Gûbelin, the icon of ‘Inclusions of Gemstones’, as mentioned before. He developed his own dark field gemmoscope in 1942 using the latest Zeiss optics. His advice to his students of gemology was to be inquisitive and to remain curious to find out everything what one can find out from gemstones [8].

1.3.6 Who am I? - A self-introspection by the inclusions in diamond

A probe into the inclusions in minerals suggested by Gûbelin appears to be a self-enquiry or a self-introspection by the inclusion itself. This is reminiscent of the
profound, question of the great Hindu seers, Adi Sankara and Bagwan Ramanan, who inquired, ‘Who am I’, Gübelin began publishing on gemstone inclusions since 1940 and the select solid inclusions in some of the important minerals from his collection are included in my thesis out of my infectious interest to assimilate his knowledge.

1.3.7 Inclusions in inorganic minerals

The chemistry of inclusions in minerals is known to be of inorganic and organic nature and they are explained below with examples from each type of such minerals. A few examples of tremolite and actinolite (an amphibole fibrous variety of silicate) in emerald, (Be, Al silicate- a green variety of Beryl) and calcite (CaCO$_3$) in ruby (Al$_2$O$_3$) and tourmaline, a boron aluminium silicate in quartz (SiO$_2$) are shown in Figure 1.3.

![Image of inclusions in minerals](image.jpg)

Figure 1.3: (A) Inclusion of tremolite (amphibole fibres) Ca, Mg, Fe, Al silicate are from the emerald (Be, Al silicate, a green variety of beryl). These amphibole fibers, which Gübelin believed as tremolite, are characteristic of emeralds from Sandawana, Zimbabwe. (B) Protogenetic inclusion of actinolite, a variety of amphibole in Austrian emerald. (C) Calcite (CaCO$_3$) in Burmese ruby (Al$_2$O$_3$) is protogenetic inclusion (formed before the growth of the host minerals). (Source: Dr. Gübelin’s classified mineral inclusions, Photo Atlas of Gemstones, 1942).
Tourmaline

Tourmaline is a complex silicate mineral of boron and aluminium formed at high temperature and pressure, found in igneous and metamorphic rocks best developed in granitic pegmatite (i.e. acidic rocks, silica > 67%). It is a reaction product by pneumatolysis by enriched boron vapour on the pre-existing acidic rocks. Boron as Be₂O₃ is expected to be more than 10% in tourmaline. Needles of tourmaline inclusions in quartz (highly acidic variety) are shown below in Figure 1.4.

![Tourmaline inclusions](image)

(magnified 20×)

(A)  

(B)

**Figure 1.4:** Inclusions of tourmaline (boron aluminium silicate) in quartz. (A) Needles and (B) Schorl type (black iron rich variety). (Source: Dr. Gübelin’s classified mineral inclusions, Photo Atlas of Gemstones, 1942.)

1.4 Inclusions in crypto crystalline quartz

The word ‘crypto’ is to distinguish from macro and micro dimensions of the inclusions in quartz and they are seen well under a microscope rather than by naked eyes. Some of the important crypto crystalline varieties of quartz such as agate, onyx, tiger’s eye and opal are considered important to be included in my thesis as explained below.
1.4.1 Agate

Agate is a semiprecious crypto crystalline variety of quartz (silica mineral) commonly found in cavities in eruptive volcanic rocks or in lavas of earlier eruptions. These agates have banded crystal architecture with successive parallel layers to the sides of cavities. These are the features of a cooling magma fluid in the form of bubbles of steam and other gases which overtake the process of solidification and are frozen in cavities. Later, the fluid carrying alkali silicates percolates into these bubbles and triggers coagulation and to become a silica gel. The soluble mineral oxides like iron oxide from iron bearing rocks diffuse into the silica gel and produce the regular layers of iron oxide (Fe₂O₃). Ultimately, the whole mass gradually hardens with loss of water and most of its silica gel crystallized as quartz or chert but faithfully retaining the banded structures of its other mineral contents of iron oxides, as inclusions. Varieties of agate are indicated by the variation of their coloured bands of inclusions and are called as chert for iron and white bands with alternating layers of black, brown or red called chalcedony and onyx. The different shades of red variety are known as sardonyx. An important agate with green landscaping inclusions denotes vegetable growth resembling fern, moss or other vegetation, reflecting the paleo environs at the time of its crystallization as shown in Figure 1.5.
**Figure 1.5 (A):** Landscape agate: (Asia Minor), an oval shaped agate encloses a fossil conifer tree in 30 mm height. (Source: Jaroslav Bauer and Vladimir Bouska, A guide in colour to precious & semiprecious stones, Secaucus, N.J: Chartwell Books, 1989).

**Figure 1.5 (B):** Polished surface of variegated variety of agate (chalcedony) from Lake superior, N. America shows zonal growth in concentric bands mostly of manganese oxide derived from organic moss (Source: Gemrocks: Agate J. Barron, Seaman Museum Michigan Technological university, Photo by John Jaszczak), 10 Feb 2012).
Figure 1.5 (C): Moss agate is a green solution deposit in silica. The Green coloured mineral is derived from organic source of iron or manganese oxide (width 8 cm) (Source: Gemrocks: Agate www.cst. cmich. edu/users/dietrlrv/agate.htm, specimen collected and polished by J. Barron, Seaman Museum, Michigan Technological University, Photo by John Jaszczyk), 10 Feb 2012).

1.4.2 Tiger’s eye

Tiger’s eye is the best known variety of chalcopyrite quartz (or cat’s eye quartz). Agate and jasper are the chameleons of the gem world displaying bewildering varieties of subtle colours and patterns. The inclusions in these types of minerals are minute fibers and grains that are visible only at high magnification.

Tiger’s eye, with its bands resembling the eye of a tiger, received its name due to this similarity. Tiger’s eye is also called crocidolite cat’s eye or African cat’s eye. Tiger’s eye has rich yellow and golden brown stripes, with a fine golden lustre when polished. Tiger’s eye is a pseudomorph of a silicate as a result of one mineral replacing another containing oriented fibres of crocidolite, a fibrous variety of riebeckite like asbestos, an amphibole of Na, Fe, (SiO₃)₂ FeSiO₃ which has been replaced by silica. Tiger’s eye displays chatoyancy, an optical effect of a vertical luminescent band like that of a cat’s eye while tiger’s eye typically has lustrous alternating yellow or brown bands as shown in Figure 1.6.
Figure 1.6: Tiger’s eye from Griqualand, South Africa is seen with chatoyant lustrous yellow and brown bands. (size 6 cm x 4 cm) (Source: Jaroslav Bauer and Vladimir Bouska, A guide in colour to precious & semiprecious stones, Secaucus, N.J: Chartwell Books, 1989).

1.4.3 Opal

Opal derives its name from ‘Upala’, a Sanskrit word meaning a valuable stone and it was known as a crypto crystalline variety of quartz. Opal is amorphous in nature and technically not to be grouped under minerals for want of a regular crystal structure. Its essential chemical composition is silica with water molecules as SiO$_2$.nH$_2$O, where ‘n’ varies from 4 to 20. These water molecules are the cause of its unorganized crystal structure. Electron microscopy and later spectroscopic findings enabled us to have a better understanding of its chemistry as well as its physical structure. Opal is found to possess nano-sized 3-dimensional closely packed non-crystalline (amorphous) silica spheres of about 100–200 nm size, analogous to a pack of oranges or apples in a carton as shown in Figure 1.7. These nano grains of silica spheres form the fundamental building blocks of nanoscience. These spheres of opal are interspersed with a regular sub-lattice voids or annular spaces between the adjacent spheres filled with molecular water. These voids are accessible for filling by other elements such as iron oxides or any other substance as inclusions. These voids filled with molecules
also accommodate other elements as impurity; therefore, opal provides a natural substrate model with a patterned appearance.

There are two varieties of opal and they are known as precious and common or ‘potch’. The precious types of opal display iridescence (flashes of colours) depending on the angle of view of the observer. The common or potch variety is often opaque and, hence, we do not expect iridescence at all from such types of opal.

**Figure 1.7:** Structure and colour in precious opal (Source: Christiane Woodward and Roger Harding, Gemstones, Sterling publishing Co. Inc, New York, 1988).

When light rays impinge on these internal structures of opal, these hydrous interfaces also called inverted opal undergo the process of scattering, becoming a natural **diffraction grating** displaying the constituent colours of the source of light from violet on one end to the red on the other of the electromagnetic spectrum.
1.5 Inclusions of organic minerals

The chemistry of inclusions in certain geological and geochemical environments is found to be in organic state such as amber, pearls, corals, etc.

1.5.1 Amber

Plants and animals had contributed to provide organic gems for making ornaments with carved bones and beads of ivory to our ancient nomadic societies. Organic gems gained importance along with the growth of civilization.

Amber is a collective name for all petrified polymers of animal oozes from ancient trees which are polymerized. Amber is known to chemists as succinite from the Latin word succinum to mean amber. Germans knew amber by finding it to become soft on heating and eventually gets burnt by which it earned its name as Bernstein. But amber is a sticky aromatic resin which oozed down the barks of paleo trees of several million years ago – in the range of 30–90 million years old in some parts of the world. These resins began filling internal crevices, trapping debris such as seeds, leaves, feathers and even more popularly insects, which are about 10 million years old. In the course of geological time, these amber bearing trees were buried during geological processes of upheaval of the geological formations. These fossilized resins or ooze material became hardened into a soft, golden or honey coloured amber. This kind of fossilized amber will be found attractive as a gem category especially if they are found with their imprisoned fossils of insects of different species or plant amber is also found with the various attractive fossilized creatures of the earth such as an insect, bug or a cockroach as inclusions inside the host organic mineral as shown below. Amber becomes a beautiful, valuable gemstone of ornamental pendants when it is cut and polished. Some of the curious amber fossils with their organic inclusions are shown in Figures 1.8 and 1.9.
Figure 1.8: Baltic amber mine in Kaliningrad oblast, Yantarny, Russia, (Bug of 1 cm across in amber) (Source: www.gia.edu/research-resources/gia-gem.../W05-Gubelin.pdf Dr. Gübelin's, Photo Atlas of Gemstones, classified mineral inclusions, 1975).

Figure 1.9: 50 million year old amber with dragon fly (Source: www.gia.edu/research-resources/gia-gem.../W05-Gubelin.pdf Dr. Gübelin's, Photo Atlas of Gemstones, classified mineral inclusions, 1975)
Figure 1.10: Natural imprisonment of a cockroach in amber (Source: www.gia.edu/research-resources/gia-gem.../W05-Gubelin.pdf Dr. Gübelin’s, Photo Atlas of Gemstones, classified mineral inclusions, 1975)

1.5.2 Pearls

Pearls and corals belong to the organic origin produced by marine organisms and their mineralogy and architecture are unique in combining inorganic minerals and organic proteins. The chemistry of minerals is due to the periodical secretion by moluskan organisms – extracted by marine organisms and microbes from the marine environment and combines them with the proteins of chitin like fluids.

Pearls are found in both marine and freshwater environs, and are produced within the soft mantle tissue of pearl oysters which belong to the bivalved shell family or clams of marine environment. When any foreign material of dust or organic debris gets trapped inside their soft folds of the mantle they become irritated to secrete a nacreous fluid as a protection in self-defence mechanism as a protection against its parasites. This secreted fluid is found to be of aragonite (Orthorhombic crystal habit) with a CaCO₃ composition combined with a chitin like protein which causes the inner
layer of the shells with nacreous lustre. The globalized nacre of this process becomes the natural pearl inside the bi-valves of the shell by chance and, hence, all shells harvested may not contain pearls. They exhibit iridescence from these concentric layers of a nacreous surface. The word nacre is also known as mother of pearl. Pearl oyster and abalone (organic chitin like protein) are the sources of mother of pearl gained importance in the jewellery and other in-lay works of musical instruments or artefacts due to their iridescent nature of lustre.

All shells do not undergo these processes of pearl bearing and it is a rare and fortuitous product of marine harvest. Pearls of artificial processes known as cultured pearls are less attractive than the natural ones and are not preferred in the jewellery markets.

Some of the important figures with pearly nacreous lustre in its parts and fossils with pearly lustre are included in this section.

Figure 1.11: (A) Pearls, (B) the iridescent nacre inside a nautilus shell and (C) Pearl Harvest (Source: Christiane Woodward and Roger Harding, Gemstones, Sterling publishing Co. Inc, New York, 1988).
1.5.3 Corals

Corals are the rainforest of seas and may resemble a rock formation but they are structures made up of calcium carbonate produced by coral polyps. These marine organisms living in compact colonies of many identical coral polyps which are related to sea anemones and jellyfish ultimately become the skeletal remains. These create a hard base of limestone skeleton called calicle which forms the structure of coral reef.

The polyps begin to attach themselves to the rocks on the sea floor, and the polyp calicles begin to connect and proliferate themselves into buds and thousands of clones into colonies. These tiny organisms of polyp calicles connect to one another to become colonies that begin to act as a single organism. As these colonies grow over several hundreds and thousands of years and join with other colonies to become a major coral reefs and atoll. The Great Barrier Reef and atoll of Australia began growing over 50 million years ago. Illustrations of this Coral reef and some of the corals of importance are shown below in Figures 1.12 (A-C). In India corals are believed to have medicinal values and are used in the jewellery of women and children.

Figure 1.12(A) : The Great Barrier Reef, Australia (Source: http://web.archive.org/web/20060831073819/http://sea.unep-wcmc. Archived from the original on 31 August 2006).
Figure 1.12(B) :  The Great Barrier Reef, Australia, close up of polyps arrayed on a coral, waving their tentacles. There can be thousands of polyps on a single coral branch. (Magnified view of polyps) (Source: http://web.archive.org/web/20060831073819/http://sea.unep-wcmc. Archived from the original on 31 August 2006).

Figure 1.12(C) :  The largest of all molluscs, the giant clam prefers the warm waters around Australia's Great Barrier Reef. (Source: http://web.archive.org/web/20060831073819/http://sea.unep-wcmc. Archived from the original on 31 August 2006).
1.6 Methods of investigations of such inclusions in minerals in general

Methods of studies of inclusions are chosen to be appropriate in fulfilling the objective of my research. Hence, they are to be recognized based on the dimensions of such inclusions from micro and sub micro minerals which can always be identified under optical microscopes. In the case of submicroscopic inclusions sometimes called as ‘infra-minerals’ which are found in several micrometres to thousands of nanometres in sizes are detectable using EPMA – electron probe micro analysis. With reference to the minerals of nanometric dimensions with which my research studies are involved. Raman spectroscopy and, electron microscopy such as scanning electron microscope with EDAX provision (Energy dispersive analysis of X-ray) are very much useful. Raman effect from the scattering properties of molecular inclusions in the host minerals using appropriate laser energy sources in conjunction with photoluminescence studies are found informative. In addition mass spectrometry with MALDI (matrix assisted laser desorption ionization) is found necessary for an accurate quantitative elemental analysis of the inclusions as revealed by Raman studies and SEM EDAX data. The use of infra-red spectroscopy, Mossbauer spectroscopy, nuclear magnetic resonance and X-ray scattering and absorption are though used to study nanometric objects, they are found not suitable with respect to the nature of my sample, i.e. diamond. Hence, only non-destructive methods of analysis are considered suitable to realize the objective of my research.

As the inclusions in minerals are known to occur in all the three phases as solid, liquid and gas, studies of inclusions of minerals in such different phases require different techniques of instrumentation. I have adopted these techniques of other institution for my studies of inclusions.

Inclusions from chrome diopside, a calcium magnesium silicate (pyroxene) and polyphase inclusions from alkali sulphate melts with Ca, Ba and Sr admixtures, phosphates etc. including hydrogen in its gaseous phase from Yakutia, Russia, were studied by V.B.Naumov et al. This method involved some heat treatment and sudden quenching for few seconds as most of the inclusions contained salt melt instead of a-
silicate in a sulphate dominated composition. The chrome inclusions from the host pyroxene (diopside) were conspicuously seen with a green tinge of colour. The above nature of inclusions is thus detectable by using electron microprobe analysis and Raman spectroscopy [9].

Besides, immiscibility in granitic melts of quartz and alkali feldspar revealed three types of its trapped fluid as inclusions of a silicate glass with a gas bubble (type I), a dense saline fluid with more than 50% of by weight with NaCl developing into rock crystal of Halite (NaCl) at room temperature (type II) and the type III was found to be with a dense fluid or steam which on room temperature becomes into a dilute saline water and with a very large CO₂ gas bubble indicating its high-pressure environment [10].

1.7 Inclusions in Diamond

1.7.1 Importance of nanoinclusions

When inclusions are expected to be in nanometric sizes, electron microscopic methods are the only choices to be made use of in their detection. Fluid inclusions can reveal anything as Everest or Alps and much more through a microscope and, hence, such inclusions are objects of great wonder and natural aesthetic beauty, thus becoming great relevance to gemology.

The objective or the rationale of my research is to identify nanometric or submicroscopic inclusions that are found in different samples of diamond. The terminology of ‘nano’ relating to the material science is a visionary concept of the Nobel Prize winning geophysicist Dr. Richard Feynman on December 29, 1959. He expressed in his talk on a scientific forum entitled as ‘There’s plenty of room at the bottom’ and in this talk he stated “The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom. He, in a way, suggested the bottom up approach, “...it is interesting that it would be, in principle, possible (I think) for a physicist to synthesize any chemical substance that that the
chemist writes down, Give the orders and the physicists synthesizes it.....Put the atoms down where the chemist says, and so you make the substance. The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed---a development which I think cannot be avoided.” [11].

The term ‘nano’ refers to the dimension of matter as small as $10^{-9}$ m and it is one thousandth of a micron which is $10^{-6}$ m whereas an atom is $10^{-10}$ m (1Å-unit) in its dimension. The nano scale of materials adopted is considered to be in the range from 1–100 nm. With the advent of scanning tunnelling microscope during 1981 and with the development of analytical tools collectively called scanning probe microscopes, the scope of putting down atoms at the required place has brightened.

Diamond is named from the Greek ‘adamas’ meaning unconquerable, an early recognition for its superior hardness of natural mineral. This supreme hardness when combined with exceptional lustre and dispersion of light gives diamond the lasting laity which is a combined optical effect of highest diffraction of light causing total internal reflection. This is the prime reason for the fiery brilliance also known as its ‘fire’ (play of colours due to repeated total internal reflections) from the interior of the crystal structure.

Diamond, the ultra hard cubic form of carbon is a mineral requiring a long string of superlatives of attributes to describe its physical properties, its technological, commercial importance and its roots into our human culture and physical world.

But with the advent of electron microscopy, sub-microscopic inclusions of nitrogen and even boron in very minute quantities can be detected as this is essentially a non-destructive method of analysis. Based on those values of impurities, they are classified and assigned into different types of diamond as type Ia, Ib, Iia and Iib etc. The type Ia category was found to contain 0.1 atomic % of nitrogen in the form of small aggregates (i.e. $1 \times 10^{17}$ - $5 \times 10^{20}$ atoms cm$^{-3}$) and in type Ib diamond with not more than 500 ppm. Type II diamonds contain least nitrogen. In type Iia diamonds,
there is so little nitrogen and it is difficult to detect either by U.V. or infra-red absorption methods. But this type is very rarely found in nature. Among the four types, type IIb contains the least nitrogen content. In the other three types of diamond (Ia, Ib, and IIa), the amount of nitrogen is great enough to compensate the small amount of boron naturally present. In view of the least amount of nitrogen in type IIb, they qualify to become the natural p-type semi-conductors. These values of impurities of N and B were made applicable in the study in the chemical vapour deposition (CVP) method.

Hope diamond or even the Kohinoor for that matter may now be considered to belong to the II b type of diamonds which may contain the least amount of nitrogen among the four types described. But with the advent of electron microscopy, sub-microscopic inclusions of nitrogen and even boron in very minute quantities can be detected as this is essentially a non-destructive method of analysis.

One common categorization scheme is based on defect structure, and is called typing. The properties of bulk diamond are often stated with particular reference to the diamond type. In this typing system, diamond is divided into two groups, given the Roman numeral designates "I" and "II". Each of these groups is divided again, distinguished with the lower case letter "a" or "b". Diamond

Based on those values of impurities, they are classified and assigned into different types of diamond as type Ia, Ib, IIa and IIb, etc. The type Ia category was found to contain 0.1 atomic % of nitrogen in the form of small aggregates (i.e. \(1 \times 10^{17} - 5 \times 10^{20} \) atoms cm\(^{-3}\)) and in type Ib diamond with not more than 500 ppm. Type II diamonds contain least nitrogen. In type IIa diamonds, there is so little nitrogen and it is difficult to detect either by UV or infra-red absorption methods. But this type is very rarely found in nature. Among the four types, type IIb contains the least nitrogen content. In the other three types of diamond (Ia, Ib, and IIa), the amount of nitrogen is great enough to compensate the small amount of boron naturally present. In view of the least amount of nitrogen in type IIb, they qualify to become the natural p-type semi-conductors. These values of impurities of N and B were made applicable in the study in the chemical vapour deposition (CVP) method elaborately studied as a
research project. This work was carried out over a period of about 6 years by late professor David A. Stevenson who died of cancer before the submission his thesis. Hence, this document on the fundamental studies of the chemical vapour deposition of diamond was compiled and submitted by the professor William D. Nix of Stanford University, California [12].

Hope diamond or even the Kohinoor for that matter may now be considered to belong to the II b type of diamonds which may contain the least amount of nitrogen among the four types described.

Thus, the traditional belief that the natural diamonds considered as pure and free from any inclusions is unfound through the research work carried out over a period of about 6 years by the Professor of Stanford University, California. Inclusions in diamond are, therefore, considered as the barcodes of the chemistry and the evolutorial history or origin of the host diamond and the included minerals. Thus, the methods of their detection using electron microscopy are faster and easier sequencing techniques to obtain the spectra of the interior of diamond.

Later, several other physical properties of its state from solid to liquid, optical, surface area, strength, and thermal, electrical and all other electronic properties of material science were opened up like a flood gate changing the classical science of physics into chemistry as an analytical tool. Thus, nanometric materials are developed with several enabling technologies in view of their various natures of revolutionary physical properties.

An illustration of the historical nanogold now preserved in the institute with a diary entry dated 2nd April 1956 made by Faraday himself from an appropriate reference of publication, ‘The Nano, The essentials’ [13]. This nanogold has been referred as ‘divided gold’ and the solution prepared by him out of them are colloidal gold preserved in sealed glass bottles as shown in Figure 1.13. Hence, nanogold became the cynosure of a nanomaterial and to the discipline of the nanoscience.
Figure 1.13: Faraday’s Gold preserved in royal institution (Source: http://www.rigb.org/rimain/heritage/faradaypage.jsp).

Reference to the Lycurgus Cup from glass with 70 nm gold and silver particles dated to 4th century AD included in the reference is reproduced in Figure 1.14 to focus on the colour change from red in transmitted light and green in reflected light.

Figure 1.14: 4th century Lycurgus cup from glass with 70 nm particles of gold and silver as seen in the transmission electron micrograph, appears red in transmitted light and green in reflected light (Source: http://www.thebritishmuseum.ac.uk, reproduced by Pradeep, T. Nano: The Essentials, Tata McGraw-Hill, New Delhi, 2008).
1.7.2 Morphology of diamond crystal

Before describing the properties of diamond, the external crystal morphology of well faceted diamond is considered to be useful and informative. Hence, the same is shown below with the names of the elements of its geometry. The top flat surface of the diamond crystal is known as Table while the portion just below the table up to the widest edge is known as Crown and when they are faceted, it is identified as Bezel. The major conical portion below the crown is known as the Pavilion and the tip of the pavilion at the bottom when ground flat is called the Culet. A diagram with its geometrical elements is shown in Figure 1.15.

![Diagram of a diamond crystal with various angles and percentages]

1.7.3 Physical properties of diamond

Diamond is the king of gemstones to be categorized as a precious one along with other gemstones such as ruby, emerald, sapphire etc. They have long been admired for their beauty and value based on their 4Cs (Colour, Carat, Cut and clarity). Every other gemstone is all faceted using the above geometry, only with their desired innumerable number of facets of crystallography, by skilled hands sourced from Antwerp, Belgium or Surat, Gujarat, India. All Natural diamonds have been studied as scientific curiosity for most of the twentieth century because of their unique set of physical properties. They are less well known for their unusual engineering properties which lie at one extreme or another of the appropriate scale (1–7). Diamond is a remarkable mineral and has been long recognized for its unusual physical and chemical properties: robust and widespread in industry, yet regally adorned. This diversity is even greater than formally appreciated because diamond is recognized as an extraordinary recorder of astrophysical and geodynamic events that extent from the far reaches of space to Earth’s deep interior [14]. The strong sp³ bonding character in diamond leads to a number of extreme properties of diamond, especially its highest hardness in Mohs scale as 10 in the scale of hardness proposed by Friedrich Mohs, a German mineralogist, in 1922 from 1 to 10 and its corresponding Knoop hardness up to 9000 kg/mm at 110 GPa of pressure. Thus, we find diamond to possess the highest hardness of all materials and with a high density of 2.4391 causing a slower speed of light transmission into 77,000 miles per second as against the natural speed of light at 186,000 miles per second or 300,000 km/s (Harlow 1988). The thermal conductivity is found to be four times than that of copper or silver at room temperature (20 W/cm-°C); an electrical resistivity that ranks with the best insulators when undoped (10¹⁶ ohm·cm). Diamond is found to be with high chemical inertness and stability in air to over 600°C; and a very high index of refraction (2.43 @ 514.51 nm). In addition, its large band gap (hv = −5.5 eV) makes it transparent to the entire Maxwell’s spectral region from the near ultra-violet to the far infrared. Consequently, diamond has been developed for optical windows and also as an exceptional material for electronic devices requiring high power.
1.7.4 World Famous Diamonds

A brief reference to these world famous diamonds has been considered relevant in this context and hence the same is covered in my thesis. Discovery of large sized diamonds varies in time from the earliest discovery of Kohinoor (Koh-i-Noor) also known as ‘Mountain of Light’ in India (Golconda mine – A.P. State) was found during early 1500 A.D. Later, this valuable diamond was acquired by the English East India Company in 1877 well before the independence of our country. A natural diamond crystal with an octahedral face naturally developed in the host rock is found as a phenocryst as shown in Figure 1.16 [A]. The cut and faceted Kohinoor diamond is also shown in Figure 1.16 [B] was gifted to Baber the great, the mogul king in India in 1526 and this diamond became the cynosure of the British crown jewel since then.

![Diamond A](image1)
![Diamond B](image2)

**Figure 1.16:** (A). An octahedral natural diamond in its host rock. (B). Cut & faceted Kohinoor diamond (Source: Gemstones, National gem collection of the U.S.A., Sterling Publishing Co., Inc. New York, 1970).

Yet, the Cullinan diamond was the largest rough gem quality diamond ever found and this illustrious rough diamond found in 1905, from the Cullinan mine, S.Africa, weighing 3,106 carats (621gm). A carat weight is 200mg or 0.2 gm and the term carat is from ‘carob’, name of a Mediterranean plant seed used in the measurements of standard weights in the 16th century onwards in the trade of precious
gemstones and this term carat is retained even now. The original Cullinan diamond was later cut into a smaller piece of 530 carats and named as Cullinan I or the Great star of Africa [15]. I had the privilege of visiting the Natural History museum at London as an invitee by the British council while undertaking an U.N. fellowship studies in the University of Wales, Cardiff followed by a practical training in the field of Geophysics in Huntsing Survey, Hertz, London during 1969-70.

1.8 Significance of diamond as a system of host with nanometric inclusions

Much research has been done with so small of 1 nm size of single molecule of carbon isotope, i.e. C60, the fullerene to realize the benefit of opening up amazing possibilities of solid state synthesis of them. Later, several other physical properties of its state from solid to liquid, optical, surface area, strength, and thermal, electrical and all other electronic properties of material science were opened up like a flood gate changing the classical science of physics into chemistry as an analytical tool through Raman effect. Thus, nanometric materials are developed with several enabling technologies in view of their various nature of revolutionary physical properties overriding all the achievements attained so for in this world after the great industrial revolution. Diamonds have formed as mantle derived products as well as cratonic diamonds even before the evolution of lithosphere was completed and also prior to the availability of their host rocks of kimberlites or eclogites.

Diamond is the most intensively mined and carefully graded of all minerals and hence it is grouped under gemstones because of its rarity. Diamond is the only mineral formed earlier to the evolution of our planet earth with its paleo geography. Hence, the inclusions as probes into its origin became my first love of research. Finally, the study of nano inclusions in diamond or in any mineral warrants an integrated knowledge of multi-disciplinary sciences such as geology, paleo geography, geophysics, petrology, mineralogy, mineral physics, physical chemistry and material science which in all aspects turns to be of a hybrid nature, an attribute to the Nano science itself. Hence, diamond is chosen as a system of research and nothing else.
Raman spectroscopy is a useful tool to study the chemical/molecular composition of the materials, their bonding, crystal and electronic structure, phases as well as strain at micron and sub-micron sizes. This technique is highly useful for the identification of inclusions with its paragenesis because each carbon allotrope displays a clearly identifiable Raman signature, which can be easily distinguished from that of the inclusions with different chemistry. It therefore provides a clear fingerprint by which the material can be identified even from a micron or nanoscale sample area or volume under analysis. Internal pressure inside the diamond can be monitored from the inclusions, since diamonds are capable of sustaining high internal confining pressure on its inclusions. This internal pressure reflects as a shift in the peak position of the Raman features of the inclusions. Raman spectroscopic data when combined with scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) can give a very clear picture of the inclusions present inside diamonds and thereby the history of the host and the paragenetic relationship with the inclusions of other molecules of minerals. In several earlier reports, fragmentation and combustion of the host have been used to liberate the inclusions for their chemical analysis [16]. In the case of diamonds with inclusions of different parageneses, this method is not effective as the spatial relationships between the mineral grains themselves and the different growth zones of the host diamond will be lost upon crushing [16c, 17]. Herein, we demonstrate the characterization of sub-micron or nanometric inclusions inside diamonds in a non-destructive manner by using a wide range of spectroscopic and microscopic techniques.

Finally, the study of nano inclusions in diamond or in any mineral warrants an integrated knowledge of multi-disciplinary sciences such as geology, geophysics, petrology, mineralogy and material science which in all aspects turns to be a central or nodal science with a hybrid nature, an attribute to the nanoscience itself.
1.9. Importance of Nano inclusions –smart materials

Inclusions in diamond of submicroscopic Pyrochlore, which is a niobium–tantalum oxide happens to be the main host of Uranium and light rare earth elements. The importance of Niobium is realized in view of its corrosion resistant and super conducting properties whose applications are found in the manufacture of high-grade structural steel used in the gas pipe lines. Besides, Niobium bearing super alloys using powder metallurgy forms the important component in jet engines in view of its temperature stabilizing properties and all other relevant physical properties to qualify as a smart material as established by the Hudson Resources Inc. in their REE project in Greenland. As fossil fuels are depleting into a wasting asset of natural resource the use of Niobium plays an important role as a catalyst for treating bio-diesel fuels. Niobium and columbium are synonymous names for the same chemical element with atomic number 41 but the International Union of Pure and Applied chemistry [IUPAC] adopted the name Niobium when the use of Columbium is still used by the metallurgists in the U.S.A. However, the Nb/Ta ratio of the Earth’s major silicate reservoirs – the crust and mantle – is subchondritic, hinting at the existence of a complementary reservoir with high Nb/Ta.

Eclogites, one of the host rocks of diamond formation which are high-pressure metamorphic rocks that often found in subduction zones can contain the mineral rutile (titanium dioxide) with high Nb/Ta. They have, therefore, been inferred to constitute a complementary reservoir. More recent evidence from natural samples, however, suggests that residual eclogites have low Nb/Ta, which is confirmed by number of experiments as referred therein. Here, we may find that Nb and Ta concentrations and hafnium (Hf) isotope compositions of rutiles from eclogite fragments that were entrained from the subcontinental lithospheric mantle in kimberlite melts [18]. Nanoinclusions in minerals are found useful in finding strategic elements which will be of economic importance as minerals are considered as wasting assets and non-renewable natural resources.
1.9.1 Diamond genesis – Its native place

The study and detection of inclusions in natural diamond, presupposes to have good background knowledge on the genetic history of diamond unambiguously. Diamonds of primary origin of peridotitic source occur in one place in the interior of earth over a significant period of 3.57 Ga (Richardson et al. 1984 peridotitic, and those of eclogitic diamond in the range of 990-1670 Ma) to 88 Ma but are found in the surface of earth in different geographical locations in different periods of time [19]. The first discovery of diamond was reported in 1600 in India in the Godavari basin of Krishna district and out of these, the age determination of diamond by radiometric methods clearly showed that the period of formation of one type of diamond is contemporaneous with the age of the planet earth. It is to be known that though diamonds are formed both in the lithosphere beneath the cratons and also deep in the mantle region of earth in different geological period during the evolution of planet earth.

Diamonds of primary nature but are found on the surface of earth only by volcanic eruptions of kimberlitic rocks in different periods. The host rock in which the inclusions reside can be specifically identified and their relationships are to be viewed as the host inclusion pair. All these studies into the origin of diamond began only after the discovery of a volcanic kimberlite pipe rock in 1871 at Kimberley, Pretoria in S. Africa. Later, all other diamond occurrences in other parts of the world with no geographical boundaries or their periods of their discoveries were also named as kimberlite after the type area of ‘Kimberley’ from S. Africa in view of their petrological and mineralogical similarities. The Kimberley pipe rock was initially mined manually during diamond rush in Kimberley near Johannesburg and remain as a big hole enlarged into deep well now becoming a symbol of their national heritage for the earliest diamond mining activity as shown in Figure 1.17.
Figure 1.17: The Big Hole, Kimberley, S. Africa (Source: http://en.wikipedia.org/wiki/File: Open pit-mine.jpg, Martin Meredith, Diamonds, Gold, and War, (New York, Public Affairs, 2007)).

1.9.2 Host rocks of diamond

It is common knowledge of petrology (study of rocks) that diamond bearing host rocks of Peridotite and eclogite are derived from kimberlite or lamproite types of magmas from the interior of earth. This depends upon the mobilization of the mantle diapirs and associated physical and thermal convectional aspects of the proximal mantle rocks in the incorporation of diamond bearing xenoliths. The term xenolith refers to a foreign rock not related to the place of its occurrence but from the subducted oceanic crustal blocks during plate tectonic events. Xenolith is referred to a foreign rock unrelated to the place of its occurrence. Similarly xenocrysts or phenocrysts seen are found to be inclusions embedded in xenolith indicates a similar state of its origin with no petrological relationship between the host rock (matrix) of kimberlite and the phenocryst of diamond.
A photograph of the xenocryst of a diamond in the kimberlite of xenolith of USA is shown in Figure 1.19 to distinguish the petrological relationship between the diamond (white-phenocryst) and its dark host rock of kimberlite.

![Xenocryst](image)

**Figure 1.18**: A picture of a diamond phenocryst in kimberlitic xenolith of U. S. A. (Source: http://en.wikipedia.org/wiki/File: Open pit-mine.jpg, Martin Meredith, Diamonds, Gold, and War, (New York, Public Affairs, 2007)).

Both xenoliths and phenocrysts are mantle derived products transported to the Earth’s surface by kimberlites and alkali basalt (lamproite) provide direct information on the nature of lithospheric mantle and mantle processes. Therefore, this becomes a natural geological record of regional magmatic and metasomatic processes [20].

Diapirs are piercing structures of volcanism in the interior of earth. Depending upon the locations of such diapirism relative to the lithosphere kimberlite and lamproite are found to be the magmatic end products. As a consequence of these diapiric processes in the mantle, rapid transport and ascent of the payload of diamonds was found through crack propagations to the crust. It is very interesting to know that the thick cool lithosphere (heels of cratons) became an optimal thermal regime which caused to find diamonds in as metastable conditions without being reverted back into graphite in little loss of diamond. Thus, the mantle geochemical environment and diamond bearing rocks from mantle region was found surviving the onslaught of high
pressure-high temperature (HPHT) conditions beneath the pre-cambrian shield rocks or cratons. Hence, diamonds are also appropriately called as ‘time capsules’ from the Earth’s mantle [21]. Prof. Lawrence Taylor who was kind enough to provide me a photograph of his personal collection of diamonds of Siberia after having read the findings from my synopsis of this thesis and is included in Figure 1.19.

![Image of diamond collection]

**Figure 1.19:** Personal collection of diamonds by Prof. Lawrence Taylor, University of Tennessee, Knoxville, USA, complimentary photo, 8th June-2011.

### 1.9.3 Host rock minerals

Peridotite and eclogite are universally accepted as the original cognate hosts of diamonds. Peridotite and eclogite are mantle derived rocks (plate tectonic products) and these reveal nature’s geological diary from the interior of earth on the growth conditions of diamond (P&T). The genesis of natural diamond is governed by different P-T conditions before they are found on the surface with a complex growth history due to the magmatic processes taking place in its host rocks such as kimberlite or lamproite as the case may be.
Besides, the mineral assemblies from them indicate whether they are in-situ or subducted material from the oceanic crust. Diamonds are found well before the formations of its host rock of kimberlite from which the origin of peridotite and eclogite are traced.

1.9.4 QUEMSCAN - Quantitative Evaluation of Minerals by SCAN

QUEMSCAN is an acronym for quantitative evaluation of minerals by scanning electron microscopy and a registered trademark owned by FEI company since 2009. QUEMSCAN aims to obtain an integrated automated mineralogy and petrography solution providing quantitative analysis of minerals, rocks and man-made materials. The specimen’s surface is scanned by a high-energy accelerating electron beam along a predefined raster scan pattern. Low count energy-dispersive X-ray spectra (EDX) are generated to provide information on the elemental composition at each measurement point. QUEMSCAN data includes mineral and calculated chemical assays. By mapping the sample surface, textural properties and contextual information such as particle and mineral grain size and shape, mineral associations are obtained.

Quantitative reports can be generated for any selected number of samples, and for particle classes sharing similar compositional and/or textural attributes, such as size fractions or rock types. This system comprising a Scanning Electron Microscope (SEM) with a large specimen chamber, up to four light element (Z=4) energy dispersive X-ray spectrometers (EDS), and a proprietary software controlling the automated data acquisition. A separate software package known as iDiscover provides data processing and reporting functionally from QUEMSCAN.

A cross section of mineral map kimberlite rock from South Africa generated from this novel system of data acquisition was donated by De Beers, the leading diamond producer in the world to intellectual property which is shown in Figure 1.20.
Figure 1.20: QEMSCAN Cross sectional Mineral of South African kimberlite rock donated by De Beers to intellectual property. Mineral map of olivine macro crystal (in green) is spectacularly altered into various generation of serpentine. (Source: http://en.wikipedia.org/wiki/File: kimberlite cross section of QEMSCAN.png, 15th November 2010).

1.9.5 Regional geological setting of primary diamond deposits

"Clifford's Rule", states that diamondiferous kimberlites are almost exclusively found in regions underlain by Achaean cratons, i.e. continental crust older than 2.5 billion years in age. In Africa, Russia and Canada, all of the significantly diamondiferous kimberlites are "on-craton". The only significant exception to Clifford's Rule is the Argyle lamproite in Australia. It lies "off-craton" in a proterozoic mobile belt [22]. Craton means a part of the continental crust that has been stable (not subjected to any orogenic (mountain building) activity for at least 1000Ma. The oldest parts of cratons are often more than 2500Ma old. (Ex) Tamil Nadu, Karnataka and Kerala are part of a craton that sit on this and this craton is well known as the Archaen shield rock of the peninsular India.
This region of high pressure and relatively low temperature (less than about 1200°C) provides a "window" in which diamonds can form and be preserved. Kimberlitic magmas are generated at or below these depths (as evidenced by their xenoliths), and may "sample" the lithospheric roots, thus collecting diamonds en route to surface. Kimberlites formed away from the craton do not sample the diamond window and, thus, are unlikely to be diamondiferous as can be seen in Figure 1.21.

![Image of cratons](image)

**Figure 1.21:** Window of diamond formation and preservation in the interior of earth  
(Source: De Beers donation to intellectual property, Wikipedia.org/Wiki/significance of cratons, 2010)

The growth of diamond was neither a continuous feature nor did diamonds grow necessarily in identical geochemical environments. Geochemical and isotopic studies of carbon δ¹³C show that diamonds contain many elements in traces and also in concentrations similar to those present in silicate and sulphide magmas indicating their growth in a similar environment to most silicate bearing rocks. Majority of diamonds studied (e.g. Deines 1980) have δ¹³C values in the range of −4 to −8%. The isotopic values of carbon are found to be different indicating different sources of carbon for diamond genesis. Importantly, the above studies enabled to assign diamonds to either ultramafic or ultrabasic (SiO₂ ≤ 45%) or ultra potassic (eclogitic) suite inclusions [23].
1.9.6 Mineralogy of peridotite and eclogite

1.9.6.1 Peridotite:

Peridotites have two primary modes of origin, as mantle rocks formed during the accretion and differentiation of the Earth, or as cumulate rocks formed by precipitation of olivine ± pyroxenes from basaltic or ultramafic magmas; these magmas are ultimately derived from the upper mantle by partial melting of mantle peridotites.

Peridotite with olivine (Mg₂SiO₄) is the dominant rock of the Earth's mantle above a depth of about 400 km from the transitional zone (TZ) 410-660 km and below that depth. Olivine, the early formed / silicate mineral (orthorhombic) is converted to the higher-pressure mineral wadsleyite. Oceanic plates consist of up to about 100 km of peridotite covered by a thin crust; the crust, commonly about 6 km thick, consists of basalt, gabbro, and minor sediments. The peridotite below the ocean crust, "abyssal peridotite," is found on the walls of rifts in the deep sea floor. Oceanic plates are usually subducted back into the mantle in subduction. However, pieces can be emplaced into or overthrust on crust by a process called obduction rather than carried down into the mantle (subduction). The emplacement may occur during orogenesis (mountain building events) during collisions of one continent with another or with an island arc. (Ex) Java, Sumatra and Borneo islands). The pieces of oceanic plates emplaced within continental crust are referred to as ophiolites.

1.9.6.2 Eclogite:

Eclogite mainly consists of pyroxene with garnet (mafic or ferromagnesian peralkaline aluminous silicate group) and are deliberately excluded with its mineral constituents in my thesis, as their presence was found negative in the results from the SEM studies and through the elemental analysis using EDS in our diamond samples.
1.9.6.3 Types of peridotite

Peridotites are further divided into two types and a Pie diagrammatic presentation of their mineral distributions are shown in (Figure 1.22) which will be found useful to understand the concept of these two types of peridotite as Harzburgite and Lherzolite from which the host rocks of diamond are traced.

Harzburgite is mostly composed of olivine, orthopyroxene, and relatively low proportions of basaltic ingredients as garnet and clinopyroxene are found in minor amounts.

Lherzolite is mostly composed of olivine, orthopyroxene (commonly enstatite), and clinopyroxene (diopside). These mineral assemblages have relatively high proportions of basaltic ingredients (garnet and clinopyroxene). Partial fusion of lherzolite and extraction of the melt fraction can leave a solid residue of harzburgite.

**Figure 1.22**: Xenolith - Mineral proportions of peridotite in pie diagrams (Source: Smithsonian national museum of natural history-Mineral sciences, U.S.A. figure modified).
1.9.6.4 Raw materials for diamond formation or nucleation

Mantle carbonate has an important role in sharing the earth's carbon budget. Carbonates, diamond, and graphite are viewed as the chief reservoirs of mantle carbon. Many CO$_2$ rich and silica under-saturated (ultrabasic) mantle derived suites of rocks are believed to be present in the mantle region of the interior of earth. Besides studies on the range of oxygen fugacity in which the mineral assemblages were captured enable to infer into the mineralogy of the original mantle assemblages and the chemical reactions which must have taken place in its transformations. Evidence of the specific processes that stabilize and preserve carbonates in the mantle is very important in understanding the redistribution and transportation of carbon including diamond. These natural inclusions now found in nano and sub-micro dimensions in diamond are also described as 'mantle stowaways' to mean that, they are neither conspicuously seen nor can be easily identified with a definite chemistry posing analytical and petrological challenges or uncertainties due to its complex micro mineral assemblages [24]. They also give a vital knowledge of the mass balance and the depth dependant distribution of certain elements such as carbon and sulphur. Mineral assemblages found in the inclusions of a single diamond cannot represent the chemistry of the major volume of entire mantle.

The syngenetic multiphase inclusion of a euhedral rhombohedron shaped magnesite (MgCO$_3$) in a natural diamond from the Finsch kimberlite of S. Africa provides unambiguous evidences of earth's mantle to become mostly a major carbon reservoir in the world. The inclusion mineral assemblages in diamond suggest two reactions involving decomposition of carbonates in mantle peridotite during decompression. This is also one of the clues that other parts of the world wherein the mantle petrology is found with paucity of magnesite. The hypothesis that mantle carbonates are the major source of carbon needed for the formation of diamond has been proved before two decades ago by which the Ca- and Mg-carbonates were found to be more stable in the peridotitic systems under the pressure and temperature environs of the mantle. This view was based on model from a simple system of CaO-
MgO-SiO₂-CO₂-H₂O. This involves reactions between the different silicates and the carbonates of Mg and Ca in various stages displaying how their reactions delimit the stability of carbonates in that system.

Most important in this system of carbonates, is not its stability in the mantle environs during the nucleation of diamond but its preservation in the post diamond formational geologic processes during its ascent in a volcanic rocket like eruption of a pipe rock of kimberlite with the payloads of diamonds. Thus, we find that the critical schedule of the time of delivery of diamonds to the surface in a clock like precision took only a day or so though the residency period for the nucleation of diamonds in the interior of earth last in billions of years. When xenoliths of diamondiferous rocks were engulfed by ascending magma, the inherited diamonds were further transformed by processes of dissolution, replacement and overgrowth. A very low sublimation temperature (3,773 K) of diamond enables it to recrystallize and overgrow on its seed grains in the metastable conditions aided by CO₂, fO₂ and other mineralizers like H₂O as steam en-route. Besides, the presence of other minerals which have crystallized from a kimberlitic magma along with diamond can provide more information as to how well these diamonds in a given host rock (Kimberlite) have been preserved during their ascent to surface.

For example, the presence of low iron and high magnesium picro ilmenites (Cr₂O₃-(Fe, Mg)TiO₃) in a kimberlite is a positive indication of an oxidizing conditions through fO₂ and CO₂ of a kimberlite magma were favourable for the preservation of diamonds with its sp³ structure without being reverted back into the sp² structure of graphite. The salient feature in the preservation of diamond far from the diamond stability field, its place of genesis, is due to its highest hardness of any known material and its unusual thermodynamic properties including its anomalous low entropy value of S₀ 298 = 0.197 J/(gK) compared to that for graphite with S₀ 298 = 478 J/(gK) [25].
1.9.6.5 Nomenclature of kimberlite volcanic Pipe

The kimberlite volcanic pipes are referred to the entire worldwide as the diamond bearing volcanic pipe rocks which are carrot shaped volatile charged **piercement** structures or **diatremes**. The type area of the kimberlite pipe rock from South African diamond mining towns is of a classical nature and, hence, its nomenclatures with old terminology were assigned with different terminology of its facies. These were based on the aspects of their appearance and characteristics of their host rock. Yet, these new terminology faced technical controversies on the conditions of its origin in all international kimberlite conferences. This compelled the concerned authors of this subject to find a simpler two fold revised terminology. For a visual concept of this express elevator kimberlite volcanic pipe with the payload of diamonds, a model of the classic South African kimberlite pipe with their old & revised terminologies is shown in Figure. 1.23.

![Diagram](image)

**Figure 1.23**: Kimberlite, A volcanic pipe rock, with the structures of piercement or diatremes (Source: Kjarsgaard, 2003, Sparks et al. 2006).
**Legend:**

The classic South African model of kimberlite with its old nomenclature (left side of figure) and a simpler revised two-fold nomenclature system (right side of figure) to describe rocks from kimberlite magmatic system (Mitchell 1995, Kjarsgaard, 2003, Sparks et al. 2006) is reproduced with its legend as therein. PK = pyroclastic kimberlite, RVK = resedimented volcanioclastic kimberlite, MVK = massive volcanoclastic kimberlite, HK = Hypabyssal kimberlite.

### 1.9.6.6 Kimberlite Geochemistry

Kimberlite exhibit distinctive and unique mineralogical signature with its ultramafic and alkaline mineral assemblages which cannot be found in any other rocks with rare exceptions in a couple of other petrological environs. These are highly enriched with ultramafic minerals of the first order transition elements of Mg, Ni, Cr and characteristic geochemical signature being rich in the incompatible elements of Sr, Ba, LRRE and with Nb, Ta, Zr, P, Th and U (alkaline signature) [26].

### 1.9.6.7 What is ‘Little effect’?

Little effect describes a concept of a novel electronic dynamics (sub-shell rehybridization and shell rotation) developed by the concerted understanding of a fundamental science by giant scientists of the world starting with Newton, Boyle, Lavoisier et al. numbering more than 36 and also by Sir. C. V. Raman. The author of this draft resolution was by Reginald B. Little from Roache of Florida A & M University and Joseph Roache.

The concept of a problem relating to the physicochemical synthesis of diamond is two centuries old. It relates to the analysis and contributions on most of the salient aspects relating to the ring current in graphite causing the difference in the magnetic susceptibilities between graphite and diamond. This was the hallmark of contribution by the Nobel laureate Sir. C. V. Raman. The joint effort of discussions and deliberations by all resulted in the passing of a resolution based on the orbital
dynamics involving sub-shell hybridization, valence shell rotation and magnetic quantum resolution etc. involving the wonder element of carbon.

Thus, the concept of "Little effect" became a resolution passed after 200 years by Reginald B. Little and his colleagues. The crux of their resolution bears fruit and is explained very briefly. Their experiments on the physics of carbon nano tube (CNT) for the synthesis diamond from graphite revolve around the electronic density of atoms in graphite to squeeze them into diamond allotrope is virtually an electronic alteration. This involves the conditions of high temperature, high volume and low pressure (HTHVLP) to break ‘cut off’ the graphite spring sp² and to be in low temperature, low volume and high pressure (LTLVHP) continuum conditions to fix ‘cut on’ the diamond spring sp³. This electronic mechanism of synthesis of diamond from graphite further involves creation of an energy barrier of semi conducting property in diamond with an anomalous property of entropy as described earlier under the physical properties of diamond [27].

1.9.6.8 Delivery mechanism of diamond from mantle earth

Diamonds, when the process of their nucleation are completed, require a transport medium or container service to quickly deliver them from the mantle in their meta stable state to the surface of the earth at supersonic speed within a day lest the diamonds should be reverted back into graphite. The delivery mechanism of transport of diamonds is naturally provided by volcanic pipe rocks known as kimberlite or lamproite derived magma which is the primary ultra basic igneous host rocks of diamonds in the whole world. Diamond in turn becomes the host mineral for enclosing the inclusions of other elements or molecules that become its progeny or successive daughter minerals. They are, henceforth, addressed as inclusion elements or molecules in diamonds.

Diamonds can exist either under high pressure and high temperature or in a low pressure and in cooler temperature conditions only. We should also know that the system or the mechanism of delivery of these shielded diamonds to the surface of
earth was by different specialized natural transport modes of volcanic eruptions. These transport modes of the diamond bearing volcanic pipes of eruptions are globally recognized as kimberlite and lamproite whose role of functions are like an express elevator type of transport system. The processes of delivery of these diamonds by the host rock of kimberlite from the mantle region are very important and crucial as they cruise into a **supersonic speed** during the final stage aided by the mineralizers such as (fugacious) $fO_2$, $CO_2$ and $H_2O$ as steam in their passage of ascent through crustal regions of low pressure shielded with high temperature to the surface. Fundamental physics indicates that pressure increases with increase of depth and it drops down with decrease of depth till it becomes in equilibrium with atmosphere on the surface of earth. The speed of propulsion of the express volcanic elevator with its payload of diamonds is regulated by the fluids of $fO_2$ and $Co_2$ from the mantle as fast as possible lest diamond should be reverted back into its sp$_2$ structured graphite due to the HTHP conditions of the mantle.

![Diagram of magma and diamond formation](image)

**Figure 1.24:** Providential delivery of diamonds to the surface of earth (Image: James W. Head III) (Source: Providence R.L, Brown university, Rapid thrust of diamond bearing structures, 24$^{th}$ May 2007).
A cone of liquid carbon dioxide changes rapidly to gas when it reaches the surface, creating an instantaneous 'catastrophic cooling' effect.

A new comprehensive theory on the kimberlite origin with a leading wedge of fluid CO\textsubscript{2} by Prof. Lionel Wilson, the professor of volcanology shown above offers with a plausible explanation in this regard. His theory is based on the wedge of fluid CO\textsubscript{2} above the source of a CO\textsubscript{2} rich magma gets propelled upward due to a sudden chilling effect on reaching the surface of the earth causes the expansion of the confined CO\textsubscript{2} bubbles like the uncorking a soda or champagne bottle. The rapid chilling soon seals off the magma supply completely, ending the process any further chemical reactions protecting the diamonds. The whole process of the delivery mechanism of the payloads of diamonds is completed in less than an hour. One implication of this new theory is that the surface geological conditions have little to do with where kimberlites form and that where diamonds are deposited. The tip of the chamber of these expanded bubbles of fluid CO\textsubscript{2} breaks the surface jettisoning CO\textsubscript{2}, magma foam with rock fragments with a speed of about 5000 km per hour typical of a booster rocket surviving the pay load of diamonds in metastable conditions while erupting into a kimberlite volcanic pipe rock to the surface of earth with no loss of time lest the diamond should be reverted back to graphite (clock like precision).

This looks like a contradiction to the general theory of fundamental physics. But, with this new theory as above it becomes clear by recalling the quotation of the Professor of Volcanology Prof. Lionel Wilson of the university of Lancaster, U.K that 'as long as they are hot, you want them to stay at high pressure and then if you are going to decompress them, you have got to get them cold really fast.' Thus, we find that the delivery mechanism of the payloads of diamond from the interior of mother earth to the surface of the earth in a single day is found to be really a providential function of nature like the gyration of our planet earth around the sun. The following figure will explain the new theory of its proponents on the role of fluid CO\textsubscript{2} in the safe delivery of diamonds to the surface from the mantle of earth [28].