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MESSAGES FROM THE DEEP

A Lecture by

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GRESHAM COLLEGE

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Message from the deep

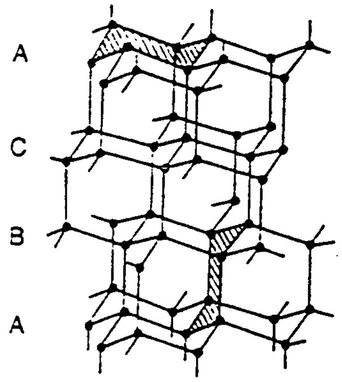
It is sometimes said that the interior of the Earth is every bit as inaccessible as outer space. Attempts to drill into the planet have penetrated little further than a few kilometres, just scratching the crust. There is, however a natural geological route through to the Earth's mantle afforded by kimberlite or lamproite pipes. By literally picking through the weathered remnants of these ancient eruptions, which originated perhaps 150kms down, we get information about the elements of life far below our feet. Kimberlite (and lamproites) bring to the surface diamonds, man's most precious mineral, and as Sir Charles Frank described them, a message from the deep.

Despite their enormous value as gems and industrial tools, we did not know where natural diamonds came from until 1870, when a so-called dry source was found on the Koffiefontein Farm in the Orange Free State, South Africa. In mediaeval times diamonds came from "the East" as recounted in the 14th century manuscript "The Travels of Sir John Mandeville" who describes the stones in his accounts of a visit to India. Nowadays the largest sources of the mineral, are the Argyle mine in Australia and Siberia. Before 1870, however all the diamonds from South Africa, beginning with the Eureka, found probably in February 1867, were placers, that is they were deposited by water along the banks of the Orange or Vaal rivers. Following the discovery of the Koffiefontein source, other kimberlite pipes were found bursting through the ancient South African Craton. The areas in which they were discovered had not long been settled by homesteaders and the mines and pipes are still known by the names of the farms on which they were located. One of the most famous farms launched diamond fever in 1871 when men clamoured to hammer in the pegs to stake their 31 x 31 feet claims. The original claimant took fright and sold out for £110, whilst the farm owners bewildered by the mayhem all around them accepted £6300 from developers for the whole property. Later they claimed they had been cheated because a wagon and new implements were never delivered. Their farm eventually realised 1 billion pounds worth of diamonds and the farmer's name, like the mineral, is set to last for ever since it was taken on by the company, DeBeers, which still regulates the diamond industry.

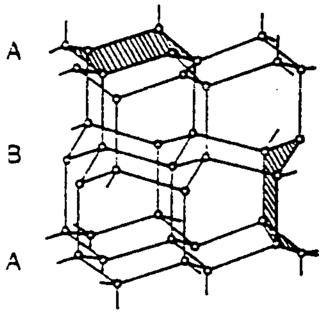
One of the largest pipes ever, was discovered by a cook who was sent to dig in a previous unproductive area as a punishment for getting drunk. The Kimberly mine, the place which actually afforded its name to the geological source material, was the result of the amalgamation of almost 4000 individual staked claims, which produced "Big Hole" - a 38 acre gash in the Earth, a mile round and a quarter of a mile deep. Just 3 tons of diamond of diamond have been recovered from 25,000,000 tons excavated; a success rate of about 0.1ppm by wt for one of the most successful mines in South Africa. The man (Fleetwood

Rawstone) who sent the cook on what he thought was a wild goose chase, having already gambled away his claim at DeBeers Farm, chose locations outside the perimeter of the Kimberly pipe, and ended up with virtually nothing.

Diamond was actually shown to be pure carbon only in 1797 by Tennant. It is found in a variety of crystal forms, octahedrons and cubes are common, as might be expected from the bonding nature of the carbon atoms. A less common form is a hexagonal crystal, named lonsdaleite, after Dame Kathleen Lonsdale, one of the first two lady fellows of the Royal Society. Hexagonal and cubic (octahedral) diamonds differ according to their stacking patterns, ABAB vs ABCABC respectively, of their Sp^3 network of "chairs".



DIAMOND



LONSDALEITE

Lonsdaleite is never found alone and is the kind of diamond often encountered in meteorites when shock pressures are involved. Incidentally diamond (more correctly lonsdaleite) has been known in meteorites since 1879, almost as were identified as the source. The amounts recovered from some meteorites, upto 1000ppm, would make the yields for which men fought and died laughable. Whilst diamonds are thought of as a crystal, it is most often dug out of the ground as an ill-formed lump. The world's biggest stone, the Cullinan was an uninspiring 4 x 2½ ins chunk which weighed 3106 carats (a carat is 200 mgs and the name derives from the fact that carob seeds were the original weights) before it was cut and polished. The final product, 105 gems, form part of the Crown Jewels.

The art of cleaving, cutting and polishing stones appears to have originated in Venice at the beginning of the fourteenth century but rapidly spread to the low countries, Bruges, Antwerp and finally Amsterdam, all seaports, trading with the East becoming centres. The most prized diamonds are colourless and their beauty depends entirely upon their optical properties, to produce brilliance and lustre. A material which is transparent might be expected not to be a good jewel, but diamond reflects 17% of the light which falls on it compared to only 5% for glass. Diamond also has a very high refractive index and has cleavage planes which allow it to be faceted in such a way as to arrange for the maximum amount of light to be internally reflected from the sides and back, out through the front, giving it its unique sparkle.

The diamonds optical properties are by no means its only claim to fame. It is of course well known that diamond is the hardest substance in existence giving it the most vital role in machining and cutting. Nothing made naturally or artificially approaches it. The scale of hardness, the Mohs scale, which has diamond as its end member of ten does not actually convey how hard the mineral is: if the Mohs scale was linear then diamond should have a rating of 42. Diamond is not just used for cutting metals etc. it makes the most delicate incisions when employed as a medical scalpel. Amongst the other extremes of scale, diamond is the most thermally conducting substance available at room temperature. It cannot be compressed much or expanded by heat and the atoms in the mineral can be made to vibrate with the greatest range of frequencies. Although it conducts heat, unlike metals it does not conduct electricity, so has enormous values as a heat sink in microelectronics.

Only the purest diamonds have the properties which are at the ends of the measurable scales. And whilst the popular concept of diamond is that of extreme purity this is far from true in reality. The carbon constituting the mineral is frequently contaminated with the other elements of life. Some thousands of ppm atomic hydrogen is concentrated at the surface. This is not water (diamond is totally hydrophobic); the hydrogen is actually bonded there. Another abundant contaminant is oxygen, much of which exists in a variety of discrete silicate minerals. The silicates brought to the surface trapped in diamond provide two fold information. Firstly diamond itself cannot be dated, it has no sufficiently long lived radioactive isotope (^{14}C has $t\frac{1}{2}$ ca. 5500 years) but of course the minerals do have appropriate constituents and these can afford maximum (but not minimum ages) billion years for some diamonds. Secondly, the silicate are indicators of the pressure and temperature at which the diamonds formed, the best estimates being 50 to 60 kbars and 1100 to 1300^{o}C corresponding to a depth of at least 140 to 180 km down in the continental lithosphere.

By far the most important trace element in diamond is nitrogen, it modifies virtually all the mineral's properties and is used for classifying stones into different categories because it is the cause of a variety of spectral characteristics, which can be easily measured without damaging the precious samples. Nitrogen exists substituted for carbon atoms in the crystal lattice. The simplest situation of all is for a single N atom to replace a C. Although this sounds as though it might be common in Nature, it is not and almost all the so-called type Ib diamonds are synthetic. A far more regularly encountered type are IaA stones; here the nitrogen constitutes pairs of atoms located at adjacent sites. An extension of this philosophy, suggest even bigger defects which are clusters of four nitrogen atoms plus a vacancy (type IaB). In the most complex situation of all, nitrogen has coalesced into ever greater agglomerates, hundreds to thousands of atoms, which lie as linear features in lattice planes and are known as platelets. Each of the above kinds of diamond have very characteristic infrared (IR) spectra. A problem is of course that with a natural substance finding a pure end number is almost impossible, so arguments, centred on interpreting mixed IR spectra and absolutely celebrating them for the abundance of nitrogen are frequent and probably almost as violent as disputes amongst the early miners.

Even allowing for the disputes mentioned above the transition from Ib to IaA to IaB to platelets is interpreted as a progression. It can be reproduced in the laboratory and understood in terms of a thermal processing history of the diamonds involved. For example, it can be calculated from high pressure, high temperature simulation experiments that 500ppm N in Ib form can 99.9% convert to IaA in 410 years at 1000°C, which accounts for the very low natural abundance of Ib. Other activation energies are higher and can be used to work out events which took millions of years of burial at high temperatures in the Earth's mantle.

There is one other form of diamond which has a nitrogen contaminant believed to be part way between IaA and IaB. Three nitrogen atoms exist in what is called an N3 centre; it does not give rise to an IR absorption and therefore does not have a typed designation. Both the other types of diamond known, called type II, are believed to be the ultimate end numbers of the mineral which exist with no nitrogen at all. Originally they were thought very uncommon in nature when most knowledge was based on South African sources, but Type IIa diamonds seem to be much more prevalent from Australian mines. Most uncommon of all are the type IIb; these appear to have incorporated small amounts of boron to give semi-conductor properties.

Perhaps not surprisingly, being pure carbon, diamonds were amongst the first materials for which carbon isotopic compositions were obtained. The vast majority have a $\delta^{13}C$ of ca -5‰ just slightly removed from the standard marine carbonate. This would seem to mean that the isotopic composition of deep seated carbon and hence the bulk Earth was of such a value. Other sources of carbon which come up from the Earth's mantle, including lavas erupted at the spreading centres of geological plates, called Mid Ocean Ridge basalts, are more difficult to measure, but give similar confirmatory results.

Of course science never learns to quit when it is ahead, so as more and more diamonds were measured (many of these analyses done by Russian investigators), it was found that outliers, which were originally thought to be analytical errors, were in fact real. These odd diamonds are almost all isotopically lighter (enriched in ^{12}C) than the main population; just one group is slightly heavier. The diamonds for which the $\delta^{13}C$ values are different, are often type IIa, or have silicate mineral inclusions of a type called eclogite paragenesis. Eclogites are a rock which forms as material from the Earth's crust is subducted from the ocean floors beneath the continents. The interpretation put on diamonds of variable carbon isotopic composition is that they reflect a mixing between primitive mantle material and carbon which has been processed, by amongst other things biology on the planet's surface. Biological carbon is isotopically light and the ideas just expounded would appear verified by the analysis of gases in basalts erupted just beyond active subduction zones. Carbon dioxide trapped in magmas from what are called Back Arc Basins is indisputably about -6‰ lighter than pristine mantle because of admixes of organic biological carbon reentering the mantle and contributing to the lava sources.

The real heterogeneity of the Earth's mantle in terms of the elements of life however is seen from conjoint measurements of carbon and nitrogen isotopes. Because the amounts of nitrogen were small, almost always less than 1000ppm, until the mid 1980s the $\delta^{15}N$ of diamonds could not be carried out at all without destroying whole stones of several carats not a very popular experiment. A breakthrough in technique made at the Open University allowed specimens a thousand times smaller to be studied and this meant that small areas could be excised from plates cut across crystals. Using these methods, it was found that diamonds often grew like onions or tree rings with different generations of the stones being discerned readily from the isotopic composition. Thus diamonds can have a complicated history within the mantle, with stop, start, stop events being a regular occurrence.

The strategic importance of diamonds made them something which would be very desirable to synthesis in the laboratory. Many claims, counter claims and even frauds, planned and possibly unintentional, were purportrated before success was achieved in the early 1950's. The principle, which became a well controlled commercial process known as the reconstitution method, relies on carbon dissolved in a metal catalyst under one of set of conditions and being reprecipitated under another. It was also found in the late 1960's that diamond could be made in the extremely high pressures created by explosions. Most peculiarly, it was also manufactured by accident in a low pressure (few millibars) low temperature (800-1000°C) process but not appreciated. This process was rediscovered and now uses various electrical discharges, in carbon containing gases, to produce a plasma which can be made to coat just about anything with diamond. The method works because hydrogen atoms, also in the plasma, destroy graphite and other forms of carbon deposited but not diamond.

To return to the reconstitution method, this frequently grows diamonds of mixed crystal habit, being cubic in one direction and octahedral in another. The different forms of diamond, for an unknown reason, have a markedly different preference for nitrogen. Out of sheer curiosity, the isotopic composition of the C and N in reconstituted diamond was measured and it was found that a fractionation of nearly -40‰ existed between nitrogen in the two forms. There was also a small shift in the carbon isotopes. Large fractionations are almost always found only in low temperature processes but reconstitution happens at very high temperatures, over 1500°C, and the fractionation is associated with a structural phenomenon. This observation is quite unique, but perhaps not surprising, since diamond is a substance quite without parallel.

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