

The Early History of Synthetic Diamond

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Abstract: As synthetic diamonds become increasingly prominent in the jewellery market, this article honours the incremental steps taken by scientists, over a quarter of a millennium, to understand and ultimately replicate the world’s most valuable gemstone. This story begins in the early 18th Century, with Isaac Newton musing on the nature of diamond, and ends in the middle of the 20th Century as the secret of diamond synthesis is finally revealed.



Figure 1. The Bregans Lens. The instrument’s primary lens had a reported diameter of “two thirds of a Florentine arm”, equivalent to around 40cm (Averani and Targioni, 1711, p.225). However, as the lens is still in existence, we know its actual diameter to be 45cm. Its secondary, condensing lens, was mounted on a sliding mechanism, allowing the sun’s rays to be focussed on a specimen which would be held on the metal plate (to the lower left of the picture). Image courtesy of Museo Galileo, Creative Commons, licence CC BY-SA 4.0.

The Adamantine Matter

Isaac Newton took an early step to identify the constituent material of diamond, which would soon be known as “adamantine matter”. In his treatise on optics, Newton wrote:

“... the refraction of Camphire, Oil-Olive, Lintseed [sic] Oil, Spirit of Turpentine and Amber, which are fat sulphurous unctuous [i.e. oily] Bodies, and a Diamond, which is probably an unctuous substance coagulated, have their refractive powers in proportion to one another as their densities without any considerable variation ...

“It seems rational to attribute the refractive power of all Bodies chiefly, if not wholly, to the sulphurous parts with which they abound. And as Light congregated by a Burning-glass acts most upon sulphurous Bodies, to turn them into fire and flame; so, since all action is mutual, Sulphurs ought to act most upon light.” (Newton, 1704, pp.75-76)

Newton implies that, since diamond has considerable refractive powers, it must be combustible. In reality, there is little causal relationship between a material’s refractivity and its combustibility. But in other respects, Newton was correct in surmising that:

- if diamond was viscous, it would likely be considered an oil, given its high carbon content, hydrophobicity, and attraction to other oils; and
- diamond is combustible (although not to the extent Newton imagined).

The first demonstration of the vulnerability of diamond to heat had been provided in 1694-95 when Italians Giuseppe Averani and Cipriano Targioni placed a diamond beneath the Bregans Lens (a large burning-glass / magnifying lens that was owned, along with the diamond, by Cosimo III de’ Medici (Figure 1). It was hoped that the heat generated by the lens would be sufficient to transform the diamond to fire and flame. But instead, the diamond was merely “exhaled away” (Averani and Targioni, 1711, p.232).

The possible fate of Cosimo's diamond was further investigated by the French chemist Jean Darcet in 1768. Darcet had placed two small diamonds in separate porcelain crucibles: one had a tightly-fitting lid, the other had a pierced lid to permit the flow of air. He then subjected the two crucibles to the violent fire of a porcelain furnace, after which neither diamond remained. Darcet, quite reasonably, concluded from this experiment that his diamonds had evaporated, since combustion should not have been possible without a supply of air (as in the closed crucible).

Two years later, Darcet repeated his experiment at the request of the French Academy of Sciences (Darcet, 1771). This time, the closed crucible was replaced by a ball of porcelain paste encasing one of the diamonds. The results were the same. Nevertheless, as Darcet's experiments were reworked by others in the scientific community, some curious results emerged. Most curious of all were those of Pierre-Joseph Macquer, who employed a 'muffle furnace' in his experiments. This apparatus had separate compartments for the burning fuel and the specimen, allowing Macquer to open his 'muffle' at the moment of the diamond's destruction and observe the stone surrounded by flame!

Despite Macquer's observation, the nature of diamond's destruction continued to be debated. The Academy's policy on such topics was for investigations to be carried out cooperatively (Guerlac, 1961). And so it was that, in 1772, Macquer began collaborating with Louis Claude Cadet de Gassicourt (Cadet) and Antoine-Laurent Lavoisier. The group set themselves the challenge of distilling vapours from the evaporation of diamond. But, after placing their diamonds in a ceramic retort and subjecting this to a very violent fire for three hours, no vapours were obtained. Instead, "the diamonds were found in the retort, almost as they had been put in, but nearly all frosted, coated with a kind of black-brown varnish like the inside of the retort; but they had lost more than two grains of their weight and had begun to melt." (L'Académie Royale des Sciences, 1772, pp.18-19).

The question of the destruction of diamond was finally settled with the assistance of a Parisian jeweller, Monsieur Maillard. Not satisfied with Darcet's original crucible with the tightly fitting lid, Maillard placed three diamonds in a ceramic pipe-head filled with powdered charcoal, which would presumably have absorbed any oxygen that penetrated the pipe-head. This was then sealed with a strip of sheet metal, surrounded by silica sand, placed in a crucible coated with chalk, then sealed between two further crucibles! Not all of the protective layers survived two hours in Macquer's large furnace, but the pipe-head and its contents did, proving beyond doubt that diamond could withstand extremely high temperatures when sheltered from air.

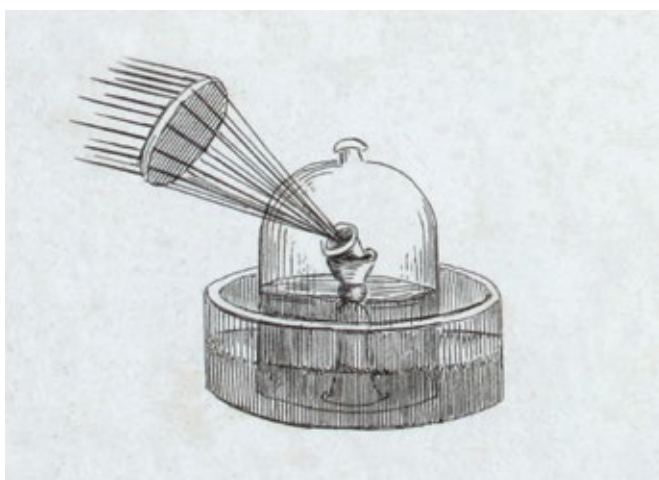


Figure 2. The apparatus used by Lavoisier in his combustion of diamond. Image from Lavoisier (1789, plate 3), and edited by the author.

What had caused the initial confusion? Further experiments by Macquer demonstrated that porcelain paste was not impermeable, as had been assumed. Given that diamond had survived in a ceramic retort, its destruction in Darcet's closed crucible was presumably due to some small gap between his crucible's base and its lid (however tightly fitting the lid was reported to be).

A further contribution from Antoine Lavoisier was then to place several diamonds in a porcelain crucible, which sat atop a glass pedestal, in the middle of an earthenware bucket filled with distilled water (Figure 2). A glass bell-jar was then placed over the diamonds before the Lens of the Royal Palace was focussed upon them (Figure 3). The point of the experiment was seemingly to smell the odours arising from diamond's destruction. But no odours were produced. Nevertheless, after the apparatus had cooled, it was noticed that the water level inside the bell-jar had risen. This led to further investigation. Lavoisier poured 16 ounces of limewater (calcium hydroxide) into the jar and found a cloudy solution (calcium carbonate) arose, as would be expected from air after the combustion of charcoal. He therefore concluded:

"According to this experience, it is difficult not to believe that the air in which one has evaporated diamond, acquires at least in part the properties of fixed air [now known as carbon dioxide]." (L'Académie Royale des Sciences, 1772, p.26).

An Englishman, Smithson Tennant, took the final step to identify adamantine matter in 1796 (three years after Lavoisier's execution during the French Revolution). Replicating Lavoisier's quantitative approach, Tennant weighed the fixed air produced from diamond's combustion and found it equal to that produced by the same weight of charcoal, concluding that:

"... the nature of the diamond ... consists entirely of charcoal, different from the usual state of that substance only by its crystallized form." (Tennant, 1797, p.124).



Figure 3. The Lens of the Royal Palace. This instrument's primary lens had a diameter of 89cm and thus a surface area nearly four times larger than the Bregans Lens.¹ Image by Michael Lange, courtesy of the Mathematics-Physics Department of the Dresden State Art Collections; ©Staatliche Kunstsammlungen Dresden/Mathematisch-Physikalischer Salon and reproduced with permission.

¹ This lens is not to be confused with 'The Great Burning Glass of Mr Trudaine' ('Du Grand Verre Ardent de M. Trudaine') which would have a diameter of around 260cm and thus a surface area thirty-three times larger than the Bregans Lens.

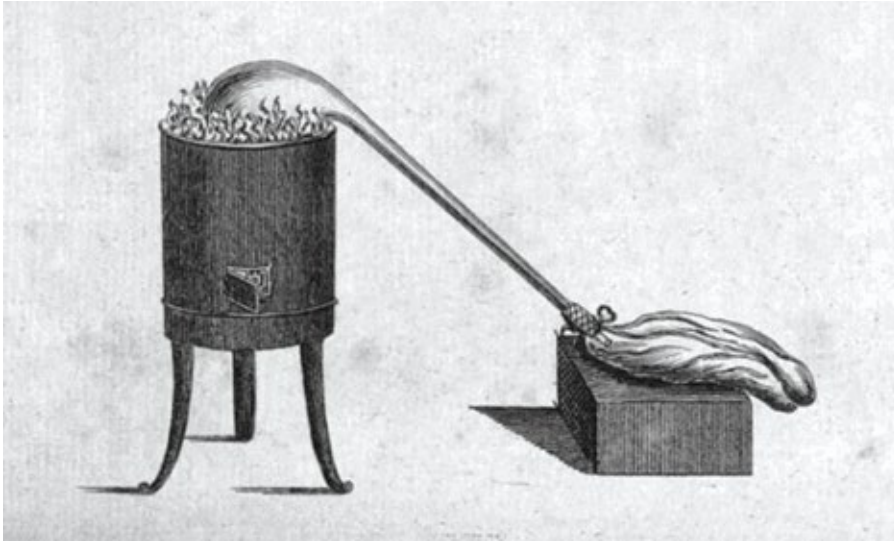


Figure 4. Scheele's apparatus.
Image from Scheele (1780, p.xvi-xvii).

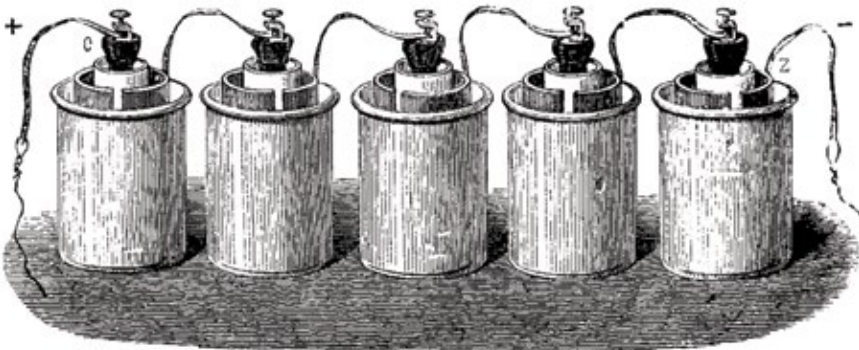


Figure 5. A Bunsen Pile. Each cell of this battery contains a carbon cathode at its centre, immersed in nitric or chromic acid, and surrounded by a tubular zinc anode in sulphuric acid. The two acids are separated by a ceramic pot through which electrical ions, and thus an electrical charge, can pass. Image from Figuier and Nansouty (1911).

The Synthesis of Graphite

Having discovered the composition of diamond to be carbon, at the time known as charcoal, the next challenge was to synthesize it. But before getting to this, we must first consider another form of carbon: graphite.

Carl Scheele, the Swedish chemist, identified graphite as a form of carbon in 1779. Scheele had no access to the extravagant laboratory equipment enjoyed by Lavoisier, instead, he burnt a mixture of 'plumbago' (as both graphite and the ores of lead were known) and arsenic acid within a small retort of thick glass, upon which a large ox bladder was bound (Figure 4). The role of the arsenic acid was to provide sufficient oxygen for the combustion of graphite. Or, as Scheele would have understood it, to absorb phlogiston, because he, like others at this time, believed that materials released phlogiston during combustion, rather than absorbing oxygen. But regardless of the prevalent theory of combustion, Scheele's finding was that, during the experiment, the heated 'plumbago' (graphite) had given off pure "aerial-acid" (as carbon dioxide was then known).

"I am convinced that plumbago is a kind of mineral sulphur or carbon, the constituents of which are aerial-acid, combined with a large amount of phlogiston." (Scheele, 1779, p.243).

Seven years later, three Frenchmen, Messieurs Vandermonde, Berthollet and Monge, found that blades of plumbago would form from molten cast iron as it cooled, and that "the quantity of this substance is always greater when the cast iron is greyer, that is to say, when more charcoal has been placed in the charge of the furnace" (Vandermonde *et al.*, 1786, p.136). The trio correctly identified the blades as being

the same material used in England to make pencils. But it wasn't until the end of the 1780s that the German mineralogist, Abraham Gottlob Werner, labelled the material as "*graphit*" (from the Greek "*graphein*", to write).

By the late 1840s, César-Mansuète Despretz (another Frenchman) was investigating the synthesis of diamond with an influential new tool: the battery. In 1841, the German chemist Robert Wilhelm Bunsen had improved upon the existing Grove Cell by replacing its expensive platinum cathode with carbon. The lower price of the new Bunsen Cell meant many more cells could be joined together to form a powerful battery (also known as a 'pile'; Figure 5). Despretz used his Bunsen Pile to pass an electric current through numerous varieties of carbon, at pressures of up to three atmospheres, to find that "diamond itself changes, like the other species of coal, into graphite" (Despretz, 1849, pp.46-47).

It had therefore been established that charcoal, graphite and diamond were three forms of the same material. But whilst graphite had been synthesized, first from charcoal and then from diamond, a method to synthesize diamond remained elusive. Despretz had already employed a Bunsen Pile with 600 cells in his attempts to form diamond. Having failed, he concluded:

"... diamond is not like the graphite that can be produced artificially in blast furnaces, the product of the action of intense heat on organic or carbonaceous matter. Rather, it would appear ... to have a vegetable origin and to have been initially in a state of softness and to have hardened gradually as one sees a gum harden [to amber]." (Despretz, 1849, pp.46-47).



Figure 6. A rough mellite crystal. Image by Rob Lavinsky, iRocks.com, Creative Commons, licence CC BY-SA 3.0.



Figure 7. One of Hannay's diamonds (approximately 0.4mm long). Photo courtesy of The Trustees of the Natural History Museum, London, Collection number: BM.87756.

The Synthesis of Diamond

Despretz was following the work of the Scottish physicist David Brewster when he suggested a vegetable origin for diamond. Although this now seems a fanciful notion, Brewster supported his argument with reference to "mellite" (Figure 6), a mineral with a distinct crystalline form that emerges from vegetable matter (namely coal) "by the influence of time, and the slow action of corpuscular [molecular] forces" (Brewster, 1835, p.457).

Brewster's rationale was that the properties of diamond were, in some respects, similar to those of amber:

- they were found in similar localities;
- they were both based on carbon;
- they behaved similarly under a polariscope; and
- most significantly, both contained inclusions of air; the expansive force of which could induce strain patterns surrounding the inclusion (when viewed under a polariscope).

On this final point, Brewster believed that strain anisotropy could "arise only from the expansive force exerted by the included air in the diamond and the amber, when they were in such a soft state as to be susceptible of compression from so small a force. That this compressible state of the diamond could not arise from the action of heat is manifest from the nature and recent formation of the soil [i.e. the matrix of sedimentary rock] in which it is found." Brewster further stated: "It is obvious that such an effect cannot arise from any mode of crystallization; ... I have never observed the slightest trace of it in more than 200 mineral substances which I have examined, nor in any of the artificial salts from aqueous solutions." (Brewster, 1835, p.456).

Having first proposed a vegetable origin of diamond in 1820, Brewster updated his work in 1835 to consider further evidence. A certain Captain John Franklin had found diamond within a new, possibly igneous, matrix from Bundelkhand, India, and Franklin believed the diamond had withstood the heat required to produce its rocky matrix because of a great pressure. Furthermore, Franklin surmised that this pressure might also account for the gem's original crystallisation. Brewster admitted this was quite conceivable, and that fusion under pressure could account for the gemstone being in a sufficiently soft state to produce strain anisotropy. But he did not believe it, for it was a fact that 'compressive cavities' did not occur in minerals of igneous origin.

By 1862, Brewster had changed his mind. Having re-examined several plates of topaz, he realised that his 'compressive cavities' were frequently seen in this mineral also (Brewster, 1862). As such, the most notable attempts at diamond synthesis would henceforth operate under increasing pressure.

Early claims of diamond synthesis

A compatriot of Brewster, James Hannay, claimed to have synthesized diamond in 1879 (Figure 7). His method was later described by Gardner Williams, as follows:

"A [wrought iron] tube twenty inches long by four inches in diameter was bored so as to have an internal diameter of half an inch [and thus walls of 1 ¾ inches]. In the tube was placed a mixture of ninety per cent of rectified bone oil, and ten per cent of paraffin spirit, together with four grams of the metal lithium. The open end of the tube was welded air-tight, and the whole mass was heated to redness for fourteen hours." (Williams, 1906, p.138).

Hannay reported the results of his experiments as being small, transparent pieces of “crystalline carbon”, stuck to the sides of the tube within a black mass of iron and lithium (Hannay, 1880). However, the majority of his account focussed on the carnage wrought by numerous violent explosions – hardly encouraging for those looking to validate his work. Added to the significant risk of injury was the risk of failure, for Hannay reported just three successful experiments out of eighty. It was almost as if he was trying to put people off! Later tests would find that Hannay’s diamonds were in fact natural, rather than synthesized (Davies, 1984), presumably added by Hannay at the start of his experiments.

Henri Moissan claimed to have synthesized diamond in 1893. By the time of his experiments, diamonds had been discovered in the ‘blue earth’ (i.e. Kimberlite) of South Africa and in the meteorites of Canyon Diablo, Arizona. Both sources supported the role of high pressures in the diamond’s formation. To replicate these conditions, Moissan dissolved sugar charcoal (a pure form of amorphous carbon derived from sugar) in a crucible of molten cast iron then plunged the crucible in water (Figure 8). Cast iron expands as it solidifies then contracts as it cools. Moissan therefore believed the outside of the iron mass would be contracting whilst the inside expanding, creating immense pressure within the crucible. This approach was found to produce graphite, brown charcoal, and “a small quantity of a fairly dense carbon which, when separated from its iron matrix by a series of acid baths, displayed all the characteristics of diamonds”. These characteristics were listed as:

- a specific gravity close to 3;
- being harder than ruby; and
- being entirely combustible in oxygen.

Of these, Moissan considered combustibility the most important, for the other characteristics were shared with a “number of metallic silicides and carbides” (Moissan, 1893, pp.221-224).



Figure 8. Henri Moissan quenching molten cast iron (alongside the electric arc furnace he invented). Image from Archive Pics, Alamy stock photo.

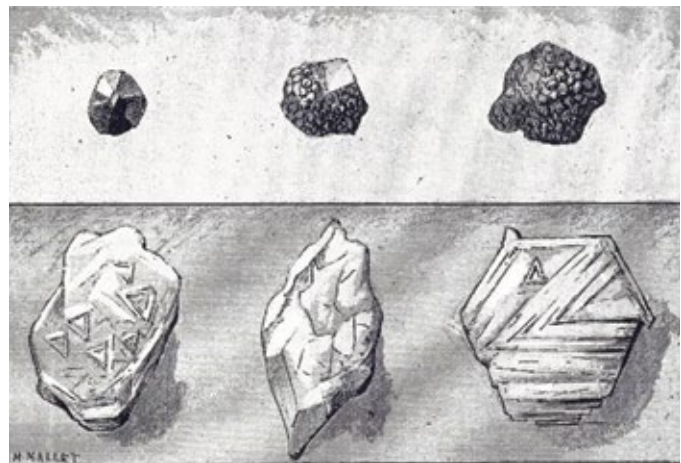


Figure 9. Some of the crystals produced by Moissan. Image from World History Archive, Alamy stock photo.

Moissan’s diamonds, however, were not entirely combustible. Those specimens which burned left an ochre-coloured ash which Moissan considered analogous to the combustion of low-grade diamond (Moissan, 1893). The experiments were later replicated by Charles Parsons, who found that more crystals were formed when impurities (such as silicon, aluminium, magnesium and chromium) were present in the iron; and that few crystals would emerge from pure iron. The suspicion then, was that Moissan’s diamonds were in fact either carbides (such as silicon carbide, also known as moissanite) or spinels (Desch, 1928).

Figure 9 shows some of the crystals produced by Moissan. They were comprised of two groups, described by Moissan as having “a chagrined appearance and a shade of grey black identical to that of certain carbonados” (Figure 9, top row); and “the transparent fragments which appear broken into small pieces have a greasy appearance ... [and] possess a certain number of parallel streaks or triangular impressions.” (Figure 9, bottom row; Moissan, 1893, pp.221-222).

An approach similar to Moissan’s was later used by J. Willard Hershey and his students at McPherson College, USA. In 1940 Hershey reported that:

“Since we first began our experiments in their manufacture [in 1929] more than 50 diamonds have been made synthetically ... , ranging in size from the smallest, one millimeter in diameter, to the largest, which is two millimeters by one and one half millimeters by one millimeter, weighing 1/30 carat.” (Hershey, 1940, p.140).

As Moissan’s largest specimen had measured 0.75 mm, Hershey believed he had produced the largest synthetic diamonds on record. However, by this point several of Hershey’s diamonds had already been examined by the GIA laboratory and found to be a mixture of natural diamonds and quartz (Figure 10)². The GIA rather charitably concluded that “there may have been too much confusion of specimens in the system followed by Hershey and his assistants” (GIA, 1938, p.198).

² Hershey later acknowledged that the first stone (Figure 10) was a natural diamond. It might be questioned how the GIA laboratory could have identified synthetic diamonds, assuming that none had ever been produced, but inclusions were observed within Hannay’s stones that were typical of natural material. The uncertain verdict on the fifth stone was explained as follows:

“The surface is not sufficiently clear to allow a detailed study of the inclusions to be made, but from its appearance this stone might possibly be diamond produced by Dr. Hershey’s method. However, in view of the outcome of the tests on the other stones of this group, plus the appearance of the specimen, which likewise is quite similar to that of many South African stones, its synthetic origin may reasonably be doubted” (GIA, 1938, p.197).

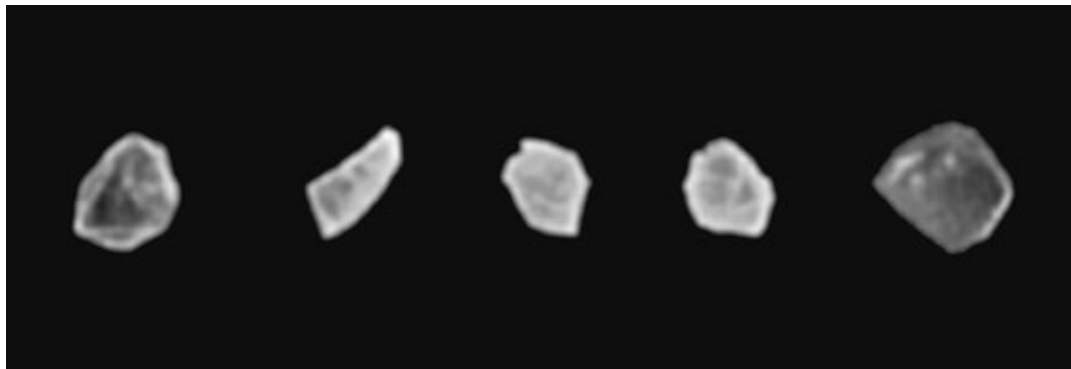


Figure 10. The five specimens examined by GIA. Left to right: natural diamond, natural diamond, quartz, quartz, possibly synthetic but more likely natural diamond. The largest of these specimens weighed less than 1/100th of a carat. Image courtesy of GIA (GIA, 1938, p.195), edited by the author.

The first true synthesis of diamond

At the same time as Hershey's experiments at McPherson College, Percy Bridgman was working at Harvard University developing apparatus to maintain astonishingly high pressures. By 1947, he reported that at room temperature, not even 400,000 atmospheres of pressure was sufficient to transform graphite to diamond (Bridgman, 1947). Yet it had previously been calculated that diamond was the preferred form of carbon at pressures of just 15,000 atmospheres (Davies, 1984). The problem was that, without sufficient heat to break apart its carbon bonds, graphite's transformation to its more lustrous counterpart was occurring at a negligible pace. But to maintain both high temperatures and pressures was a formidable engineering challenge.

Success would finally be achieved in 1953. On 15th February that year, Erik Lundblad and the Swedish company ASEA employed their 'sphere' apparatus – designed for the purpose by Baltzar von Platen – to produce the first 'high pressure, high temperature' synthetic diamonds.³ (For a full account of Lundblad's work, see *Diamond (1984)* by Gordon Davies.) Lundblad had replaced the cast iron employed by Vandermonde, Berthollet and Monge with cementite – an iron carbide with a far higher density. But Lundblad's method was in some senses an evolution of their work, along with that of Newton, Averani and Targioni, Darcet, Macquer, Cadet, Lavoisier, Maillard, Tennant, Scheele, Despretz, Brewster, Franklin, Hannay, Moissan, Bridgman and von Platen. The slow progress of science and engineering over a quarter of a millennium had finally revealed the secret of diamond synthesis.

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³ Although a significant achievement, Lundblad's synthesis of diamond was not actually the first. Just one month earlier, William Eversole and the Union Carbide Corporation had achieved new growth atop a seed of natural diamond, using a low-pressure technique of Chemical Vapour Deposition (Angus and Hayman, 1988). Lundblad and ASEA were, however, the first to synthesize diamond without a natural diamond seed.

