

Edward Charles Howard

Explosives, meteorites, and sugar

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ABSTRACT

To Edward Charles Howard (1774–1816), a self-educated scientist without formal education in chemistry, we owe the (accidental) discovery of mercury fulminate, the finding that meteorites contain nickel and have a composition different from any material originated in the earth, and the design of the vacuum evaporator and other accessories that resulted in a substantial improvement in the economic balance of sugar production.

KEYWORDS: Fulminates, meteorites, nickel, vacuum evaporation, sugar

Resumen

A Edward Charles Howard (1774–1816), un científico inglés autodidacta, sin formación formal en química, se le conoce como el descubridor (accidental) del fulminato de mercurio, el hallazgo de que los meteoritos contienen níquel y que su composición es totalmente distinta de toda sustancia originada en la Tierra, y del diseño del evaporador al vacío y otros accesorios, que condujeron a una economía sustancial en la fabricación de azúcar.

Palabras clave: fulminato, níquel en meteoritos, evaporación al vacío, azúcar.

Life and career

Edward Charles Howard was born on 28 May 1774 at Darnell Hall near Sheffield. His father, Henry Howard (1713–1787) was an unsuccessful wine merchant in Dublin. After his failure in business the 9th Duke of Norfolk, a kinsman, paid his debts and put him in charge of his Sheffield estates (Kurzer, 1999, 2000; Sears, 1976).

At the age of nine Edward was sent to be educated at the Catholic English College in Douay, in Northern France, where his two elder brothers were already enrolled. At that time it was thought impossible to receive a good Catholic education in Protestant England; families who wished their sons to receive their education in the proper religious background had to look for it abroad; consequently. In 1788, at the age of fourteen, after he had completed less than half the course, he returned to England. His father had died six months previously and there were already signs of the French revolution, which was to break out a year later. The Revolution government would later close all the French scientific institutions as well as religious schools and offices (Kurzer, 1999; Sears, 1976).

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There is no information about his further education but clearly it was enough to make him a very skilled chemist, as demonstrated by the publication of his first paper in which he announced the discovery of mercury fulminate, a most powerful explosive (Howard, 1800). This paper made Howard well known at home and abroad and gained him the Copley Medal of the Royal Society. In his address at the presentation of the Medal, Joseph Banks (1743–1820), the President of the Royal Society, described Howard's achievements, mentioning the accidental explosion of mercury fulminate in which Howard had been injured in his eyes and other parts of his body, and also brought up the next subject of his researches: "...Mr. Howard has not stopped here. He has announced to us the discovery of a fulminating silver, analogous in some degree to his fulminating mercury, and he is now employed in the analysis of certain stones, generated in the air by fiery meteors, the component parts of which will probably open a new field of speculation and discussion to mineralogists as well as to meteorologists" (Kurzer, 1999; Sears, 1976).

In the year 1799–1800 Howard was elected a Fellow of the Royal Society and became a member of the Royal Institution and of the Society of Arts. His candidature for Fellowship of the Royal Society was supported by the 11th Duke of Norfolk (his third cousin), by William Henry Francis, 11th Baron Petre (1793–1850), and another five fellow scientists interested in his work; John Abernethy (1764–1831, a surgeon and teacher of anatomy), who participated in some of Howard's experiments on fulminates, John Richard Anthony Pearson and George Shaw (1751–1813), who shared Howard's interest in meteorites; Peter Woulfe (1727–1803, a chemist and mineralogist), and Charles Hatchett (1765–1845, the discoverer of niobium). Within a year of his election, he was appointed member of Permanent Committee of Chemistry of the Royal Society, which was "authorized to make such experiments in the laboratory of the Institution as they may think fit" (Kurzer, 1999; Sears, 1976).

One interesting and significant activity of Edward was his participation in the polemic related to the discovery of palladium by William Hyde Wollaston (1766–1828) in solutions of platinum in aqua regia. Initially, Wollaston did not publish

his discovery in order not to hurt his platinum business; instead he offered samples of palladium for sale anonymously through the Soho mineralogical shop of Jacob Forster. Several members of London's scientific community received a small printed notice in the mail advertising the properties of a new noble metal dubbed *Palladium* or *New Silver*, without mentioning the source of the new metal, the procedure employed in its isolation and purification, or the identity of its discoverer. Nicholson, the editor of the *Journal of Natural Philosophy, Chemistry and the Arts*, received a copy and printed the notice in his journal (Nicholson, 1800). Richard Chenevix (1774–1830) read the palladium notice on April 19, 1803 and believing it to be a bad taste prank, he made a comprehensive study of the metal; after 13 days of intensive research he read a 31-page paper to the Royal Society where he declared that the unusual announcement of the discovery of the new metal hinted of fraud, and although the metal had all the advertised properties, he believed it was actually an alloy of platinum and mercury (Chevenix, 1803). Wollaston then put a anonymous notice in Nicholson's Journal (Nicholson, 1804; Wollaston, 1805) offering £20, to anyone who could succeed in making only 20 grains of real palladium, before three competent "gentlemen chymists", the Editor being one of them. Nicholson appointed Charles Hatchett and Howard to serve with him as judges of the competition and in the following number of his journal expressed his hope that "the commission will enable me to present to my readers an account of whatever may be the result of this public invitation". No one came forward to claim the prize. Shortly thereafter Wollaston revealed to Banks that he was the discoverer of platinum and also sent a letter to Nicholson with the same notice (Wollaston, 1805; Wisniak 2006).

Howard married, on July 12, 1804, Elizabeth (–1810), the daughter of William Maycock. They had one son, Edward Giles (1805–1840), and two daughters, Julia (1807–1856) and Elizabeth (1806–1835). Howard died suddenly in 1816 at the early age of 42. According to Kurzer, it is reported that having spent an excessively long time in the steam-heated rooms of a sugar refinery, Howard suffered a hemorrhage and died shortly thereafter. He was buried in the cemetery of Old Saint Pancras Church, Middlesex (Kurzer, 1999).

Scientific achievements

Howard published less than 10 scientific papers, mostly in the areas of chemistry and meteorites. He was also awarded several patents related to improvements in the manufacture of sugar and other engineering elements.

Mercury fulminate

The alchemists of the 17th century, among them Cornelius Drebbel (1572–1633) and Johann Kunckel (1630–1703), knew that mixtures of *spiritus vini* with mercury and silver in *aqua fortis* could explode. Kunckel, a well-trained alchemist, believed that mercury was a constituent of all metals, in accordance with the modified prevailing notion that of the

four elements, earth, air, fire, and water, earth, in its many forms, consisted of mixtures of three other elemental substances, salt, mercury, and sulfur. In one of his numerous experiments using this metal, Kunckel accidentally synthesized mercury fulminate, but did not isolate it since it was immediately destroyed in the ensuing explosion: "I once dissolved silver and mercury together in aqua fortis, and having added *spiritus vini*, set the vessel aside in the stable. When by the next day its temperature had (spontaneously) risen, there occurred such a thunder clap that the groom thought someone had shot at him through the window, or that the very devil had appeared in the stable. But I realized that it was my experiment that had exploded" (Kunckel, 1716; Kurzer, 2000).

By the second half of the 18th century many chemists believed that ammonia originated from alkalis and contained an inflammable substance. Torbern Olof Bergmann (1735–1784) had noticed that ammonia decomposed gold carbonate and produced a highly unstable compound name gold fulminate (Scheele and Bergmann, 1781). Claude Louis Berthollet (1748–1822) studied the behavior of gold fulminate (an azide) and established that when heated carefully it disengaged ammonia and gold returned to the carbonate state and lost its explosive characteristics. Bergmann had proved that alkalis dissolved the oxides of lead; Berthollet extended these results to other oxygenated compounds and found that a boiling aqueous solution of calcium hydroxide dissolved all the oxides of lead (Berthollet, 1788ab).

Treatment of the decomposition product of silver nitrate by lime or alkalis produced a brown precipitate, soluble in ammonia. If previous to treatment with ammonia the precipitate was dried over a filter paper, it decomposed under the action of light, yielding silver oxide, which partly dissolved in ammonia. After 10 to 12 hours a brilliant layer formed on the surface of the solution, which dissolved when more ammonia was added. Decantation of the liquid and drying over a filter paper precipitated a black powder that presented some interesting properties. For example, when humid and pressed with a hard body, it detonated violently yielding reduced silver. Touching or rubbing it while transported, also resulted in detonation. The properties of silver fulminate (an azide) were very similar to those of gold fulminate. Boiling the solution produced a large amount of bubbles, which were found to be nitrogen; boiling precipitated small brilliant crystals extremely explosive and able to break the glass in a dangerous manner. In Berthollet's words: "Gunpowder, even gold fulminate, cannot be compared with this new product. Contact with fire is required to make powder explode; gold fulminate has to be heated to a sensible degree to fulminate it, whereas contact with even a cold object is enough to set off silver fulminate. In short, after this material has once been obtained, it may not be touched. No attempt should be made to put it into a bottle; it must be kept in the open vessel." A weight of one grain left (one grain is about 0.06 g) in a glass capsule was enough to pulverize the capsule; the particles released went through many pages of paper. According to Berthollet the

strong detonation was caused by the combination of the remaining oxygen in the silver with the hydrogen (generator of water) from ammonia, producing vapor water. This water, which vaporized instantly with all its elastic and expansive power, was the main cause of the phenomenon, although nitrogen disengaged from ammonia also played also an important role amongst others (Berthollet, 1788ab).

In 1800 Howard reported his discovery of the highly explosive mercury fulminate by reacting mercury with alcohol and a mixture of concentrated nitric and sulfuric acids (Howard, 1800). In his lengthy monograph he described its method of preparation, its chemical properties, and its remarkably violent detonating powers. Howard described several of the explosive and destructive properties of mercury fulminate that he had witnessed, but did not reveal its nature or its method of preparation (Kurzer, 1999; Nicholson, 1800). It should be noted that in 1789 Fourcroy reported the synthesis of an explosive material, which he called *mercure fulminant* (fulminating mercury), product of the reaction of mercury nitrate and ammonia (Fourcroy, 1789). This derivative is actually an azide of the metal (Hg_2N_6), and thus different from the material prepared by Howard.

Howard's discovery of mercury fulminate was accidental. In his own words (Howard, 1801): "I was led to this discovery by a late assertion that hydrogen is the basis for muriatic acid (HCl); it induced me to combine different substances with hydrogen and oxygen. With this view I mixed such substances with alcohol and nitric acid... (which) might... attract an acid combination of the oxygen of the one and the oxygen of the other... The red oxide of mercury appeared not unfit for this purpose... The acid... gradually dissolved the oxide... a smell of ether was perceptible... and a white dense smoke... was emitted with ebullition. The mixture then threw down a... precipitate... which became... nearly white... I poured sulfuric acid upon the dried crystallized mass... a violent effervescence ensued... and an explosion took place." Howard made several experiments to cause the mercurial powder to fulminate by concussion by striking it in an anvil with a hammer. With 3 or 4 grains a very disagreeable noise was produced and both the anvil and hammer were damaged. A similar effect was obtained with the shock of an electrical battery; heating the powder it exploded when the temperature reached 368°F.

Together with his friend John Abernethy, Howard made some experiments to compare the power of mercury fulminate with that of gunpowder. An ordinary gunpowder proof was filled with compound and fired in the usual way. Although the explosion was sharp but not loud and no recoil was observed, it laid open the upper part of the barrel. A similar experiment, done with a gun, burst the weapon. In order to make a better examination Howard carried on the explosion by confining mercury fulminate in the center of a hollow glass tube, 7 inches in diameter. The glass tube withstood the explosion, retaining the gases produced by the same while its interior became coated with a layer of highly divided

mercury. From these experiments Howard inferred that the "astonishing force" of mercurial fulminate must be attributed to the rapidity of its combustion (Howard, 1801).

Howard then described the procedure for manufacturing up to 500 grains mercury fulminate per batch; this upper limit was selected not because the danger of an explosion but because the amounts of nitric acid and alcohol required would generate enough heat to affect the quality of the product. He suggested using pure mercury used instead of its oxide because the results were the same and pure metal was cheaper. From 100 grains of mercury he obtained between 120 and 150 grains of fulminate, depending on the conditions of the reaction.

Analysis of the gaseous products generated during the combustion of mercury fulminate indicated that they consisted of carbon dioxide and nitrogen and some of its compounds.

Howard found that mercury fulminate was decomposed by nitric acid, sulfuric acid, and muriatic acid (HCl). Nitric acid generated nitrous gas, acetic acid, and mercuric nitrate. Very concentrated sulfuric acid produced an explosion almost instantly, probably because of the large heat of reaction, leaving a white non flammable powder, mixed with small drops of mercury, which Howard believed, was mercury oxalate. Hydrogen chloride dissolved a portion of the fulminate and transformed it into mercuric chloride. According to Howard, these results established that mercury fulminate contains nitrous etherized gas (ethyl nitrite) and mercuric oxalate combined with an excess of oxygen, and served to explain the combustion process, as follows: "The hydrogen of oxalic acid and of the etherized gas is first united to the oxygen of the oxalate forming water; the carbon is saturated with oxygen forming carbonic acid (carbon dioxide); and a part if not all of the nitrogen of the etherized gas is separated in the state of nitrogen gas..." Howard indicated that he did not want to make an accurate analysis of mercury fulminate because "the affinities I have brought into play are complicated and the contribution of the substances I have to deal with not fully known". Nevertheless, he calculated that 100 grains of mercury fulminate contained 21.28 grains of pure oxalic acid, 60.72 grains of mercury formerly united to the oxalic acid; 2 grains of mercury dissolved in the sulfuric acid after separation of the gases (giving a total of 64.72 grains of mercury), and 14 grains of nitrous etherized gas and excess of oxygen (Howard, 1800).

Howard used his process to try to impart, without success, fulminating properties to gold, platinum, antimony, tin, copper, iron, lead, zinc, nickel, bismuth, cobalt, arsenic, and manganese. Only silver yielded a gray precipitate, which fulminated with great violence. A safer method of producing the latter in very small amounts was worked out in collaboration with William Cruickshank, at the Royal Military Academy, Woolwich.

Howard closed his paper with a description of seven experiments done at Woolwich in collaboration with Colonel

Thomas Blomefield (1744–1822) and Cruickshank. The results indicated that any piece of ordinance may be destroyed by employing a quantity of mercury fulminate equal in weight to one half of the service charge of gunpowder, and that it would be possible to proportion the charge of mercury fulminate to the size of different cannons as to burst them without dispersing any splinters. Nevertheless, he cautioned that the great danger attending the use of mercury fulminate would probably prevent it being employed for this purpose.

Such was the universal interest in this new explosive that *The Times* of London twice reported about this finding (September 6, 1799 and August 5, 1800) and the Royal Society awarded him his highest distinction, the Copley Medal (Kurzer, 1999).

Berthollet examined the results reported by Howard and disagreed with his conclusions (Berthollet, 1801). According to Howard, mercury fulminate contained per weight 21.28% oxalic acid, 64.72% mercury, and 14.00% nitric gas and excess oxygen. Berthollet prepared the compound following Howard's procedure but first separated and analyzed the supernatant liquid. Addition of powdered calcium carbonate produced a black precipitate similar to the one produced from solutions of mercury that contain ammonia, results that led him to believe that the precipitate also contained ammonia. For this reason he treated the mercury fulminate with potassium hydroxide and noticed the release of ammonia. The alkali did not show presence of oxalic acid, the powder became brown and hardly melted when put on top of burning coal. He then subjected the fulminate to the action of hydrogen chloride and of sulfuric acid, the same as Howard had done. The clear solution was treated first with a suspension of potassium sulfide to precipitate the metal, followed by addition of a solution of calcium chloride, no precipitation occurred, as should if oxalic acid was present. The same experience, repeated with mercury oxalate, produced now a precipitate with the calcium chloride proving that mercury fulminate did not contain oxalic acid.

In another experiment, a similar solution of mercury fulminate was distilled alone and brought to sublimation. The sublimate consisted of fine needles in which it was easy to identify the presence of ammonia, and were similar to those obtained when distilling a mixture of a little of ammonia chloride with a dissolution of mercuric chloride. This result confirmed the presence of ammonia in mercury fulminate and also proved that the metal was in the same oxidized state as in mercuric chloride.

Berthollet confirmed Howard's claim that dilute sulfuric acid decomposed mercury fulminate reducing it to a white non-flammable powder that Howard had assumed to be mercury oxalate. Berthollet disagreed with this conclusion, believing that the powder was actually mercuric sulfate, (which he named sweet mercuric sulfate). The action of sulfuric acid was accompanied by the release of a considerable amount of gas. Howard had identified this gas to be largely carbon dioxide, but he had also assumed that the part of the

portion that is insoluble in water had the properties of what the Dutch chemists call *gaz nitreux éthère* (ethylene dichloride), because it was changed by the action of sulfuric acid. Hence, mercury fulminate had to contain *gaz nitreux éthère*. Berthollet wrote that none of his findings justified the presence of latter gas. The largest part of the gas he obtained was carbon dioxide and the rest, about 1/12 volume of the gas, was *gaz hydrogène oxicarboné* (a mixture of hydrogen, carbon dioxide, and carbon monoxide) (Berthollet, 1801).

From these results Berthollet concluded that mercury fulminate was actually a combination of (a) well-oxidized mercury, like the one present in mercuric chloride, (b) ammonia, and (c) a substance still not identified, but which is not oxalic acid or a similar acid. This substance seemed somewhat different from an alcohol because it was easily decomposed forming carbon dioxide at the same time that it reduced mercury producing *gaz hydrogène oxicarboné*.

Berthollet ended his paper indicating that "although my results were opposed to those of Mr. Howard regarding the analysis of mercury fulminate... he expected the young chemist to be more rigorous in his researches to which he will apply his talents...he congratulated the interesting experiences Howard had done in order to explain the different mode of action of detonating substances based on the fast expansion of the gases they generated and according to the amount of the same" (Berthollet, 1801).

It took many years and the work of many scientists to decipher the actual composition of mercury fulminate and fulminic acid. Its history has been described in detail by Kurzer (Kurzer, 2000). In 1989 Teles *et al.* (1989) used modern spectroscopic techniques to elucidate the definite composition of fulminic acid and to prove that the acid assumes the formyl configuration. Beck *et al.* (2007) reported the results of X-ray investigations of single crystals as well as powders of Hg(CNO)₂, which revealed, almost linear O–N–C–Hg–C–N–O bonds similar to those in mercury cyanide. The fulminate group CNO was reported to consist of a short carbon–nitrogen bond of length 1.143 Å, and a remarkably longer nitrogen–oxygen bond of length 1.248 Å. Beck and Klapötke (2008) investigated the molecular structure of mercury fulminate at B3LYP level of theory using a large and a small core scalar relativistic pseudopotential for mercury. The connectivity in mercury fulminate was found to be ONC–Hg–CNO and not CNO–Hg–ONC as previously predicted. Whereas mercury fulminate, ONC–Hg–CNO, has a C₂ structure in the solid state with an Hg–C–N angle of 169°, as an isolated molecule it is perfectly linear and possesses D_{∞h} symmetry.

Until the 18th century firing of guns was carried on by matches, fuses, glowing coals, or by sparks generated by flintlocks. The procedure was superseded in the 18th century by percussion firing, in which the sharp detonation of a small initiator induced the reliable explosion of the main gunpowder charge. The first primers were based on potassium chlorate, but their sensitivity to atmospheric moisture impaired their reliability; moreover, they liberated chlorine on detona-

tion, which promoted the corrosion of the gun. E. G. Wright, a British gentleman having a hobby for firearms, is credited with having introduced mercury fulminate as a greatly superior primer. He personally prepared the compound by Howard's method, and soon he and his friends were taking advantage of the striking improvement afforded by the new detonator (Wright, 1823). In the 1840s and 1850s its introduction throughout Europe created an ever-increasing demand for mercury fulminate, which remained, for the next 80 years, the only practical detonator for firing projectiles of every kind. In the early years of the 20th century, the annual production was estimated at 100,000 kg in Germany alone (Kurzer, 2000).

Mercury fulminate played a crucial role in the development of explosives for industrial and military applications of Alfred Nobel's (1833–1896) dynamite (Nobel, 1875). An important problem in the industrial and military application of nitroglycerine was finding a reliable method for firing the explosive. Nobel discovered that it was possible to fire nitroglycerin using an initial explosion, such as that produced by a small charge of gunpowder. The gunpowder cartridge was afterwards replaced by a small metal receptacle loaded with mercury fulminate mixed with gunpowder or potassium nitrate (Nobel's igniter). It was the firing of nitroglycerin by detonation which first rendered it useful as a blasting explosive. As described by de Mosenthal (1899), the full importance of Nobel discovery of firing an explosive by a separate initial explosion instead of a flame or flash has been considered the greatest invention since the discovery of gunpowder, and it makes Nobel not only the creator of the nitroglycerin industry but also the father of the modern high explosive industry.

Meteorites

Probably the best description of the early history of meteoritic knowledge is the one given in a brochure published in 1894 by the British Museum under the title "An Introduction to the Study of Meteorites" (British Museum, 1894): "Until nearly fifty years after the establishment of the British Museum (1753), meteorite collections nowhere existed, for the reports of the fall of stones from the sky were then treated as absurd, and the exhibition of such stones in a public museum would have been a matter for ridicule;...Hence it happened that in 1807 probably not more than four or five meteoric stones were in the British Museum; one of them was a stone of the L'Aigle fall, presented in 1804 by Biot...A fragment of the Pallas meteorite had been presented to the Museum by the Academy of Sciences of St. Petersburg as early as 1776, at which time it was regarded as "native iron."

In the year 1807...Charles Konig, the mineralogist, was appointed "assistant librarian"...thus came about that for thirty-eight years the senior officer of the Natural History Department of the Museum was one who had an intense enthusiasm for minerals and made them his own special study. It was in Konig's time (1810) that Parliament voted a special

grant of £14,000 for the purchase of the minerals which had belonged to Sir Charles Greville; (probably containing) several fragments of meteorites, including... one (from)...Tabor...During Konig's time, though numerous and excellent mineral specimens were acquired...; at his death in 1851, it numbered about 68 specimens...After the death of Mr. Konig, Mr. C. K. Waterhouse, the paleontologist, was appointed Keeper of the Department...During the time of Mr. Waterhouse, only three meteorites were added to the collection...It may be added that a stone which lately fell in India was decked with flowers, daily anointed with ghee (clarified butter), and subjected to frequent ceremonial worship and coatings of sandal wood powder. The stone was placed on a terrace constructed for it at the place where it struck the ground, and a subscription was made for the erection of a shrine.

Three French Academicians, one of who was...Lavoisier, presented to...the Academy in 1772 a report on the analysis of a stone said to have been seen to fall at Lucé on September 13, 1768. As the identity of lightning with the electric spark had been recently established by Franklin, they were in advance convinced that "thunder-stones existed only in the imagination; and never dreaming of the existence of "sky-stone" which had no relation to a "thunder-stone"; they somewhat easily assured both themselves and the Academy that there was nothing unusual in the mineralogical characters of the Lucé specimen, their opinion being that the stone was an ordinary one which had been struck by lightning.

In 1794...Chladni...brought together numerous accounts of the fall of bodies from the sky and called the attention of the scientific world to the fact that several masses of iron... had in all probability come from outer space to this planet... the Pallas or Krasnojarsk iron...irregular mass, weighing about 1500 lb...was regarded by the Tartars as a "holy thing fallen from heaven." The fragment...weighing about 7 lb, was presented in 1776 by the Imperial Academy of Sciences of St. Petersburg.

Chladni argued that these masses could not have been formed in the wet way, for they had evidently been exposed to fire and slowly cooled; that the absence of scoriae in the neighborhood, the extremely hard and pitted crust, the ductility of the iron, and, in the case of the Siberian mass, the regular distribution of the pores and olivine, precluded the theory that they could have been formed where found, whether by man, electricity, or an accidental conflagration: he was driven to conclude that they had been formed elsewhere, and projected thence to the places where they were discovered; and as no volcanoes had been known to eject masses of iron, and as, moreover, no volcanoes are met with in those regions, he held that the specimens referred to must have actually fallen from the sky. Further, he sought to show that the flight of a heavy body through the sky is the direct cause of the luminous phenomenon known as a fireball (Chlandi, 1794).

Fragments of the stones of Siena, Wold Cottage, Krakhut, (and)... at Tabor, in Bohemia, came into the hands of Edward

Howard, (who reported)...the comparative results of a chemical and mineralogical investigation...as follows: "The mineralogical descriptions of the Lucé stone by the French Academicians, of the Ensisheim stone by M. Barthold, and of stones from the above four places (Siena, Wold Cottage, Krakhut and Tabor) by the Count de Bournon, all exhibit a striking conformity of character common to each of them, and I doubt not but the similarity of component parts, especially of the malleable alloy, together with the near approach of the constituent proportions of the earth contained in each of the four stones, will establish very strong evidence in favor of the assertion that they have fallen on our globe. They have been found at places very remote from each other, and at periods also sufficiently distant. The mineralogists...agreed that they have no resemblance to mineral substances properly so called, nor have they been described by mineralogical authors" (British Museum, 1894).

In 1805 Joseph Izarn (1766–1834) published a lengthy book (422 pages) describing the development of the knowledge about celestial stones that took place between 1700 and 1805. The first section of the book describes all the historical writings about falling stones, beginning in the antiquity, and the explanations given about their origin, many of them carrying a religious tone. By the end of the eighteenth century, scientists had rejected most of the explanations as being common superstition. The book also includes reprints of the main papers published on the subject during this period (Izarn, 1805).

Ernst Florens Friedrich Chladni (1756–1827) was the only reputable scientist to entertain the cosmic hypothesis seriously. In 1794 he published a 63-page book (Chladni, 1794) in which he proposed that meteor-stones and iron masses were cosmic objects, perhaps debris ejected from a broken planet, which on crossing the Earth's orbit and entering its gravitational field, would plunge to Earth and glow as a result of the heat generated by the friction in their passage through the atmosphere. Chladni estimated that the speeds of the rocks entering the atmosphere was enormous, much faster than could be produced by the Earth's gravity alone, but possible for objects originating in outer space. Chladni's interpretations violated the belief that no small bodies exist in space beyond the Moon; aside from the stars, planets, moons, comets, and perhaps some vapors arising from their atmospheres, everyone "knew" that space itself was empty (Marvin, 2007).

Shortly after the book was published, a large cloud of smoke appeared in the sky near Siena, Italy. The cloud turned bright red and stones fell to the ground. On December 13, 1795, several eyewitnesses reported the fall of stone of about 25 kg in Wold Cottage, England. The fall was accompanied by the sound of an explosion from the air and took place in broad daylight, out of a clear, blue sky, refuting the most popular explanations for the formation of meteorites, such as lightning or condensation in clouds (Marvin, 2007).

These and similar events convinced Joseph Banks that an investigation was warranted, and consequently, asked How-

ard to analyze the chemical composition of the alleged rocks from the sky. Howard reported his results in a long paper published in 1802 (Howard, 1802a). In the first part of it he gave a short historical summary of the available information about falling stones. Their origin or whence they came was involved in complete obscurity. The accounts of these peculiar substances, in the early annals, even of the Royal Society, had unfortunately been blended with relations, which then could be considered fabulous. In very early ages it was believed that stones did in reality fall from heaven or from the gods. Keepers of European museums discarded genuine meteorites as shameful relics of a superstitious past (Howard, 1802a).

Howard indicated that the first reported chemical analysis of these substances was of the stone presented to the Académie des Science by the Abbé Bachelay. This stone was found on September 13, 1768, yet hot by the persons who saw it fall. The academicians Fougereux de Bondaroy (1732–1789), Louis-Claude Cadet de Gassicourt (1731–1799), and Antoine-Laurent Lavoisier (1743–1794) reported that the stone had a density of 3.535 and contained 8.5 % sulfur, 36 % iron, and 55.5 of vitrifiable earth. Their conclusion was "la pierre présentée par M. Bachelay, ne doit point son origine au tonnerre, qu'elle n'est point tombée du ciel, qu'elle n'a pas été formée par des matières minérales mises en fusion par le feu du tonnerre, comme on aurait pu le présumer, que cette pierre n'est autre chose qu'une espèce de grès pyriteux, qui n'a rien de particulier, si ce n'est l'odeur hépatique qui s'en exhale pendant la dissolution par l'acide marin, ce phénomène, en effet, n'a pas lieu dans la dissolution des pyrites ordinaires." (The stone did not owe its origin to thunder, it did not fall from heaven, it was not formed by mineral substances fused by lightning, and it was nothing but a species of pyrites, without peculiarity, except as to the hepatic smell disengaged from it by marine acid (HCl), a phenomenon that does not take place with ordinary pyrites). They did not believe that any conclusion could be drawn from the resemblance of this stone to another found near Coutances, "unless that the lightning had fallen by preference on pyritical matter". Prof. Charles Barthold, from the École Centrale du Haut-Rhin, had examined another body, which he named Pierre de Tonnerre, found at Ensisheim, Bohemia¹ and reported that its density was 3.233 and contained 2 % wt sulfur, 20 % iron, 14 % magnesia, 17 % alumina 2 % lime, and 42 % and silica, for a total of 97 % (Barthold, 1800). Barthold results were followed by a letter received by William Hamilton (1730–1803) from the Earl of Bristol, dated from Sienna, July 12, 1794, reporting that in the middle of a very violent thunder-

¹ A document mounted beside the stone in the Ensisheim church stated that learned men did not know what it was: it must be supernatural, a wonder of God, because never such a thing had been heard, seen, or written about (Barthold, 1800).

storm, about a dozen stones of various weights had fallen at the feet of different persons. The letter indicated that either these stones had been generated in the igneous mass of clouds, which produced such unusual thunder, or, which was equally incredible, they were thrown from the erupting Mount Vesuvius at a distance of at least 250 miles (Howard, 1802a).

In 1796 a stone weighing 56 pounds was exhibited in London, which had fell near Wold Cottage, Yorkshire, on December 13, 1795. It was stated that day was mild and hazy, with no thunder or lighting the whole day. No such other stone was known in the country; there was no eruption in the earth and from its form it could not have come from any building and not been forced from any rocks (Howard, 1802a).

In 1799 John Lloyd Williams, a fellow of the Royal Society, sent to Joseph Banks an account of the stones fallen in the East Indies. It gave a detailed description about the explosion of a meteor near Benares (Krakhut) and the falling of some stones at the same time. The report also included a detailed description of the internal and external appearance of some of the stones (Howard, 1802a).

Banks send samples of the Yorkshire and Sienna stones to Howard and Charles Francis Greville (1749–1809) and Williams provided additional specimens. Howard understood that the first task should be a mineralogical study of the stones and for this purpose he engaged the help of Jacques Louis Count of Bournon, one of the foremost mineralogists of the time. Bournon realized that the stone from Benares had the most striking features and for this reason he examined it first and used it as object of comparison when describing the other specimens. Bournon's report gave the following details: (a) *Benares stone*. The broken stones had a granulated texture and appeared to be composed of four different substances, which could be easily distinguished with the help of a lens. One of these substances, very abundant, appeared in the form of small gray to brown bodies, some perfectly globular, others rather elongated or elliptical (today: chondrules). They were easily broken; their fracture was conchoid and gave faint sparks when struck with steel. A second substance was a martial pyrite having a reddish yellow color similar to that of nickel or artificial pyrites, which was not attracted by a magnet (the existence of metal and pyrite had been previously noted by the Jesuit priest Dominic Troili in the Albereto Stone in 1766). The third substance consisted of iron in a perfectly metallic state and hence attractable by the magnet. These three substances were united by means of a fourth one, whitish gray, which was nearly of an earthly consistence. The Benares stone had a density of 3.352, (b) *Yorkshire stone*. It had a finer grain than the Benares ones; its chondrules were also in an irregular shape of a smaller size than the ones present in the Benares stone. It contained less martial pyrites, a larger amount of metallic iron, and had a density of 3.508; (c) *Sienna stone*. It contained the same globular bodies, the same kind of martial pyrites, the same particles of iron in the metallic state as in the stone from Benares, and had a density of 3.418; (d) *Bohemia stone*. Its an internal structure was

similar to the one from Yorkshire but differed materially from the others stones in that its pyrite particles could not be seen without a lens; it contained a much larger quantity of metallic iron (almost 25 % wt), and had a density of 4.281 (Howard, 1802a).

Bournon concluded that although these stones had small analogy whatsoever with any of the mineral substances already known, either of a volcanic or any other nature, they had a very peculiar and striking analogy with each other, facts that provoked a desire of knowing to what causes they owed their existence (Howard, 1802a).

The last comment led Howard to try chemical means to distinguish better between the stones. French academicians and Barthold before, had already performed a chemical analysis of the stones presented by Bachelay but their conclusions that the stones were made of pyritical matter was highly questionable because the analysis had been made of an aggregate portion of the stone instead of each distinct substance. The proportions of the different components were as accidental as the arrangement of every substance in the mass (Howard, 1802a).

Howard's chemical results were as follows: (a) *Benares stone*. The particles not attracted by a magnet were digested with nitric acid, followed by neutralization of the excess acid, filtration, and saturation with an excess of ammonia. The resulting solution was evaporated to dryness and redissolved in distilled water. Howard believed the resulting solid to be a triple salt, similar to the one described by Hermstadt as being an ammonium nitrate of nickel. The solid, treated with ammonia prussiate, yielded a white to violet precipitate, which was shown to contain nickel. Chemical analysis of the other portions of the stone led to the following analysis: 50 % silica, 15 % magnesia, 34 % iron oxide, and 2.5 % nickel oxide (adding to 101.5). Howard believed that the excess weight was caused by the oxidation of the iron. He concluded the report of his analysis cautioning that the amount of nickel was a mere estimation because not enough information was available on the metal to speak of it with accuracy. In general, it could be concluded that the pyrites were of a very particular nature, for although Johann Friedrich Henkel (1678–1744) had observed that sulfur may be separated from pyrites by hydrogen chloride, this was not the usual behavior for a pyrite; (b) *Sienna stone*. The same analytical procedure of the stone freed from its iron with a magnet, indicated that it contained 44 % silica, 21.4 % magnesia, 32.7 % iron oxide, and 1.9 % nickel oxide, (c) *Yorkshire stone*. The analysis of the earthy part of the stone indicated 46.3 % silica 22.8 %, magnesia, 29.6 %, iron oxide, and 1.2 % nickel oxide, (d) *Bohemia stone*. Analysis of the small sample available gave 42 % silica, 16 % magnesia, 39.5 % iron oxide, and 2.5 % and nickel oxide (Howard, 1802a).

Howard concluded that the main differences of his results with the ones reported by the French academicians and Barthold, were finding that all the stones contained nickel and magnesium oxide. He ascribed the difference to the fact that

he had analyzed the different parts of the stone and not its total. He ended this part of his paper with the following comments: "The metallographic and chemical analysis indicate clearly that the stones are bodies that have fallen on the Earth from outer space. They have been found at places very remote one from the other and at periods also sufficiently distant, and have no resemblance to known mineral substances. It is remarkable that Chladni has connected the descent of fallen stones with meteors. If the latter claim would prove to be true, it should not constitute a problem that such masses do not penetrate further into the earth, for meteors move more on a horizontal than in a perpendicular direction, and there is as absolute ignorance regarding the force, which impels the meteor as with the origin of the fallen stone" (Howard, 1802a).

Howard concluded his section on stones with a brief discussion of possible mechanisms for producing the light associated with meteors: "I ought not to suppress, that in endeavoring to form an artificial black coating on the interior surface of one of the stones from Benares, by sending over it the electrical charge of about 37 square feet of glass it was observed to become luminous, in the dark, for nearly a quarter of an hour; and that the tract of the electrical fluid was rendered black" (Howard, 1802a).

Howard then described the single mass of about 15 ton of what has been called native iron, discovered in South America, and portrayed by Don Rubin de Celis. Joseph-Louis Proust (1754–1826) found the mass to be actually a mixture of iron and nickel. Howard related this finding with the native iron of Siberia described by Pallas (Pallas, 1776).² It was said that the Tartars considered as a sacred relic, which had dropped from heaven. Bournon again proceeded to examine the various specimens of native iron and Howard to make their chemical analysis. Bournon observed that the Pallas iron had a ramified cellular structure due to the presence of a very large number of small cavities; these cells were sometimes filled with yellow-green hard glass globules resembling peridot, a form of olivine afterwards analyzed by Martin Klaproth (1743–1817). Bournon speculated that the destruction and removal of the interstitial mineral matter would leave the metal in precisely the porous spongy form in which it was actually found.

The South American native iron was found to contain about 10% of nickel, while the Siberian one contained 54.5% silica, 27.3% magnesia, 17.2% iron oxide, and 1.0% nickel oxide.

Howard concluded his paper as follows: (a) all the stones examined have pyrites of a peculiar character, (b) they all have a coating of black iron oxide, (c) they all contain an alloy

of iron and nickel, and (d) the earths that serve them as a sort of connecting medium correspond in their nature and nearly in their proportions, (e) all the kinds of iron called native, contain nickel. His final statements were: "From these facts I shall draw no conclusion, but submit the following queries: (1) Have not all fallen stones, and what are called native irons, have the same origin? (2) Are all, or any, the produce or the bodies of meteors?, (c) might not the stone from Yorkshire have formed a meteor in regions too elevated to be discovered?" (Howard, 1802a).

Howard's chemical results were reproduced in many countries (Howard, 1802bc, 1803a) and persuaded some of the leading scientists in England, France, and Germany that bodies do fall from the sky. On April 1803, nearly 3,000 stones fell at L'Aigle in Normandy and transformed the last skeptics into believers. At the request of the Académie des Sciences, the French minister of the interior commissioned one of its members, Jean-Baptist Biot (1744–1822), to investigate the fall. Based on extensive interviews with witnesses, Biot established that the rain of stones had taken place after the vision of a luminous meteor and that the meteor had not been seen in L'Aigle but in many surrounding villages, some of them separated widely one from the other. He also mapped the area where the stones had landed: it was an ellipse measuring 10 by 4 kilometers, with the long axis parallel to the fireball's trajectory. The weight of the fallen stones varied between 8 kg to 8 grams. Louis-Jacques Thenard (1777–1857) analyzed samples of the stones and found them to contain 46% silicon oxide, 45% iron oxide, 10% magnesium oxide, 2% nickel, and 5% sulfur (Thenard, 1806). Once again, the excess over 100% was attributed to oxidation of the iron present. Biot's results proved in an irrefutably way that celestial stones were both real and extraterrestrial, that they had a very similar composition, that their fall was always accompanied by one or more explosions, which followed the appearance of a luminous meteor, and that they fell from a very high altitude at a tremendous velocity (Biot, 1803).

Siméon-Denis Poisson (1781–1840) (Poisson, 1803) also discussed the findings and indicated that the although the phenomenon looked strange and contrary to natural laws, it was not so and could be explained using the laws of physics and assuming that the stones were ejected from the surface of the moon by an eruption or other explosion. Some of the stones expelled could perfectly have an initial velocity enough to exceed attraction of the moon, and become captured by the gravity of the earth. Friction with the earth atmosphere would cause them to become highly heated and perhaps catch fire. Poisson calculated the velocity required to overcome the moon's gravity (7592 ft/s) and the final velocity (31,508 ft/s) achieved by a stone traveling along the line connecting the earth with the moon, if the resistance of the air was neglected. The numerical results of Biot and Poisson were somewhat different because of the uncertainty on the value of the mass of the moon.

² In 1772 the naturalist Peter Simon Pallas (1741–1811) examined a huge iron mass near the town of Krasnojarsk — a mass that the Tartars said it had fallen from the sky (Pallas, 1776). Pallas sent a sample of his findings to the Royal Society.

The manufacture and refining of sugar

The art of refining sugar was first introduced into Europe by the Venetians and was practiced at there some time before other European countries adopted it. The smelly and black sugar brought from Egypt at the end of the thirteenth century was the first material upon which the art of the refiner was exercised. Initially the Venetians converted it into sugar candy, similar to that which came from India; but they soon sought to obtain the sugar by a quicker and more profitable process and for this end they invented the form of the inverted clay cone, or loaf, the use of which soon became universal. The art of refining passed afterwards to all of Europe where sugar became an article of commerce and consumption; the number of refineries increased and extended over the entire continent. As many other technologies, sugar processing developed by trial and error, without much scientific input, until probably the 19th century. According to Porter (Porter, 1830) annual raw sugar imports to England amounted to 427,573 cwt (about 22,000 ton) in 1800 and to 4,000,000 cwt (about 203,000 ton) in 1830.

In the existing refining process (Porter, 1830) the crude sugar was dissolved in hot water and the liquid clarified by the addition of lime, fresh bull's blood, or the white of egg. Although lime increased the solubility of non-sugar substances and did not allow the coagulation of the albumen, in the processes of concentration and crystallization it partly reduced the problems caused by the presence of molasses, which gave to sugar its dark color. When dissolving raw sugar, the molasses dissolved first; the lime combined with it and made the solution more fluid, favoring the formation of sugar nuclei in crystallizing. Fresh bull blood (called spice) was added together with a certain quantity of limewater, followed by heating the mixture to almost its boiling point. During this stage extraneous matters precipitated from the sugar by the joint action of the heat and the spice. Eventually all the solid matters raised to the surface of the fluid in the form of a thick brown scum, which was skimmed off and the operation repeated enough times until the syrup threw up a clean milky froth and appeared quite bright and transparent. The resulting clear solution was then heated in shallow pans heated by direct fire, until boiling and evaporation produced the desired concentration. The syrup was now transferred into the coolers where it was agitated to promote and assist crystallization (the granulating stage). This was a critical part of the refining operation because if the syrup was not agitated enough the grain would be large and loose and its color not sufficiently white; if it was agitated too much the grains would be broken and the resulting sugar be without luster. When the sugar was cold enough it was punctured with an awl and the molds set upon pots to collect the syrup drain. The first draining was called *green syrup* on account of the new or green state of the sugar from which it ran. This green syrup was also boiled and after sufficient evaporation poured into large moulds, yielding the variety called *bastard sugar*. The solution thus seeded was transferred to the molds to complete the crystallization pro-

cess. In general, the process described above yielded, per 100 kg of raw sugar, 54.5 kg of refined sugar, 16 kg of bastards, 25 kg of molasses, and 4.5 kg of waste (Porter, 1830).

Exposure of the unprotected sugar pans to the direct action of fire led to charring and decomposition of part of the sugar; about two-thirds of the uncrystallizable syrup, which drained from the sugar, was produced by the corresponding high temperatures. Howard's patent was the first successful attempt to eliminate this problem; its advantages were so large that it was adopted by most of the sugar manufactures and to Howard receiving a large income from royalties. Howard's first patent (Howard, 1812) represented a significant improvement in the method of preparing and fining the sugar, while the second (Howard, 1813), in the manner of applying and regulating heat. Previous to boiling the raw sugar was mixed with enough water as to form a magma of the consistency of well-worked mortar and after resting for about an hour or more, it was heated to a temperature of 190° to 200°F. A thinner magma of sugar was now added and the whole let to cool in molds, followed by draining of the molasses. At the end of the draining the upper portion of the mass of sugar was pared down to an uniform surface and then mixed with cold water until the magma acquired such a consistency that it would not allow of its closing behind the stirrer; in which condition it was replaced on the firm even surface before prepared. As soon as the magma was moderately dry, a saturated solution of fine sugar in cold water was poured upon it; these operations were repeated as often as the nature of the sugar required. The neat sugar was drained from its molasses and then refined by pouring upon it boiling water. Stirring dissolved the sugar; the impurities allowed to deposit, and the clear solution separated. Finings (substances are usually added for removal of organic compounds to either improve clarity or adjust flavor/aroma) were now added to complete its clarification.

In his second patent (Howard, 1813) Howard recommended that the refining of the sugar be carried on by mixing it with a proper proportion of the finings, in a vessel having a perforated bottom, through which steam was allowed to enter until the sugar was fully dissolved and heated to 200°F. The most important feature of Howard's invention consisted in using the known fact that the boiling point of a fluid is reduced as the pressure is lowered. The syrup was now put in a closed vessel heated in the outside by steam while vacuum was applied to the vessel with the help of an air pump. The operating pressure was about 25 mmHg. This method of concentrating sugar solutions avoided all danger of overheating; it reduced the amount of sugar lost through caramelization, and the solid sugar presented a boldness and brilliancy of crystal, which had never been attained before. In addition, it saved fuel (Porter, 1830).

Since the use of a closed vessel did not allow examining the progress of concentration in the syrup in the old manner, Howard provided a table relating the pressure with the temperature to help control the process, and also developed an

instrument (called a proof stick) by means of which it was possible to sample the contents without admitting air into the pan. The details of its construction constitute another example of Howard's technical ingenuity.

Once the sugar became sufficiently concentrated it was discharged into the usual granulating vessel, which was heated on the outside with steam at a temperature of 150° to 180°F and the contents agitated to effect granulation. The temperature was raised to 200° before filling the moulds (Porter, 1830).

A German translation of the full text of Howard's patents was made available some years later (Howard, 1828).

Thomas Thomson (1773–1852) applauded Howard's improvements with these words: "I consider this process as by far the greatest improvement which has been made in sugar refining since it began to be practiced in this country. It will enable the manufacturer to produce a greater quantity of loaf-sugar, from raw sugar, than has hitherto been done. It will, ultimately, reduce the price of that article" (Thomson, 1816).

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