



TO GET RID OF ITS DUST

Charles Hatchett: The discoverer of niobium



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PALABRAS CLAVE

Bitúmenes;
Huesos;
Columbio;
Monedas de oro;
Lac;
Molibdeno;
Niobio;
Conchas;
Zoofitas

Abstract To Charles Hatchett (1765–1847), a self-educated scientist and first class analytical chemist, we owe the discovery of niobium, the analysis of a series of important minerals and animal substances such as shells, bones, dental enamel, a detailed study of bitumens, the separation of an artificial tanning material from mineral and animal sources.

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Charles Hatchett: el descubridor del niobio

Resumen A Charles Hatchett (1765–1847), un científico autodidacta y hábil químico analítico, le debemos el descubrimiento del niobio, el análisis de minerales importantes y de sustancias animales como conchas, huesos y esmalte dental, un detallado estudio de los bitúmenes, la separación de taninos artificiales de fuentes minerales y animales, etc.

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Life and career (Barrow, 1849; Coley, 2004; Griffith et al., 2003; Walker, 1862; Weeks, 1938)

Charles Hatchett was born at Long Acre, London, on 2 January 1765, the only child of John (1729–1806) and Elizabeth Hatchett (1795). His father was a successful coachbuilder in

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Long Acre and later became a magistrate in Hammersmith. Charles took his basic education at Fountayne's, a fashionable private school Marylebone Park. On leaving school he continued to live for some time with his father, intending to follow the same business, while continuing improving his scientific knowledge and becoming a self-formed mineralogist and analytical chemist. His father supported this activity and provided him with a generous allowance, to enable him to continue his studies without financial worries. On 24 March 1786 Charles married Elizabeth Martha Collick (1756–1837), the only daughter of John Collick, a London wigmaker. After the wedding the couple traveled to Russia and Poland, where they remained for nearly two years. On their return to England they lived in Hammersmith, where Charles "set up an excellent laboratory and collected a good library". In 1790 his father sent him to St. Petersburg to deliver a coach to Catherine the Great (Griffith, Morris, & Charles Hatchett, 2003). The couple had three children, John Charles, born in 1788, Amelia, born in 1793 but lived for only a few days; and Anna Frederica (1797–1881) born in 1797, who eventually married William Thomas Brande (1788–1866) (Griffith et al., 2003).

Hatchett became a Fellow of the Linnaean Society in 1795 and of the Royal Society in 1797. In 1808, together with Sir Everard Home (1756–1802), they founded the Animal Chemistry Club, as a subgroup interest of The Royal Society, who met at distant intervals under a regulation that the papers read at their meetings, should be afterwards communicated to the parent body (Griffith et al., 2003). In 1809, Hatchett was elected to the Literary Club, which had been founded in 1764 by Dr. Samuel Johnson (1709–1784) and Sir Joshua Reynolds (1723–1792); and on the death of Dr. Charles Burney (1726–1814), he was elected treasurer of the club (Barrow, 1849).

After his father's death in 1806 Hatchett began to put more and more time into the business and little by little decreased his scientific activities, becoming instead a noted collector of books, paintings, musical instruments, and musical manuscripts. This change brought criticism by some of his colleagues, who lamented the loss of a gifted researcher. Thus, Thomas Thomson (1773–1852), wrote in his *History of Chemistry* (Thomson, 1831) that Hatchett "was an active chemist. . . but unfortunately this most amiable and accomplished man has been lost to science for more than a quarter of a century; the baneful effects of wealth, and cares of a lucrative and extensive business, having completely waned him from scientific pursuits." Sir Benjamin Brodie (1783–1862) made a similar comment in his autobiography: "After his father's death. . . Hatchett inherited a considerable fortune and seems to have concentrated on the coach-making business. He did very little more chemical research" (Brodie, 1865). Sir Joseph Banks (1743–1820), the President of the Royal Society, argued with Hatchett for stopping to do any chemistry and remarked that "he would find being a gentleman of fortune was a confounded bad trade".

Hatchett died of pleurisy on 10 February 1847, at the age of 82. He was buried in St. Laurence's Church, Upton-cum-Chalvey, Buckinghamshire, near his wife and parents (Griffith et al., 2003).

Hatchett first scientific paper described the complete analysis he carried on the Carinthian lead molybdate, at

that time thought by some to be lead tungstate, and also reported the properties of molybdic acid (Hatchett, 1796). This was followed by another one reporting the analysis of the water of the mere at Diss, in Norfolk (Hatchett, 1798a). Here he showed that this water contained very little sulfur and iron, in spite of the fact that the deposit at the bottom contained iron pyrites. In the same year he reported that an earthy substance, called Sydneia from New South Wales, was not a primitive earth but one made of siliceous earth alumina, iron oxide, and graphite, and hence should not be considered as a genus of the mineral system (Hatchett, 1798b). Between 1798 and 1807 and Hatchett published three papers about bitumen where he stated that the bituminous substances originated from the organized kingdoms, and especially from the resin and juices of vegetable substances, by the action of some of the mineral principles (Hatchett, 1798c, 1804d; Span, Tobin, Hatchett, 1807). The last paper reported the analysis of some samples from a pitch lake of Trinidad, where he claimed that most of the lake was not pure mineral pitch or asphaltum, but rather a porous stone of the argillaceous genus, much impregnated with bitumen. This conclusion was afterwards proven mistaken. This work led to other projects related to artificial tannins and to lac. Hatchett found that treating carbonaceous materials, such as wood, coal and charcoal, with nitric acid produced a substance very analogous to tannin (Hatchett, 1805a,b, 1806). In his work on lac (stick lac, seed lac, and shell lac) he proved that although this substance was the result of the action of insects, most of its components were of vegetable origin (Hatchett, 1804b).

Further research was related to the constituents of marine shells, fish bones, of fossils from Gibraltar, and the enamel of sharks' teeth (Hatchett, 1799c). His results indicated that while calcium phosphate was the main component of bones and tooth enamel, shells were mainly made of calcium carbonate with little phosphate. In a following paper about zoophites he investigated the presence and general proportions of calcium carbonate and phosphate, and examined the substance in and upon which the hardening or ossifying principles were secreted and deposited (Hatchett, 1800).

His most significant achievement was the discovery of a new element, columbium (niobium), in an ore specimen in Sir Hans Sloane's collection at the British Museum, which had been brought from Massachusetts. He understood it was a new element, in spite of his unsuccessful attempts to reduce the oxide to the metal (Hatchett, 1802a).

In 1798 a Privy Council appointed Hatchett and Henry Cavendish (1731–1810) to investigate the apparent loss that the gold coin appeared to have sustained in the course of circulation, and to establish whether this loss was caused by any defect, either in the quality of the standard gold or in the figure or impression of the coins. Hatchett studied the alloying of gold with a wide variety of metals and non-metals and concluded that copper and silver were the best metals for alloy formation with gold and that "there was no important defect in the composition or quantity of the standard gold" (Hatchett, 1803a).

Additional publications were related to magnetic pyrites (Hatchett, 1804c), the composition of an iron ore (Hatchett, 1804e), a method for separating iron from manganese

(Hatchett, 1813), on the utility of copper prussiate as a brown pigment with a lilac tinge (Hatchett, 1802b), on a calomel from Tibet, used by its inhabitants to treat venereal diseases (Hatchett, 1803b), a triple sulfide of lead, antimony, and copper (Hatchett, 1804a), a procedure for purifying corn tainted with mold (Hatchett, 1817), a review of the electrophoretic experiments of Hans Christian Ørsted (1777–1851) and André-Marie Ampère (1775–1831) (Hatchett, 1821), and a description of the medical uses of the oil of spikenard (Hatchett, 1836).

As a result of his scientific findings, Hatchett was awarded the 1798 Copley Medal of the Royal Society and the 1828 Fullerian Medal of the Royal Institution [together with Humphry Davy (1778–1819), Brande, William Hyde Wollaston (1766–1828), and John Frederic Daniell (1790–1845)].

Scientific contribution

Hatchett published about 20 scientific papers in the areas of chemical analysis, mineralogy, bitumens, tanning materials, and animal substances such as shells, bones, dental enamel, and zoophites. Here we describe some of his most important activities.

Mineralogy

Niobium

On November 26, 1801, Hatchett read to the Royal Society his most important work: the discovery of a new metal, which he named columbium (Hatchett, 1802a). He said “when I was examining and arranging some minerals in the British Museum, I observed a small specimen of a dark colored substance, which attracted my attention, on account of some resemblance which it had with the Siberian chromate of iron, on which I that time was making experiments. Upon referring to Sir Hans Sloane’s catalog, I found that this specimen was only described as a very heavy black stone with golden streaks, which proved to be yellow mica, and it appeared that it had been sent. . .to Sloane by Mr, Winthrop, of Massachusetts.”

Hatchett went on to describe the physical properties of the ore and the chemical treatments he had carried on it. The external and internal color of the mineral was dark brownish gray; its longitudinal fracture was imperfectly lamellated and the cross fracture showed a fine grain; it had a vitreous luster, was moderately hard and very brittle, the particles were not attracted by a magnet, and had specific gravity 5.918 (18.3°). The mineral was only slightly attacked by HCl, nitric acid, and sulfuric acid so that it could not be decomposed by their direct action. In order to do so, Hatchett mixed the mineral with five parts of potassium carbonate, fused it in a silver crucible, and noted a slight effervescence once the mixture began to flow. After cooling the mass, he treated it with boiling water and separated the solution from the remaining solid residue. The latter was melted consecutively with potassium carbonate until complete decomposition; the alkali was washed off with water, and the remaining solid digested with HCl. The resulting solution had a deep yellow color resulting from the iron that had been dissolved. The first filtrated liquid was treated with an excess of nitric acid and yielded a copious white

flocculent precipitate. According to Hatchett calculations, 12.96 g of the ore afforded 2.72 g of iron oxide and 9.72 g of the white precipitate (for a total of 12.44 g) (Hatchett, 1802a,b).

An exhaustive analysis of the white precipitate indicated, among other things, that it was insoluble in boiling nitric acid; boiling HCl dissolved it when recently prepared; put upon litmus paper moistened with distilled water turned the paper red, it effervesced when fused with potassium carbonate or sodium carbonate and the resulting saline combinations were soluble in water; and with ammonium phosphate it yielded a deep blue derivative. Treatment of the HCl solution with different reagents produced different colored precipitates: olive green with KCN, orange with tincture of galls, white with phosphoric acid, purple blue with ammonium phosphate, white with a piece of zinc, chocolate with ammonium hydrosulfide, etc. (Hatchett, 1802a,b).

Hatchett remarked “the preceding experiments show that the ore which has been analyzed consists of iron combined with an unknown substance and that the latter constitutes more than three fourths of the whole. This substance is proved to be of a metallic nature by the colored precipitates which it forms with prussiate of potash and with tincture of galls; by the effects which zinc produces when immersed in the acid solutions; and by the color which it communicates to phosphate of ammonia, or rather to concrete phosphoric acid, when melted with it. . .It seems to be one of those metallic substance which retain oxygen with great obstinacy. . .it is an acidifiable metal. . .but different from the other acidifiable metals which have of late been discovered. . .These properties completely distinguish it from the other acidifiable metals, viz. arsenic, tungsten, molybdena, chromium. . .other metals such as uranium, titanium and tellurium. . .are still farther removed from it” (Hatchett, 1802a,b).

“Considering, therefore, that the metal which has been examined is so different from those hitherto discovered, it appeared proper that it should be distinguished by a peculiar name. . .I. . .give it the name of Columbium” (Hatchett, 1802a,b).

In a postscript to his paper Hatchett described the unsuccessful attempts he had made to reduce the white oxide and added the comment: “The above experiment show that the white oxide. . .may be deoxidated to a certain degree without difficulty, but that the complete reduction. . .is still far from being easily effected” (Hatchett, 1802a).

In 1802 Anders Gustaf Ekeberg (1767–1813) announced the discovery of a new element, which he named tantalum (Ekeberg, 1802). Some years later, Wollaston became suspicious that columbium and tantalum were the same metal (Wollaston, 1809) and obtained from Hatchett some of the ore he had originally used in his experiments about his new element. After much experimental work, in which he compared the physical and chemical properties of the materials used by Ekeberg and by Hatchett, Wollaston concluded that except for a large difference in the specific gravities of the two minerals (5.918 for columbite and 7.953 for tantalite), which he assumed to be due to a different state of aggregation or of oxidation, there was no reason to consider that columbium and tantalum were different elements. Wollaston opinion was generally acknowledged until 1844 when

Heinrich Rose (1795–1864) showed that the American mineral contained a metallic acid different from that contained in tantalite. Rose named his acid niobic and its metallic component *niobium* (after Niobe, one of the children of Tantalus) (Rose, 1844, 1845).

A paper by Griffith and Morris (Griffith et al., 2003) and a book by Weeks and Leicester (1968) describe further developments in the history of columbium (niobium).

Gold coins

In February 1798, a committee of Privy Council was appointed to examine the state of the British coin. One of the objects of inquiry was to investigate the apparent loss that the gold coin appeared to have sustained in the course of circulation, and to determine whether this loss was caused by any defect, either in the quality of the standard gold or in the figure or impression of the coins. The committee appointed Hatchett and Henry Cavendish (1731–1810) to carry on the necessary experiments to provide an answer to this query. Although Cavendish took an active part in this task, he requested from Hatchett to write the corresponding report. Hatchett did so, took upon himself the responsibility of any inaccuracies that may have been introduced, and gave Cavendish the corresponding credit by stating that the new machinery to produce friction and the dies used in the experiments were entirely designed by Cavendish (Hatchett, 1803a,b).

Hatchett wrote that the wear of a coin was an effect produced by mechanical causes, possibly modified by certain physical properties, such as ductility and hardness, which varied according to the chemical effects produced by different alloying metallic substances. Hence, he felt appropriate to examine (a) the effects, which the different metals produced upon gold when combined in different proportions, starting from 1/12, which was the standard proportion of alloy, and decreasing it gradually to 1/1920 parts of the mass. He studied the alloys of gold with arsenic, antimony, zinc, cobalt, nickel, manganese, bismuth, lead, tin, iron, emery, platinum, copper, and silver; (b) the specific gravity of the different alloys of gold and the causes of its variations, and (c) the comparative effects of friction produced by different procedures upon soft and hard gold, and upon smooth and flat, and rough surfaces (Hatchett, 1803a,b).

The resulting long report (150 pages) described in detail all the numerous experiments carried on to give a satisfactory answer to these questions. Their results indicated that (a) fine gold alloyed with silver, copper, or tin, did not suffer any loss during the experiment, (b) gold alloyed with lead, iron, bismuth, antimony, zinc, and arsenic, suffered a loss caused by different physical and chemical reasons, and (c) only silver and copper were appropriate for the alloy of the gold coin; all the others either considerably altered the color or diminished the ductility of gold (Hatchett, 1803a,b).

Hatchett's experiments also showed that the specific gravity of gold alloys was different from that which resulted from a calculation of the respective density of the component ingredients. In addition, another anomaly arose from the unequal mixture of the heterogeneous particles, which resulted in the lower part of a bar (when cast in a vertical position) having a greater specific gravity than the upper one. This led to a considerable difference in the results of

an assay if the specimen was taken from one end or the other end of the bar (Hatchett, 1803a,b).

The third section discussed the effects of friction on the comparative wear of gold and its alloys, which was tested under three regimes: (a) the friction between gold coin of the same or different qualities, (b) the friction of gold coin against silver and copper coin, and (c) the friction of gold against gritty powders, metal filings, etc., representing the different circumstances under which gold, in the course of circulation, was subject to wear (Hatchett, 1803a,b).

Hatchett's final conclusion was that the great loss which the British gold coin was stated to have sustained, could not be attributed to any important defect in the composition or quality of the standard gold, and that all that could be said was that some portion of this loss may have been caused by the rough impression and milled edge now in use, by which each piece of coin acted and was acted upon by the others, or in the manner of a file or rasp (Hatchett, 1803a,b).

Magnetic pyrites

According to Hatchett, iron sulfide (magnetic pyrite) was the sulfide most universally dispersed throughout the world (Hatchett, 1804a,c,d). Of the many varieties of this ore, magnetic pyrite had not been subjected to any regular chemical examination, in spite of its possessing the remarkable property of strong magnetic polarity. It was not known if this particular property was proper of the iron sulfide or it was due to particles of another sulfide intimately mixed with the former. The ore had been found only in some parts of Norway, Silesia, Bavaria, and Germany; but it seemed that it was also part of Charles Greville's (1749–1809) collection, and originating from Caernarvonshire. The magnetic power of this ore was very strong; it affected a well-balanced needle at a distance of 10 cm.

Hatchett gave first a detailed description of the physical characteristics of the ore and the results of treatment with heat, ammonia, sulfuric acid, nitric acid, HCl, KCN, etc., and went on to determine its composition, and compare it with that of other pyrites. For the latter purpose he analyzed pyrites in the form of dodecahedrons with pentagonal faces, pyrites in the form of striated cubes, pyrites in the form of polished cubes (found in the lapis ollaris, which accompanies magnetic pyrites), and two varieties of radiated pyrites. The results indicated that ordinary pyrites contained sulfur and iron in the approximate ratio (weight) 53:47, with very little variation from one species to the other; for magnetic pyrites this ratio was substantially different, 37:63 (Hatchett, 1804a,b,c,d,e).

In hopes of discovering the causes of the magnetic property he paid particular attention to the experiments reported by other scientists, particularly those of Joseph-Louis Proust (1754–1826). Proust had concluded that there were two types of iron sulfide, one artificial, and the other natural (Proust, 1801, 1802). The first was prepared in the laboratory by adding sulfur to red-hot iron or exposing their mixture to heat in a retort. The sulfur to iron ratio in the artificial species was 37.5:62.5 and 47.4:52.6 in the natural one.

Hatchett carried on a series of experiments preparing artificial pyrite using Proust's method and comparing the properties of the product with those of natural

magnetic pyrite. His conclusion were as follows (Hatchett, 1804a,b,c,d,e): (a) Magnetic pyrites are composed of sulfur, and iron in the metallic state, in the proportion nearly of 37–63 per weight, respectively; (b) the chemical properties of magnetic pyrites was very different from those of the martial pyrites; the latter were also composed of sulfur and iron, but in the weight ratio 53:57; (c) the chemical composition and properties of magnetic pyrites agreed with those of iron sulfide so that they may be considered identical; (d) during the formation of natural pyrites, iron and sulfur combined in a different ration from that present in iron sulfide, sulfur became a predominant ingredient, varying in quantity between 54 and 55%; (e) pyrites containing more than 45.5 or 46% of sulfur had no magnetic power, although the upper limit may be around 52%; (f) carbon, when combined in a certain proportion with iron (forming steel), enabled it to become a permanent magnet; a certain proportion of sulfur and of phosphorus communicated the same quality to iron; (g) the combination of carbon, sulfur, and phosphorus, with iron led to many similar chemical effects, so do each of them, when combined with iron in certain proportions, not only permitted it to receive, but also gave it the peculiar power of retaining the magnetic properties; and thus henceforth, in addition to that carbide of iron called steel, certain sulfides and phosphides of iron could be regarded as bodies peculiarly susceptible of strong magnetic impregnation (Hatchett, 1804a,b,c,d,e).

Molybdenum

Hatchett's first paper was related to the analysis of a yellow sparry lead ore found at Villach in Carintia, Austria (Hatchett, 1796), which had been examined by the Abbé Franz Xaver Wulfen (1728–1805), Nicholaus Joseph Jacquin (1727–1817), Justus Christian Heinrich Heyer (1746–1821), and Martin-Heinrich Klaproth (1743–1817), and assumed to be lead combined with molybdic acid. Carl Wilhelm Scheele (1742–1786) was the first to examine molybdenum ore and to determine that two very different substances formed it, one composed of carbon and iron, that he named plumbago, and the other he called molybdena. In 1778 he had analyzed the latter component and obtained sulfur and a whitish powder, which possessed the properties of an acid, and for this he named it acid of molybdena. In 1782 Peter Jacob Hjelm (1746–1813) succeeded in obtaining a metal from acid of molybdena by mixing it with linseed and subjecting the mixture to a strong heat. Hjelm named the new metal molybdenum. Afterwards, Bernard Pelletier (1761–1797), J. C. Ilsemann (1727–1822), and Heyer repeated Scheele's experiments and confirmed the metallic nature of molybdic acid. Klaproth made a detailed analysis of the Carynthian ore and concluded that it was composed of lead oxide combined with molybdic acid, but he was unable to determine the proportions of the ingredients because of the small sample he had available. For these reasons, Hatchett decided to make a complete analysis of the mineral and determined the properties of molybdic acid (Hatchett, 1796).

The ore was described as having a limestone matrix, of a pale brownish-gray color; it was a heavy brittle substance, with relative density 5.092 at 15.6 °C. Heated with the blowpipe it first split and crackled and then melted into a dark colored mass. With borax it formed a brownish-yellow

globule and with ammonium sodium phosphate it formed a sea-green glass. Hatchett then subjected the ore to the action of water, KOH, potassium carbonate, sulfur, ammonium carbonate, ammonium chloride, black flux (finally divided carbon and potassium carbonate), HCl, and sulfuric acid, and described the results of these experiments. These indicated that lead molybdate was insoluble in water, that it was decomposed by strong solutions of potassium hydroxide and carbonate, that it was composed of the oxides of lead and iron mineralized by molybdic acid, and that these ingredients were in the ratio 146, 5, and 95, with a small amount of siliceous earth (Hatchett, 1796).

An additional important result was that "when molybdena is not in the metallic state, it appears to suffer 4 degrees of oxidation. The first one is the black oxide, the second is the blue oxide, the third is the green oxide, which as it seems to be intermediate between and oxide and an acid, I am inclined to call molybdous acid, and the fourth degree is the yellow acid, or that which is supersaturated with oxygen" (Hatchett, 1796).

Sydneia

The first sample of the fine white earth "Sydneia" was collected by Arthur Phillip (1738–1814), Governor of New South Wales, from the shores of Sydney Cover, and sent to Sir Joseph Banks, President of the Royal Society. Banks requested from Josiah Wedgwood (1730–1795) to carry on an analysis of the same and give his opinion regarding its possible use. In his report to Banks (Wedgwood, 1790), Wedgwood wrote that "the clay from Sidney Cove is an excellent material for pottery and may certainly be made the basis of a valuable industry. . .The other material. . .seems. . .to contain one substance hitherto unknown, and another not known in the state of purity in which it is here found". Wedgwood described the material as a "mixture of fine white sand, a soft white earth, some colorless micaceous particles, and a few black ones resembling black mica or black lead. . ." After carrying on a chemical analysis of the components Wedgwood concluded that the soft white earth. . .is strongly discriminated from all the known earths and metallic calces. . .and as it suffers no decomposition from any of the alkalies. . .I presume I cannot be considered a combination of any of those earths or calces with any of the known acids. . .whether this substance belongs to the earthy or metallic calces, I cannot absolutely determine, but I am inclined to refer it to the earths. . ." Wedgwood identified the black particles as a pure species of plumbago (graphite) or black lead, fact that had not been mentioned previously by any writer (Wedgwood, 1790)

In 1796 Banks asked Hatchett to carry on additional experiments on Sydneia to verify Wedgwood's results. In the preface to his report, Hatchett wrote that Wedgwood's findings had led the European mineralogists to assume the white substance to be a primitive earth and arrange it as a distinct genus in under the names Sydneia, Australa, Terra Australis, and Austral Sand. He then went on to give a detailed description of his major findings: (a) Sydneia consisted of siliceous earth, alumina, iron oxide, and black lead or graphite. The presence of the latter appeared to be accidental and was probably the result of materials being transported and deposited by water, (b) the visible particles of quartz

and mica indicated a granitic origin and the soft white earth had probably been formed by a decomposition of feldspar, (c) Sydenia had been formed by the disintegration and decomposition of granite or gneiss (metamorphic rocks), (d) Wedgwood's mistake was probably due to his using impure acids to react with the mineral, and (e) the mineral did not contain any primitive earth, or substance possessing the properties ascertained to it, and consequently, that the Sydenian genre, in the future, should be omitted in the mineral system (Hatchett, 1798b, 1799a).

Bitumen

In his opening paper about bitumen (Hatchett, 1798c) first described the state of the knowledge about these substances and then discussed in particular three bitumens, the Bovey coal, the Derbyshire elastic bitumen, and the Surturbrand coal of Iceland.

Bituminous substances were regarded as having formed from certain principles of substances belonging to the organized kingdoms of nature, which after death had experienced profound changes following their contact with mineral bodies. These changes were so profound that the bitumens were not referred to their origin but were considered to form part of the mineral system. The known bitumens could be divided into two groups, those consisting of simple species (e.g. naphtha, petroleum, mineral tar, mineral pitch, and asphaltum) and the compound ones, formed of bitumen mixed with or combined with the earths, vegetable matter and metallic oxides (e.g. bituminous wood, pit-coal, peat, and turf). Hatchett remarked that the two groups were not clearly separated and it was appropriate to assume that there was a gradual transition from one to the other. Jet and cannel coal were examples of substances in the intermediate range (Hatchett, 1798c).

Carbon was known to be one the largest components of vegetable matter. During the combustion of vegetable matter, the more volatile principles contained in the vegetable fiber were the first to separate, and in proportion to this separation, carbon, the more fixed substance, was developed. Thus by combustion, wood became brown and afterwards black. In other words, combustion could be considered a species of analysis by which the principles of vegetables were separated according to their affinities and according to their volatility. Hydrogen and nitrogen (if present) were first discharged and formed new combinations, while the carbon remained fixed and unchanged (if the combustion was carried on with an insufficient amount of air). The same separation took place whenever the vegetables were exposed to circumstances that favor putrid fermentation. The same as in combustion, as putrefaction progressed, the wood became brown and afterwards black, while a gas mixture of hydrogen, nitrogen and CO₂, was discharged. If the putrefaction process was interrupted, the vegetable matter retained part of its original principles and contained more or less carbon depending on the degree of putrefaction achieved. The residual vegetable matter would look like wood, partially charred (Hatchett, 1798c).

According to Hatchett, this process of partial putrefaction explained the formation of the coal found in Bovey, near Exeter, and a similar fossil coal found in Iceland, known by the name of Surturbrand. Bovey coal was known to

burn readily with a flame like half-charred wood, and not to crackle. When moderately burned it formed coal and when completely burned it left a small quantity of white ashes exactly similar to those of wood. Hatchett mentioned that the portion of oily and bituminous matter that he had obtained from both of the above coals, was nothing more than the remainder of the vegetable oils and juices, which had been modified by mineral agents (Hatchett, 1798c).

Hatchett wrote that about 1786 a new species of bitumen (in twenty-two different varieties) was discovered near Castleton in Derbyshire, which much resembled in elasticity and color, to caoutchouc or Indian rubber. When the different varieties were melted, they lost the elastic property while releasing a quantity of gas. The residue was either petroleum, or mineral tar, mineral pitch, or asphaltum, according to the particular variety. This latter fact led Hatchett to suspect that the elastic property was the result of interposition of small amounts of air or other gas between the bitumen particles, which had become enclosed by some unknown reasons during the putrefaction process. The melting liberated the gas, and the bitumen lost its elasticity and fine spongy structure (Hatchett, 1798c, 1799b).

In a second memoir about bitumen, Hatchett repeated his claim that bituminous substances were derived from the organized kingdoms (especially from the resin and juices of vegetable substances) by the action of some of the mineral principles (Hatchett, 1804d).

Hatchett first distilled a sample of the Surturbrand coal and found that 250 parts of the schistus yielded 42.50 parts of water, 7.50 of thick brown oil bitumen, 23.57 of a gas mixture, 54.25 of charcoal, 98 of silica, 6 of iron oxide, and 15 of alumina (for a total of 247 parts). Since the water and the vegetable matter should be considered extraneous, the real composition of the schistus (by weight) was 82.30% silica, 12.61% alumina, and 5% of iron oxide, pointing to an argillaceous origin. Distillation of 200 parts of the Bovey coal yielded 60 parts of water, 21 of thick brown oily bitumen, 90 of coal, and 29 of a gas mixture. Hatchett pointed out that the charcoal was very similar to the one made from fresh vegetables, its ashes did not contain alkali, it yielded no signs of vegetable extract, a small portion of true resin (about 0.19 g in 200 of coal) still remained inherent in the wood, and the lignite consisted of woody fiber in a state of semi carbonization, impregnated with bitumen and a small portion of resin (Hatchett, 1804d).

In 1760 Jeremiah Milles (1714–1784) (Milles, 1760) had carried on an inspection and analysis of the Bovey coal and reported that "adhering to the veins of coal are found lumps of a bright yellow loam, extremely light and so saturated with petroleum, that they burn like sealing wax, emitting a very agreeable and aromatic scent." Hatchett analyzed samples of this material and concluded that it was not loam impregnated with petroleum but a peculiar bitumen and hitherto unknown substance, which was partly in the state of asphaltum and partly in the state of vegetable resin. Analysis of this substance indicated that it contained 55 wt% resin, 41% asphalt, and 5% of an earthy residue. Hatchett suggested naming this substance *retinasphaltum*, as suggestive of its composition (Hatchett, 1804d).

In 1807 Hatchett analyzed some samples of the Pitch-Lake in the Trinidad Island and concluded that a considerable part of the aggregate mass of this deposit was not pure

mineral pitch or asphaltum, but rather a porous stone of the argillaceous genus impregnated with bitumen. The samples contained 32–6% of pure bitumen, and residue 60 wt% alumina, 10% alumina, 10% iron oxide, and 11% carbonaceous matter. Hatchett was afterwards proven wrong because the samples he received for analysis did not correspond in character with the great mass of the lake (Span et al., 1807).

Tannins

In his first paper about tannins (Hatchett, 1805a) Hatchett mentioned that Nicolas Deyeux (1744–1837) and Armand Séguin (1767–1835) had been the first to report on the principles that influenced the operation of tanning. Deyeux had separated from galls a substance, which he considered a species of resin, and Séguin had proved that this resin (which he named tannin) was the principle that converted skins of animals into leather. Séguin believed that tannin was a vegetable material that had the unique property of precipitating glues or gelatin from water as insoluble matter. George Biggin, Proust, and Davy had made further contributions to the understanding of the tanning process. Previous work had proven that tannin was a peculiar substance, naturally formed, and existing in many vegetable bodies such as oak bark, galls, sumach, catechu, etc., frequently accompanied by gallic acid and mucilage. No one had reported about the possible synthesis of tannin, although Richard Chenevix (1774–1830) had mentioned that a brew of coffee berries was able to precipitate gelatin only after the beans had been roasted. Hatchett now mentioned that the experiments he had recently carried on lac (Hatchett, 1804a) and on bitumen (Hatchett, 1804d) had convinced him that tannin could also be prepared from mineral and animal substances (Hatchett, 1805a). His results indicated that almost all resins were completely dissolved by nitric acid, that the resulting solution was not precipitated by addition of water, and that evaporation of this solution left a deep yellow viscous substance soluble in water or in alcohol. In the case of asphaltum and jet, addition of nitric acid formed a dark brown solution accompanied by separation of an orange colored mass. Further treatment of the latter with nitric acid resulted in its complete solution. Evaporation of this solution left a yellow viscous substance, quite similar to that obtained from the resins, except that when burned it released an odor somewhat akin to that of fatty oil. Coal, which contained little or no bitumen, did not yield this yellow substance, but charcoal was found to dissolve more readily, yielding a reddish brown solution and leaving no residue (Hatchett, 1805a).

All the above solutions, when gradually evaporated to dryness, left a brown glossy residue, having a resinous fracture. These residues were readily soluble in water and in alcohol, had a highly astringent flavor, and when heated up they smoked little, swelled much, and generated a bulky coal. Their solutions precipitated metallic salts, particularly tin chloride, lead acetate, and ferric sulfate. Addition of water immediately precipitated glue or isinglass, similar to the ones produced by a tannin solution. Reduction of isinglass to coal, followed by digestion with nitric acid and evaporation to dryness, left a residue having similar properties as the ones originating from a mineral source. All these experiments demonstrated that substances

analogous to tannin could be prepared from vegetable and animal sources, by treating carbonaceous substances with nitric acid. Hatchett validated his conclusions by converting skin to leather by means of materials, which professional men would think surprising, such as wood plank, sawdust, asphaltum, turpentine, pit coal, wax candle, and even a piece of the same skin (Hatchett, 1805a).

In a second paper on the subject (Hatchett, 1805b), Hatchett wrote that some important British chemists had objected his naming this tannin artificial or factitious because it was produced by the action of nitric acid, while the same acid destroyed the varieties of natural tannin. Hatchett carried on some additional experiments to verify his claim that this substance was not affected by nitric acid. For example, he subjected it to repeated distillations with nitric acid and found that it remained unchanged; he mixed it with white sugar or gun Arabic, distilled the mixture to dryness, dissolved the residue in boiling distilled water, and then examined the solution with gelatin and other reagents; again, no changes were detected. When the substance was dissolved in HCl and then distilled to dryness; no changes were detected in the residue. Similar experiments conducted with solutions prepared from galls, sumach, Pegu cutch, common cutch, and oak-bark, proved that tannin was essentially destroyed by the action of nitric acid, although for certain varieties it took a longer time (Hatchett, 1805a,b).

After many additional experiments, Hatchett concluded that the artificial substance resembling tannin could be produced in three ways: (a) digesting any carbonaceous substance (animal, vegetable, or mineral) with nitric acid; (b) distilling the same acid from indigo, resins, and various other substances, and (c) treating resin, camphor, etc. with alcohol, after a previous digestion with sulfuric acid. Hatchett found that the first method was the simplest and most efficient: One hundred parts of vegetable charcoal yielded about 116 parts of the substance. The experiments proved also that the artificial substance was composed of hydrogen, oxygen, and nitrogen, on a carbon base (Hatchett, 1805a,b).

In this final paper on the subject of artificial tannins, Hatchett reported the results of his experiments on the action of sulfuric acid on a number of other vegetable substances, including many of the resins, balsams, mucilage, gum resins, and gums (Hatchett, 1806). After digestion with the acid, the residue was neutralized and then digested with alcohol. The liquid was separated by distillation and the remaining residue dissolved in cold distilled water. The resulting solution was then examined with a solution of isinglass, tin chloride, and iron sulfate. The results indicated that the above set of operations resulted in the formation of the tanning substance and coal, accompanied by SO₂, CO₂, water, and vegetable acids (particularly benzoic acid when the initial material was a balsam), in different proportions. Turpentine, common resin, elemi, copal, camphor, benzoin, the balsams of Tolu and of Peru, and amber, yielded a large proportion of the tanning substance, while asphaltum, gum Arabic, gum tragacanth, natural rubber, liquorice, and myrrh gave none or a very small amount. The tanning substance was also produced from olive oil, linseed oil, bleached wax, and animal fat, but if the action of the acid was too long continued, the tannin was converted into a kind of coal (Hatchett, 1806).

Hatchett observed that acids were powerful solvents for resinous bodies; acetic acid dissolved them without changing their composition, while sulfuric, as already described, converted them first into tannin, and afterward into a kind of coal. Nitric acid, initially converted the resins into a pale orange brittle substance, then into an intermediate product having the properties of vegetable extractive matter and resin, and finally, into tanning substance (Hatchett, 1806).

The final section of this paper was devoted to speculations regarding the formation of the immense deposits of coal, which exist in various parts of the world. Hatchett believed that the most probable explanation was the one claiming that mineral coal was derived from vegetable substances, which after being buried under layers of earth, had been mineralized by some unknown process in which, the sulfuric acid played a principal role. The action of sulfuric acid had led to the conversion of the oils present in different varieties of wood into bitumen and coal (Hatchett, 1806).

Physiology

Shells and bones

In 1799 Home reported on the composition of the teeth of quadrupeds, particularly the elephant and an extinct warthog (*Sus Aëhipicus*) and included the results of the experiments that Hatchett had made for him (Home, 1799). Home found that the teeth of the elephant had "a complex structure composed of three different structures, each of which had a peculiar process for its formation"; a result that led him to "an inquiry whether the materials themselves were different, or only differently arranged." Hatchett found that, contrary to the accepted knowledge, the enamel of the tooth was composed of calcium phosphate and not of calcium carbonate. He believed that the error arose from the solubility of the enamel in acetic acid or distilled vinegar (Home, 1799).

According to Home, Hatchett considered that "lime (calcium) and phosphoric acid were the essential principles" of the three structures, and differed only in their proportion and arrangement of the integrant particles. Hatchett also found that calcium phosphate was present in synovia, although in a small proportion (Home, 1799).

In a paper published in the same year, Hatchett wrote that the experiments he did for Home induced him to make "a chemical examination of shell and bone, especially as the former appeared to have been hitherto neglected" (Hatchett, 1799c). His results indicated that the most marine shells could be classified in two large groups with respect to the substance that composed them: (a) porcellanized shells, having an enameled surface and when broken, presenting a fibrous texture. Within this category Hatchett examined species such as *Voluta* and *Cypræa* and (b) shells composed of nacre or mother of pearl, having a strong epidermis under the shell. Here the species inspected were oyster, river muscle, *Haliotis iris*, and the *Turbo olearious*.

The porcellanized shells dissolved with great effervescence in acids and the solution remained colorless and transparent. Their analysis indicated that they were composed of calcium carbonate cemented by a small portion of animal gluten. When exposed to red heat in a crucible

crackled, they lost the colors of their enameled surface, without emitting smoke or smell. When dissolved in acids they deposited a small amount of animal charcoal and showed the presence of some gluten. Their solution did not show the presence of calcium phosphate or any other combination of phosphoric acid (Hatchett, 1799c).

The experiments on shells formed of mother of pearl showed that they contained less calcium carbonate than the porcellanized ones, and that the carbonate, instead of being cemented by animal gluten, was intermixed with a membranaceous or cartilaginous substance, which retained the figure of the shell, even when deprived of the carbonate (Hatchett, 1799c).

Additional experiments were conducted on the covering substance of crustaceous marine animals, such as echini, starfish, crabs, and lobsters. The results indicated that crust of the echini is different from that of marine shells, approaching that of the shell of the eggs of birds. Regarding the crustaceous and testaceous substances, it was found that the difference in the qualities of each was caused by the proportion of the hardening substance relative to the gluten which cements them, or by the abundance and consistency of the gelatinous, membranaceous, or cartilaginous substance in and on which the calcium carbonate or the mixture of calcium carbonate and phosphate, was secreted and deposited (Hatchett, 1799c).

Realizing that the presence of calcium carbonate in the substance which covers the crustaceous marine animals suggested their similarity to the nature of bone, led Hatchett to perform the same time of experiments on the bones of fish (salmon, mackerel, brill and skate), and on human and animal bone and teeth. The bones of fish showed the presence of calcium phosphate and a larger ratio of cartilaginous substance, compared what was commonly found in the bones of quadrupeds, etc. Enamel appeared only to be different from tooth or bone, by the absence of cartilage and of being principally formed of calcium phosphate cemented by gluten (Hatchett, 1799c).

An additional piece of work involved the examination of the fossil bones of Gibraltar, as well as some glossostræ or shark's teeth. The former consisted principally of calcium phosphate, with the cavities being partially filled by the calcium carbonate, which cemented them together. The latter showed the presence of calcium carbonate and phosphate.

Hatchett opened a following paper (Hatchett, 1800), explaining that "his friend Dr. Edward Whitaker Gray (1748–1806), had suggested that many marine substances still remained to be examined in a similar manner, and that a series of experiments on Zoophytes would be very interesting and probably lead to some improvements in their classification" (Hatchett, 1800).

Here, a great part of Hatchett's effort was directed toward ascertaining in this animal substances the presence and general proportions of calcium carbonate and phosphate (the materials employed by nature to communicate rigidity and hardness to certain parts of animals), and an examination of the substance in and upon which the hardening or ossifying principles were secreted and deposited. In the first part of this long memoir (76 pages) he made a thorough chemical analysis of five species of *Madrepora*, six of *Millipora*, one of the *Tubipora*, the *Flustra foliacea*, the *Corallina apuntia*, two species of *Isis*, thirteen species of

Gorgonia, two of *Antipathes*, five species of *Sponges*, and three of *Alcyonium*. Some of his results indicated that (a) the Madrepores and Millipores studied (like the various shells studied in the previous works) were formed of a gelatinous or membranaceous substance, hardened by calcium carbonate, and the only difference was the mode according to which these material have been employed, (b) in the Tubipora, Flustra and Corallina, some calcium phosphate appeared mixed with calcium carbonate, (c) in the Isis the basis was a regular organized membranaceous, cartilaginous and horny substance hardened by calcium carbonate, (d) the hardening substance of the *Gorgonia nobilis* was also calcium carbonate, with a small proportion of the phosphate, but that the matter forming the membranaceous basis consisted of two parts, the interior being gelatinous, and the external a complete membrane, (e) the Sponges were of a nature similar to the horny stems of the *Gorgoniæ*, and (f) the *Aleyonia* were likewise composed of a soft membranaceous substance, slightly hardened by carbonate, mixed with a small portion of calcium phosphate (Hatchett, 1800).

From this mass of evidence it emerged, in general, that the varieties of bone, shell, coral, and the numerous tribe of zoophytes, only differed in composition by the nature and quantity of the hardening or ossifying principle, and by the state of the substance with which this principle was mixed or connected (Hatchett, 1800).

Conflict of interests

The authors declare no conflict of interest.

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