

Rediscovery of the Elements

The Platinum Metals



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In 1735, the French Academy commissioned a scientific expedition to New Granada¹ to measure a degree of the meridian at the equator to detect any deviancy from a perfect sphere of the earth. The results would determine who was correct: Newton, who thought the earth was flattened at the terrestrial poles, or Descartes, who predicted the earth bulged at the poles.² The expedition included 13 professionals, including Antonio de Ulloa y de la Torre-Giralt (1716–1795), mathematician-explorer and a sailor in the Spanish navy¹, (Figure 1). When de Ulloa returned in 1744, his ship was captured by the British, and he was taken to England. Because of his scientific stature, he gained the respect of the scientific community and was even elected a member of the Royal Society in London. He was allowed to return to Spain and he published a full account of his travels to the New World.³ In this account de Ulloa described a new metal which was known in the Spanish colonies as *platina di pinto* (“worthless little silver of the Pinto River”) or *oro blanco* (“white gold”).⁴ Antonio de Ulloa is generally credited with the “discovery” of the metal in the New World because his was the first published account of the metal in Europe¹ (Figure 2).

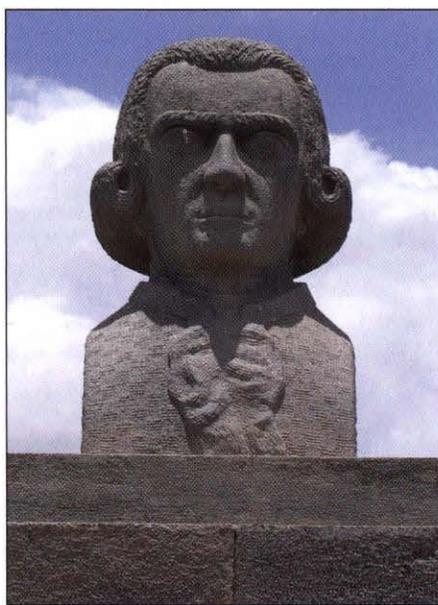


Figure 1. Bust of Antonio de Ulloa (S 0° 00.19 W 78° 27.27) at *Mitad del Mundo* (“Middle of the World”) at Pichincha, Ecuador, 35 km north of Quito, Ecuador. *Mitad del Mundo* is a park commemorating the astronomical measurements made at the equator by de Ulloa and colleagues in 1736. de Ulloa’s statue is only one of 13 including that of his principal colleague Jorge Juan y Santacilla (1713–1773). The park holds a museum, planetarium, other monuments, and other usual tourist attractions. de Ulloa had a varied career, credited with the discovery of platinum (Note 1), then becoming the first governor of Spanish Louisiana (1766–1768), and later establishing the first mineralogical laboratory in Madrid.¹ Courtesy, Miguel A. Monjas, under GNU License.

Originally, platina was recognized as useless, because it was difficult to work, its melting point being beyond normal forging temperatures (700–800° above copper, silver, or gold).¹ Found mainly in Chocó, Colombia, it interfered with the preparation of malleable forms of gold and was considered as “useless slag.” The Spanish government was concerned that gold might be adulterated with platina and ordered

it discarded; from the river sands, the gold and platinum grains were laboriously separated by hand and the unwanted platina was dumped into rivers and landfills. However, de Ulloa suspected the new metal might be of value, and he apparently was able to deliver some of the metal to Spain for further investigation.¹

In spite of Spain’s attempts to maintain secrecy of platinum and its potential use to “debase” gold, reports of the new metal from the New World began to circulate in Europe. Shortly after de Ulloa’s report, Sir William Watson (1715–1787) and Dr. William Brownrigg (1711–1800) contributed a paper to the Royal Society of London⁵ more fully describing the properties of this new metal (Note 1).

After the report of Watson and Brownrigg of platina, research on the new metal commenced in Europe. It was becoming clear that platina was a new metal in its own right, even though George-Louis Leclerc, Comte de Buffon (1707–1788), the famous scientist known for his *Histoire naturelle*, considered the metal merely as an alloy of iron, gold, and mercury.^{6,9a} In 1777 the Swedish Torbern Bergman (the mentor of Scheele^{7c}) proposed that platina be named platinum in accordance with Linneaus’ protocol,⁸ although full acceptance of the new name did not occur until the mid-1800s.^{9a}

The curiosity of skilled laboratory chemists led to further knowledge of the platina. Marggraf^{7c} in Berlin in 1757 found that platina, like gold, would dissolve in aqua regia¹⁰; he marveled that the chloride of platinum compounds could not be precipitated by lead solutions (we now know that chloride is covalently coordinated in the hexachloroplatinate anion, PtCl₆²⁻).

Scientists rued the intractability of platinum but realized its chemical inertness promised usefulness in chemical laboratory ware. Pierre-Joseph Macquer, chemist at the Jardin du Roi in Paris, was able in 1758 to melt small buttons of platinum by means of a large burning mirror¹¹; but to melt platinum in quantity required extreme means such as the oxy-hydrogen torch which was not readily available until the beginning of the 19th century.^{9b,1}

First attempts to create a fusible form of platinum involved the addition of arsenic. Henrik Theophilus Scheffer (1710–1759) in Stockholm in 1752 showed that platinum could be melted if arsenic was added.⁶⁶ Franz Carl Achard (1753–1821), who worked with Marggraf in Berlin^{6b} and is best known for the industrial development of beet sugar,⁷¹ was able in 1784 to prepare a malleable form of platina by fusing it with arsenic and then driving off the arsenic by heat.^{6b} Dealing with poisonous arsenic and the impure platinum thus obtained prevented this method from being used profitably.

Some chemists sought a more workable form of platinum by producing a purer form. In 1772, Carl Heinrich von Sickingen (1737–1791), Austrian Ambassador to Paris (whose father was an alchemist^{6d}), in his spare time found that the solution of platina in aqua regia, when treated with ammonium chloride, gave a precipitate (ammonium chloroplatinate) which could be separated from the original contaminants still in solution, such as iron and copper.^{11,12} Heating the precipitate would regenerate the platina when heated; the resulting divided form of platina could be hammered into coherent form, albeit the procedure was not consistent and much too often simply produced a brittle, powdery product.¹¹

The Platinum Age in Spain. In 1770, Carlos III of Spain established the Real Seminario Patriótico at Vergara in northern Spain in the Basque Country (Figures 3 and 4). In 1781, the two Elhuyar brothers^{7b} Don Fausto (1755–1833) and Juan José (1754–1796), who had been studying at Freiberg,^{7a} arrived at the Seminario Vergara (Note 2). These two brothers in 1783 were successful in preparing, for the first time, metallic tungsten^{7c} by a straightforward procedure of heating tungstic acid (discovered by Scheele^{7e}) and powdered charcoal in a sealed crucible. When the crucible was broken open, a crumbling black button was found with pinhead-sized metallic globules of metallic tungsten.

This work on refractory tungsten presaged research on platinum. The Elhuyar brothers recruited Pierre-Francois Chabaneau (1754–1842), a native of southern France, to teach chemistry and experimental physics at the Seminario Vergara. Chabaneau arrived in 1778, and two years later he became chemistry chair at Vergara.

In 1784, new shipments of platinum arrived at Vergara, and Chabaneau began collaborating with the Elhuyar brothers on the problem of preparing malleable platinum. Chabaneau was soon on his own, because the Elhuyar brothers were preoccupied in their preparations for their

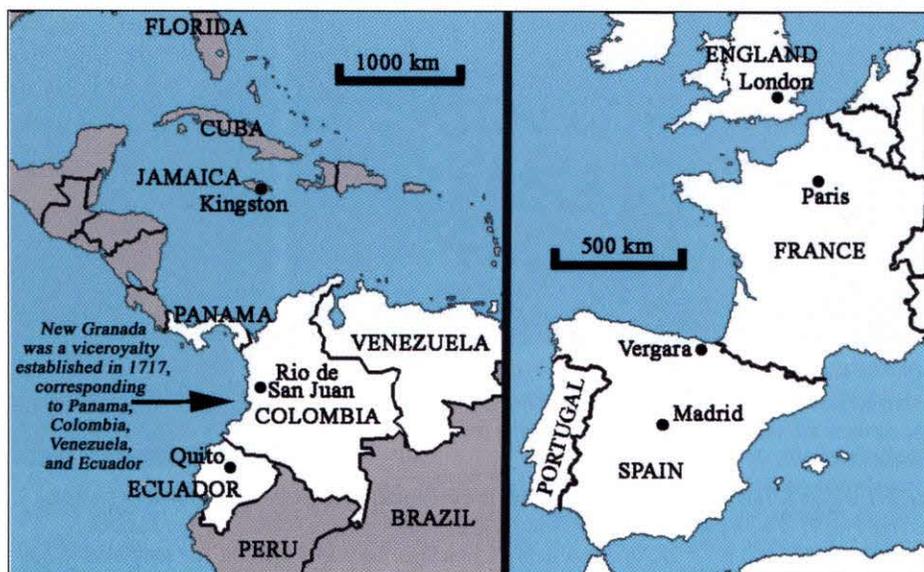


Figure 2. Sites associated with the early history of platinum. Platina di pinto was originally found in placers of “Rio di Pinto,” one of the tributaries of Rio de San Juan of southwestern Colombia. Rio di Pinto cannot be located today.²⁷ Today Condoto, in the heart of the San Juan drainage basin, is known as the “Platinum Capital of Colombia” (N 05° 06' W 76° 39'). Platina was originally worked in the Spanish laboratory at Vergara, Spain. Meanwhile, samples of platina were smuggled to Jamaica, a British colony, whence it was taken to England for study. In London, a commercial basis was developed for the production of platinum for laboratory crucibles and other uses. Also in London, the elements palladium, rhodium, osmium, and iridium were discovered as impurities in platinum.



Figure 3. Seminario Vergara (corner of Bidekurutzeta Kalea and Herrilagunak Kalea), Vergara, Gipuzkoa, Spain (N 43° 07.06' W 02° 24.80') where the Elhuyar brothers first prepared metallic tungsten and where Chabaneau devised the first practical method of preparing malleable platinum.

next calling by the Spanish King—in 1786 Juan José was sent to New Granada, and Don Fausto was sent the same year to the mining school at Schemnitz (then Hungary, now Slovakia)^{7c} to study amalgamation methods which he was to use in Mexico^{7b} two years later.

Chabaneau was successful by 1786, developing a procedure which included Sickingen’s use of aqua regia and ammonium chloride. His process was ordered by the king to be kept secret; its details have only recently become known when a pamphlet¹¹ published in 1862



ABOVE: Figure 4. Plaque on the wall of the Seminario Vergara, commemorating on June 19, 1977, the two hundredth anniversary of the founding of the chemical laboratory. The plaque is inscribed in both Spanish (top) and Basque (bottom).



RIGHT: Figure 5. This platinum chalice was given to the Spanish King Carlos III in 1788 who presented it to Pope Pius VI. It is on public view in the Treasury at St. Peter's in Rome (Basilica di San Pietro in Vaticano, N 41° 54.13 E 12° 27.20). It measures 29.5 cm high, diameter 8.5-15 cm, and weighs 55.45 troy ounces. Courtesy of Johnson Matthey PLC, reference 13.



Figure 7. Tennant's birthplace, 12 Finkle St., Selby, England (N 53° 47.07 W 1° 04.15). This photograph was taken in 2004, before a "blue plaque" was mounted on the outside wall (see next figure). The building is now the Elizabethan Inn, serving food and spirits. Selby is in York, 250 km north of London.

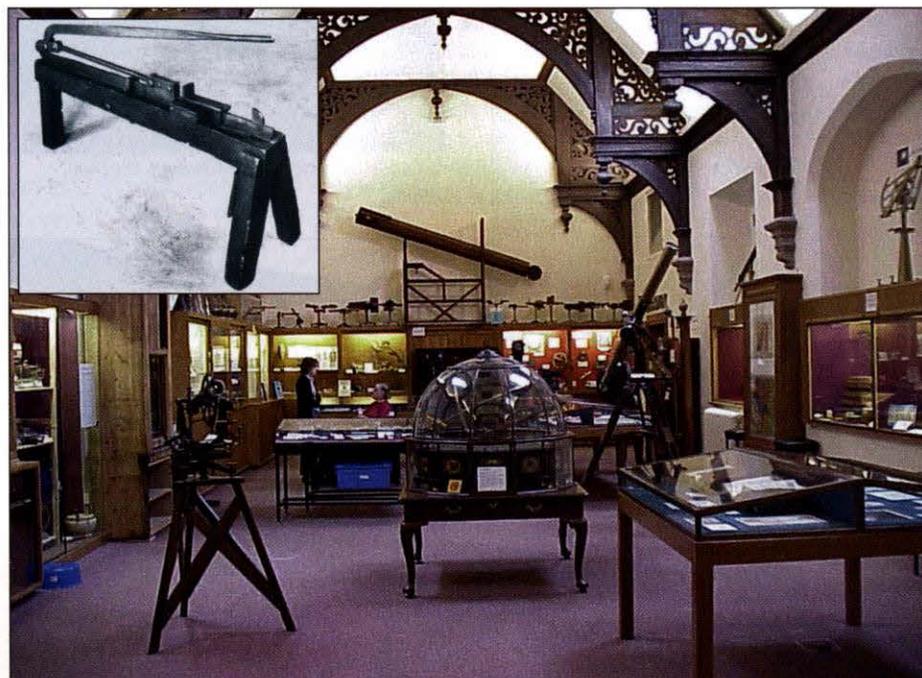


Figure 6. Top: The Whipple Museum of the History of Science, Free School Lane, Cambridge, England (N 52° 12.16 E 0° 07.15), known (among other things) for its collection of Isaac Newton's optical devices. Newton was a professor at Cambridge and invented the reflecting telescope. Inset: Among the archived items at the Whipple Museum is the "toggle press" used by Wollaston to produce his malleable platinum. The mechanical force of the press is x300. Courtesy of Johnson Matthey PLC, reference 11.

came to light in 1914. The research was not carried out without frustration; at one point the Count d'Aranda,¹¹ who furnished the raw platinum, visited the laboratory one day to find Chabaneau in a frenzy, smashing all of his equipment and throwing out his solutions which he had prepared with such patience. However, a consistent procedure was worked out using a new sequence of extractions, washings, and sintering; only three months later a

large cube of malleable platinum was prepared. This cube, measuring 10 cm,³ weighed 750 troy ounces, translating to 23.3 kg! In 1786, Chabaneau presented a platinum plate to de Ulloa with the inscription: "To the Hon. Mr. Don Antonio de Ulloa, the first to bring platina to Europe in 1748, here it is returned as a perfect gift in 1786, Don Francisco Chabaneau."¹ In 1788, the first platinum work of art was produced (Figure 5), a chalice which was present-

ed to Carlos III.¹³ Most impressed with Chabaneau, the King moved him to Madrid in 1787 to head the newly founded Royal School of Mineralogy (Note 3), where 14,000–18,000 troy ounces of platinum per year were produced until French troops destroyed the laboratory during Napoleon's second invasion of 1808.

The overthrow of the Spanish empire during the Napoleonic Wars ruined the Spanish platinum industry. Platinum continued to be produced in the New World, but it found its way to Europe mostly via smuggling through Jamaica. The next chapter in the history of platinum took place in England.

Wollaston and Platinum. Independent of the researches in Spain, William Hyde Wollaston (1766–1828) developed a method of preparing malleable platinum in London by 1800. This was the same scientist who formulated the theory of chemical equivalents and who was involved in the promotion of Dalton's atomic theory.⁷⁸ His procedure was essentially that of Chabaneau, and like the Spanish chemist he kept his procedure secret (until just before his death). Unlike Chabaneau, however, who produced all of his product secretly and privately for the Crown, Wollaston publicized his product, marketed it, and made a handsome profit which allowed him to retire from his medical profession in 1800 to continue other independent researches.¹¹ This work was developed at a laboratory in his first home (Note 4),

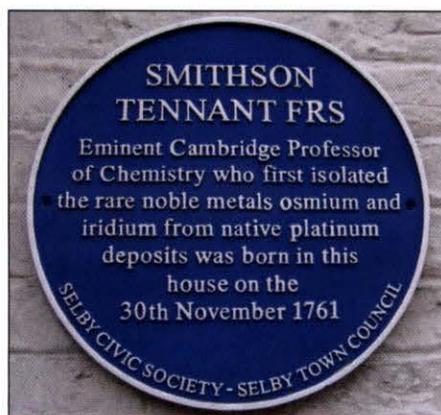


Figure 8. This plaque was prepared for one of the famous “Selebians,” as denizens of Selby are known, and was mounted on Elizabethan Inn in 2005. In the United Kingdom, a blue plaque is a historical marker for famous persons and events. In spite of Tennant’s major contributions and his membership in the Royal Society, no likeness of him exists nor is likely to have ever been produced.²³

within walking distance of the Crown and Anchor, where the Royal Society held frequent meetings.⁷⁸ It is clear from his notes that he experienced similar initial frustrations as did Chabaneau, with cracking of the final metal as the mortal enemy. One of Wollaston’s major improvements is the “toggle press”¹¹ which he used to compress his platinum sponge before forging into metallic bars (Figure 6). He found, as did Chabaneau, that a key step was the sintering of the powder to white heat before compression.

The pioneering efforts of Chabaneau and Wollaston are recognized today as the first attempts at powder technology of metals.¹¹ Their final procedures were not so much a result of the understanding of the science but instead simply a hit-and-miss discovery of a recipe that works—today’s science of metallurgy with its understanding of eutectics and grain boundaries was over a century in the future.

Wollaston and Tennant—four more elements from platinum. Smithson Tennant (1761–1815), a native of Selby, Yorkshire, (Figures 7 and 8) and Wollaston (Figure 9) were acquaintances at Cambridge University where they both earned their medical degrees. When Wollaston moved to London in 1797, they became close friends, working on various scientific projects and relaxing together on vacations, e.g., the Giant’s Causeway in Ireland. Their first successful collaboration was an investigation of the nature of diamond,¹⁴ where they showed that charcoal and diamond upon combustion gave the same amounts of carbon dioxide, and thus must be forms of the same element (i.e., allotropes, a term invented by

Berzelius⁷⁹ in 1841). This was an advancement beyond Lavoisier’s experiments^{7d} where the French scientist showed that the combustion of diamond gave carbon dioxide but he did not elucidate the nature of diamond (some speculated that diamond was simply another form of carbon oxide).

Wollaston and Tennant also collaborated on their analysis of platinum. In 1797, they entered into a partnership, with Tennant providing the original financial investment.¹⁵ On Christmas Eve of 1800 they purchased 5959 troy ounces of alluvial platinum ore (containing 80 percent Pt.). The cost was £795 (today’s \$30,000).¹⁵ This was the capital which allowed Wollaston to retire early from the medical profession and to give him ultimately a return from his malleable platinum business of £30,000 (over \$1,000,000 today).¹⁵ Wollaston moved into his new house and set up a new laboratory in the back garden (Note 4).

Wollaston and Tennant conducted a detailed analysis of platinum, dividing their work into two assignments: the soluble portion when platinum is dissolved in aqua regia (Wollaston’s task) and the non-soluble residue (Tennant’s task). In less than three years, they found four new elements.

Wollaston took his soluble fraction and found the addition of mercuric cyanide precipi-



Figure 9. Perhaps the only commemorative site for Wollaston is the Chislehurst church, Church Lane, Chislehurst, England (N 51° 24.58 E 0° 04.50), 15 km SE of London. Wollaston’s father, Francis Wollaston (1769–1815), astronomer and a member of the Royal Society, was rector of this church 1731–1815; commemorative plaques can be found inside. The family vault, where William Hyde Wollaston is buried, is located on the NNE side of the church.

tated out a yellow solid ($\text{Pd}(\text{CN})_2$). By ignition of the solid he produced a new element, which he named palladium after the newly discovered asteroid Pallas.¹⁶ His notes show he had considered the name Ceresium in 1802, but Berzelius and Hisinger were at that time announcing the discovery of cerium from the Bastnäs mine in Sweden.^{7h} Wollaston’s original announcement of palladium was most peculiar, being in the form of an anonymous public handbill; possibly he was avoiding orthodox publication because he was concerned about competition from others who were investigating crude platinum and was purposely keeping his detailed researches secret.¹⁷ This was perhaps the first example of “publication by press.”

To the remaining solution after palladium had been removed, Wollaston then added sodium chloride, evaporated the solution to dryness, and washed it with alcohol. Remaining was a dark red powder, which was the chlororhodate salt, $\text{Na}_3\text{RhCl}_6 \cdot n\text{H}_2\text{O}$. From this the metallic rhodium could be prepared by reducing with a stream of hydrogen.¹⁸ Wollaston named the new element rhodium from the rose color of the chlororhodate salt he had isolated. The homes where Wollaston did his research on palladium and rhodium no longer exist (Note 4).

Tennant’s research (Figure 10) was concerned with the black residue,¹⁹ which had been noticed previously but which was thought simply to be plumbago (graphite).²⁰ A density measurement by Tennant showed the residue to be much heavier (10.7).²¹ Tennant heated the residue with sodium hydroxide to redness, cooled, and dissolved in water. The resulting yellow solution (mostly $\text{Os}(\text{OH})_2\text{O}_4^{2-}$) had a very pungent smell; upon acidification and distillation a white oxide was obtained (OsO_4). Reaction with copper, tin, zinc, or phosphorus gave a black powder, which Tennant named osmium [Greek “odor”] from the wretched stench.²¹

Tennant took the black residue after the aqueous osmate solution was removed and treated with marine acid (hydrochloric acid). Concentration of the aqueous solution gave dark red crystals, probably $\text{Na}_2\text{IrCl}_6 \cdot n\text{H}_2\text{O}$. Heating the solid returned the new metallic element, which Tennant called iridium because of the variable colors of the hydrochloric acid solutions.²¹

Tennant in his publications mentions the simultaneous work on the “black residue” by the French chemists Collet-Descotils (the “undiscoverer of vanadium”^{7c}) and Vauquelin (discoverer of chromium^{7e}) and Vauquelin (who believed they had discovered a new element.²² The French workers fused the black residue with potash which was then treated with aqua regia and ammonium chloride. A red precipitate was

observed which the French workers believed was a new element. This precipitate, probably residual ammonium chloroplatinate, *might* have contained $(\text{NH}_4)_2\text{IrCl}_6$ —or the rhodium analog.¹⁹ The authors also later described a pungent odor (OsO_4) when the fused potash residue was extracted with water, and which they mistakenly believed was due to the same unknown element. The French authors later admitted that Tennant's work was superior and that he deserved credit for discovery of iridium and osmium¹⁹ (Note 5).

Were there any more elements in crude platinum? Wollaston and Tennant, in the space of a year, had announced four new elements in crude platinum—palladium, rhodium, iridium, and osmium. It was natural to ask, are there more elements? A flurry of activity resulted in many such claims—but no more substantiated discoveries were recognized for 40 more years. A modern student studying the Periodic Table sees that the six platinum elements form a block with platinum as its southeast cornerstone, and that in addition to Wollaston and Tennant's new elements only one remained—ruthenium. Unfortunately, no one had any idea how many elements might still be hidden—the Periodic Table was more than half a century in the future.

Vauquelin and Tennant both had clues but missed them. First, a stench was observed *before* acid was added to the alkali fusion; second, they both noticed that an aqueous solution of the alkali residue is *yellow*. Vauquelin, the discoverer of chromium, naturally thought the color was due to that element, but Tennant performed chemical tests and found no such evidence. Neither realized that they were dealing with the oxide of the sixth platinum-group element. The discovery of this element had to await the discovery of prodigious quantities of platinum in the Urals of Russia. This story will be told in a future issue of *The HEXAGON*. ☉

Acknowledgments

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Notes.

Note 1. There is not a solid consensus regarding the “true” discoverer of platinum. Some scientists ascribe the discovery to William Brownrigg,^{2,24} who contributed the first scientific description of platinum (William Watson is listed as the author only because he, as a member of the Royal Society, made the formal read-



Figure 10. 4 Garden Court, *The Temple*, London (N 51° 30.73 W 0° 06.70), famous and occasionally mentioned in Sherlock Holmes stories. Tennant moved here (then 1 Garden Court) in 1788 after he obtained his M.D. degree, where he lived the rest of his life. He never practiced medicine, but instead pursued research in chemistry and mineralogy, with a rich background gained by extensive travel of Europe. He frequently gave lectures to large gatherings of his friends in his rooms at Garden Court.²³ *The Temple* was only 200 meters east of the Crown and Anchor, the favorite haunt of members of the Royal Society. Tennant also purchased a farm in Shipham where he conducted agricultural experiments; Berzelius visited the farm in 1812.²³ This farm, now called Longbottom Farms, still exists (N 51° 18.45 W 2° 46.68), 190 km east of *The Temple*, near Bristol.

ing).²⁴ But perhaps with equal claim was Sir Charles Wood (1702–1774), “Assay Master of Jamaica” 1721–1740 who performed the first chemical tests at his laboratory in Kingston on platina obtained from the Spanish colonies.²⁵ He determined its density, noting it was the same as that of gold; and he recorded its resistance to nitric acid. He carried samples of platina when he returned permanently to England in 1741 and presented them to Brownrigg, his brother-in-law, who did no new chemistry, only repeating Wood's experiments.²⁵ And an even earlier, if vaguer, claim might be Joseph Justus Scalinger (1540–1609) who made the first published report of platinum in 1557—he mentioned a metal (without referring to it by any name) in the Spanish colonies “which proves the word ‘melt’ cannot be applied to all metals,”⁴ referring to its intractability. Finally, credit might be best given to the Indians in Colombia and Ecuador, who originally used platinum in jewelry, as early as the 2nd century B.C.²⁶

Note 2. When Carlos III founded the Real Seminario in Vergara, to establish the chemistry program he first brought in the Frenchman Joseph Louis Proust (1754–1826), who later was to gain fame by his Law of Definite Proportions, where in 1799 he disproved⁷⁸ the variable composition views of C. L. Berthollet.^{9c} Proust stayed three years at Vergara, leaving in 1780. Proust then returned in 1786 to Spain to hold various posts at Segovia and Salamanca. In 1799, he succeeded Chabaneau, who was now at Real Escuela de Mineralogía at Madrid. In 1808, when Napoleon destroyed the Madrid laboratory, all Proust's records and equipment were lost and he returned to France.

Note 3. Antonio de Ulloa was involved in the founding of the School of Mineralogy in Madrid.¹ It is not clear where in Madrid the school resided during the period 1787–1789, but it is known that the permanent school was established at the calle de Turco (today the Marquess de Cubas, address #13 (N 40° 25.06 W 3° 41.71), which is the current Real Academia de Jurisprudencia y Legislación (Royal Academy of Law and Legislation). Immediately to the north was established the Banco de España, which still exists.

Note 4. Wollaston lived in three homes while in London, none of which still exist: (1) 1797–1801, 18 Cecil St. (N 51° 30.51 W 0° 07.22), where he originated his method of producing malleable platinum; the street has been supplanted by Ivy Bridge Lane (just north of the Thames River), which today is an alley crammed between high buildings; (2) 1801–1825, 14 Buckingham St. (N 51° 31.38 W 0° 08.57), where he perfected his platinum process and made his fortune, and where he discovered palladium and rhodium, all in a laboratory structure set up in his back garden; a plaque existed on the house before it was taken down after WWII; now the site is a parking lot and the street is renamed Greenwell St.; (3) 1825–1828, 1 Dorset St. (N 51° 31.20 W 0° 09.28), where Wollaston lived his final years; and where Charles Babbage (1791–1871), originator of the concept of the programmable computer, lived 1829–1871; the newer house bears a plaque dedicated to Babbage. The two latter sites were 2.5 km northwest of the first residence.

Note 5. Partington suggests Vauquelin and Descotils “should rank as independent discoverers of iridium,”^{9c} but this is not universally accepted. Before Tennant's publication, the French chemists' experiments were preliminary and they never proposed a name for their “element.” There are references that *ptene* [Greek, “winged”] was proposed for osmium, but this cannot be validated in the literature, and the source of this name is not clear.¹⁹

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