Rediscovery of the Elements

Thallium, Crookes, and Lamy

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With the development of spectroscopic analysis by Bunsen and Kirchhoff and their discovery of cesium and rubidium (1860-1861),[1i] the hunt was on for more element discoveries using this new tool. Almost immediately, ***thallium*** *was independently discovered by* ***William Crookes*** *(1832–1919) and* ***Claude-Auguste Lamy*** *(1820–1878) (Figure 1).*

Crookes, the "Commercial Scientist."[2a] Crookes was an entrepreneur and scientific journalist with research achievements in chemistry, physics, and photography. His many inventions included the Crookes tube, the radiometer, and the spinthariscope (Note 1), and he was awarded Fellowship of the Royal Society (1863), knighthood (1897), the Davy Medal (1888), and the Order of Merit (1910).

William Crookes was born to Joseph (1792–1884) and Mary neé Scott (1806–1884) Crookes; Joseph was a well-to-do tailor with a home and shop on Regents Street on the west end of London with its prospering gentry (Figure 2). Soon the family would move westward with expanding London. William's schooling was gained at the new Royal College of Chemistry (Figure 3), founded in 1845 by Prince Albert (consort of Queen Victoria) who was keen on promoting the technology base of Great Britain.[3] Using the German model, Albert invited August Wilhelm von Hofmann (1818–1892) from the group of Justus von Liebig (University of Giessen). At the Royal College Crookes researched selenocyanides (-SeCN compounds)[4] using material procured by Hofmann from the Harz Mountains of Germany.[5]

At an early age Crookes developed a passion for photography, a hobby he pursued in his Brook Green home laboratory built for him by his parents in 1851 (Figure 2). Here he developed new photographic techniques which required a wide broadening of his chemical knowledge. Blending his expertise in photography and chemistry, he designed instrumentation and devised techniques in the spectroscopic examination of chemical substances. Hence, by the time Bunsen discovered cesium spectroscopically in 1860, Crookes had already launched his own search for new elements. When his old mentor Hofmann needed a spectroscope in 1861 for a demonstration lecture on Bunsen and Kirchhoff at the new South Kensington Museum, he turned to Crookes for the only high quality instrument equal to the task in the entire British Isles.

The Role of the Independent Editor. Modern research journals, such as *The Journal of the American Chemical Society*, utilize a formal protocol of submission and peer review. In earlier years, however, it was common for a journal to be owned and/or managed by an independent editor free to pontificate on various matters. Often a journal would be more easily recognized by the editor's name, e.g., "Gilbert's Annalen" (*Annalen der Physik*) or "Liebig's Annalen" (*Annalen der Chemie*). For example, the editor Ludwig Wilhelm Gilbert (1769–1824) would editorialize on on the significance of Döbereiner's Triads[1g] (precursor to the Periodic Table[1f]), or he would suggest alternate possible names for Stromeyer's new element isolated from zinc[1n]—not only "Kadmium," but also "Junonium" and "Melinium." Berzelius in his *Jahres-Bericht über die Fortschritte der Chemie und*

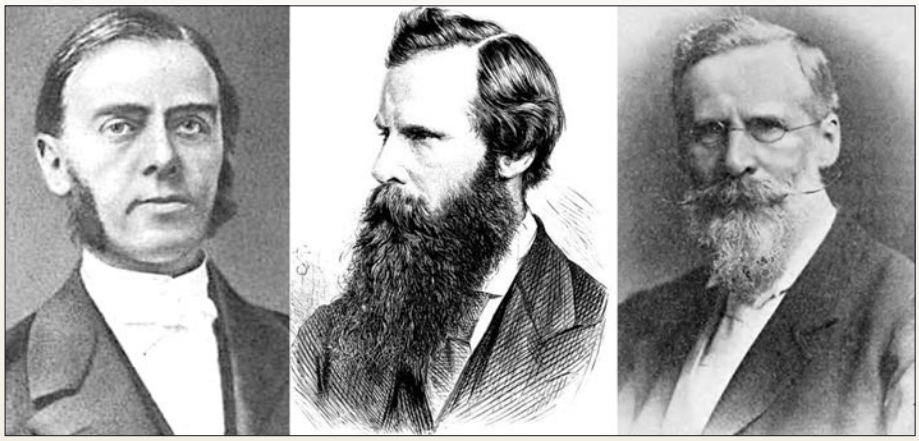

Figure 1. Claude-Auguste Lamy (left) and William Crookes (middle) are shown when thallium was discovered and characterized (early 1860s). Crookes lived well into his eighties and his elderly portraits (right) with his classic waxed mustache and goatee, at the apex of his career, are more familiar in the biographical literature. Lamy did not live so long after the thallium work, and is only known by this portrait.[8]

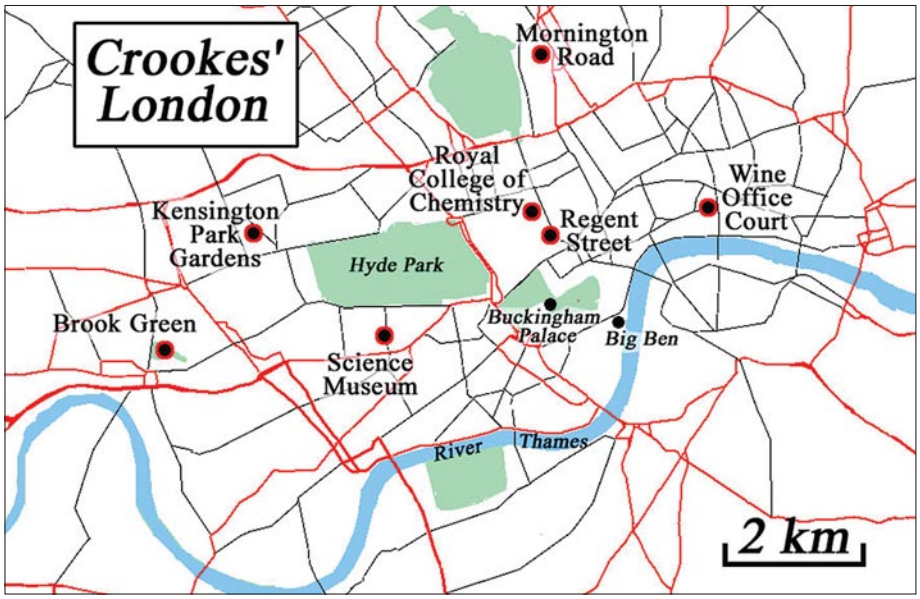

Figure 2. Sites pertaining to William Crookes in London (asterisk denotes edifice no longer exists).
***Father's tailor shop**,* Crookes' birthplace, 143 Regent St.–N51° 30.68 W00° 08.35.*
Family home 1846–1856 in Brook Green (Masborough House)–N51° 29.72 W00° 13.03.*
***Royal College of Chemistry**, founded 1845, 16 Hanover Square (N51° 30.86 W00° 08.67); then (in 1848) 299 Oxford Street* where Crookes attended–N51° 30.89 W00° 08.69.*
Crookes' home 1857–1879, 20 Mornington Road 1857–1878, discovered thallium and performed spiritualism experiments here–N51° 32.08 W00° 08.58.*
***Crookes' home** 1880–1919, 7 Kensington Park Gardens, Notting Hill–N51° 30.69 W00° 12.16.*
***Science Museum**, Exhibition Road, South Kensington, London, wealthy repository of Crookes' exhibits—N51° 29.86 W00° 10.44.*
***Publishing houses of William Crookes.** Wine Office Court, site of Crookes' periodical* Chemical News *1861–1867 (there were also several other sites in the general locality during the life of the journal)–N51° 30.86 W00° 06.43.*
NOT SHOWN:
***Home at 15 Stanley St.** [now Ovington St.] in Brompton (0.7 km east of Science Museum), residence in 1856 with new bride Ellen Humphrey (1836–1916) before moving to Mornington Road–N51° 29.73 W00° 09.90.*
***Royal Institution**, 21 Albemarle St. (300 meters southwest of Regent Street), exhibits on Crookes and other scientists–N51° 30.58 W00° 08.55.*

Mineralogie[1h] coined the term "catalyst" for his concept of a special agent in plants, anticipating enzymes by almost half a century. The announcement in the Western World of the spurious "vestium" by Sniadecki[1l] and its rejection by the French Science Academy was made by Jean-Claude de La Métherie (1743–1817) in his private *Journal de physique, de chimie, d'histoire naturelle et des arts*. In *The HEXAGON* "Discovery" series we have seen back-and-forth discussions of Hevesy and Coster's hafnium and Urbain's celtium,[1m] Soddy's transmutating elements,[1k] Rutherford's atom,[1k] and Moseley's atomic numbers,[1j] all discussed in *Nature*, the journal founded in 1869 by Joseph Norman Lockyer (1836–1920); co-discoverer of solar helium. And lastly there was William Crookes, who after two years as editor of various photographic journals, in 1859 founded *Chemical News* which lasted for 73 years, 13 years past his death (Figures 4, 5). In this journal Crookes emphasized commercial chemistry but did not hesitate to venture into many areas of pure research. And it was in this medium that he announced his own discovery of thallium, the "first element discovered by an Englishman since [Sir Humphry] Davy's discovery of the alkali metals."[6]

The Discovery of Thallium. Crookes was caught up in the race to "discover a new element before they ran out."[1m] Returning to the Harz Mountains sample previously used in his selenocyanide studies, Crookes subjected it to spectral analysis. His observation filled him with excitement: "Suddenly a green flash appeared before my eyes!"[5] (Figures 6, 7) He surmised that the element was of the "sulfur family,"[5] because sulfur, selenium, and tellurium were known to occur together in ore

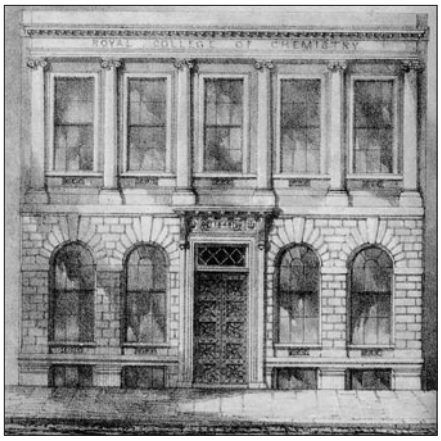

Figure 3. The Royal College of Chemistry at 299 Oxford Street, where William Crookes was trained in chemistry and published his first paper on selenocyanides. Today this site is occupied by a men's apparel store. By 1872 the institution had moved to New Kensington (200 meters west of the present Science Museum) and by 1907 had evolved to the modern Imperial College (N51° 29.86 W00° 10.66), where the original dedication stone laid by Prince Albert in 1846 is on display.

deposits. In his following publication[7] he categorized his new element as a "metalloid," and he named it "thallium" ("thallos," *Greek* for "green budding twig").

Crookes was a meticulous observer, careful not to confuse stray lines with new elements. He had previously corrected others who had "discovered" new elements—for example, John F. W. Herschel (1792–1871; son of William Herschel 1738–1822, discoverer of the planet Uranus) in his naive exuberance originally interpreted the manifold spectral lines now appearing in modern spectroscopes as new elements—which he named junonium, vestium, neptunium, asataeum, and hebeium—until more careful study showed the lines belonged to known elements.[6] In Crookes' study of thallium,[5a] he cautiously precluded all other possibilities by both spectroscopic and chemical means, in all 55 other known metals and metalloids, as well as the gases and carbon.[5]

The Surprise at the International Exhibition of 1862. Eager to introduce his new element at the 1862 International Exhibition at Hyde Park in London, Crookes received a rude shock—another scientist, a Frenchman Claude-Auguste Lamy (1820–1878), a professor of the Université de Lille (northeast France), was bringing his own exhibit of thallium.

Lamy[8] was born in Ney, in the Jura region of southeast France. He was the son of Désiré (1782–1865) and Rosalie neé Melet (1796–1853) Lamy; Désiré was a career officer in the major battles of Napoleon I. Claude-

Figure 4. Wine Office Court, the site of Crookes Chemical News *publishing houses 1861–1867, retains the Georgian atmosphere of earlier times. Samuel Johnson, who wrote the first comprehensive dictionary of the English language, lived here 1748–1759. The name of the court is derived from the Excise Office that existed here until 1665. It presently holds* Ye Old Cheshire Cheese *(see next figure).*

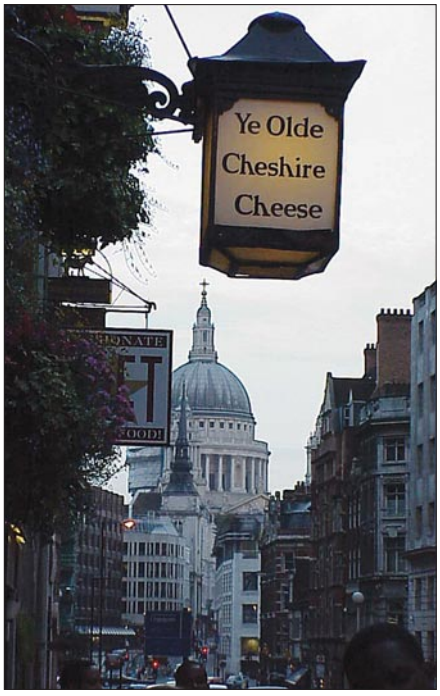

Figure 5. Ye Old Cheshire Cheese *is a pub with a rich heritage of Tutor windows, oak panels, and sawdust-covered floors, dating from 1667, rebuilt in that year because of the great London fire of 1666. Patrons have included Samuel Johnson, Charles Dickens (mentioning the tavern in* A Tale of Two Cities*), Sir Arthur Conan Doyle, Mark Twain, and Theodore Roosevelt. The dome in the background is St. Paul's Cathedral, built by Sir Christopher Wren and finished by 1697.*

Auguste Lamy studied at École Normale Supérieure, where Henri-Étienne Sainte-Claire Deville (1818–1881) made his fame with aluminum.[1d] There Lamy met fellow-student Louis Pasteur (1822–1895), also from the Jura region; the two became close friends there. After graduating in 1842 Lamy taught at Lille, then Limoges, then finished his doctorate at the University of Paris in 1851. In 1854 he joined the newly founded Université Lille Nord de France (Université de Lille) as the professor of physics (Figure 8), along with Louis Pasteur who was first dean of the University as well as professor of biology (Figures 9,10). After achieving his reputation with thallium there,[9,10] Lamy moved in 1879 to l'École Central des Arts et Manufactures in Paris (today the Musée Picasso).[1e]

In 1854 Claude-Auguste Lamy married Cécile Honorine Kuhlmann (1832–1906),[8] daughter of the prosperous chemical industrialist Charles Frédéric Kuhlmann (1803–1881).[11] Kuhlmann's company had a branch in Loos (a suburb of Lille) whose sulfuric acid factory proved to be a rich source of thallium (Figure 11). Kuhlmann also lent Lamy a spectroscope with which Lamy immediately observed the strong green line in his laboratory. With such an abundant supply of this new element, Lamy was able to prepare sizable amounts of metallic thallium.

At the London Exhibition of 1862, Lamy inspected Crookes' sample of the element—merely a few grains of dark powder—and proclaimed it was a sulfide derivative (immediately disputed by Crookes). Although Crookes had prepared many derivatives of thallium in a full chemical study, Lamy's exhibit stood out because he had prepared an *ingot* of the metal. The Exhibition jury, headed by A. J. Balard, of bromine fame,[1b] awarded Lamy a prize for his accomplishment. Crookes protested bitterly—"What would one expect when the majority of jurors were foreigners!"[2a] The fight was on. Much rode on this priority issue—both Crookes and Lamy "had a reputation to establish."[2a]

Crookes had the advantage of immediate control of a British journal, and his propaganda campaign, coupled with a general British zeal for priority, led to his being elected as a Fellow of the Royal Society—new credentials which gave considerable weight to the International scene. Meanwhile, the famed Jean-Baptiste André Dumas (1800–1884)[1e] came to the aid of Lamy. Dumas argued that Lamy should be credited with the discovery of the *metal* since Crookes had originally characterized it as a *metalloid*.[12] To the credit of Crookes, he published Dumas' (translated) article in his *Chemical News*.[12c]

Lamy and Dumas[12] argued that thallium must be a member of the alkali metals: It could form oxides of the formula M_2O, and its spectrum was strong and sharp, just as those of the alkali metals (Li, Na, K, Rb, Cs) (Figure 7). However, other properties were more puzzling; Dumas dubbed it the "ornithorincus [duckbill platypus] of metals," referring to the fact that taxidermic specimens of this Australian species were first thought to be a hoax, a composite of different animal parts stitched together. Indeed, thallium more closely resembled lead (Pb) in appearance, high density, and chemical reactivity, and was capable of multiple oxidation states (+1 and +3). Thallium's proper categorization was clarified by the Periodic Table presented a few years later (1869) by Dimitri Mendeleev and by Lothar Meyer, both of whom placed the element in the aluminum family.[1f]

The reason why Lamy was so successful in preparing large amounts of thallium was given by Kuhlmann himself[13] who had developed a cleaner method of preparing sulfuric acid. He inserted an intermediate chamber between the roasting chamber (which heated pyrites to generate sulfur dioxide) and the final reaction

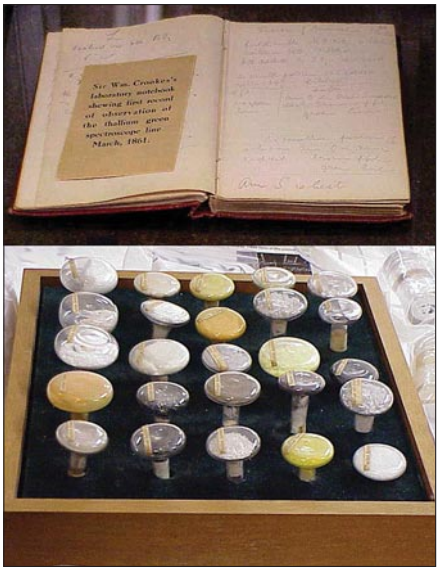

Figure 6. In the Science Museum of South Kensington, London, are many exhibits on Crookes, including (top) the laboratory notebook of William Crookes, documenting his observation of the green spectral thallium line, and (bottom) his collection of thallium compounds. (A collection of Lamy's thallium compounds resides in the bibliotheque de l'École Normale Superieure Physique, 24, Rue Lhomond, Paris, France–N48° 50.57 E02° 20.82).

chamber.[13] This intermediate chamber was designed to separate out nonvolatile impurities (arsenic as the main culprit). When this nonvolatile deposit was taken up in aqua regia and diluted with water, copious amounts of yellow thallium sesquisulfide hexagonal crystals ($3TlCl \bullet TlCl_3$, or Tl_2Cl_3) could be collected.[10] (It was now clear that in previous manufactory designs, the thallium had been carried on to become a contaminant in the final sulfuric acid.) Another reason for Lamy's success was that his ores taken from Theux, Belgium, were blessed with a greater concentration of thallium. Crookes finally found alternative sources for thallium, but Lamy's good fortune allowed an initial burst of research that rapidly caught up with Crookes. The bitter debate between Lamy and Crookes continued for several years,[6] until a Swede christened the first thallium-containing mineral "crookesite."[14a]

The Discovery of Crookesite by Nordenskiöld. Readers of *The HEXAGON* may recall that Berzelius discovered selenium[1h] in a sulfuric acid manufactory in Gripsholm, Sweden, in 1817. Half a decade after Crookes announced his discovery of thallium, Adolf E. Nordenskiöld (a Swedish arctic explorer and mineralogist, also a biographer of Scheele[1c]) was rummaging through old selenide minerals

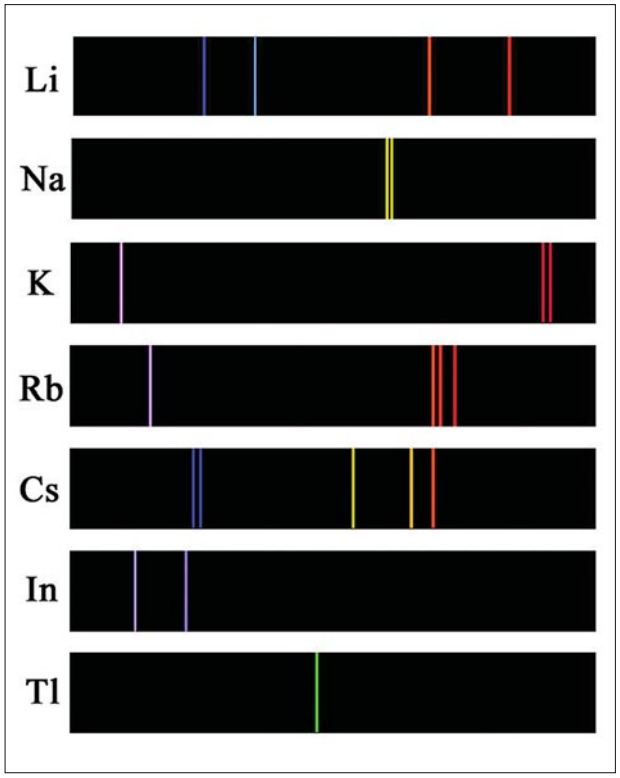

Figure 7. The emission (flame) spectra of the alkali metals (upper five) are relatively simple and facilitated Bunsen's discovery of cesium (1860) and rubidium (1861).[1i] Owing to their fortuitously simple spectra, thallium (one green line at 535.0 nm) was then promptly discovered by Crookes (1861) and indium[1a] (two lines at 451.1 and 410.2 nm) by Reich and Richter (1863). Even the "monochromatic" yellow spectrum of sodium exhibits a close doublet (589.6 nm and 589.0).

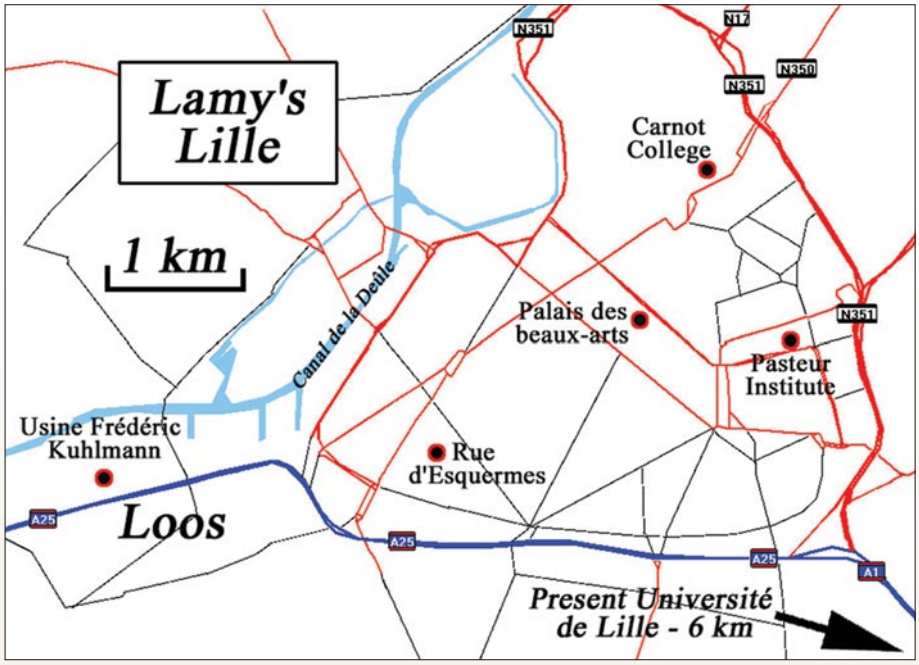

Figure 8. Sites pertaining to Lamy in Lille (asterisk denotes edifice no longer exists):
***Carnot College** (original site of Université de Lille,* where Lamy researched thallium),–43, Boulevard Carnot–N50° 38.38 E03° 03.99.*
***Usine [factory] Frédéric Kuhlmann**,* source of thallium for Lamy, 22 rue Georges Clemenceau, Loos–N50° 37.28 E03° 00.45.*
***Rue d'Esquermes sugar beet manufactory**,* whose lactic acid problem was solved by Louis Pasteur–N50° 37.37 E03° 02.45.*
***Palais des Beaux, Place de la République**, marble bust of Frédérick Kuhlmann by Albert-Ernest Carrier-Belleuse (1870)–N50° 37.88 E03° 03.67.*
***Pasteur Institute**, devoted to biochemical research, Blvd Louis XIV–N50° 37.74 E03° 04.47.*

Figure 9. This was the building where Lamy performed his thallium research. It was originally the Lycée [high school] Faidherbe, before Napoleon III founded the Université de Lille at this site in 1854. The physics department, where Lamy did his work, was on the premier étage (second floor).

Figure 10. Carnot College now occupies the original site of the Université de Lille where Lamy performed his work on thallium. The monument in the foreground is in memory of Louis Pasteur; the plaque on the disk rim reads [translated]—"Tribute to Louis Pasteur, founded here the science of microbiology. Lille 1857." In Lille Pasteur solved the problem of ruinous lactic acid production at a sugar beet factory by postulating bacteria as the source of the problem.

in Stockholm collections. He identified eucairite (AgCuSe) and berzelianite (Cu_2Se) but also found other unidentified minerals containing up to 19 percent of thallium! Some of these specimens could be traced back to collections of Carl Gustaf Mosander (1797–1858), a student of Berzelius and the discoverer of the elements lanthanum, "didymium," erbium, and terbium.[1h] Nordenskiöld isolated and characterized crookesite,[14] describing it as (Cu,Ag,Tl)Se (now known to be $Cu_7(Tl,Ag)Se_4$).[15] In his original article[14a] Nordenskiöld muses that the "keen-eyed and alert" Berzelius and Mosander surely observed the vivid green flame color of thallium in their blowpipe studies.[1a] These Swedish masters, he concluded, apparently mistook the green flame of thallium for that of omnipresent copper, which can appear emerald green to azure blue.[14a]

Priority of discovery of thallium. Most texts credit both Crookes and Lamy as co-discoverers of thallium. The French think they have the better case[2a]—Lamy was able to produce large ingots of the new element, thus recognizing it as a metal. Lamy was also the first to appreciate the extreme toxic nature of thallium. But Crookes seized on Nordenskiöld's new mineral named in his honor.[14b] Although in Crookes' *Chemical News* the Swede explained he chose "crookesite" after the discoverer of the metal,[14b] in his original article[14a] he specifically credited Crookes and Lamy as independent discoverers, but he honored Crookes who had "observed it first."[14a] At last, Crookes thought, this clinched it: He really was "the first Englishman since Davy to have identified a new chemical element"![2]

A historical lesson of this "Rediscovery" episode might be: if you want to be recognized as the discoverer of an element, not only must you *see* it first, but you must *publish* it first, but most importantly—just as in the French episode with Urbain and lutetium[1m]—you must *name* it first. There have been some 50 different thallium minerals discovered—but none has been named "lamyite."[15]

The legacy of Crookes and Lamy. The lengthy (11-page) obituary[16] of Crookes was written by William A. Tilden (1842–1926), noted biographer and researcher in terpene chemistry, and friend of the deceased. Tilden lauds Crookes' success story as he worked from humble beginnings to great achievements including editorship of *Chemical News*; many inventions and scientific discoveries, including his further spectroscopic verification of helium; even his dabblings in spiritualism where he intellectually investigated the psychical force, requiring proof while the "spiritualists" only needed faith (Crookes was president of the Society for Psychical Research); service to his community as he sought ways to solve such problems as sewerage and sanitation deficiencies, "The Wheat Problem" (nitrogen fertilizers), and the "Cattle Plague" (phenol as an antiseptic); and his many honors and awards.

Lamy's eulogy was delivered by his mentor Louis Pasteur in Paris, archived in "four typewritten pages,"[8] who described Lamy as a "simple man, upright, fearing God and shunning evil." With major accomplishments in chemistry (principally thallium), Lamy was praised as a scientist of "the first order," eventually becoming président de la Société française de chimie in 1873. Pasteur emphasized Lamy's triple

Figure 11. Appearance of the Loos factory site today. The sign on the headquarters building is expanded in the lower left inset. "Chemical products of Loos. Factory Frederic Kuhlmann/Chemilyl." The thallium-bearing pyrite used in sulfuric acid manufacture here in the 1860s was obtained from Le Rocheux Mine, Oneux, Belgium (200 km east; N50° 32.43 E05° 49.83).

sense of "honor, discipline, and duty," carrying on the tradition of his father who was among those who "carried the flag gloriously in all the capitals in Europe during the Napoleonic campaigns." (Note 2)

Next episode: In the following *HEXAGON*, we will travel to the Harz Mountains to explore the source of Crookes' thallium.

Acknowledgments.

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Notes.

Note 1. The Crookes tube was a low-pressure discharge tube which emanated "cathode rays" (electrons). The radiometer is an evacuated bulb enclosing a spindle with vanes, blackened and silvered on opposite sides, which rotates when exposed to light; this device is common in educational institutions. The spinthariscope was a device for observing individual scintillations from a radioactive alpha source (Ra or Po) on a phosphorescent zinc sulfide sceen—old-timers may recall the "Atomic Bomb Ring," which could be ordered in the late 1940s by mailing in 15¢ and the top of a KIX breakfast cereal boxtop.

Note 2. The father Désiré Lamy was wounded and captured in the Moscow campaign of 1812. After he was released he participated in the 1815 Waterloo defeat and then returned home to have five sons. The eldest son (Claude-Auguste) turned to science and the other four served in the military; one was killed in 1863 during the Maximilian Affair during the Battle of Puebla, Mexico (which is commemorated today in Mexico as "Cinco de Mayo").

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