

Rediscovery of the Elements

The Harz Mountains and Göttingen



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The Harz Mountains. In central Germany lie the Harz Mountains, a natural preserve and a National Park (Figure 1). This region, which lies astride of the boundary separating West and East Germany during 1949–1990, was a “no-man’s land” which served as a protected area allowing natural plants and wildlife to flourish. Today one may gain an appreciation for the beauty and expanse of the region by traveling the narrow-gauge Brockenbahn (train) from Wernigerode (the birthplace of Klaproth, the discoverer of uranium;^{1f}) to the summit of Brocken, the highest peak of the Harz (1141 m) and the mythical home of witches in Goethe’s *Faust*.

For over a millennium mining was widespread in the Harz; this region produced silver, iron, lead, and zinc, and small amounts of copper and gold. Cadmium was a by-product of the zinc industry in Goslar and was discovered by Friedrich Stromeyer (1776–1835) at the University of Göttingen, 50 kilometers to the southwest. Tilkerode in the southeastern part of the Harz provided the ores in which William Crookes (1832–1919) discovered thallium in London in 1861.^{1h}

The Discovery of Cadmium. The Goslar region has historically been the center of the



Figure 1. The Harz Mountains, stretching 100 kilometers from Eisleben (the birthplace of Martin Luther) through Goslar (UNESCO World Heritage site for its historic mines), is located 80 kilometers southeast of Hannover, Germany. The two elements discovered in this region were cadmium and thallium.

RIGHT: Figure 2. An ancient woodcut of the Oker manufacturing region during its productive period of the 1800s (courtesy, Museum der Göttinger Chemie). Oker is a suburb of Goslar which was active in the processing of silver, copper, lead, and zinc.



mining industry in the Harz Mountains (Figures 2, 3). The Rammelsberg Museum in Goslar (Figure 4) is an expansive network of buildings holding elaborate exhibits of mining equipment, uniforms and tools, and scientific displays of the metals mined in the area.

Zinc has played an important part in the history of Rammelsberg region. A special exhibit in the Rammelsberg Museum describes the first published description of purified zinc (Note 1) at Goslar by George Engelhard von Löhneys (1552–1625)² (Figure 5). When the smelters of silver and lead were operating, volatile zinc would sublime from the furnaces and condense in the gaps between the slate stones. This metal, described as “white as tin but harder,” could be scraped from the walls but was not commercially valued because it was too brittle. However, it was soon discovered that when mixed with copper it made superior brass to the previous recipe from tin and calamine (zinc silicates and oxides).

Another exhibit in the Rammelsberger Museum provides a spectacular example of goslarite (Figure 6). This mineral specimen has the typical appearance of cave formations, but instead of being composed of calcium carbonate it was formed by the leaching of oxidized zinc sulfides in the geological layers above to form zinc sulfate stalactites and stalagmites.

The zinc ores of the Rammelsberg region are particularly rich in cadmium, the element immediately below zinc in the Periodic Table. A special exhibit in the Rammelsberg Museum shows various hues of cadmium formulations used in dyes and paints, including the famous yellows of Vincent van Gogh’s (1853–1890) paintings (Figure 7).

Cadmium was discovered in 1817 by Friedrich Stromeyer (1776–1835) at the University of Göttingen.³ Stromeyer was not only a professor but also General Inspector of Pharmacies (Apotheken) throughout the Kingdom of Hannover (stretching from



Figure 3. The present appearance of Oker. This manufacturing region lies at the foot of the Harz Mountains (far distance, to the right), the rich source of many metals and minerals. This northwestern portion of the Harz is sometimes called the “Classic Geological Square Mile” because of its continuous sequence of tilted geologic layers from the Paleozoic era to the present, 400 million years.

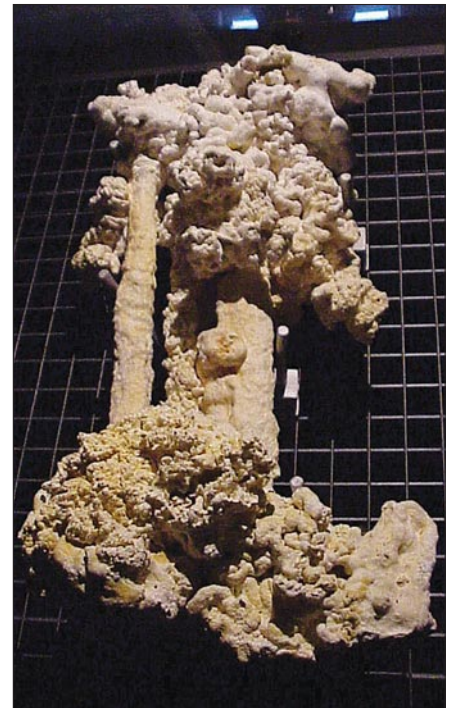


Figure 6. Found in a nearby mine, this is a magnificent example of “goslarite” ($ZnSO_4 \cdot 7H_2O$), also known as zinc vitriol. This 62x28-cm stalactite formation was found in the “Vitriolkammer” [“vitriol room”], a chamber dripping with sulfate solutions. It is believed that the “prongs” of zinc minerals (and/or sublimed zinc) gave rise to its modern name (Ger. antler’s prong = Zinke).



Figure 4. The Rammelsberg Mining Museum in Goslar (N51° 53.39 E10° 25.09) has a fascinating display of equipment and exhibits describing the 1000-year history of the Goslar-Oker area; tours are also offered through the historic mines.

BELOW: Figure 5. In the Rammelsberg Museum a wall-size reproduction of an excerpt from Löhneys’s 1617 treatise² refers to “Zinck or Conterfeht” (see arrows) collected by the accidental sublimation of volatile metallic zinc onto the walls of the smelter. The name “Conterfeht” [counterfeit] was used because when zinc was blended with copper in the correct proportions, the color changed to a golden hue. Alchemists sought the Rammelsberg zinc, which gave them much hope — albeit false — for easy riches.

Göttingen to Hamburg, see Figure 1). Upon reports that zinc medicines were turning yellow upon heating, he initiated a study of medications prepared at Salzgitter-Bad (15 kilometers north of Goslar) which were believed to be the source of the problem. This company preparing the zinc preparations was originally known as Gesellschaft Saline Liebenhalle,⁴ (Figures 8,9) named for the salt mined for centuries in the village. During the 1800s the company’s name was changed to Johann Ludwig von Unger’s Erban & Company, a Chemischen Fabrik which produced magnesia, tartaric acid, sulfur, zinc and ammonia compounds, oils and extracts, and other pharmaceutical products.⁵

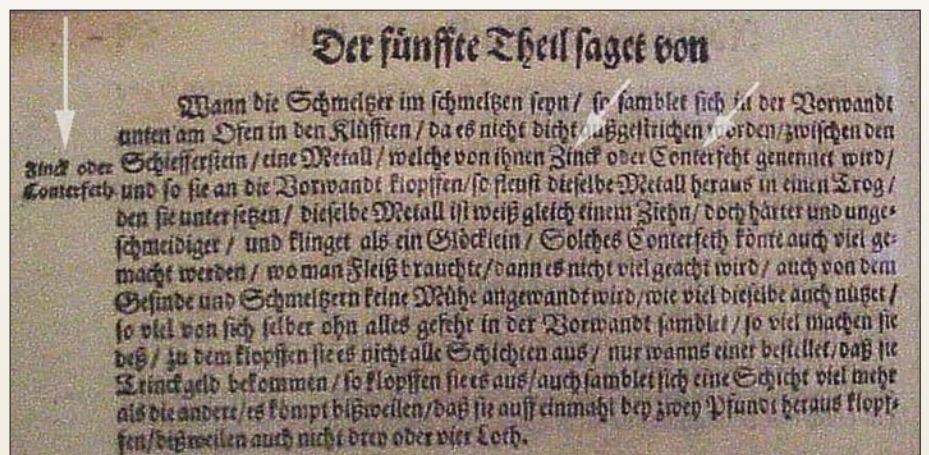




Figure 7. In the Rammelsberg Museum is this display of mineral pigments, including the yellows, oranges, and reds of cadmium/zinc sulfides and selenides, used in ceramics by 1830 and in paints by the 1840s.

Originally the undesired yellow discoloration of zinc preparations was thought to be due to iron impurities or arsenic, but Stromeyer was able to separate a yellow sulfide by reaction of solutions of zinc salts with hydrogen sulfide. After extraction with aqueous ammonium carbonate to remove zinc sulfide, he was able to isolate the cadmium, from which he obtained a small ingot by reaction with charcoal. He verified that zinc preparations from Silesia (now southwestern Poland) were similarly contaminated. He named the new element cadmium from the Latin word for zinc ores (cadmia). Stromeyer conducted his analytical work at a building which is now the Department of Physics (Figure 10).

The contributions that Stromeyer made to chemical laboratory instruction are not well known. Despite widespread belief that Justus von Liebig (1803–1873) erected “the first laboratory ever . . . for the teaching of chemistry”⁶ at Giessen in 1824 which “may be regarded as the prototype of all teaching laboratories,”⁷ Stromeyer actually developed the first teaching laboratory in 1806 at Göttingen.⁸ His most celebrated student was Robert Wilhelm Bunsen (1811–1899), the discoverer of rubidium and cesium.¹⁶ Bunsen was a native of Göttingen and the home of his family is marked in the city with a plaque (N51° 32.10 E09° 55.76, Untermasch-Strasse).

Immediately to the east of the historic chemistry building at Wöhlerplatz is a statue of Friedrich Wöhler (1800–1882) (Figure 11), who moved to this university in 1836 to replace the deceased Stromeyer. *The HEXAGON*^{1b} readers may recall that after a postdoctoral stint with Berzelius in Stockholm during 1823–1824, Wöhler accepted a post at the Gewerbeschule



Figure 8. This painting was found in the town public library (Stadtbibliothek; 11 Marktplatz; N52° 02.81 E10° 22.33) of Salzgitter-Bad. Dating from 1905, this painting shows the east panorama of the village, and on the hilltop beyond, the chemical industrial complex of Johann Ludwig von Unger's Erban & Company which produced zinc preparations with the cadmium impurities detected by Stromeyer (see next figure). The town is named for the salt mined in the center of the village (beside the St. Mariae-Jakobi Church, the tallest structure in the figure). The pharmacy which sold these zinc medications was in Wagenfeld in Hildesheim, 25 km to the west.



Figure 9. Today the Chemischen Fabrik of Unger's Erban & Company is gone and is replaced by a “Wohnstift”—an old folks’ home on Kurpark am Greif (“Healthpark of the Griffin”) (N52° 02.38 E10° 22.65).

in Berlin in 1825 where he prepared metallic aluminum, yttrium, and beryllium, verified del Río's discovery of vanadium in Mexico¹⁹, and most notably disproved the “vital force” in organic chemical theory (Figure 12). At the new campus of the University of Göttingen (4 Tammannstrasse, N51 33.49 E9 56.90), an attractive museum of chemistry (Museum der Göttinger Chemie) boasts historical displays of Wöhler, Stromeyer, Otto Wallach, Walther Nernst, and others. Earlier chemical preparations from Wöhler's research with Berzelius are also included, e.g., the original metallic selenium preparation (Figure 13).

Tilkerode, the original source of thallium. In the previous issue of *The HEXAGON*,^{1b} the discovery of thallium was described. William Crookes wrote “In the year 1850 Professor Hofmann placed at my disposal upwards of 10 lbs of the seleniferous deposit from the sulfuric acid manufactory at Tilkerode in the Hartz [sic] Mountains for the purpose of extracting from it the selenium . . .”⁹ As Crookes was pursuing a spectral analysis of the residue in 1861, “suddenly a bright green line flashed into view . . . which was caused by the presence of a new element . . .”⁹ which he called “thallium” meaning “green twig.”¹⁰



Figure 10. This “Fachwerkhau” (Ger. = medieval half-timbered building) served as the Chemical Institute since the latter part of the 18th century, and recently was transferred to the Physics Department of the University of Göttingen (N51° 31.82 E09° 56.19). This is where Stromeyer discovered cadmium and developed the first chemistry laboratory program.



Figure 11. The statue of Friedrich Wöhler at Wöhlerplatz (N51° 31.81 E09° 56.17), stands next to the old Chemical Institute (see next figure).



Figure 12. At the base of the statue of Wöhler is the chemical structure of urea inlaid in brick. Wöhler stated, “I can make urea without the use of kidneys, or either man or dog.” He prepared urea $OC(NH_2)_2$ by heating its inorganic isomer, ammonium isocyanate, NH_4CNO . Wöhler’s famous organic laboratory was located immediately to the east (razed in 1977 and replaced by apartment buildings).

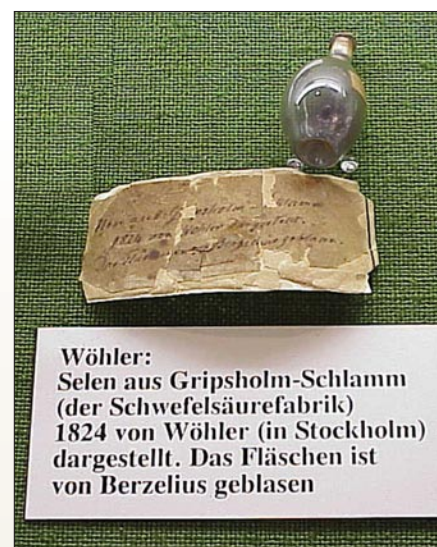


Figure 13. This original sample of selenium in the Museum der Göttinger Chemie (4 Tammannstrasse; N51° 33.49 E09° 56.90) dates from Wöhler’s days with Berzelius. The label reads, “Wöhler: selenium from the Gripsholmsludge (of the sulfuric acid factory) prepared in 1824 by Wöhler (in Stockholm). The glass flask was blown by Berzelius.” Even though Berzelius gets official credit for the discovery of selenium, it was his postdoc Wöhler who did the work.

Figure 14. These rolling hills are the Tilkerode area (N51° 37.26 E11° 18.34), the historic site of silver and lead mining, and the source of the thallium discovered by Crookes in 1861. Today the fields are lush with peas and rye (“Erbsen und Roggen”). The “-rode” suffix is common in the Harz, meaning “forest clearing” in the local dialect.



The German literature verifies that thallium was discovered by Crookes in a Harzer Bleikammerschlamm (lead-chamber sludge in the Harz)¹¹—just as Berzelius had discovered selenium in 1817 (Figure 13) in the “golden-brown mud” deposited in a lead chamber in his sulfuric acid manufactory at Gripsholm, Sweden,¹⁶ a residue from the roasted iron pyrites from Falun (175 kilometers northwest).¹²

It is true that selenium-rich ores abound in Tilkerode (Figure 14) and were certainly the source of Crookes’ “seleniferous deposit” (Figure 15), but a visit by the authors to Tilkerode proved that a sulfuric acid manufactory (German: “Vitriolfabrik” or “Schwefelsäurefabrik”) never existed there—nor did smelters of any kind.¹³ The only sulfuric acid manufactories that existed in the Harz area in the mid-1800s were in Oker (65 kilometers northwest of Tilkerode), first appearing in 1846 (Figure 16).^{11,13a} Local scholars agree^{13a} that Oker is the clear choice for the site that produced the seleniferous sludge that Crookes obtained from Hofmann. (Note 2)

Hofmann, the provider of the “seleniferous deposit.”

August Wilhelm von Hofmann (1818–1892) had studied under Justus von Liebig at the University of Giessen. Hofmann, the first Director of the newly formed Royal College of Chemistry in London¹⁴ (the school Crookes attended), remained at that post during 1845–1864 before returning to Germany. Hofmann is probably best remembered for his work on anilines and dyes, derived from coal tar, originally a waste liquid product derived from the destructive distillation of coal. His work with amines led to the eponymous Hofmann rearrangement and Hofmann elimination. Hofmann promoted the modern systematic names for the alkanes¹⁵ and coined “aromatic” for coal tar derivatives.¹⁶ He proposed the term “quantivalence” (instead of “atomicity”) which has led to our modern term “valence.”¹⁷ Before returning to Germany, he delivered a famous lecture at the Royal Institution “On the Combining Powers of Atoms” (April 7, 1865), where he used two-dimensional ball-and-stick molecular models constructed from “croquet balls” to explain organic structures and multivalent atoms—even proposing a model for unsaturation in olefins and acetylene. The color scheme Hofmann chose is the same as that used today: C = black, H = yellow, O = “fiery” red, N = “dye” blue, Cl = green.¹⁸ (Three-dimensional models were developed later with the 1874 concepts of the tetrahedral carbon of van’t Hoff and Le Bel).¹⁹

The final tantalizing question remains, how and when did Hofmann procure the Tilkerode

Figure 15. The Eskeborner-Goldschacht mine complex (N51° 38.01 E11° 19.13 was the source of the selenium-rich ores which held Crookes’ thallium. The mines are now all filled in and taken over by forest. The sign reads: “Former mine entrance. Old Eskeborner gallery [horizontal tunnel]. Began in 1784, total length ca. 1300 meters. Distance to Goldschacht ca. 500 meters, shut down 1862. Eponymous source for the mineral Eskebornite” (CuFeSe₂). The sign is one of many erected in Tilkerode by the Tourist Museum at Wippra (6 kilometers south).



Figure 16. These historic smelting ladles sit outside the Harz Metals in Oker (6 Hüttenstrasse; N51° 54.05 E10° 29.09), the site of an old sulfuric acid works which probably furnished the Crookes’ seleniferous sludge. This manufactory, dating from 1527, was originally the Frau-Marien-Saigenhütte, later (1968) the Hütterwer Harz, then the modern name Harz-Metall GmbH in 2001. The long history of this smelter site includes the production of lead, copper, and silver, and then the first major sulfuric acid manufactory in the Harz (1846).

deposit? As Director of the Royal College of Chemistry, Hofmann traveled frequently to the Continent,²⁰ and “with amazing energy and an astonishing range of acquaintances”²¹ he frequently associated with “agricultural-landowners and mine operators; apothecaries, druggists, and physicians; industrialists and businessmen”²²—all affording much opportunity for his acquisition of the sample. Specifically, he maintained close contact with the sulfuric acid industry,¹⁵ writing a series of review articles on the subject, mentioning Oker as a primary industrial site.²³ Unfortunately, it is unknown

how Hofmann laid his hands on this sample of nondescript gray soot (Figure 17), and it appears that we will never know the complete story!

Next issue: Crookes uses spectral analysis to confirm the discovery of terrestrial helium. ☉

Acknowledgments.

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Figure 17. This display in the Science Museum of South Kensington, London, includes (1) "Seleniferous deposit from the sulfuric acid chambers of Tilkerode in which Crookes first noticed the existence of a new element"; (2) "Residue left on distilling crude selenium from the deposit and which was shown to contain thallium." Tilkerode never had a sulfuric acid manufactory; hence the seleniferous ore was processed elsewhere, most certainly at Oker in the Harz region.

Dr. Günther Beer, Director of the Chemistry Museum. The two furnished much information (both published and unpublished) regarding Stromeyer, Wöhler, and the history of cadmium. The authors are indebted to Dr. Dieter Klaus, Museum Schloss Bernburg, Germany; Andreas Karcher, Verwalter der Tilkerode (curator of Tilkerode Area; erected park signs, e.g., Figure 15); and Heinz Mentz ("best historian of the Harzgerode/Silberhütte region" and author of *Harzgerode in alten Ansichten*, 1992, Europäische Bibliothek) for furnishing mine and Vitriolwerk information for the Harz region.

Notes

Note 1. The first reference to "zinck" specifically as a metal was in 1556 by Agricola (1494–1555)²⁴ and in a (ca. 1570) publication questionably attributed to Paracelsus (1493–1541).^{1c,25} Although Andreas Sigismund Marggraf (1709–1782) is credited in 1746 with the first laboratory preparation of metallic zinc,^{1d,26} descriptions of metallic zinc in the East and Europe appeared previously. Perhaps the first European reference to zinc was by Marco Polo²⁷ during his journey through Persia (1272) where it was called "tutty" or "Tutia."

Note 2. Actually, there had been a Vitriolfabrik even closer to Tilkerode—but

much earlier. Silver and lead ores from Tilkerode were transported to the smelters of Mägdesprung and its suburb Silberhütte as early as 1693 (15 kilometers to the west; see Figure 1).^{13b} A minor Vitriolfabrik was established at Silberhütte, perhaps as early as the late 1700s,²⁸ but it ceased production in 1832—long before Hofmann, originally studying law and languages at the University of Giessen in 1836, was attracted to chemistry and won his doctorate with Liebig in 1841.^{15,22} By 1845 the rich selenium content of the Tilkerode ores had been established by the blowpipe method of Berzelius,²⁹ giving one reason to collect lead-chamber residues to procure quantities of this element. (A major sulfuric acid factory was again started up at Silberhütte in 1885;^{13b} today this community is well-known for its fireworks factory, Pyrotechnik Silberhütte).

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