Rediscovery of the Elements

Klaproth

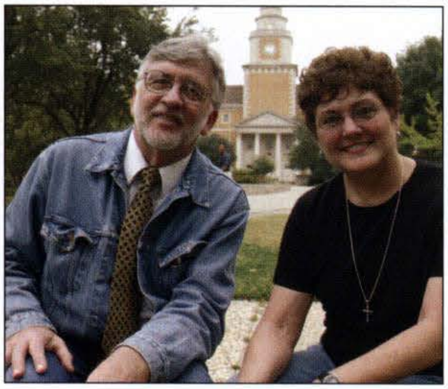

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Figure 1. Sites associated with Martin Heinrich Klaproth are concentrated in northeastern Germany: his birthplace in Wernigerode, his career in Berlin, and Johanngeorgenstadt, the source of the uranium he discovered. "Rode" is a common suffix in the Harz region, meaning "clearing in the woods" in old German.

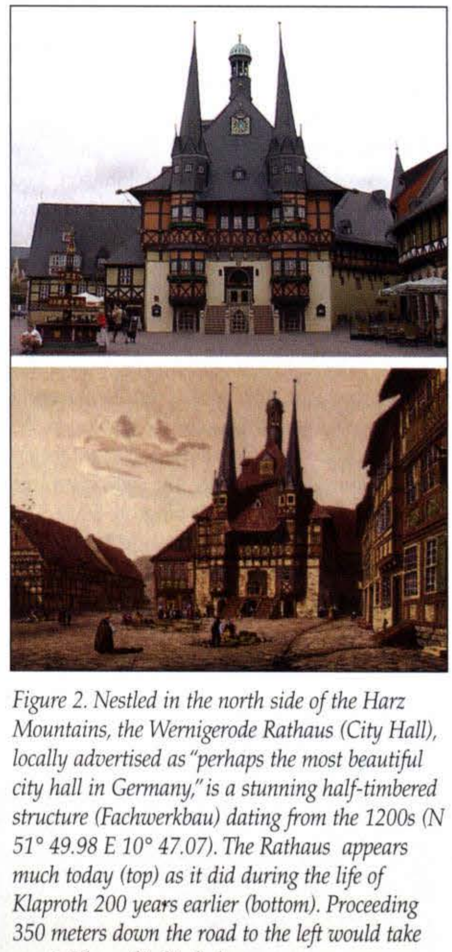

Figure 2. Nestled in the north side of the Harz Mountains, the Wernigerode Rathaus (City Hall), locally advertised as "perhaps the most beautiful city hall in Germany," is a stunning half-timbered structure (Fachwerkbau) dating from the 1200s (N 51° 49.98 E 10° 47.07). The Rathaus appears much today (top) as it did during the life of Klaproth 200 years earlier (bottom). Proceeding 350 meters down the road to the left would take one to Klaproth's birthplace.

Klaproth. . . entirely altered the face of mineralogy. When he began his labours, chemists were not acquainted with the true composition of a single mineral.[1b]

"The Creator of the Art."[1b] Martin Heinrich Klaproth (1743–1817), whose genius flourished as Lavoisier's New Chemistry was replacing the phlogiston theory of Stahl, was recognized as the best analytical chemist of his time (Note 1). He systematized analytical chemistry and independently invented gravimetric analysis. Before Klaproth, analyses could be slipshod and minor components were often missed. Chemists would gloss over calculated surpluses or losses in analyses, ascribing such inconsistencies as "errors in laboratory procedure." But Klaproth, with his neatness and precision, reported analyses exactly as he found them.

With his alertness to detail, he realized that laboratory vessels themselves could contribute to reported residuals, and he became careful in his choice of earthenware, glass, graphite, silver, iron, or platinum. He realized that "unreported" mass was often due to waters of hydration. He initiated the method of using barium carbonate in alkali treatments, so that he could detect the lighter alkali metals, and thus was able to discover potassium and sodium in feldspars.

Figure 3. This is the birthplace of Klaproth, a tiny house on Liebfrauenkirchhof 6 ("Church of our Lady Courtyard," N 51° 49.92 E 10° 47.34). For inscription in the plaque, see the next figure.

His growing understanding of the composition of minerals led to the discovery of many elements. He is perhaps best known for his discoveries in 1789 of uranium and zirconium, but he was also responsible for the characterization of many other newly found elements. However, because of his modesty and generosity of character,[1b] he gave credit for original discovery to others even when their work was cruder and often tentative.[1b] In 1795, he discovered titanium (and named it) in red schorl (TiO_2) from Eastern Europe, but when he analyzed menachanite (ilmenite, $FeTiO_3$) from Cornwall,

*Figure 4. "Birthplace of the famous chemist Martin Heinrich Klaproth born 1 December 1743, died in Berlin 1 Januar y 1817." The customary method of recording vital statistics in historic Germany was to designate birth with a star *, death with a cross †, and marriage with a lemniscate ∞.*

Figure 5. The Klaproth showcase with authentic specimens from which he made his famous elemental and other mineralogical discoveries. In the mineralogical hall are also comprehensive exhibits on Humboldt, Wöhler, Heinrich and Gustav Rose, Mitscherlich, and others.

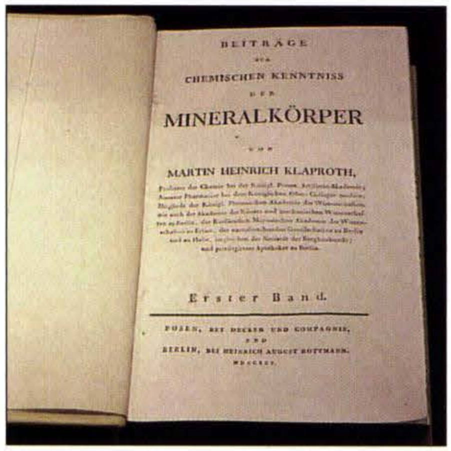

Figure 6. Here is the famous work by Klaproth, "Contributions to the chemical knowledge of mineral bodies,[9] delivered in six volumes from his life's work 1795–1815. At the bottom of the title page of this tome is listed "Erster Band" ("First Volume"). In these works, Klaproth essentially defined the systematic composition of minerals, and includes, for example, the analysis of gadolinite and confirmation of yttrium described in the previous "Rediscovery" article on Gadolin.[2j]

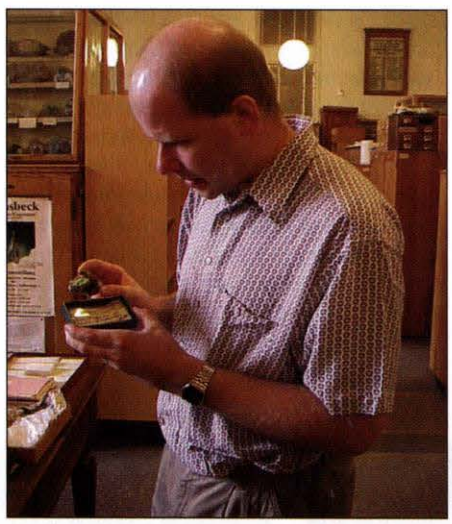

Figure 7. Dr. Ralf-Thomas Schmitt, Professor at the Institut für Mineralogie, Museum für Naturkunde, displays archival mineralogical specimens of Klaproth. There are over 300 samples dating from Klaproth's work, some of which with original labels. Dr. Schmitt is holding a sample of torbernite (copper uranyl phosphate, $Cu(UO_2)_2(PO_4)_2\ 11\ H_2O$),[10] the original specimen from which Klaproth discovered uranium. The labels are original, in Klaproth's own handwriting. Klaproth called torbernite "Grüner Uranglimmer" = "green uranium mica" (Note 5).

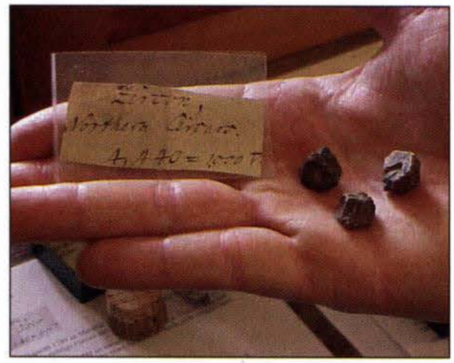

Figure 8. These are the original zircons ($ZrSiO_4$) that Klaproth analyzed to determine the formula of the mineral in 1802. These are from Northern Circars (Andhra Pradesh, India), but the precise location of the zircon mine is not known.

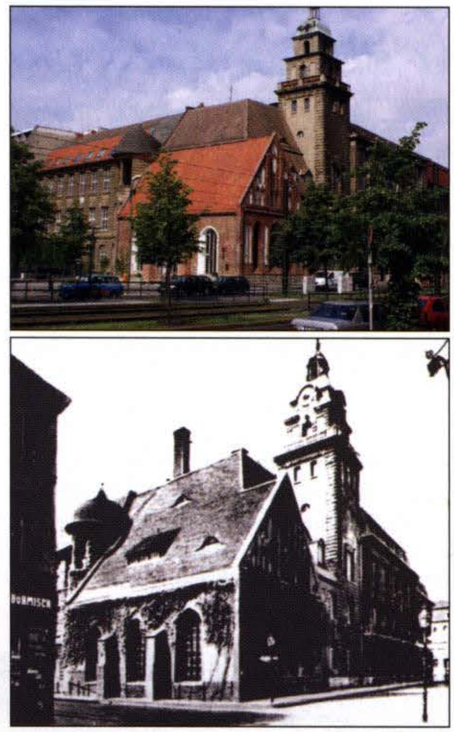

Figure 9. Heilge Geist Kirche (Holy Ghost Church), across the street from the "Apothecary of the White Swan." The church is now part of Humboldt-University, located at Spandauer Straße 1 (N 52° 31.26 E 13° 24.19). The current appearance of the church (top) is remarkably similar to that in the late 1800s (bottom), when the apothecary still existed. On the original site of the apothecary, there now exists modern multi-storied construction, including a University bookstore. Lower photograph, courtesy, Berlin Catholic Archives.

which had been investigated by William Gregor[2b] in 1791, he realized Gregor's new element was the same as his own titanium, and he gave Gregor the credit for the discovery. In 1793, he distinguished strontium from barium, but when he found Charles Hope of Edinburgh had been independently investigating strontianite ($SrCO_3$) from Western Scotland,[2c] he allowed Great Britain to claim the discovery. In 1798, he investigated the gold ores of Transylvania and confirmed the discovery of tellurium by Müller von Reichenstein[2a] and helped to resolve the priority of dispute of tellurium between Müller and the Hungarian chemist Paul Kitaibel.[3] In 1803, he independently discovered cerium in the mineral cerite but graciously acceded recognition to Berzelius and Hisinger.[2i] Because his reports were so highly regarded, his confirmations of Vauquelin's discovery of chromium and beryl[2e, 4a] and of Gadolin and Ekeberg's announcement of yttrium[2j] were welcome corroborations—by some he is given credit for the co-discovery of chromium and beryllium.[4b]

When Lavoisier proposed his anti-phlogiston theory in Paris[2f, 5] it was natural for the German chemical community to close ranks and defend the phlogiston theory of Georg Stahl (professor at Halle, Germany[2f]), claiming Lavoisier's new theory was "just another French speculation."[6a] Klaproth volunteered to repeat

Figure 10. Hidden beside the Nikolaikirche on the narrow Probststraße is the historic site of Apothek zum Bären ("Apothecary of the Bear"), where both Marggraf and Klaproth worked. While Marggraf was at this apothecary, he isolated zinc from calamine. Through the arcade is Spandauer Straße; above and to the right of the passageway is the Klaproth plaque. Behind the viewer are numerous souvenir shops, some specializing in Berliner Bären (giant Teddy bears).

key experiments in an attempt either to refute or to validate Lavoisier's views. With Klaproth's reputation as an unbiased authority, the Berlin Academy had full confidence in his work. When Klaproth, in 1792, successfully duplicated Lavoisier's experiments[6b] (Note 2), the Berlin Academy "became antiphlogistians."[1a]

Revisiting Klaproth's Career. Klaproth's life was spent mostly in northeastern Germany (Figure 1). Klaproth's birthplace in Wernigerode (Figure 2) still stands (Figures 3, 4). In Berlin, where his famous work was carried out, his legacy is honored at the Museum für Naturkunde (Museum for Natural History). This museum (Invalidenstraße 43, N 52° 31.79 E 13° 22.76), perhaps best celebrated for the most nearly complete specimen of Archeopteryx, also houses an astonishingly rich mineral collection tracing the history of chemistry in Germany. This is the same museum that houses the famous vanadinite specimen transported by Alexander Humboldt from Mexico to Europe.[2d] In the spacious mineralogical hall is a superb display on Klaproth, which includes samples of minerals from original sites (Figure 5) as well as his famous work *Beiträge Zur Kentniss der Mineralkörper* (Figure 6). Klaproth's mineralogical archives are also carefully preserved, which include, for example, the exact specimens which he studied in his discoveries of uranium (Figure 7) and zirconium (Figure 8).

The life of an apothecary in 18th century Germany typically included 5–6 years as an apprentice (Lehrling) and then 6–8 years as a journeyman (Geselle).[7] After 12 years as Lehrling and Geselle in apothecaries in Quedlinburg, Hannover, Berlin, and Danzig, Klaproth, in 1771, joined Valentin Rose, owner of the Apotheke zum weißen Schwan (Apothecary of the White Swan) in Old Berlin. Unfortunately, Rose died within the year, but Klaproth, with his legendary kindness, took on the responsibility of raising the children. One of these children (Valentine Rose the Younger) grew to have two famous sons of his own (Heinrich and Gustav Rose), who worked in the Berlin Academy and whose accomplishments are displayed in the Natural History Museum. The White Swan apothecary is now gone, but the identifying landmark across the street still exists, the Heilige Geist Kirche (Holy Ghost Church) (Figure 9).

In 1780, Klaproth moved into his own apothecary "Apotheke zum Bären" (Apothecary of the Bear), one-half kilometer southeast, once owned by Marggraf (discoverer of "aluminum earth"[2h]). The Apotheke zum Bären structure no longer exists; the site can be found nestled beside the Nikolaikirche (St. Nicholas Church) on Probststraße, now a pleasant and relaxing part of town with restaurants and souvenir shops (Figures 10, 11). At this pharmacy, Klaproth discovered uranium and zirconium. The precise origin of Klaproth's zircons in India

Figure 11. "Berlin memorial plaques. At this site, in his apothecary 'Zum Bären,' Martin Heinrich Klaproth (Jan 12, 1743–Jan 1, 1817) lived and worked from 1780 until 1800. Member of the Academy of Sciences in Berlin from 1788 and first Professor of Chemistry in the Berlin University, which was founded in 1810. In this apothecary laboratory, he discovered many chemical elements, among which were uranium in 1789. In 1799, he produced the first Prussian physician's manual."

Figure 12. Two hundred kilometers south of Berlin is Johanngeorgenstadt, the source of Klaproth's uranium ore. A docent of the community museum explains how the old mine was exploited by the Soviet Union, who shipped tons of uranium ore back to Russia during the days of the DDR (Communist East Germany). Portions of the bricked-up Georg Wagsfort mine can be seen to the left (N 50° 25.98 E 12° 43.77). A city museum 1.5 km up the hill (N 50° 25.84 E 12° 42.58) describes mining practices of the past. One-half kilometer to the south is the Czech border, where a busy "border town" offers souvenirs for German tourists.

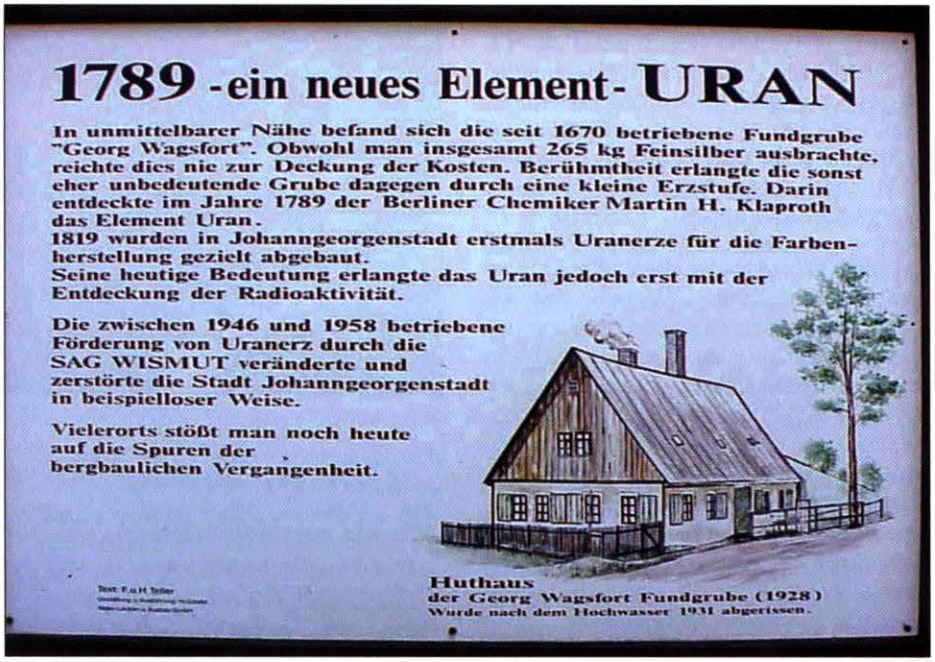

Figure 13. The plaque beside the mine. "1789—A New Element—Uranium. In the immediate vicinity is the Georg Wagsfort Mine, which started operating in 1670. Although a total of 265 kilograms of fine silver was extracted, this is never enough to cover the costs. Fame had to wait until a small amount of ore was procured in which the Berlin chemist Martin Heinrich Klaproth discovered uranium in 1789. In 1819 in Johanngeorgenstadt, the first uranium ore was processed for the color [yellow used in glasses and porcelain]. But the major significance of uranium became apparent with the discovery of radioactivity. Between 1946 and 1958, uranium production was carried out by SAG WISMUT [Sowjetisch-Deutsche Aktiengesellschaft Wismut, Soviet-German Bismuth Corporation], which altered and exploited the Johanngeorgenstadt community in many ways. [A great deal of the old mining town had to be torn down 1953–1960 because of the mining damage during Soviet occupation]. Fortunately, there is still much left here to remember of the mining past." Under the drawing of the house: "Mining house of Georg Wagsfort Mine, 1928. Destroyed by the flood of 1931."

are not clear, but that of uranium is known to be the Georg Wagsfurt Mine at Johanngeorgenstadt, which can be visited today (Figures 12, 13).

The apothecaries of the 18th century were an integral part of community life (Figure 14), numbering about twenty in Berlin. There were various classes of apothecaries across Europe—ranging from simple providers of published recipes, to institutions where advanced chemical investigations were provided alongside the pharmaceutical preparations.[7] Klaproth "stood on the top of an iceberg"[7] and after the passing of Scheele (1742-1786),[2g] Klaproth's apothecary laboratory "became the most productive artisanal site of scientific chemical investigation in all of Europe."[7] With increasing fame, he was invited in 1800 to move to the Akademiehaus near the famous University on Unter den Linden boulevard (Note 3). With the inauguration of the newly founded University of Berlin in 1810, he became its first Professor of Chemistry (Note 4).

Märkisches Museum. For a historian of Berlin, a visit to the Märkischen Museum (Wallstraße and Am Köllnischen Park, N 52° 30.84 E 13° 24.88) is recommended, where a large collection of exhibits and paintings eloquently describes Old Berlin and its environs. Of particular interest to the chemical historian is the expansive wooden city model occupying the center of a room and including every building and house as accurately as can be rendered from available records from the 1750 time period (Figure 15). One can compare and match locations in the modern city with Old Berlin and its developing suburbs, Cölln, Friedrichswerder, Friedrichsstadt, and Dorotheenstadt. The three main areas of Klaproth can be identified in the city model—Heilige Geist Kirche and Apotheke zum weißen Schwan; Nikolaikirche and Apotheke zum Bären; and the Akademiehaus.

The legacy of Klaproth. Thomas Thomson, the contemporary of Klaproth who wrote the History of Chemistry,[1] has given us a rich personal sketch of the famous German chemist: "Among the remarkable traits in his character was his incorruptible regard for everything that he believed to be true, honourable and good; his pure love of science, with no reference whatever to any selfish, ambitious, or avaricious feeling; his rare modesty, undebased by the slightest vainglory or boasting. He was benevolently disposed towards all men, and never did a slighting or contemptuous word respecting any person fall from him. When forced to blame, he did it briefly, and without bitterness, for his blame always applied to actions, not to persons. His friendship was never the result of selfish calculation, but was founded on his opinion of the personal worth of the individual. . . . To all this may be added a true religious feeling. . . of duties of love and charity . . . [shown] by the honourable care which he bestowed upon the education of the children of Valentine Rose. . ."[1b] ○

Acknowledgments.

The authors are indebted to Drs. Vera Enke and Wolfgang Knoblock of the Archiv der Berlin-Grandenburgischen Akademie der Wissenschaften, Jägerstraße 22/23, Berlin for detailed accounts of historical sites associated with Martin Heinrich Klaproth. We are also thankful to Dr. Ralf-Thomas Schmitt, Professor at the Institut für Mineralogie, Museum für Naturkunde, for an extended tour of the mineralogical archives of the Museum and much biographical information about Klaproth.

Notes.

1. A close second was Louis Nicolas Vauquelin (1763–1829) of Paris.[1c,2d] Vauquelin and Klaproth had parallel apothecary careers, each of whom was a pioneer in the art of analytical chemistry, deciphering the composition of substances. Although Vauquelin made numerous analyses of minerals, thereby discovering chromium and beryl, he was foremost an organic pharmacist—he discovered, for example, asparagine in asparagus, and he went on to become director of Faculté de Pharmacie in Paris. Klaproth's chemistry career by contrast was focused on mineralogy, and he eventually became the first Professor of Chemistry at the newly organized University of Berlin.[4a] Thomson[1c] suspected that Klaproth's edge was due to Vauquelin's bad choice of specimens (put in his hand by Haüy, the head of the Paris School of Mines[2e]) and perhaps somewhat inferior apparatus and reagents.

2. Klaproth obtained two samples of mercury calx (HgO), one from Britain whose quality was apparent from its fine crystalline state and its failure to emit white vapor (contaminant) when heated; and the other prepared by Klaproth himself. Klaproth, in the presence of witnesses, quantitatively measured the process when the mercury calx (HgO) was heated. He

Figure 14. This painting in the Märkisches Museum in Berlin portrays an apothecary (probably in the Friedrichstadt suburb) around 1775, when time Klaproth was at the Zum weißen Schwan. Apothecaries would import raw opium, willow bark (source of aspirin), oak-galls (for preparing inks) and other herbs, barks, roots, and seeds for grinding and distilling into prescriptions; but a major part of their profits would often come from tobacco, sugar, and drink (e.g., Branntwein or brandy). In addition, pharmacies would sell soaps, perfumes, grooming ointments, and cosmetics, pigments (white lead paint, black lead powder, etc.). Apothecaries were often places for social gatherings, sometimes with dispensaries for tobacco and drink to be consumed at the site, leading to complaints that too many apothecaries were evolving into "pubs."

found the mercury calx definitely produced oxygen, with the weight of the oxygen gas equal to the weight loss as mercury calx was transformed to metallic mercury.[6b] One would think such a simple experiment would have earlier settled the argument, and indeed this very experiment had previously been performed several times in Germany. However, so many issues had been raised[6b] by the nationalistic Stahlians, such as the possibility of air leaks, water contamination, etc., that it took someone of Klaproth's stature and known scientific integrity to sway the German community. Within a year after Klaproth's experiment, most of the German chemists had adopted the "new chemistry."[1b]

Note 3. The Akademiehaus (N 52° 31.14 E 13° 23.46), built in 1711, was located at Letzte Straße 7 (changed later to Dorotheenstraße 10, now 28), one block north of Unter den Linden. The house originally served principally as a lodging for astronomers from the Sternwarte (Observatory) across the street. The Berlin Academy of Sciences established a laboratory here in 1753, and Marggraf moved in immediately. His research here included, for example, the distinction of potassium from sodium saltpeter (by the color of their flame tests). In 1800, Klaproth moved from Apotheke zum Bären to the Akademiehaus to replace Marggraf, who had passed away earlier (1709–1782). Among the researches Klaproth made here was the co-discovery of cerium in 1803. The building was totally destroyed during World War II and the site is now occupied by a parking garage, and there is no trace of the original building. A beautiful bust of Marggraf adorned the facade of the Akademiehaus (Figure shown in previous "Rediscovery" article[2h]).

Note 4. Other sites associated with Klaproth are: (1) Quedlinburg (25 km east of Wernigerode), where he spent his first apprenticeship 1759–1764 at the apothecary which still stands—the Ratsapotheke at Kornmarkt 8 (N 51° 47.43 E 11° 08.59); (2) the prestigious Apotheke zum Engel (Apothecary of the Angel) in Berlin, then at the "Street of the Moors" (Mohrenstraße 5), where Klaproth spent a short time in 1768 as a journeyman. The pharmacy (long gone) was situated near the present U-Bahn Mohrenstraße station, about 600 meters southeast of the Brandenburg Gate.

Note 5. A misconception in the literature is that Klaproth discovered uranium from pitchblende (uranium oxide). It is true that pitchblende furnished the bulk of material for subsequent studies, but the initial discovery was on the secondary mineral torbernite.[8] "Secondary" minerals, formed by the long-term geological leaching of "primary" intractable minerals such as pitchblende, are more water-soluble and easily handled in the laboratory. Other examples of secondary minerals include malachite and azurite (basic copper carbonates), formed from copper sulfides.

References.

1. T. Thomson, *The History of Chemistry*, **1975**, Vol. II, 1–25, reprint of 1830–1831 edition, H. Colburn and R. Bentley, London. (a) 135-136; (b) 191–211; (c) 211–215.
2. J. L. Marshall and V. R. Marshall, *The HEXAGON of Alpha Chi Sigma*, (a) **2000**, *91(3)*, 43–45; (b) **2001**, *92(1)*, 4–5; (c) **2002**, *93(3)*, 42–47; (d) **2003**, *94(4)*, 60-65; (e) **2004**, *95(2)*, 24–28; (f) **2005**, *96(1)*, 4–7; (g) **2005**, *96(1)*, 8–13; (h) **2006**, *97(2)*, 24–29; (i) **2007**, *98(4)*, 70–76; (j) **2008**, *99(1)*, 8–11.
3. M. E. Weeks, *Discovery of the Elements*, 7th ed., **1968**, *J. Chem. Ed.*, 293–304.
4. J. R. Partington, *A History of Chemistry*, **1961**, Vol. III, Macmillan, London. (a) 551–557; (b) 654–658.
5. A.-L. Lavoisier, *Traité Élémentaire de Chimie*, **1789**, Paris.
6. K. Hufbauer, *The Formation of the German Chemical Community* (1720–1795), **1982**, University of California Press (a) 102; (b) 125–127.

Figure 15. In the Märkisches Museum in Berlin is this 6-meter wooden model of 1750 Berlin, whose streets match closely with a contemporary layout of the city. The view is eastward, looking down the famous Unter den Linden ("2"), which stretches from the Brandenburg Gate ("1") (at this time just a narrow opening in a low wall, before the present famous structure was built 1788–1791) to the Prince Heinrich Palace ("3") (becoming the Berlin University in 1809, later the Humboldt-University). The zum Bären/Nikolaikirche ("4"), and the zum weißen Schwan/Heilige Geist Kirche ("5") mark the apothecaries of Klaproth. Today, the prominent 358-meter Fernsehturm (TV Tower) lies just on the other side of "5". The Akademiehaus is located at "6", where both Marggraf and Klaproth spent the latter parts of their careers. The Spree River meanders through the city and separates the original Old Berlin ("4" and "5") from Cölln and Friedrichswerder (just to the right of "4"), Friedrichstadt (to the right of "2"), and Dorothenstadt ("2"). It is interesting that these historic sites "1"–"6" all resided in the old Soviet-occupied zone of Berlin.

7. U. Klein, "Apothecary-Chemists in Eighteenth-Century Germany," in *Archimedes New Studies in the History and Philosophy of Science and Technology*, **2007**, *18*, 97–137, Springer-Link.
8. Dr. Ralf-Thomas Schmitt, Professor at the Institut für Mineralogie, Museum für Naturkunde, private communication.
9. M. Klaproth, *Beiträge Zur Kentniss der Mineralkörper*, **1815**, Berlin.
10. *Dana's New Mineralogy*, 8th Ed., John Wiley & Sons, N.Y. **1997**.