Rediscovery of the Elements

Germanium: Freiberg, Germany

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Half a millennium ago, alchemy was maturing into chemistry by advancing on two fronts: medicine and mining. In medicine, Paracelsus (Phillipus Aureolus Theophrastus Bombastus von Hohenheim, 1493–1541) was promoting the use of chemical preparations and preached that a medicine possessed a quintessence that could be extracted and used to combat disease.[1] In mining, Georgius Agricola (Georg Bauer, 1494–1555) was preparing classic treatises on mining and metallurgy.[2] The most famous work of Agricola was De Re Metallica, which appeared a year after his death.[3] Agricola lived most of his life in Saxony and Bohemia; he was born in Glauchau, Saxony; worked in Sankt Joachimsthal, Bohemia; and later became Burgermeister of Chemnitz, Saxony (Note 1). De Re Metallica, translated from the original Latin into English by Herbert and Lou Henry Hoover,[4] not only contains full textual descriptions of the construction of mines and the assay and smelting of metals, but also abounds with detailed woodcut figures. Agricola was one of the first to differentiate among bismuth, antimony, tin, and lead.

Figure 1. Freiberg is the focus of mining activity in the Saxony area and boasts the major mining university in the region, the Technisches Institut Bergakademie (the technical institute and mining academy).

The rich mining tradition of this Saxony-Bohemia region carries on to this day and centers about Freiberg, Germany (Figure 1). Annual festivals and parades are held with the miners in their uniforms with the classic crossed hammers (Figure 2). The uniforms are worn with pride, as they commemorate a centuries-old guild tradition that gifted the miners with rank and respect. The crossed hammers, known as "Eisen und Schägel" originated in the thirteenth century near Kremnica, Bohemia,[5] and are now the universal symbol of mining throughout eastern Germany and the western Czech Republic. Not only can visitors to the region attend these festivities, but they can also roam through scores of mines which in past centuries have delivered silver, gold, nickel, tin, bismuth, tungsten, and copper, and which today are open to the public as "museums."

Figure 2. Frequent festivities are held celebrating the mining tradition. On the hat of this musician are the famous "crossed hammers" ("Eisen und Schlägel"), the symbol of the miners in the Saxony and Bohemia regions. Inset: close-up of pewter chalice with "crossed hammers" and the miner's greeting "Glück auf!"

One of the famous mining institutes in this region is the Technisches Institut Bergakademie (Mining Academy) in Freiberg, founded in 1765. Freiberg had become the economic and scientific center of the Saxony Erzgebirge region, where silver ore had been discovered in 1168. During the early days of the Bergakademie, chemistry and mining had not yet separated into different disciplines. The best known mineralogist of this time, Abraham G. Werner (1749–1817) of the Bergakademie, was a proponent of the Neptunian hypothesis, which held that geological structures were laid down by water deposition.[6] Indeed, the present famous Mineralogical Museum at the Bergakademie is named after him.[7]

Of the hundreds of mines about the region, one particularly rich mine named the Himmelsfürst Mine in St. Michaelis (about 15 kilometers south of Freiberg) yielded an unusu-

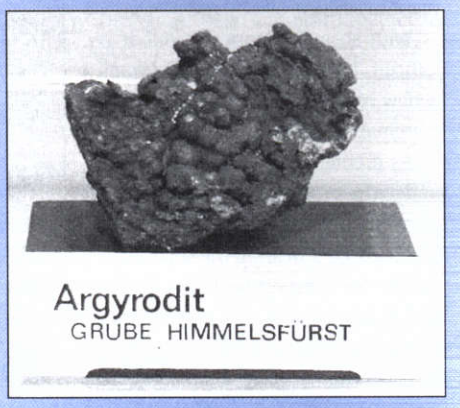

Figure 3. Argyrodite, Ag_8GeS_6, collected from the Himmelsfürst Mine south of Freiberg, and displayed in the Werner Mineralogical Museum. Argyrodite was the source of the germanium discovered by Winkler. "Grube" translates as "mine."

Figure 4. Winkler's laboratory on 5 Brennhausgasse. This small museum may be visited by appointment through the university.

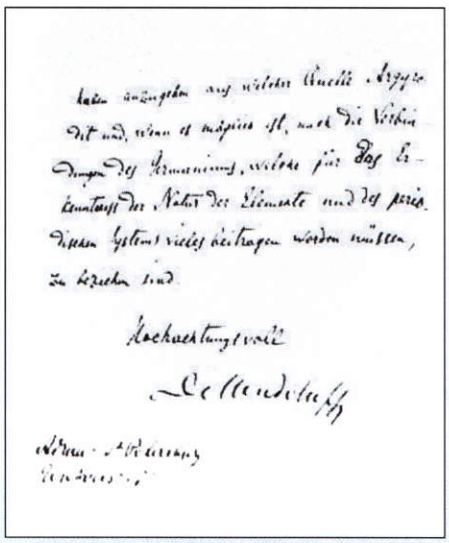

Figure 5. The last page of a four-page letter from Mendeleev's 1886 letter to Winkler, where the famous Russian speculates on exactly what Winkler has discovered. His conjectures range from —a new element between antimony and bismuth—to "eka-silicon." This latter guess turned out to be correct, i.e., directly below silicon on the Periodic Table. This letter is written in excellent formal German, and Mendeleev's signature can easily be discerned at the bottom of the page.

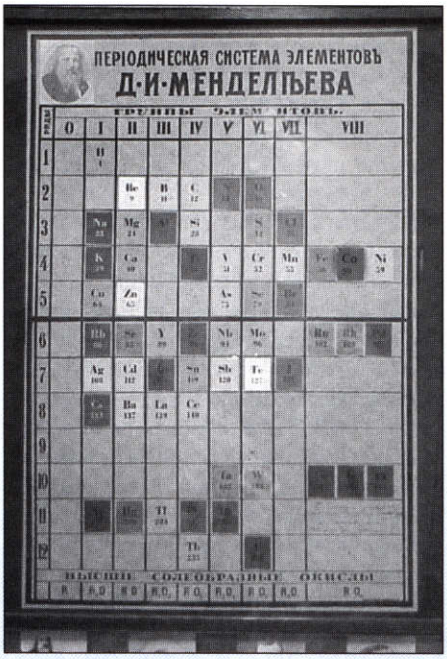

Figure 7. Mendeleev's earlier Periodic Table, in Russian, on the wall inside Winkler's laboratory. This Periodic Table dated from before Mendeleev's predicted elements.

al mineral called "argyrodite" (named from the Greek "silver-bearing;" see Figure 3). From this mineral Clemens A. Winkler (1838–1904), a professor at the Bergakademie, discovered germanium in 1886. He first performed detailed blowpipe analysis (Note 2) and ascertained the mineral held 75% silver and 18% sulfur, hence a loss of 7%. Searching for the unaccounted material, Winkler fused a sample with sodium carbonate and sulfur, separated the aqueous filtrate from the black silver sulfide, and added concentrated hydrochloric acid, which threw down a new flaky, white sulfide. He isolated the new element by passing hydrogen over this sulfide.[8] Argyrodite is now known[9] by the formula Ag_8GeS_6.

Winkler's laboratory still exists in the university and is one of the very few famous chemical laboratories of the nineteenth century that have not been torn down (Figure 4). This laboratory is a private museum and can be visited by appointment through the Freiberg Tourist Bureau (Freiberg Fremdenverhekrsampt). In one corner of the museum is a letter (Figure 5) from Mendeleev to Winkler (Figure 6), congratulating him on filling a void in Mendeleev's periodic table. In this letter, dated 1886, Mendeleev prematurely predicts that the new element will be inserted between "antimony and bismuth"—but later corrects the identification of the new element as his predicted "eka-silicon" between silicon and tin. On a wall hangs one of Mendeleev's earlier Periodic Tables, in Russian (Figure 7). Freiberg Institute, proud of its heritage and famous chemists (Note 3) has not only preserved the original laboratory but also built a museum within the main Akademie building with a monument to Winkler erected nearby.

The Himmelsfürst Mine can be reached in one-half hour by driving from Freiberg to St. Michaelis (Figure 8). In contrast to other mines which still exist intact (for example, the Fața Băii Mine in Romania[10]), the Himmelsfürst Mine region is disappointingly barren—the mine has been closed, the shafts have been filled in, the area has been cleaned of talus and

Figure 6. Dmitri I. Mendeleev and Clemens A. Winkler. This famous pose of Mendeleev, 1834-1907, and Winkler, 1838-1904, (left and right, respectively) was taken in Berlin in 1900.

debris, and only abandoned, torn-down stone ruins may be occasionally found (Figure 9). An occasional tourist sign marks the site of a previous shaft (Figure 10).

For visitors interested in an active mine, perhaps the most interesting, and certainly the most convenient, is the Himmelfahrt Fundegrube Mine which produces silver to this day on the outskirts of the city. Other important sites which may be reached by day trips in a rented automobile include St. Joachimsthal (Jáchymov, Czech Republic), whence the Curie's radium ore originated, and Johanngeorgenstadt, the source of Klaproth's uranium ore—but descriptions of these will have to wait until a future installment of Rediscovery of the Elements. To the interested tourist who wishes to visit mines and mining museums, a most informative brochure has been developed by the Tourist Bureau.[11] Visitors to the Erzgebirge are greeted with a friendly "Gluck Auf!"—the historic standard miner greeting (Note 4)—as they visit mines, museums, hotels, and restaurants in this very beautiful and scenic region of the world.

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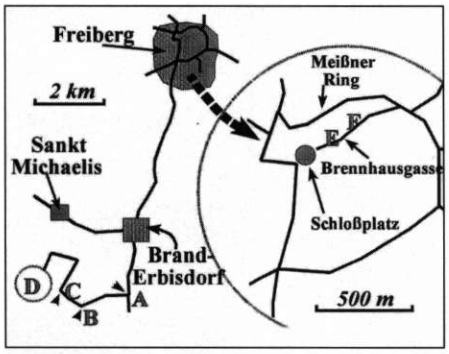

Figure 8. Maps of Freiberg and Himmelsfürst Mine. Olbernhauer Strasse from Freiberg proceeds south (Route 101) through Brand-Erbisdorf, about 5 km south. About 2 km south of Brand-Erbisdorf, a right turn (west) at "A" (N 50° 51.48', E13° 19.15') leads one into the general Himmelsfürst region south of Sankt Michaelis. "B" = N 50° 51.30', E 13° 18.37'; "C" = N 50° 51.38', E 13° 18.12'. The "D" region holds several historical markers and evidence of mines (talus, stone ruins): N 50° 51.74', E 13° 17.77'; N 50° 51.84', E13° 17.62'; N 50° 51.57', E 13° 17.40', among others. The inset of Freiberg shows the location of Winkler's laboratory at 5 Brennhausgasse ("E" = N 50° 55.21', E 13° 20.70'). About 100 meters down the street (west) is the famous Werner Mineral Museum (Mineraliensammlungen der Bergakademie).

Figure 10. Historical post identifying an old shaft. The shafts have long been filled in and little evidence remains except for a few talus piles and stone ruins.

Notes

1. Saxony is present-day Eastern Germany and Bohemia is the Czech Republic. Joachimsthal is the etymological source of "thaler" and "dollar," St. Joachimsthal is now known by its Czech name "Jáchymov."

2. Blowpipe analysis originated in Sweden in the 1700's and its methods were further refined at the Bergakademie during the next century.[12] By blowing through a 20-cm curved pipe through a candle or burner, an operator could project smelting-furnace temperatures on a test sample as small as a pepper seed. By directing the stream either through the oxidizing portion or reducing portion of the flame, and by varying the types of fluxes or reagents, the analyst could gain a great deal of information about the constituents of a sample. Typical tests included: color of the oxide layer; behavior during decrepitation; physical aspects of a glass or borax bead; color of the flame itself. Blowpipe analysis was an art that demanded experience and talent, but in the right hands was capable of even quantitative analysis by measuring the amount of a chemical derivative bead.[12]

3. The Technische Universität Bergakademie Freiberg Institut für Wissenschafts—und Technikgeschichte boasts a long line of well-known faculty and students. A few are mentioned here: Carl F. C. Mohs created the Mohs hardness scale for minerals; Hiernoymus R. Reichter and Ferdinand Reich discovered indium; the famous world traveler Alexander Humboldt was a student there.

4. Historically, a typical greeting among city folk was "Glück zu [Sie]," i.e., "Luck to you." The country folk (miners) distinguished themselves with a play on words by using "auf" ("on") instead of "zu" ("off"). The expression "Glück auf" has stuck ever since, and can be found on buildings, signs and documents. The famous Werner Museum has such a greeting on its stone edifice.

Literature Cited

1. J. R. Partington, *A History of Chemistry*, Vol. 2, pp 115–151, Macmillan & Co., Ltd, London, **1961**.
2. Ref 1, pp 42–62.
3. *Agricola, G.* (Latinized from Bauer, G), *De re metallica*, Frobenius, Basel, Switzerland, **1556**.
4. Hoover, Herbert, translator of 1556 edition of *Agricola,G., De re metallica*, Dover Publications, New York, **1956**.
5. Heřko, I. I. *Mineralogical Record*, **1988**, 19(1), Jan-Feb, pp 7–8.
6. Caswell, L. R. *The Southwest Retort*, **2000**, 53, Dec., pp 5–9.
7. Weber, W. *Mineralogical Record*, **1992**, 23(3) May–June, p 255.
8. Weeks, M. E., *Discovery of the Elements*, 7th ed., *Journal of Chemical Education*, **1968**, pp 655–662.
9. *Dana's New Mineralogy*, 8th Ed., John Wiley & Sons, N.Y. 1997.
10. Marshall, J. L. and Marshall, V. R. *The Hexagon of Alpha Chi Sigma*, **2000**, 41, No. 3, Fall pp 43–45.
11. "Schaubergwerke im Erzgebirge" and "Technische Museen im Erzgebirge," Herausgeber, *Regionaler Fredenverkehrsverband Erzgebirge e.V.* 09456 Annaberg-Buchholz, Johannisgasse 23.
12. Burchard, U. *Mineralogical Record*, **1994**, 25(4) July–August, pp 251–277.

Figure 9. One of the few mine entrances remaining in the Himmelsfürst ("heavenly prince") region.