

Rediscovery of the Elements

Niobium and Tantalum



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In the last issue of *The HEXAGON*¹ we described how in 1809 William Hyde Wollaston (1766–1828) proclaimed² the two elements columbium (known today as niobium), discovered in 1801 by Charles Hatchett (1765–1847), and tantalum, discovered in 1802 by Anders Ekeberg (1767–1813), were identical. However, there was a lingering suspicion among some chemists that something was not quite right, because the densities of the source minerals columbite (from Connecticut) and tantalite (from Finland) were different (5.918 and 7.953, respectively). This problem was investigated in detail by Heinrich Rose of Berlin in the 1840s.

The birth of analytical chemistry in Germany. The origins of modern German chemistry can be traced to two apothecaries in Berlin—the Apotheke zum weissen Schwan (Apothecary of the White Swan) and the Apotheke zum Bären (Apothecary of the Bear). Each of these pharmacies is now gone, but their exact locations can be identified by neighboring historic churches that still stand (Figure 1). In the 18th century, workers in these apothecaries worked closely with the Berlin Akademie der Wissenschaften (Academy of Science).³

The Apotheke zum weissen Schwan was purchased in 1761 by Valentine Rose, the elder (1736–1771), (Figures 2, 3), who invented the

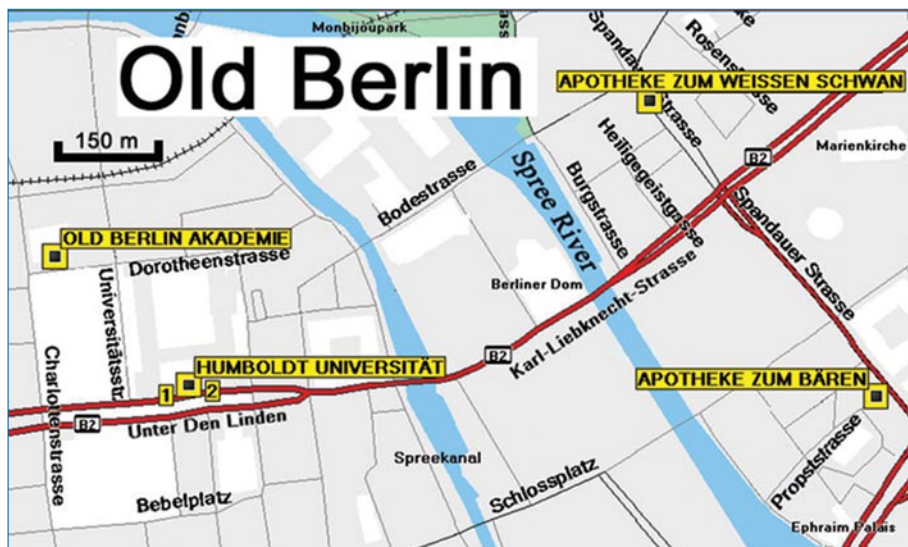


Figure 1. Map of Berlin. The Apotheke zum weissen Schwan (Apothecary of the White Swan) no longer exists; it was across the street from the present Heilige Geist Kirche (Church of the Holy Ghost), which still stands today, Spandauer Straße 1, N52° 31.26 E13° 24.19. The Apotheke zum Bären (Apothecary of the Bear) no longer exists; it was next to the present Nikolaikirche (Nicholas church), Probststraße - N52° 31.04 E13° 24.46. The Akademiehaus (Old Berlin Akademie) was at present 28 Dorotheenstraße (originally 7 Letzten Straße, then 10 Dorotheenstraße); now a parking garage - N52° 31.14 E13° 23.46. The Humboldt Universität zum Berlin (Berlin University) is located at Unter den Linden 6 - N52° 31.06 E13° 23.63, with statues of Wilhelm Humboldt, founder of the university (located at “1”) and his brother Alexander Humboldt, the biogeological explorer (located at “2”).

eponymous Rose’s metal, a low-melting (100°C) alloy of bismuth, tin, and lead.^{4a} In 1771, Martin Heinrich Klaproth (1743–1817), the discoverer of uranium,¹⁸ joined the pharmacy. That same year Rose died, and Klaproth assumed care of the two Rose sons, one of whom lived to maturity, Valentin Rose, the younger (1762–1807).^{4a} The apothecary remained in the Rose family for three generations, passing on to the grandchildren Gustav (1798–1873) and Heinrich (1795–1864).

The Apotheke zum Bären (Figure 4) was owned (1738–1753) by Andreas Sigismund Marggraf (1709–1782),¹⁴ who isolated zinc from calamine, identified alum, and differentiated potassium and sodium.¹⁴ In 1753, Frederick the Great (1712–1786) built a state laboratory for the Akademie (Figure 1), and Marggraf moved there a year later (Figure 5).²

Klaproth left the weissen Schwan apothecary in 1780 to become manager of the Bären

apothecary, and moved on to the Berlin Academy in 1800, becoming professor of the University of Berlin when it was founded by the Humboldts in 1810. Klaproth was arguably one of the best two analytical chemists of his time, to whom all would send doubtful specimens to be confirmed¹⁶ (the other being Louis Nicolas Vauquelin (1763–1829) of Paris¹⁶).

In 1823, Gustav and Heinrich Rose joined the University of Berlin.³ Gustav’s specialty was mineralogy;^{4b} he accompanied Alexander von Humboldt (1769–1859)¹³ during the celebrated 1829 geological expedition to Russia. Heinrich’s expertise was chemistry^{4b} (Figure 6); he developed qualitative and quantitative analytical techniques, including group separations and systematic tests, and wrote many analytical treatises. Heinrich and his brother worked closely together as Gustav furnished specimens for his laboratory work, while in return Heinrich furnished critical chemical analysis as



Figure 4. Looking north on Propststrasse with the Nikolaikirche (originally built 1220–1230) on the right. The zum Bären pharmacy was at the end of Propststrasse, where a plaque is posted, the site where Klaproth discovered uranium and zirconium. On the left is the famous shop for "Berliner Bären" (teddy bears).

Gustav devised the "crystal-chemical mineral system," organizing minerals on the basis of crystalline form and composition.^{4b}

Heinrich takes on the columbite-tantalite problem. Ever since Wollaston "proved" columbium and tantalum were identical,² Great Britain and the U.S. called the new element "columbium," but Jöns Jacob Berzelius (1779–1848) campaigned for "tantalum."³ The name "tantalum," Berzelius argued, conveyed the important distinction of the element that it resisted solution in acid, alluding to the legend of Tantalus who, although immersed in water up to his chin, could not quench his thirst.⁵ (Metal oxides are ordinarily basic, but tantalum oxide could not be dissolved in acids, even in excess.) Scientists of the European continent dutifully followed the suggestion of the respected Swedish chemist.

Although columbium and tantalum were considered to be "the same element," it was known that the parent minerals columbite and tantalite, which were isomorphous^{4c} (same crystal structure), had different densities. The nagging question persisted, was there actually more than one element? And if there was, could they be separated chemically? Thirty-five years after Wollaston's report, Gustav Rose, the

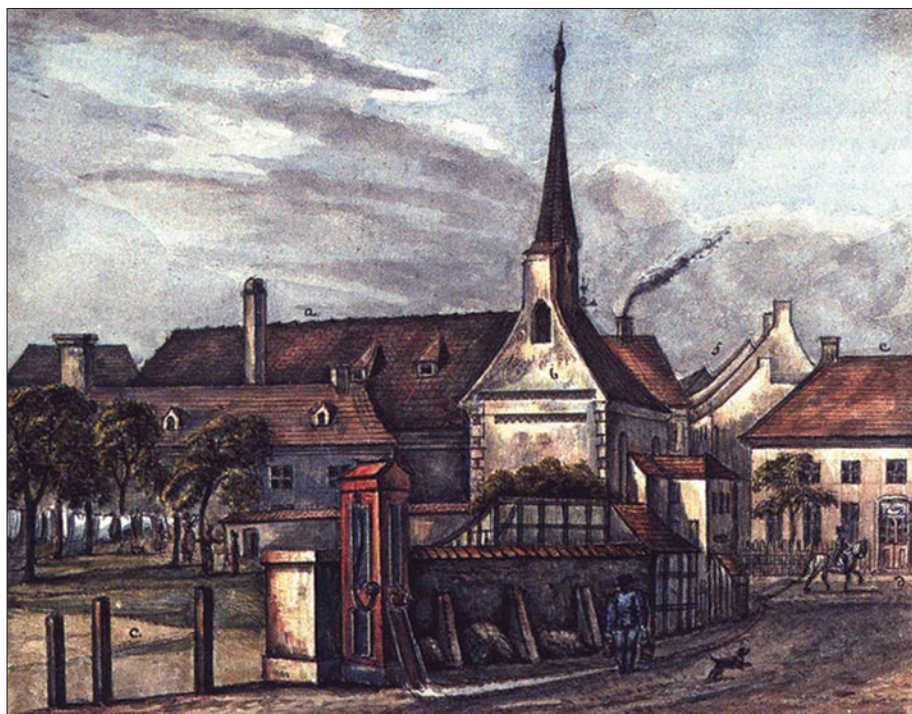


Figure 2. This water-color painting of the Heilige Geist Kirche was done by Leopold Ludwig Müller in 1804. The church is in the center; to the right is the Apotheke zum weissen Schwan, with a white swan visible above the door on the transom. To the left is the hospital which the church supported; the field to the left is the "Wurstthoff" used for raising hogs to furnish food for the hospital. Courtesy, Kupferstichkabinett, Staatliche Museum zu Berlin.



Figure 3. This photograph, taken from the Catholic archives, shows the Heilige Geist Kirche (center) which looks much the same today. To the right is the apothecary, destroyed in the War. Today the site of the apothecary is occupied by high-rise buildings. The date of the photograph is uncertain, but must be after 1906, the construction date of the tower.

mineralogist, enticed Heinrich Rose, the chemist, to review this question in more detail, utilizing the more modern analytical techniques that had been developed since the beginning of the century. Thus Heinrich embarked on a two-decade research, fully

chronicled in Poggendorff's *Annalen (Annalen der Physik und Chemie)*.⁶

By now, more localities had been discovered for the source minerals, low-density "columbite" and high density "tantalite." Tantalite could be found in Finland and Sweden, while columbite

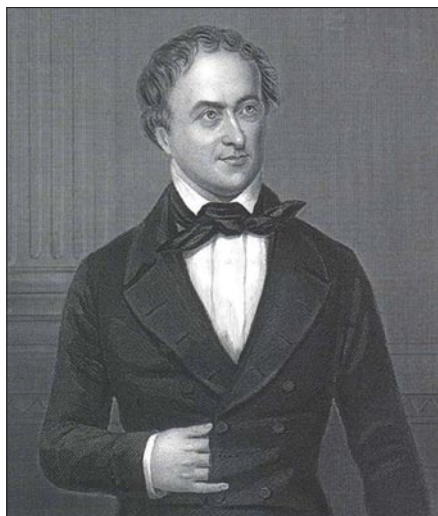


Figure 6. Heinrich Rose, portrait. Courtesy, Berlin-Brandenburgische Akademie der Wissenschaften.

could be found in Connecticut⁵¹ and in the Bavarian region of Bodenmais—today a historical mine and museum exist at Silberberg 28 in Bodenmais (N49° 3.54 E13° 7.29). In 1844, Rose announced^{6a} the Finnish/Swedish tantalite was composed of one metal, while the Bodenmais tantalite was composed of two metals—tantalum and a new element he called “niobium,” after Niobe, the daughter of Tantalus. What distinguished niobium and tantalum, Rose said, were the chlorides of the two elements, prepared by reaction of the oxides with charcoal and gaseous chlorine. Tantalum chloride was yellow, easily fusible and volatile; niobium chloride was white, infusible, and not volatile.^{6a} Two years later^{6b} he reported *another* yellow chloride had been produced from the Bavarian columbite—another element had been discovered, he asserted, which he called “pelopium” after Pelops, the son of Tantalus.

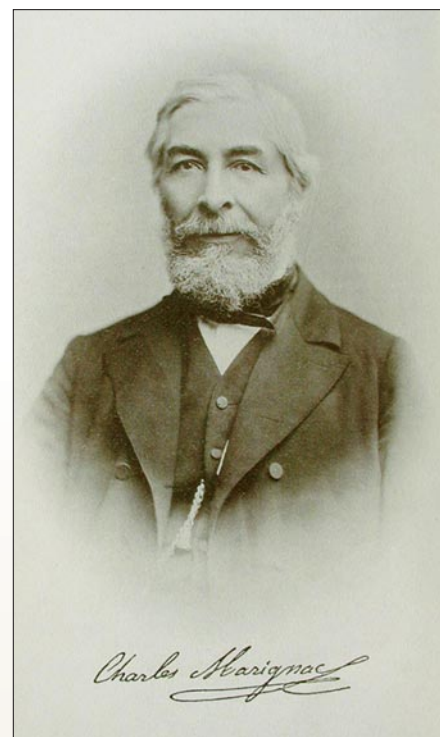
Thus followed a long series of publications^{6c,d} where Rose attempted to characterize the new elements. First he tried to separate the three elements, but then concluded that “niobium” and “pelopium” were actually different oxidation states of the same element^{6c}—he called these “Niobsäure” (niobium acid) and “Unterniobsäure” (lower niobium acid). Through two decades Rose never resolved the problem.^{6e-h}

Rose was misled because the *two* elements which were present—niobium and columbium—gave *three* different chlorides when the minerals were treated with charcoal in the presence of chlorine gas: NbCl_5 , NbOCl_3 , and TaCl_5 (but not TaOCl_3). Complicating the situation was the fact that niobium chloride (NbCl_5) and tantalum chloride (TaCl_5) had virtually identical physical properties (both yellow-white, respective mp 205 and 216, bp 248 and 240), and were



Figure 5. This photograph of *das Akademiehaus* was taken about 1900. The Berlin Academy of Sciences established a laboratory here in 1753 and Marggraf was made its director. On some maps the *Akademiehaus* is called the “Marggrafisches Laboratorium.” Klaproth did some of his latter work here, e.g., the distinction of potassium and sodium saltpeter by the color of their flame tests. Heinrich Rose performed his niobium/tantalum research here during 1844–1861. The building was destroyed in the War; the present site is occupied by a parking garage. Photograph, courtesy, Berlin-Brandenburgische Akademie der Wissenschaften.

Figure 7. Jean-Charles Marignac, a native of Geneva, Switzerland, attended the *École polytechnique* in Paris,⁵² and became professor of chemistry (1841) and mineralogy (1845) at the Geneva academy. He discovered the isomorphism⁵³ of fluorostannates (K_2SnF_6) and fluorosilicates (K_2SiF_6), thus establishing the formula of SiO_2 for silica (and not SiO_3) and producing “a revolution in mineralogy.”⁵⁴ He studied columbites/tantalites and determined how many new elements actually existed in this group of minerals—just two, niobium and tantalum. Portrait, courtesy of Dr. Rolf Haubrichs, University of Geneva.



very difficult to separate from one another. Undoubtedly all his preparations were mixtures;⁵⁴ today we know pure TaCl_5 is off-white; hence, evidently his TaCl_5 was always contaminated with NbCl_5 . A final flaw in his research was his not recognizing that one of these chlorides (NbOCl_3) contained oxygen. Both Rammelsberg⁷ and Partington^{5b} have marveled that Rose, “the discoverer of the volatile oxychlorides of Cr, Mo, W,”⁷ missed the oxygen in nearly all of the compounds he analyzed.

The subtle differences in the tantalite system were underscored by the claim, by other miner-

alogists, of three *additional* elements in columbites and tantalites—danium (1860), by Wolfgang Franz Kobell of Munich (1803–1882), and ilmenium (1874), and neptunium (1877) by Hans Rudolph Hermann of Moscow (1805–1879). All these latter “discoveries” were later shown to be mixtures of niobium/tantalum and other impurities.⁵⁹

These “earth acids”⁵⁴ were unlike the basic rare earths and other metal oxides to which chemists were accustomed. Rose was overwhelmed by contradictory chemical data, not understanding that some of his “separations”



Figure 8. This is the old site of the Geneva Academy—the Société de lecture (Grand Rue 11, Geneva, Switzerland, N46° 12.14 E06° 08.70). This academy dates from 1559, founded by Jean Calvin (1509–1564). Marignac resolved the chemistry of niobium and tantalum in a “dark damp cellar lab” in back of this building (no longer exists).



Figure 9. Marignac retired in 1878 and established a laboratory (“third floor”) in his Geneva home at Rue Jean-Sénevier, 16 (N46° 11.84 E06° 08.88). Here he discovered gadolinium (1880, separated from didymia) and ytterbium (1878, from erbia).

were merely chemical transformations between chlorides and oxychlorides. Rose had experienced the first example of two elements of a chemical group which, because of the lanthanide contraction,^{1b} were of similar size and exhibited the same chemical behavior. He final-



Figure 10. Blomstrand's laboratory at the University of Lund. Magle Stora Kyrkogata 12A (now History Dept.), U. of Lund, Malmöhus, Sweden (N55° 42.17 E13° 11.92). Here he prepared the first pure sample of niobium, a “spiegelnden stahlgrauen metal” (shiny steel-gray metal).¹² A bust of Blomstrand (see inset) stands in the University of Lund, Kemicentrum, at Getingevägen 60 (N55° 42.99 E13° 12.54).

ly lamented, “Ein solches Verhalten ist aber ein so eigenthümliches, dass wir im ganzen Gebiete der Chemie kein analoges kennen.”^{6c} (“Such behavior is so unusual that in the whole realm of chemistry I know of no analog.”)

A Swiss chemist resolves the problem. In 1866, Jean-Charles Galissard Marignac (1817–1894), (Figure 7) a professor of chemistry at l'Académie de Genève,^{4d} (Figure 8) separated and characterized the double fluoride salts of niobium and tantalum.^{10b} These salts, K_2NbF_7 and K_2TaF_7 , established the oxides of niobium and tantalum as Nb_2O_5 and Ta_2O_5 (and not NbO_2 and TaO_2 , as presumed by Rose). Marignac's determination of the pentavalency of niobium and tantalum, and of accurate atomic weights of each (1866), was delivered just in time for proper placement in the first Periodic Tables of Dimitri Mendeleev and Lothar Meyer (1869).¹¹

Marignac's separation procedure involved the initial treatment of a niobium oxide/tantalum oxide mixture with hydrofluoric acid/potassium fluoride, which produced a mixture of potassium fluorotantalate K_2TaF_7 and potassium oxyfluoroniobate K_2NbOF_7 .^{10a,b} The tantalum salt precipitated out, while the niobate salt remained in solution. (Further treatment of K_2NbOF_7 with HF could produce K_2NbF_7 .) This separation method was used as the basis of industrial production of the two

elements until the middle of the 20th century. Later, liquid-liquid extraction using, e.g., methyl isobutyl ketone, would preferentially extract the tantalum compounds from a hydrofluoric or hydrochloric acid solution.¹¹

Marignac suffered from ill health, owing to his hours of labor in the cramped damp laboratory of l'Académie de Genève. He moved with the Academy (now the University of Geneva) to its new site in 1872 (Uni-Bastion, Rue de Candolle, 5 - N46° 11.93 E06° 08.65). In 1878, he retired and continued research in his own home laboratory (Figure 9) for the rest of his life.

The work of Blomstrand. Christian Wilhelm Blomstrand (1826–1897) (Figure 10) of Lund University contributed to the final solution by studying the chlorides,¹² identifying the oxychloride of niobium ($NbOCl_3$) which had been proposed by Marignac.^{10a} Thus the riddle of Rose's three chlorides of $NbCl_5$, $TaCl_5$, and $NbOCl_5$ was solved. Henry Enfield Roscoe (1833–1915), an expert himself in the complex chemistry of vanadium (he was the first to prepare metallic vanadium,¹³) lauded the final success: “It is to Marignac and Blomstrand that we owe a deliverance from this state of uncertainty and contradiction that surrounded the metals existing in such minerals as columbite and tantalite. They have independently proved that only two metals in reality exist—niobium and tantalum, and that all the other supposed met-

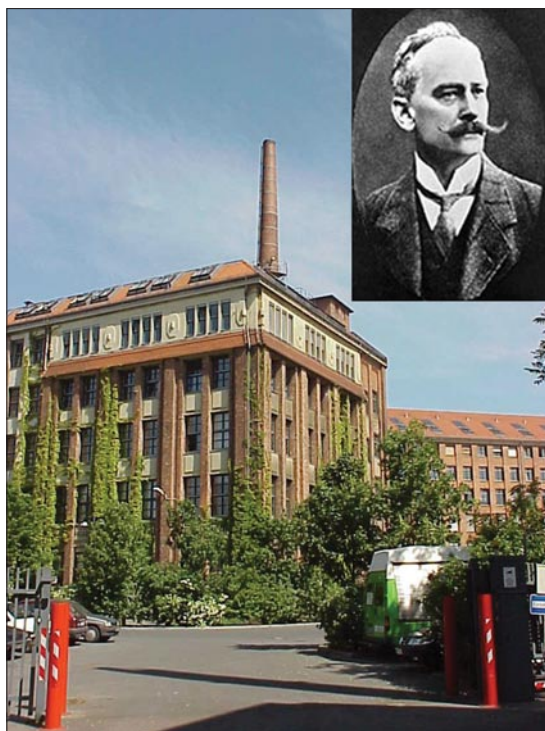


Figure 11 (left). Pure tantalum was prepared by Bolton (see inset) for use as filaments in incandescent bulbs at Siemens A.G. (then Siemens-Halske Company), Helmholtzstrasse 2-9, Berlin, Germany. Today the original building is used for business offices and workshops of various trades (N52° 31.28 E13° 19.42).



Figure 12 (right). The Swanson pegmatite quarry in the Haddam area in Connecticut was a commercial source of lithium in the early 20th century. Recently it has been filled in and must look much as it did centuries ago (except for the transmission lines) when columbite was first collected by Native Americans or colonists.³ It was closed to collectors in 2010.

als, pelopium, decinium, and ilmenium, are either simple mixtures of niobium and tantalum in varying proportions, or such a mixture containing, in addition, some other metals, such as tungsten, titanium, or iron.⁸

The conclusions of Marignac and Blomstrand were supported by vapor pressure studies of his French colleagues¹³ H. Saint-Claire Deville of the École Normale¹⁴ and L. Troost of the Sorbonne¹⁴ in Paris.¹³

Pure metals. The purification schemes of Marignac allowed the preparation of pure samples of metallic niobium and tantalum. Blomstrand prepared the first pure sample of niobium by treating the niobium chloride in a stream of hydrogen in red heat¹² (Figure 10). Producing a tractable, pure sample of tantalum was more difficult, owing to its very high melting point (3017 vs. 2477°C); early attempts resulted only in brittle, crude material. Werner von Bolton (1868–1912) of Siemens AG (then Siemens-Halske) in 1903 prepared the first pure tantalum suitable for making filaments for incandescent light bulbs, by treating potassium fluorotantalate with potassium in an electric arc vacuum oven¹⁵ (Figure 11).

“Columbium” or “Niobium”? Now that it was clear that Hatchett’s “columbium” was the same as Rose’s “niobium,” the question remained, which name should be used for the element? The European chemists, captivated with the large amount of work performed by Rose, preferred his choice of “niobium.” Even the British, whose Sir Humphry Davy and

Thomas Thomson originally favored “columbium,”³¹ accepted the choice of the Continental scientists.

However, in the United States the name “columbium” was preferred. In 1877, J. Lawrence Smith, the second (1877) president of the American Chemical Society and 21st (1874) president of the American Association of Advancement of Science,¹⁶ and himself a specialist in mineralogy, made the case for “columbium”:¹⁷ “It is the common practice of all American chemists and mineralogists to speak of the metal which is called Niobium by English and continental chemists, as Columbium. This is eminently just, since the metal was discovered and well defined, and named columbium, forty-five years before the name niobium was given to it. . . . Subsequent examination . . . convinced Rose . . . that the two metallic acids obtained from the Bodenmais columbite were really the original columbic acid of Hatchett, discovered in 1801, and the tantalic acid discovered by Ekeberg in 1802. Instead, however, of calling the first mentioned acid niobic acid, its original name should have been left to it . . . In addition to the above, . . . [columbite has] been discovered in greater quantities and in larger crystals in the United States than in other known localities . . . [including] where the specimen was obtained that was sent to Hatchett . . .”¹⁷ (Note 1).

For more than seventy years, Periodic Tables published in the United States continued to utilize “columbium.” Despite a latter attempt by Roscoe to adopt the American usage of “columbium,”⁹ the European choice prevailed.

In 1949, at the 15th meeting of the IUPAC (International Union of Pure and Applied Chemistry) in Amsterdam, it was declared that “niobium (and not columbium) is accepted”¹⁸ (Note 2). Dutifully complying, American textbooks and Periodic Tables adopted the new name, although the use of “columbium” persisted for decades. In 1960, the international committees reaffirmed “the name niobium for element 41 in spite of the fact that many in the United States, particularly outside of chemical circles, still retain the name columbium.”¹⁹ Even today one occasionally sees “columbium,” notably in engineering or trade journals.

What was the actual composition of the original columbite and tantalite? The table on page 51 demonstrates that columbite/tantalite (Fe,Mn)(Nb,Ta)₂O₆ can have wide ranges of Fe-Mn and Nb-Ta (Note 3). By luck the original sample of Hatchett still exists and has been analyzed by the London Museum of Natural History.²⁰ Also included in the table are data from Connecticut specimens of columbite collected by the authors. The original specimen of tantalite from Skogsböle, Finland (the source of Ekeberg’s tantalite⁹) is not available for analysis, and the site is depleted of tantalite. Nevertheless, a chemical analysis was performed 70 years after Ekeberg’s discovery by Rammelsberg on a Skogsböle specimen.⁷

The Ti, Sn, W impurities can serve as isomorphic substituents^{3c} in naturally occurring minerals for Nb/Ta²¹ and were noted by the early analytical chemists. Hatchett missed the presence of manganese in his original analysis

(he lumped it together with iron). Berzelius used Hatchett's oversight as an argument attesting Ekeberg's superior analysis, thus bolstering his case that "tantalum" was a better name for Hatchett's original discovery.⁵

The abundance of niobium in the earth's crust is 10 times that of tantalum (20 ppm vs 2 ppm).²¹ Hence, the low Nb/Ta ratio of Finnish tantalite is quite remarkable. This geological concentration of tantalum has been explained²¹ by the partitioning of fluorine complexes under special acid-alkaline conditions of the crystallizing medium. These were the very conditions found serendipitously by Marignac to be an efficient separation method in his laboratory!

The legacy of Heinrich Rose and Charles Marignac. In spite of the fact that Rose was the master of analytical separations in the mid-1800s,¹⁴ the niobium/tantalum system in his hands defied purification.¹⁴ An excellent review of Rose's "lengthy and exhaustive publications" research, and "how he was diverted from the right way and fell unconsciously into error" is given by Karl Friedrich Rammelsberg (1813–1899), professor of mineralogy and chemistry, University of Berlin⁷ (Rammelsberg was a student of Rose, and succeeded him at the University of Berlin^{6c}). Rammelsberg appreciated the difficulty of his task and commented, "The discovery of a new element, niobium, was a splendid result of this great, laborious, and . . . difficult investigation, and history will forever attribute to it an honourable place in science. And although the celebrated founder of Analytical Chemistry [*Ausführliches Handbuch der analytischen Chemie*] failed to discover the right path, nevertheless young chemists, in studying that long series of memoirs on tantalum and niobium, published in *Poggendorff's Annalen*, will also understand by what circumstances the guide was diverted from the right way and fell unconsciously into error."⁷

Readers of *THE HEXAGON* may recall similar difficulties in the discovery of hafnium.^{1h}

The problems generated by the lanthanide contraction with hafnium were even more severe. The element lay hidden in zirconium minerals until 1923, when it was detected by X-ray analysis.^{1h} It is astonishing that the analytical chemists 60–80 years earlier progressed as far as they did. ☉

Notes.

Note 1. Rose referred to the mineral from both New England and Bodenmais as "columbite."^{6c} After analyzing a portion of half a pound of New England columbite from Benjamin Silliman (1779–1864; the first ever to deliver a chemistry lecture at Yale College), Rose concluded^{6c} North American and Bodenmais columbite were the same, "both containing niobium and pelopium," differing only slightly in their specific gravity. Rose was familiar with Hatchett's work and his naming his element "columbium."^{6a} In a paper one year before his death,^{6h} Rose admitted, by implication, that Hatchett's "columbium" was the same as "Unterniobsäure"^{6h} (which he considered to be the lower oxide, actually NbOCl₃).

Note 2. In the same meeting "wolfram" was adopted as the official name for element 74. However, the British announced that "... the name 'tungsten' will not be replaced by 'wolfram' [in British scientific literature]"¹⁸ This is the reason for the present use of the German "W" and "Wolfram" for the original Swedish "tungsten."^{1c}

Note 3. Mineralogists recognize four mineral names encompassing the Fe/Mn/Nb/Ta system: ferrocolumbite, manganocolumbite, ferrotantalite, and manganotantalite.²²

**Next Rediscovery:
the two missing elements of the
manganese family are found!**

SELECTED ANALYSES OF COLUMBITE/TANTALITE

	Nb ₂ O ₅ ^d	Ta ₂ O ₅ ^d	FeO	MnO	TiO ₂	SnO ₂	WO ₃	Y ₂ O ₃
Hatchett's specimen ^a	54.2	25.7	15.0	3.5	0.6	-	0.2	-
Hadam sample ^b	60.2	16.6	16.8	4.3	0.8	1.3	-	-
Hadam (Swanson) ^b	56.0	25.8	8.2	9.3	-	-	-	0.7 ^e
Skogböle Quarry ^c	10.9	70.4	10.9	3.3	0.3	3.5	-	-

^aMicroprobe, ref 20a. ^bEDX, ref 20b. Swanson quarry in Connecticut is a famous mineral collection site (Figure 12). ^cRef 7. ^dExtreme ranges of Nb/Ta include 0% of Ta (Greenland) to 91% (certain Finland specimens, ref 9). ^eProbably an yttriotantalite impurity, YTaO₄.

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