Introduction

The classification of the elements had long been a subject of interest before Mendeleev’s monumental achievement of composing his periodic system of the elements. The first seeds of this endeavor were planted by Antoine-Laurent de Lavoisier in his textbook *Traité Élémentaire de Chimie* (Elementary Treatise of Chemistry) published in 1789, which was the first chemistry textbook to contain a listing of the known elements at the time. By elements, Lavoisier referred to materials that could no longer be broken down into simpler substances, and this list included 17 metals (1). The binary compounds of oxygen with various metals and non-metals, as well as numerous other binary compounds, were also compiled (1). Then, in 1829 Johann Wolfgang Döbereiner first reported the organization of certain elements into groups of three that he called “triads.” These triads were based on the trends in the atomic weights of the elements, and in each of the four triads he proposed the atomic mass of the second heaviest element was very close to the average mass of the lightest and heaviest element (2).

Dumas carried out more precise measurements of the atomic weights between 1858 and 1860, and he reported the atomic weights of a number of elements in 1859 with hydrogen being assigned an atomic mass of one, therefore establishing a system of equivalents or relative atomic weights (3). Building upon this, another more detailed attempt to classify the elements into groups came in the form of the “Law of Octaves” proposed by John Alexander Reina Newlands in 1865 (4). In his method that was based on atomic weights, every eighth element ended up being placed in the first group, such that every eighth element showed a repetition of properties. In contrast to the modern periodic table, the groups of elements were arranged from left to right while the periods of elements were arranged from top to bottom. There were numerous errors, however. For example, lithium was listed as element 2 since it was the second lightest element known at the time, followed by glucinium (beryllium) as element 3, boron as element 4, etc. In his system, cerium and lanthanum shared the same element number. From most accounts, his proposed ordering of the elements was not taken seriously and the Chemical Society of London would not publish it. Newlands is generally credited for the general idea of a periodic system, despite the fact that his system appears to be quite unsystematic.

The major breakthrough in organizing the elements in a systematic way came shortly thereafter by Lothar Meyer and Dmitri Mendeleev. In his textbook, *Die Modernen Theorien der Chemie* (Modern Theories of Chemistry) published in 1864, Meyer included an early version of the periodic table consisting of 28 elements (5). The elements were arranged in a series of six columns and in this case the elements were grouped for the first time...
according to their valence and their equivalent atomic weight. When this was done, it was shown that when the elements were arranged in order of their atomic weight they also lined up in groups by their valence. Each row or period of Meyer’s table ended with a divalent alkaline earth metal and the columns, which would later become groups in the modern periodic table, were essentially correct except that thallium was grouped with the alkali metals. It is easy to see why this was done, however, as thallium prefers the +1 oxidation state. Moving away from the relative atomic weights and using a system of valence resulted in Meyer’s 1864 periodic table strongly resembling the modern one. However, although Meyer had spaces in his table for elements that were unknown at the time, he did not offer any predictions of the properties of the new elements that had yet to be discovered.

In 1869, Mendeleev published a periodic table containing all known elements at the time, including a few that were not completely characterized, first in Russian (6) with a short summary appearing in German (7). The system he proposed was based both on valence and atomic weight, and he recognized that there were unknown elements that would be analogous to existing elements next to them in their respective groups. For example, Mendeleev indicated that there were missing elements beyond both aluminum and silicon that he later called eka-aluminum and eka-silicon, respectively. In 1871, he published an account with an updated periodic table that contained extensive details on the properties of the predicted elements (8, 9). This version of the periodic table is typically regarded as the basis for the one that is used today (Figure 1). Lothar Meyer also published an updated version of his periodic table in 1870 (10).

Ekasilicon, with an atomic mass of 72 as predicted by Mendeleev, would of course turn out to be the element germanium. It would be about fifteen years after the appearance of Mendeleev’s 1871 periodic table before this element was actually discovered. This discovery took place in 1886 in Freiberg, Saxony, by Clemens Alexander Winkler, and the story of this discovery is the focus of this paper.

**Figure 1. Dimitri Mendeleev’s 1871 Periodic Table (9).**

**Clemens Winkler**

Freiberg, which is located in present-day Saxony near Dresden, is known as “die Silberstadt” or The Silver City, due to its proximity to the Himmelsfürst mine that has produced vast amounts of silver-containing ores. Freiberg is also home to the Technische Universität Bergakademie Freiberg, which is the oldest mining and metallurgy university in the world, established by Prince Franz Xavier in 1765.

Clemens Winkler was born in Freiberg, Kingdom of Saxony, on December 26, 1838, to Kurt Alexander, a chemist and metallurgist who had studied under Berzelius, and Antonie Elmonde Winkler. He was the third oldest of seven children. He first attended a private school and then secondary school in both Freiberg and Dresden. He then attended the Royal Trade School in Chemnitz (now Technische Universität Chemnitz) from 1855 to 1856, where he acquired his knowledge base in chemistry. He then attended the Bergakademie Freiberg from 1857 to 1859.

Following the work of his father, grandfather, and great-grandfather, Winkler then began his professional career at the Niederpfannenstiel Blue Dye plant. In 1864 he received his doctorate from the University of Leipzig, where his thesis focused on the alloys of silicon and silicon/arsenic metal compounds (11). He was promoted to head smelter at the plant in 1864 as well. During his time there, Winkler developed a pioneering method of technical gas analysis, and eventually published a book on the subject entitled *Handbook of Technical Gas Analysis* in 1885 (12). In this work, Winkler described his invention of the three-way stopcock (Figure 2). Also, he was successful in producing the first large castings of nickel and cobalt (Figure 3) that he presented at the 1867 World’s Fair in Paris.
In 1873, at the age of 34, Winkler (Figure 4) was appointed Professor of Inorganic Chemistry at his alma mater, the Bergakademie Freiberg. He succeeded his former teacher Theodor Scheerer, who passed away in 1875. He would remain at Bergakademie Freiberg for the rest of his scientific career.

Winkler was known to be very personable and had an excellent sense of humor. He was a very popular instructor due to the inspiring lectures that he continuously delivered. Winkler also wrote poetry and played several musical instruments (13). He married Minna Laura Pohl in January 1863, and they had six children together.

**The Discovery of Germanium**

In September 1885, a previously unknown mineral was discovered in the Himmelsfürst mine outside Freiberg during the excavation of a cross passage in the mine. It was gray, silver-rich, and also had a coating of iron and pyrites on the outside. A sample of this was given to Albin Weisbach and he determined that the silver content was 73.5 percent, and also that the mineral contained sulfur and mercury. The ore was named argyrodite (Figures 5 and 6), which comes from the Greek meaning “rich in silver.” The formula of this mineral, which of course was unknown in 1885, is $\text{Ag}_8\text{GeS}_6$. This was an unusual composition for the ores normally obtained from this particular mine, and Weisbach asked his cousin and good friend Clemens Winkler to handle the mineral analysis, as he had done several times previously.
The fact that he was faced with an unknown component in argyrodite that could potentially be a new element was bothersome to Winkler, and he was determined to ascertain the identity of this unknown species. He worked day and night to attempt to identify this mysterious substance, but the typical analyses he used to determine the composition of other minerals were unsuccessful. To further complicate matters, only a small amount of argyrodite was available and samples were also significantly contaminated with antimony and arsenic.

Winkler refused to give up and spent four months of solid work to identify the unknown component present in the argyrodite ore. Finally, on the morning of February 6, 1886, his efforts came to fruition. Winkler had been using the “Freiberger digestion” to analyze the argyrodite. This involved mixing the ore with sodium carbonate and elemental sulfur and heating the mixture until it was red hot. This method had been widely used for the analysis of sulfur salts, which were very common in the ores obtained from the Himmelsfürst mine.

Using this method with argyrodite, the same process occurs as for mixed silver/arsenic and silver/antimony sulfides as shown in Equation 1. Upon digestion, a soluble sodium thiogermainate is formed that dissolves when water is added after the heating process, and the silver sulfide does not dissolve.

\[ \text{[1]} \quad 2 \text{Ag}_8\text{GeS}_6(s) + 2 \text{Na}_2\text{CO}_3(s) + 3 \text{S}(s) \rightarrow \]
\[ 2 \text{Na}_2\text{GeS}_3(s) + 8 \text{Ag}_2\text{S}(s) + 2 \text{CO}_2(g) + \text{SO}_2(g) \]

Since the argyrodite ore was contaminated with both arsenic and antimony the aqueous extract also contained the thiosalts \( \text{Na}_3\text{AsS}_4 \) and \( \text{Na}_3\text{SbS}_4 \). The key to isolating the germanium salt was to separate it from the arsenic and antimony contaminants. Winkler ultimately achieved this by weakly acidifying the aqueous solution with hydrochloric acid and allowing the solution to sit overnight in order for precipitates to form.

On the morning of February 6, 1886, Winkler filtered off the precipitates that had formed, which from experience he expected were sulfide salts of antimony and arsenic. To the resulting clear filtrate he added a large quantity of hydrochloric acid, and this resulted in the formation of a spongy white precipitate. Winkler strongly suspected that this was the sulfide salt of the new unknown element. The fact that this material was insoluble in only strongly acidic solutions was what had prevented its discovery and accounted for Winkler’s previous failures to isolate the sulfide salt of the new element. The \( \text{Na}_3\text{SbS}_4 \) and \( \text{Na}_3\text{AsS}_4 \) are also highly colored, such that the white \( \text{Na}_2\text{GeS}_3 \) salt was easily hidden in the precipitates of these two salts.

The final isolation of germanium was achieved by slow acidification of the material obtained by the Freiberg digestion. In solution are the anions \( \text{AsS}_4^{3−} \), \( \text{SbS}_4^{3−} \), and \( \text{GeS}_3^{2−} \), and slow acidification results in the precipitation of the arsenic and antimony sulfides \( \text{As}_2\text{S}_5 \) and \( \text{Sb}_2\text{S}_5 \), respectively, while the \( \text{GeS}_3^{2−} \) ion remains in solution. Hydrogen sulfide gas is also formed as a byproduct in this reaction.

After all of the arsenic and antimony sulfides have precipitated out of solution, the mixture was filtered to provide a clear filtrate. The difficulty in isolating the new element experienced by Winkler, and presumably others who missed its presence entirely, stems from the unusual fact that the sulfide is soluble in dilute acids and water.
but *insoluble* in concentrated acids. Addition of excess hydrochloric or sulfuric acid then leads to the precipitation of germanium(IV) sulfide (Equation 2).

\[ \text{GeS}_2^{2-}(aq) + 2 \text{HCl}(aq) \rightarrow \text{GeS}_2(s) + \text{H}_2\text{S}(g) + 2 \text{Cl}^-(aq) \]

The sample of GeS\(_2\) initially obtained by Winkler was sealed in a glass tube and is currently located at the Bergakademie in Freiberg, and that tube is shown in Figure 7. It was later determined that washing the solid GeS\(_2\) with sulfuric acid and then alcohol would prevent it from re-dissolving in water. The element itself could be isolated from the sulfide by roasting in oxygen (Equation 3) followed by reduction of the resulting oxide by hydrogen gas (Equation 4).

\[ \text{GeS}_2(s) + 3 \text{O}_2(g) \rightarrow \text{GeO}_2(s) + 2 \text{SO}_2(g) \]

\[ \text{GeO}_2(s) + 2 \text{H}_2(g) \rightarrow \text{Ge}(s) + 2 \text{H}_2\text{O}(g) \]

**Figure 7.** Winkler’s sample of Ge\(_2\) from February 6, 1886. *Photo courtesy of Prof. Mike Haustein (Nickelhütte Aue GmbH and TU Bergakademie Freiberg).*

On the same day of his discovery, Winkler wrote a short communication entitled “Germanium, A New Non-metallic Element” about the discovery of the new element that he sent to the *Berichte der Deutschen chemischen Gesellschaft* (14). The famous quote contained therein reads (translated from German to English by this author):

> After several weeks of painstaking searching, I can state with certainty that argyrodite contains a new element that is similar to antimony, but sharply distinguished from antimony, to which the name “germanium” may be given. This discovery brought great difficulties and distressing doubts, since the minerals accompanying the argyrodite contained arsenic and antimony, which closely resembled germanium and resulted in a lack of sharp methods for their separation.

Also included in his communication was a brief description of germanium and its oxide, sulfide, and chloride. In this initial report, Winkler stated that germanium was the element eka-antimony that was predicted by Mendeleev (14) although later it would be realized that this new element was actually eka-silicon.

On February 12, 1886, Winkler received a note from Viktor von Richter, who was at Breslau in Silesia (then part of Germany, now Wrocław, Poland), describing the publications of Mendeleev and Meyer detailing their laws of periodicity. It was von Richter who correctly identified that the new element germanium was *not* eka-antimony as Winkler had proposed, but rather eka-silicon. In a letter dated February 25, 1886, von Richter wrote to Winkler to inform him of this. He stated that based on the properties of the oxide, sulfide, and chloride of the new element, it must lie in between gallium and arsenic, and that the properties of eka-antimony would be much different than those exhibited by germanium.

Next to step in to comment on the discovery of the new element was Lothar Meyer, who agreed with von Richter that the new element was indeed identical to eka-silicon rather than eka-antimony. Finally, a letter dated February 26, 1886, arrived for Winkler from St. Petersburg from Dmitri Mendeleev. This was the first interaction between Mendeleev and Winkler, but certainly not the last. In fact, the two scientists forged a friendly relationship and exchanged many personal messages over the subsequent years. This is interesting, since Mendeleev spoke little German and Winkler’s knowledge of Russian was also quite limited. Mendeleev used a translator to compose the letters he sent to Winkler, and his letter of February 26 offered a different assessment as to where germanium should lie in the periodic system. Mendeleev suggested that germanium could not lie between antimony and bismuth as eka-antimony because its atomic weight would have to be between 160 and 165 g/mol. Mendeleev suggested that germanium should fit between cadmium and mercury in the periodic system, such that it would have an atomic mass of approximately 155 g/mol, and he maintained that the new element could not be eka-silicon.

Winkler himself was by now confident that the identity of germanium was indeed that of eka-silicon, and it would be the determination of the actual atomic mass that would finally confirm this. Winkler was eager to carry out a full characterization of germanium, but there was the complication that he needed more argyrodite to provide more material in order to carry out a detailed characterization.

Fortunately, the managing director of the Himmelsfürst mine, Eduard Wilhelm Neubert, was generous and provided Winkler with a total of 5.34 kg of argyrodite, with the stipulation that the silver obtained from this material would be returned. This ore ended up yielding about 100 g of germanium. In five months of intense research, Winkler was able to obtain the majority of the compounds of the element for which Mendeleev had made predictions. The properties of both elemental...
germanium and those of its compounds agreed very well with those predicted by Mendeleev.

This confirmed the power of the periodic system of the elements proposed by Mendeleev, which at this time still had a great many doubters (15). Winkler published a second, longer and more detailed account of his findings in July 1886 (16). In this, he detailed the properties of germanium including the determination of its atomic weight of 72.32 g/mol from GeCl₄, as well as the oxide GeO₂, the sulfides GeS and GeS₂, and the iodide GeI₄. In this publication, Winkler also stated (again translated from German to English by this author):

There cannot be more convincing proof of the principle of the periodicity of the elements than that implied by the previously hypothetical eka-silicon. It serves as an important advance in chemistry and is a mighty step into the realm of knowledge.

What’s In a Name?

Interestingly, naming the new element germanium caused a bit of a stir of controversy. Winkler had at one point considered naming his new discovery neptunium, but decided against it. It was Albin Weisbach who suggested that Winkler name the element after the land in which it was first discovered, and so Winkler followed the example of Paul-Émile Lecoq de Boisbaudaran and L. F. Nilson, who named their newly discovered elements Gallium in 1875 and Scandium in 1879 after their home countries.

In June 1886, Dr. G. Quesneville, the editor of the French journal Moniteur Scientifique, accused Winkler of bringing nationalism into science, and insisted that Winkler give up the name germanium and that the naming of it should be up to him (17). However, plenty of researchers supported Winkler’s naming of the new element, including Lothar Meyer. Meyer joked that Quesneville didn’t realize that the name gallium had been derived from Gaul, but rather assumed it was based on the name of its discoverer Lecoq, as this word means “rooster” in French and Gallus is the Latin word for rooster. Further, Meyer jested that Winkler should change the name of germanium to Angularium, since the Latin word Angulus translates to Winkel in German or angle in English (18).

The same journal reiterated its challenge to change the name of germanium in March 1887 (19). In response, Winkler asked Mendeleev to comment on the matter, which he immediately did. Mendeleev indicated that the name eka-silicon, as well as eka-aluminum and eka-boron, were suggested only as temporary names and that he was delighted that they had been replaced by names that paid tribute to the nations in which the elements themselves had been discovered. He further stated that the use of provisional names was in itself rather foolish, since nature isn’t based on provisional thoughts but rather through the expression of knowledge. This ended the dispute over the name of the element (20). Of course, this trend also continued as Marie Curie named one of her newly discovered elements polonium in 1898 after her home country (which did not exist on the map of Europe at the time), and Marguerite Perey named her newly discovered element francium in 1939 after her homeland as well.

Too Quick (Silver) with Envy?

If the dispute over the name of the new element wasn’t enough, some individuals attempted to pull the rug from under Winkler’s feet after realizing they had passed over the discovery of germanium. Winkler’s careful and meticulous mind and hands in the lab resulted in the identification of the new element, and others were quick and/or eager to discredit him for his discovery. Theodor Richter, who passed away in Freiberg on September 25, 1898, was the recipient of an obituary in an Austrian Magazine that claimed that Richter was the true discoverer of germanium (20). The ore argyrodite had been in Richter’s possession at one point and he had examined it in his laboratory, but he had not the slightest idea that he had before him a new element. He clearly mistook germanium for mercury.

Winkler was swift to reply to this claim, but the editor of the Austrian journal refused to print his retort (20). The whole point was disproven of course by both Albin Weisbach and Friedrich Kohlbeck. The latter was a long-time an assistant to Richter, and clearly knew that Richter had mis-analyzed the new element. Of course, Weisbach had originally asked Winkler for an elemental analysis of argyrodite and also knew the truth. All of these false claims ultimately garnered support for Winkler and furthered his reputation as the discoverer of the new element.

Curiously enough, a mineral in the Freiberger collection from 1820 named Plusinglanz by Johann Friedrich August Breithaupt (Winkler’s uncle), was also ignored. It was not until 1900, when the mineral collection was reorganized, that this sample was identified as argyrodite.
Opportunity and a meticulous set of hands and eyes, as well as an intense passion for chemical analysis, paid off for Clemens Winkler and he remains the undisputed discoverer of the element germanium.

Clemens Winkler and Dmitri Mendeleev met in 1900 in Berlin, on the occasion of the 200th anniversary of the Prussian Academy of Sciences, and this is likely to be the most well-known portrait of the two scientists (Figure 8). It hangs in the conference room of the Clemens Winkler building at the Technische Universität Bergakademie Freiberg. It is truly an amazing capture of a predictor of a new element and the discoverer of said element. To be able to listen to what these two brilliant researchers talked about would be an amazing experience!

Figure 8. Winkler and Mendeleev in Berlin in 1900. Courtesy of Technische Universität Bergakademie Freiberg.

Clemens Winkler remained on the faculty of the Technische Universität Bergakademie Freiberg until 1902, at which point he resigned his professorship. He passed away on October 8, 1904, in Dresden due to complications from carcinoma. His legacy remains one of an intense passion for science and discovery, and he is highly revered in Freiberg to this day as well as in the chemistry community. Several monuments in Freiberg exist to celebrate his legacy (Figure 9).

Further Reading

Several additional accounts of the life and achievements of Clemens Winkler are available in the literature (13, 18, 21, 22), as well as an in-depth biography written by Mike Haustein (20).

References and Notes

5. J. L. Meyer, Die Modernen Theorien der Chemie, Maruschke & Berendt, Breslau, Germany, 1864, p 137.
17. Dr. Q [G. Quesneville], “Le Germanium,” Moniteur Scientifique, 1886, 16, 691.
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About the Author

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It will hold an online celebration on July 3. Its 8th Chemistry Congress was to have been held in Lisbon, Portugal, later this year; that conference has been postponed to 2022, in late August and early September, still in Lisbon.