Berzelius' Discovery of Selenium

"Undersökning af en ny Mineral-kropp, funnen i de orenare sorterna af det vid Fahlun tillverkade svaflet." [1]

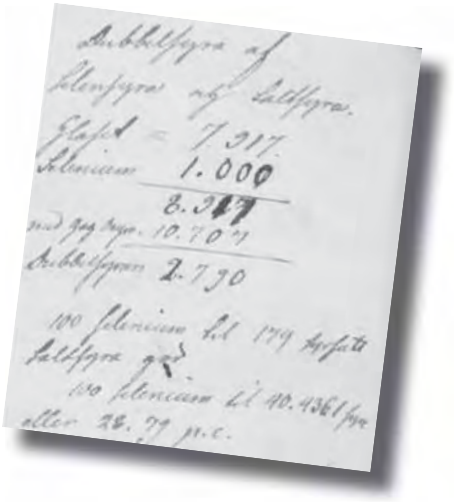
by Jan Trofast

Swedish Discoveries of New Elements

Sweden has a long tradition of mining and assaying. As early as the mid–17th century, Sweden had a chemical laboratory devoted to the study of minerals and ores and the art of mineral analysis. The resulting research was often used to improve mining, iron, and steel production. During the first decades of the 19th century, Jacob Berzelius' laboratory in Stockholm became the center of these activities. From 1803 to 1843, Berzelius (1779–1848) and his Swedish pupils J.A. Arfvedson, N.G. Sefström, and C.G. Mosander discovered and characterized no less than 10 new elements. Many of these discoveries were made using a simple instrument—the blow pipe.[2]

Elements Discovered by Swedish Chemists and Miners

Georg Brandt	cobalt	1735
Axel Fredrik Cronstedt	nickel	1751
Johan Gottlieb Gahn	manganese	1774
Carl Wilhelm Scheele	oxygen	1770s
Peter Jacob Hjelm	molybdenum	1782
Anders Gustaf Ekeberg	tantalum	1802
Jacob Berzelius	cerium	1803/4
	selenium	1818
	zirconium	1824
	silicon	1824
	thorium	1828
Johan August Arfvedsson	lithium	1817
Nils Gabriel Sefström	vanadium	1830
Carl Gustav Mosander	lanthanum	1839
	erbium	1843
	terbium	1843
Lars Fredrik Nilsson	scandium	1879
Per Theodor Cleve	holmium	1879
	thulium	1879



Determination of the composition of selenic acid. From Berzelius' laboratory notebooks, Ms. Berzelius, 24:6, Royal Swedish Academy of Sciences, Stockholm.

The Gripsholm Chemical Factory

The first major chemical factory in Sweden was established in 1800 in a former distillery adjacent to the Castle of Gripsholm. Following drawn-out negotiations, the factory owners were granted the right to produce alcohol for the manufacture of acetic acid. At that time, one of the major uses of acetic acid was for the production of white lead paint. However, a poor business climate, unfair competition, and incompetent technical management forced the Gripsholm factory into liquidation in 1816. Fortunately, the factory was soon acquired at an auction by some businessmen and the chemists Johan Gottlieb Gahn (1845–1818), H.P. Eggertz, and Jac. Berzelius. Gahn's personal commitment to the business, persuaded Berzelius to join. Thus, three distinguished chemists became linked to the company. Berzelius had been one of the experts in settling disputes concerning the manufacturing rights of white lead. In a long letter to Gahn in late 1816, Berzelius discussed the chemical processes for the production of acetic acid and the improvements he considered necessary.[3]

As a devoted scientist, Berzelius was in principle disinterested in business, but in this particular case, he saw the potential to use scientific knowledge to establish a robust and profitable industrial business. He participated actively in matters in which he considered

himself capable of contributing. A typical example is the isolation of the new element selenium from the bottom sludge of the lead chambers used for sulfuric acid production.[4]

The Discovery of Selenium

Berzelius and Gahn met at Gripsholm in August 1817. Berzelius spent more than one month there, studying, *inter alia*, technical issues related to the production of sulfuric acid and nitric acid (aqua fortis). The former owner of the factory, M. Bjuggren, had noted that a reddish sludge occurred in the lead chamber, only when pyrite (an iron sulfide) from the mine in Falun was used. The sludge was believed to be an arsenic compound and hence the Falun pyrite was avoided. However, Gahn and Eggertz both came from Falun and considered it interesting and important to use Falun pyrite. Therefore, Gahn and Berzelius—being the experts—tried to analyze the reddish sludge. By roasting 200 kg of sulfur they obtained about 3 g of a precipitate. Their subsequent chemical analysis of the sample indicated the possible presence of tellurium (discovered in mines in Transylvania in the 1780s). However, Berzelius doubted this result since tellurium had never been found in minerals from Falun. Nevertheless, he wrote about tellurium in letters to his close friends Alexandre Marcet and H.G. Trolle Wachtmeister in 1817.[5] In early 1818, Berzelius repeated the experiments in his Stockholm laboratory and concluded that the sludge must contain a new element.

Statue of Jacob Berzelius in Berzelii Park, Stockholm, Sweden.

The new element had properties of a metal, and was similar to sulfur, initially suggesting it to be a new species of sulfur. In its metallic state, it had a brilliant grayish lustre. When heated by a candle using blowpipe analysis, it burned with an azure-blue flame and emitted a strong odor of horseradish, typical of tellurium. This smell may initially have fooled Berzelius and Gahn.

Klaproth had assigned tellurium (Latin: tellus, earth) to Müller von Rechenstein's new element in 1784. Berzelius chose the name selenium (Greek: selene, moon) for the new element, noting its resemblance to tellurium. The naming was described (in Swedish):

> *. . . skola beskrifvas vara en egen förut okänd brännbar mineralkropp, hvilken jag har kallat Selenium af* ∑εληνη, *måna, för at dermed utmerka dess nära slägtskap med Tellurium.*[6]

Berzelius was able to prove that selenium was indeed a new element after establishing its properties, as well as the properties of the compounds it formed with metals, oxygen, hydrogen, sulfur, phosphorus, and different salts. Due to the similarity between selenium and sulfur and tellurium, Berzelius carefully investigated the properties of these elements (e.g., their ability to form gaseous compounds and their reactivity towards oxygen and metals). In the appendix to the third volume of his *Textbook in Chemistry*, published in 1818, Berzelius gave the formulas of 90 different selenium compounds (58 selenias, 20 selenietum, and 12 hydroselenietum) together with the atomic weight of the element itself. A remarkably high number of compounds!

Berzelius tried to reduce the selenium salts to the pure metal in different ways, but found it difficult to obtain it in a pure enough form for an atomic weight determination. The impurities, mainly mercury, copper, tin, lead, zinc, arsenic, and iron were difficult to remove. Eventually, he managed to obtain beautiful crystals of selenium, still preserved in the Berzelius collection in Stockholm, that he used to determine the atomic weight. These crystals were featured on a stamp commemorating the 200th anniversary of the Karolinska Institutet, the medical school founded by Berzelius and others and where Berzelius was a professor for 25 years.

According to Berzelius, selenium formed two oxides—selenic oxide and selenic acid. His analysis of selenic acid gave the following:

	Content of each element (by mass %)	Content % by mass of oxygen per 100 % selenium
Selenium	71.261	100
Oxygen	28.739	40.33

Selenic acid corresponds to what we today denote as selenious acid (H_2SeO_3). Berzelius reported its anhydride (SeO_2) and assumed the selenic acid contained two oxygen atoms per selenium. Today, this compound theoretically contains 28.84 percent by mass oxygen—a remarkably accurate analysis by Berzelius in 1818![7]

Berzelius determined the atomic weight of selenium to be 495.91 (O=100), corresponding to 79.34 (O=16).[8] The value today is 78.96, which again shows the accuracy of his chemical analysis.

His analysis of seleniuretted hydrogen (hydrogen selenide) gave the correct formula:[9]

	Content of each element (by mass %)	Atomic mass	Corresponding formula
Selenium	97.4	495.91	= Se
Hydrogen	2.6	13.27	= 2H

Since selenium possessed a brilliant metallic lustre, Berzelius thought it should be considered a metal. He subdivided the metals into two classes, those that are capable of forming acids, and those that act as bases: ". . . I place selenium among the acidifiable metals near arsenic . . . ."[10]

Berzelius experienced first hand the toxicity of the gaseous selenium compounds, particularly seleniuretted hydrogen (hydrogen selenide). As a medical doctor, Berzelius carefully described the sensation:

> *The gas has the odor of sulphuretted hydrogen gas [hydrogen sulfide], when it is diluted with air; but if it is breathed less diluted, it produces a painful sensation in the nose and a violent inflammation, ending in a catarrh, which continues for a considerable length of time. I am still suffering from having breathed, some days ago, a bubble of selenuretted hydrogeous gas, no larger than a small pea. Scarcely had I perceived the hepatic taste in the fauces, when I experienced another acute sensation: I was seized with a giddiness, which, however, soon left me, and the sensibility of the schneiderian membrane was so far destroyed that the strongest ammonia produced scarcely any effect upon the nose.*[11]

Berzelius' first announced the new element in a letter of 27 January 1818 to J.S.C. Schweigger in Germany, followed by a letter in April for immediate publication in his *Journal für Chemie und Physik*, XXI (1817), 342–344. In February, he sent descriptions to scientific

Jacob Berzelius (1779-1848) from a daguerreotype taken by J.W. Bergström 1844. Royal Swedish Academy of Sciences, Stockholm. ©Lennart Nilsson, photography/Scanpix.

friends including C.L. Berthollet[12] (published in *Annales de Chimie et de Physique*), A. Marcet (published in *Annals of Philosophy*) and H.G. Trolle Wachtmeister.[13] The comprehensive investigation of the discovery of selenium was finalized in April 1818 and published in *Afhandlingar i Fysik, Kemi och Mineralogi*, VI, (1818), 42–144.[14]

These *Afhandlingar* (Dissertations) were published in six volumes from 1806 to 1818 by Berzelius and a few of his friends as a practical way of publishing scientific results without being in conflict with other Swedish journals at the time. *Afhandlingar* contain the remarkable scientific achievements made by Berzelius during his most productive years. The discovery of selenium

was also included in his *Lärbok i Kemien* (*Textbook in Chemistry*), III (1818), 410–417, although the element had already been described in the second volume of the textbook. The discovery was further reported to the Royal Academy of Sciences in Stockholm by publications in its transactions for 1818.[15] Selenium was first isolated from Falun pyrite, but Berzelius also searched for selenium in other minerals. He found 38.5 percent selenium in "selen-copper" or selenite (Cu_2Se, later called Berzelianite) and also in eukairite (AgCuSe) from Skrikerum in Sweden.

Selenium was discovered thanks to the curious, analytical, and observant mind of Berzelius at a time when he was also heavily occupied with teaching medical students and overseeing his busy chemical laboratory. Selenium is now known as a trace element, which is essential for important antioxidant systems, thyroid function, and the immune system.

The discovery of selenium—just one example of Berzelius' many accomplishments—further established his reputation as one of the world's leading chemists of the 19th century. He revised the chemical nomenclature and in 1813 introduced the atomic notation system based on the Latin names of the elements, which, in principle, is still in use. He allowed these symbols to design the number of mass units given by the atomic mass of the particular element. Using this formalism, he could construct elegant and simple empirical formulas describing the composition (in mass %) of a given chemical compound. This important innovation finally translated chemistry into the language of atomic theory. For several decades, Berzelius dominated his scientific field more than any other chemist since.

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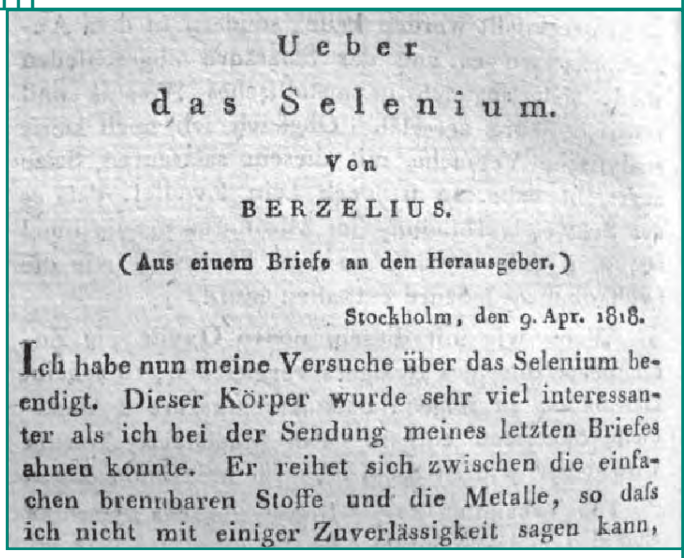

Ueber
das Selenium.
Von
BERZELIUS.
(Aus einem Briefe an den Herausgeber.)
Stockholm, den 9. Apr. 1818.

Ich habe nun meine Versuche über das Selenium beendigt. Dieser Körper wurde sehr viel interessanter als ich bei der Sendung meines letzten Briefes ahnen konnte. Er reihet sich zwischen die einfachen brennbaren Stoffe und die Metalle, so dafs ich nicht mit einiger Zuverlässigkeit sagen kann,

The letter of 9 April 1818 from Jac. Berzelius to J.S.C. Schweigger was published in* Journal für Chemie und Physik, *bd XXI (1817), 342.

Notes and References

1. "Investigation of a New Mineral, Found in the Impure Varieties of Sulphur, Manufactured at Fahlun"
2. U. Burchard, The History and Apparatus of Blowpipe Analysis, *The Mineralogical Review*, 25 (1994), 251–277.
3. Letter from J. Berzelius to J.G. Gahn 7 Oct. 1816, *Jac. Berzelius Brev*, IV:2 (1922), 140–142.
4. The laboratory notebooks describing the experiments on the discovery of selenium performed by Jac. Berzelius together with drafts to different publications on selenium are kept at the Royal Swedish Academy of Sciences, Stockholm—Ms. Berzelius 24:6; 24:8 and 27:25:1-2.
5. Letter from J. Berzelius to A. Marcet 23 Sept. 1817, *Jac. Berzelius Brev*, I:3 (1914), 155-159.
6. . . . should be described to be a characteristic, not previously known, combustible mineral body, which I have called Selenium, derived from ∑εληνη, moon, in order to indicate its resemblance with Tellurium." Ms Berzelius 27:25:1, Royal Swedish Academy of Sciences, Stockholm.
7. In his laboratory notebook Berzelius gave the value of the oxygen content as 28.79%!
8. Jac. Berzelius et al., *Afhandlingar i Fysik, Kemi och Mineralogi*, VI, (1818), 42-144, particularly 68-74.
9. Ibid., 79.
10. Letter from J. Berzelius to A. Marcet 6 February 1818, published in *Annals of Philosophy*, XI, (1818), 447–449.
11. Letter from J. Berzelius to A. Marcet 6 February 1818. Marcet wrote on 25 March to John Bostock in order for the information to be published (*Annals of Philosophy*, XI (1818), 291–93).
12. Letter from J. Berzelius to C.L. Berthollet 9 Feb. 1818. The selenium work was published in *Annales de Chimie et de Physique*, 9 (1818), 160--180, 225–267, 337–365.
13. Letter from J. Berzelius to H. G. Trolle Wachtmeister 17 February 1818, published (ed. J. Trofast) in *Brevväxlingen mellan Herr Professoren Jac. Berzelius och Hans Excellens H.G. Trolle Wachtmeister,* part 1 (1998), 40-42.
14. A complete translation into English was published in *Annals of Philosophy*, XIII (1819), 401–412; XIV (1819), 97–106, 257–265; 420–427; XV (1820), 16–27.
15. Jac. Berzelius, *Kongl. Vetenskapsakademiens Handlingar*, (1818), 13–22.