

Rediscovery of the Elements

Yttrium and Johan Gadolin

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The Beginning of the Rare Earths: Ytterby. (Figure 1). For centuries the Chinese were the masters of fine porcelain manufacture. In 1708, Europe learned the art when the two Germans, Johann Friedrich Böttger (1682–1719) and Ehrenfried Walther von Tschirnhaus (1651–1708), discovered how to make quality chinaware from feldspar and quartz.¹ Swedish porcelain factories, such as Rörstrand in Stockholm in 1726, developed a great appetite for premium feldspar and quartz available on Resarö Island (Figure 2) in the Swedish archipelago 20 kilometers northeast of Stockholm.¹ On this island near the village of Ytterby, a mine was developed (Figure 3) which could furnish this profitable raw material in abundance (Figures 4, 5, 6).

In 1787, a Swedish artillery officer and amateur geologist, Lieutenant Carl Axel Arrhenius (1757–1824), visited the Ytterby Mine^{2,3} and noticed an unusual heavy black rock which occurred in narrow layers through the mineral quartz beds (Figure 7). He passed a specimen on to Bengt Reinhold Geijer (1758–1815), Inspector of Mines in Stockholm. A year later Geijer announced⁴ to the world the “heavy rock that my friend Arrhenius found . . . in Ytterby three miles from Stockholm” (German Meile = 4.6 English miles). Geijer performed some preliminary tests, such as “Berlinblau,” proving the existence of iron (reaction with potassium ferrocyanide to form the blue pigment “Prussian blue”), and he speculated that perhaps the “Schwerstein,” (“heavy rock”) contained “Wolfram” (tungsten), recently discovered by Scheele in 1781 in Köping, Sweden.⁵

For a complete chemical analysis of his “Schwerstein” Arrhenius turned to Johan Gadolin (1760–1852), (Figure 8) a professor at the University of Åbo in Turku, Finland (the city

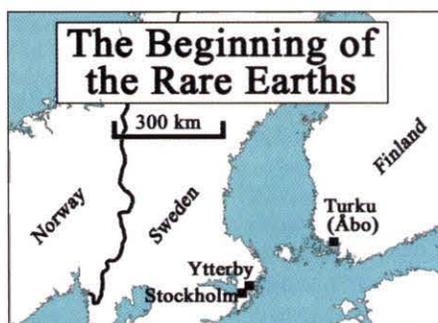


Figure 1. The history of the rare earths begins with the Ytterby Mine, where the source mineral for yttrium was found; and Åbo (now called by the Finnish name Turku), where Johan Gadolin discovered yttrium in the Ytterby Mine specimen. Ytterby, 20 km northeast of Stockholm, means “Outer village” in Swedish.

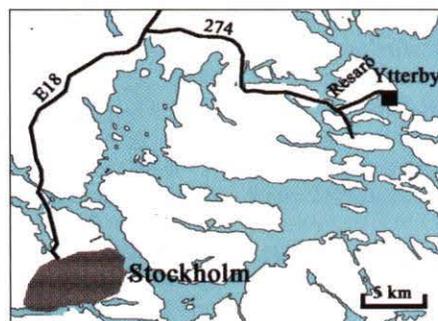


Figure 2. The village of Ytterby, on the island of Resarö, historically could be reached only by boat. It can now be accessed by road from Stockholm; public transportation (bus) is also available.

was then called Åbo, a part of Sweden). Johan Gadolin, a native of Åbo, had studied under Torbern Bergman at Sweden’s major university at Uppsala and written a dissertation on the analysis of iron.³ In addition to his native Swedish, he also was fluent in Latin, German, English, French, Russian, and Finnish.⁶ He traveled extensively through western Europe and visited universities and mines in England, Ireland, Holland, and Germany, finally returning to the University of Åbo in 1797.³ Despite



Figure 3. The Ytterby Mine (N 59° 25.60 E 18° 21.21) can be reached directly from Ytterbyvägen (vägen = road) on the eastern end of Resarö Island. The slope leading up to the mine is littered with numerous interesting minerals. About the mine area are streets named Yttriumvägen, Terbiumvägen, Gadolinivägen, Fältspatsvägen, Glimmervägen (glimmer = mica), Tantalvägen, and Gruvvägen (gruv = mine).

the high activity of chemical research in Paris, he never visited France, possibly because of his concern about the political climate there.⁶

Gadolin’s important researches included thermochemistry—he refined the values for the heat of ice and showed it was identical to that of snow^{3,7}—and the theory of combustion—his textbook was the first in Swedish to promote the new antiphlogiston theory of Lavoisier.^{3,7} His best known contribution, however, is his discovery of yttrium in the sample provided by Lieutenant Arrhenius.

Even before the end of the phlogiston era, the best analytical chemists of the late 1700s possessed a laboratory skill that was astonishingly accurate. The most famous analytical chemists of the day were Louis Nicolas Vauquelin (1763–1829) of Paris and Martin Heinrich Klaproth (1743–1817) of Berlin. These



Figure 4. This was the original reason for the Ytterby Mine—high quality feldspar (left) and quartz (right) used in the porcelain industry. Feldspar (taken from German for “Feldspat,” meaning “field spar”) is a general term for alkali and alkaline earth aluminosilicates and is the most common mineral in the earth’s crust, comprising 60 percent. Quartz (SiO_2) is the second most common mineral. Today the Ytterby area is still littered with large amounts of both minerals.

chemists’ exquisite skill allowed them to determine the composition of minerals and to discover several new elements—long before modern techniques such as spectroscopic analysis. Gadolin was an accomplished analytical chemist as well, and his research allowed him to discover in 1794 the first rare earth, yttrium.⁸

A centuries-old method for assaying ores began with the digestion of an ore in concentrated nitric acid. When Gadolin^{2a} used this procedure on “Schwerstein,” an insoluble portion was separated and identified as silica by its calcination with sodium carbonate to obtain a clear glass. The remaining soluble portion was treated with sodium carbonate to give a hydroxide precipitate, which proved to be iron by its positive “Berlinblau” reaction, corroborating Geijer’s conclusion. The remaining solution was treated with ammonia to give additional hydroxide precipitate. Further treatment of the solution with KOH gave no further precipitate, indicating that there was no calcium, magnesium or tungsten (these cations precipitate in KOH but not in ammonia)—disproving Geijer’s guess that tungsten was present. When treated with excess KOH, a minor portion of the gray hydroxide precipitate redissolved, identified as aluminum because of its amphoteric nature.⁹ The remaining precipitate of yttrium hydroxide was characterized by Gadolin with reactions with various acids and with the blow pipe. He concluded he had a new earth:^{2a}

“These properties suggest that this earth has similarities with alum and with lime, but also dissimilarities from both of these, as well as other known earths, whence it should be included among the simple earths...” He thus proposed the composition of the mineral to be 31 parts silica, 19 parts aluminum oxide, 12 parts iron oxide, and 38 parts of an unknown earth (“unbekannte Erdart”).



Figure 5. The Ytterby Mine is now heavily overgrown with trees and other vegetation. The ASM (American Society of Metals) International has erected a sign recognizing the site as a historical landmark, the “birth-place” of the rare earth elements.

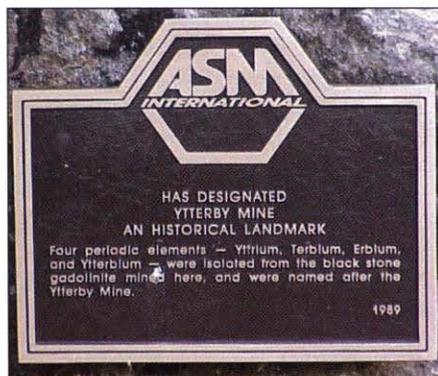


Figure 6. The ASM sign tells us that “Ytterby” was the physical and etymological source for four elements. This mine also furnished minerals for the discovery of holmium, scandium, and tantalum.

Anders Gustaf Ekeberg (1767–1813), a professor of chemistry at the University of Uppsala (who in 1802 was to discover tantalum in yttrotantalite, Y_2TaO_4 , also collected at the Ytterby Mine,¹⁰), procured a larger, purer sample of the Arrhenius “black stone from Ytterby” uncontaminated with feldspar. He confirmed and refined Gadolin’s results in 1797, giving a composition of 25 parts of silica, 18 parts of iron oxide, $4\frac{1}{2}$ parts of aluminum oxide, and $47\frac{1}{2}$ parts of the new earth.¹¹ He gave the name “Ytterjord” (Swedish for “Ytter earth”) or “Yttria” (Latin) to the new earth, and “Ytterstein” (ytterbite) to the source mineral.

Unfortunately, Gadolin and Ekeberg did not know that their “aluminum” was a new element—beryllium, not yet discovered! This oversight was understandable, because their attention was concentrated on the new earth, yttria.



Figure 7. The Ytterby Mine was special because the rocks there were formed by slow cooling, allowing the formation of pegmatites (mixtures of quartz, feldspar, and dark minerals with large crystals). Unusual minerals such as gadolinite ($\text{Y}_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$) separated out in wide bands in the special geochemical cooling process. Johan Gadolin analyzed gadolinite and found all components in this mineral—yttrium, iron, beryllium, and silicate—but the beryllium, which had not yet been discovered (in 1798 by Vauquelin in Paris), was mistaken by Gadolin for aluminum.

Beryllium was discovered a year later by Vauquelin¹² who was studying beryl and emeralds¹³ upon the suggestion of René-Just Haüy of the École des mines in Paris, who had suggested that these two minerals, with the same crystalline form, might be chemically identical.¹² Vauquelin was fortunate that beryl/emerald contained only four elements ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$), allowing simple distinction between aluminum and beryllium not confounded by the presence of other metallic ions. In the laboratory



Figure 8. Johan Gadolin, professor of chemistry at the University of Åbo (Turku, Finland) and the discoverer of yttrium. Even though Gadolin lived to the age of 92, this is the only known portrait of him, made when he was a student at the University of Uppsala, Sweden, at the age of 19.

Vauquelin fused beryl with caustic potash (KOH); the resulting mass could be completely dissolved in muriatic acid (hydrochloric acid). Upon incomplete evaporation, silicic acid (silica) precipitated and was separated out. The filtrate, containing only aluminum and beryllium cations, was treated with caustic potash to precipitate the hydroxides. In excess KOH he then redissolved the amphoteric aluminum/beryllium hydroxide mixture. The observant Vauquelin noticed that a fraction of the hydroxides did not seem to be quite as soluble. This fraction he separated and showed to have chemical behavior distinct from that of aluminum using a few key experiments,¹⁴ viz., beryllium's solubility in ammonium carbonate, its reprecipitation in boiling KOH, its inability to form an alum, and the solubility of its oxalate or tartrate salts.¹³ Vauquelin called the element glucinium because of the sweet taste of its salts—chemists then routinely reported taste and smell of new substances—but Klaproth preferred "Beryllerde" ("beryl earth") and the name stuck.^{15b} (Note 1)

After Vauquelin's discovery of beryllium, Ekeberg realized his "Ytterbite" contained beryllium instead of aluminum.¹⁶ His refined analysis gave 23 parts of silica, 55.5 parts of yttria, 4.5 parts of beryllium, and 16.5 parts of iron. Klaproth, who also analyzed the mineral, named it "gadolinite," the name by which we know it today.^{15a} By the latter 1800s the formula^{10,17} was determined, $Y_2FeBe_2Si_2O_{10}$.

Rediscovering Turku. Today Åbo is known by its Finnish name Turku (Figure 9). The labo-

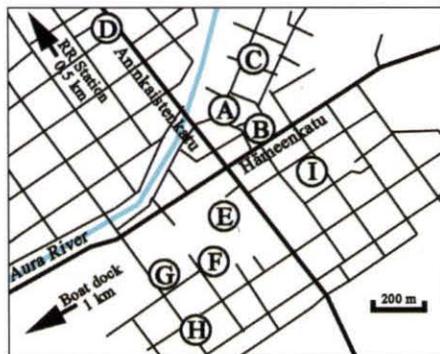


Figure 9. The predominant language in Turku is now Finnish; in Gadolin's time the city was known by its Swedish name Åbo. Key sites in Turku are: (A) Turku Cathedral (Tuomiokirkko), N 60° 27.15 E 22° 16.66. (B) First Academy Building, where Gadolin discovered yttrium, now occupied by Vanha Akatemiatalo (Old Academy Building)—Rothoviuksenkatu 2, N 60° 27.11 E 22° 16.77. (C) Modern chemistry building "Gadolinia," Porthanskatu (Porthansgatan) 3, N 60° 27.25 E 22° 16.77. (D) The origin of the 1827 fire, in Puutori square, historically a public toilet, now a restaurant Puutorin Vessa ("Public Toilet Pub"), N 60° 27.30 E 22° 16.12. Plaques are in the east side of the square, flush with the sidewalk, Aninkaisenkatu 9, N 60° 27.32 E 22° 16.20. (E) Observatory Hill, Vartiovuori ("vuori" = "hill"), N 60° 26.92 E 22° 16.65, blocked the historic fire from spreading further south. (F) Handicraft Museum (survived the 1827 fire), on Luostarinmäki (Luostarin Hill), N 60° 26.83 E 22° 16.60, a "living historic park" where guides in costume show how people lived in the early 19th century. (G) Gadolin plaques, on wall in front of fish restaurant, Kalaravintola Kaskenahde, which was the site of Gadolin's former home, 6A, Kaskenkatu, N 60° 26.80 E 22° 16.37; in back is the orphanage, site of Gadolin's laboratory, 5 Luostarininkatu, N 60° 26.80 E 22° 16.46. (H) "Old plantation," where Gadolin raised his crops, now the site of Surutoin restaurant, where formerly "Gadolin dishes" were served, Kaskenkatu 12, N 60° 26.69 E 22° 16.51. (I) Site of 1823 painter's location (see Figure 11), Kerttulinmäki (Kerttulin Hill), N 60° 27.02 E 22° 17.03. NOT SHOWN: Gadolin's grave at Mynämäki, 30 km northwest of Turku, N 60° 40.76 E 21° 59.39, in the village he retired (then known by the Swedish name Wirmo).

ratory where Gadolin performed his yttria research (Figure 10) no longer exists; it was destroyed in the Great Fire of 1827 which raced down the hill from a bakery to the center of town (Figure 11). The laboratory was beside the cathedral, which itself was badly damaged in the fire (Figure 12). In 1797, Gadolin had moved to his Turku home at Vårdberget (Figure 13), where he lived until his retirement at the



Figure 10. This is the appearance of the university ("Akademitorget i Åbo" or "Academy Square in Åbo") before the Great Fire of 1827, and where Gadolin made his discovery of yttrium in 1794 ("B" of Figure 9). The ground floor of the front right building housed the first chemical laboratory of the Academy (1764–1804). A glimpse of Vårdberget (see Figure 13), the hill where Gadolin had his garden and private laboratory, can be seen in the background at left. The top of the cathedral spire can be seen behind the building; hence, the view is southwest along the present Hämeenkatu, the main street of Turku.

age of 62. He spent his last years in Mynämäki (Wirmo), 30 kilometers to the northwest, where he lived on a manor until the age of 92.

Gadolin's legacy. Until the discovery of the transuranium elements, Gadolin shared with Samarsky (Vasili Evgrafovich Samarsky-Bykhovets 1803–1870, chief of the Russian Mining Engineering Corps 1861–1870) the honor of being the only person after whom an element was named—gadolinium and samarium, respectively. Gadolin's discovery of yttrium was the beginning of a long line of rare earths, no less than 17. Mosander (Berzelius' assistant) later in Stockholm from yttrium separated erbium and terbium, which in turn led to discovery of more of the "heavy" rare earths which were separated out—while Berzelius' subsequent discovery of cerium¹⁸ led to the discovery of the "light" rare earths^{2b} (Note 2). Berzelius later exclaimed (1843), "What a scoop it would have been if he [Gadolin] had been able to separate them!"^{2c} ○

Notes.

Note 1. Klaproth suggested glucinium be called beryllium, because "yttrium salts also were sweet."^{15b} We suspect this was an error, due to the beryllium component in the gadolinite. Modern literature (including MSDS and Merck information) does not include taste data for yttrium salts (except for redactions of Klaproth's initial comments). We conducted a private sommelier session with yttrium chloride and can report the salt to possess a pleasant tart taste, but not sweet.

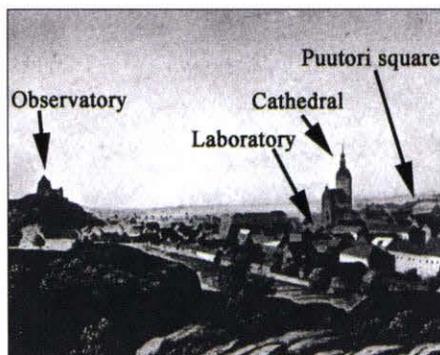


Figure 11. Postcard view of Åbo, Finland, in 1823, four years before the Great Fire, with important sites identified. This overall view emphasizes the hilly terrain of Åbo (present Turku). The view is westward from Kerttulinmäki (Kertulin Hill). The cathedral (“A” of Figure 9) and Observatory Hill (Vartiouuri) with its old observatory (“E” of Figure 9) are the prominent features. The road is the old Hämeentie (today Hämeenkatu), the historic main road out of Åbo and the present main street of Turku. Disappointingly, the old Gadolin laboratory (“B” of Figure 9) cannot be clearly discerned, although its position can be marked. The Great Fire of 1827 started in Puutori square (“D” of Figure 9) and swept relentlessly down the hill past the cathedral and the university, but it stopped at Observatory Hill. After the fire, the university continued in the observatory for several months, before it moved to Helsinki the following year. The observatory was at sea level 7000 years ago! (Scandinavia, because of geological isostasy, is lifting as the global ice melts.)

Note 2. Yttrium, discovered in gadolinite in 1794, was found over several decades to be a mixture of rare earths, yielding a series of other so-called “heavy rare earths” including erbium, terbium, ytterbium, holmium, thulium, ytterbium, scandium, and lutetium. Because of the lanthanide contraction, the “heavy rare earths” possess a smaller atomic radius, similar to that of the lighter yttrium, and they occur with it in nature.¹⁹ Cerium, discovered by Berzelius and Hisinger in 1803,¹⁸ tends to harbor in nature the “light rare earths” which are larger: lanthanum, praseodymium, neodymium, samarium, gadolinium, and europium.¹⁹

Acknowledgments.

The authors are indebted to Pekko Pykkö, professor of chemistry at the University of Helsinki, who furnished a large amount of the information regarding Turku and Gadolin (including Figure 10). Professor Pykkö actually lived at Kaskankatu 6, the site of the home of Gadolin, during the mid-1970s, and thus has a personal connection with the history of Gadolin. The home is now gone and has been supplanted by a condominium.



Figure 12. The prominent Turku Cathedral (Tuomiokirkko) was originally built of wood in the 1200s and augmented with stone 1500–1700. The cathedral (“A” of Figure 9) is in the center of historic Turku. Just to the right (out of sight) was located the chemistry laboratory where Gadolin discovered yttrium, now occupied by a modern “Old Academic Building” (“Vanha Akatemiatalo.”) The view is eastward.

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classic amphoteric hydroxides — aluminum and beryllium—will neutralize either an acid or a base. Hence, these hydroxides are insoluble in water but soluble in acids or bases, e.g., $\text{Al}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{H}_2\text{O}$; and $\text{Al}(\text{OH})_3(\text{s}) + \text{KOH} \rightarrow \text{KAl}(\text{OH})_4(\text{aq})$.

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Figure 13. Gadolin’s home and laboratory at his Turku plantation on Vårdberget (“Fire Signal Mountain”) 1797–1814 is now occupied by a fish restaurant (“G” of Figure 9). His laboratory was in back of the restaurant, a building which still exists and which is used as an orphanage (not shown). His home was not touched by the Great Fire, and his records were preserved. Two corroded copper plaques (on the stone wall above sidewalk) in both Finnish and Swedish translate “On this site at house number 161 in the Cloister Quarter the professor of chemistry at Åbo Akademi Johan Gadolin had his laboratory 1797–1814.” (Luostarinkatu, the address of his laboratory, translates into Swedish as Klostergatan, meaning “Cloister Street.”)