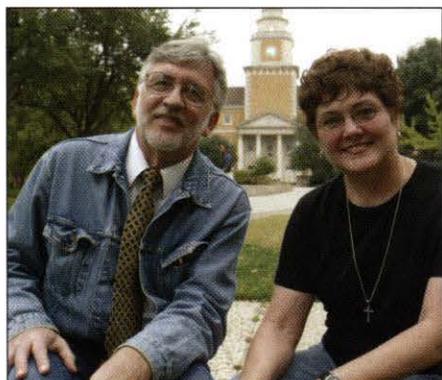


Rediscovery of the Elements

Mineral Waters and Spectroscopy



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The origin of spectral analysis: the analysis of mineral waters. In Europe health spas and community baths have been fashionable for centuries, tracing back to Roman times (Figure 1). We have seen in a previous *HEXAGON* article that Paracelsus visited several mineral baths—including Bad Pfäfers and Bad Liebenzell (see map, Figure 2)—and wrote reports on their healing powers.^{1b} When Joseph Priestley reported in 1767 that he had synthesized a synthetic carbonated water in Leeds, England, (proposing it as a cure for scurvy),² he called it “artificial Pymont water” after the famous springs at Bad Pymont, Germany (Figure 3). Another well-known Kurzentrum (health resort) in Germany was Bad Dürkheim (Figure 4), whose water was analyzed in 1861 by chemist Robert Bunsen (1811–1899) and physicist Gustav Robert Kirchhoff (1824–1887). Using their newly-founded science of spectral analysis at the nearby University of Heidelberg, they discovered two new elements, cesium and rubidium, in the Bad Dürkheim waters.^{3a} These were the first elements to be discovered spectroscopically.

Today as one enters the Altstadt (Old City) of Heidelberg, one is greeted by a towering



Figure 1. Community bath at Bad Pfäfers in the 16th century, exhibited in the Paracelsus Museum, Bad Pfäfers, Switzerland (N 46° 58.46 E 09° 29.26). The thermal baths at Bad Pfäfers hold at 37° C. Paracelsus wrote a report on these baths, deeming them “fit and healthy.”

statue of Bunsen (Figure 5). Directly across the street stands the medieval building where spectroscopy was born (Figure 6). In spite of the assertion of August Comte (1798–1857) that mankind would “never know anything of the chemical nature of planets and the stars,”⁴ upon their invention of the spectroscope in 1859 Bunsen and Kirchhoff quickly identified half a dozen elements in the sun.

“Bunsen’s greatest discovery: Kirchhoff.”^{5a} While still a graduate student at the University of Königsberg (1842–1847), Kirchhoff had for-

mulated the laws of circuitry which have been in use in electrical engineering for over a century and a half.⁶ He accepted a position at the University of Breslau (1850–1854; now Wrocław, Poland) where he met Bunsen.^{3a} He followed Bunsen to Heidelberg where the two initiated their successful collaborative work.^{3a} Thereafter Kirchhoff moved on to the University of Berlin in 1875 to accept a chair of theoretical physics.^{6a}

Kirchhoff is celebrated for his Three Laws of Spectroscopy^{6b} (1859–1962) which he formulated in Heidelberg. In these laws he differentiat-

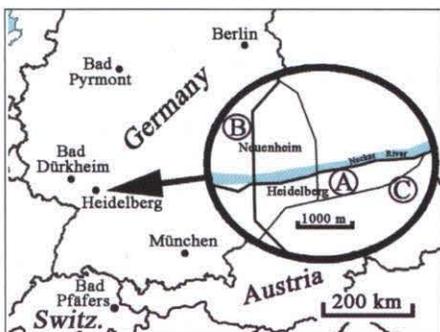


Figure 2. Bad Pfäfers, Bad Pyrmont, and Bad Dürkheim are examples of spas frequented by people seeking the curative powers of mineral waters. From the springs of Bad Dürkheim, the elements rubidium and cesium were discovered by Bunsen and Kirchhoff at the University of Heidelberg (40 km east), utilizing their newly developed method of spectroscopy. The scientific activities of the two were concentrated in one block ("A") in the Altstadt (Old City). Postwar expansion of the university spread to Neuenheim across the Neckar River, where today an impressive exhibit in the Chemistry Lecture Hall concentrating on Bunsen may be visited ("B"). Also of interest to scientific historians is the Apothecary Museum (C) located in the Heidelberger Schloß (castle), perched on a hill (N 49° 24.56 E 08° 42.81) overlooking the city.

ed (a) black-body radiation (a term he coined); (b) emission spectra, where bright lines are produced by hot gases; and (c) absorption spectra, where dark lines are observed in continuous spectra when light passes through a cooler gas.^{6c} His black-body concept had far-reaching consequences, leading eventually to Planck's quantum theory.^{6a} His understanding that the bright lines of emission spectra and the dark lines of absorption spectra were identical wavelengths (signaling the same respective elements either "hot" or "cold")⁷ allowed him to explain the puzzling Fraunhofer lines, the dark lines in the solar spectrum first described⁸ in 1814 by Joseph von Fraunhofer (1787–1826).

It had been known for a century that different elements can be distinguished by different flame tests, i.e., they glow different colors when heated in a flame.⁹ Marggraf used this technique in 1758, for example, to distinguish sodium and potassium.¹⁶ Bunsen chose this principle to analyze elements, and he used colored glass to distinguish subtle color differences, such as that between lithium and strontium, both of which give red flame tests.⁹ Kirchhoff suggested the use of a prism, which would separate the colors sharply.⁹ John Herschel in 1822 had shown that heating chlorides of strontium, calcium, barium, copper, and boric acid gave unique bright lines¹⁰ and Henry Fox Talbot dis-



Figure 3. "Dunsthöhle" [Vapor Cave], An der Dunsthöhle, Bad Pyrmont, Germany (N 51° 59.33 E 09° 15.66). Because of a unique combination of geological factors, carbon dioxide effuses up into this depression, formerly a sandstone quarry. A doctor, Johann Philip Seip, noticed rabbits and birds asphyxiating in the area, and he concluded the dry vapors would have a curative effect on human beings. In the 1720s he built stone casings on the site, in which patients lounged and recuperated from gout and edema (with heads sticking out into fresh air). Popular bathing springs in the area were saturated with the bubbly gas, and the water was sold as "Pyrmont water." Today the Vapor Cave is enclosed and locked, but can be visited with a special guide, who is careful to monitor the heavier CO₂ gas and to prevent tourists from descending below a critical level in the pit.

tinguished lithium and strontium by passing light through a prism,¹¹ but it was the team of Bunsen and Kirchhoff who combined all previous techniques and principles into one device.¹²

The invention of the spectroscope created a sensation in the scientific world, and Bunsen's "flame reaction" techniques¹³ soon replaced blowpipe analysis (pioneered by the Swedes^{14a}) which had previously been the fashionable and handy way to identify elements in mineral analysis. The more sensitive and higher resolution method of spectroscopic analysis which was used to discover cesium and rubidium soon led to the discovery of many new elements by other investigators, including thallium, indium, gallium, helium, and several rare earths.

The discovery of cesium and rubidium.

When Bunsen turned his newly-invented spectroscope to the analysis of the Dürkheim mineral waters, he found new spectral lines which announced the presence of cesium (blue line) and rubidium (red line).¹⁴ He concentrated 40 tons of mineral water to obtain weighable amounts of crude salt for chemical tests, although the original detection could be accomplished with only a minute amount of water because of the extreme sensitivity of the spectroscopic method.¹⁴

The original spectral analysis of Dürkheim waters prominently displayed the lines of cesium, but only with much effort were faint lines seen attributable to rubidium.¹⁵ Other spas signaled the presence of cesium, including Wiesbaden and Baden-Baden, but rubidium was more elusive.^{15a} A better source for rubidium was lepidolite (a lavender form of mica), principally from "Rozena in Mähren" (Moravia), today known by the Czech name Rožná, from a pegmatite outcropping on the outskirts of town (N 49° 28.82 E 16° 15.50). Lepidolite not only furnished weighable amounts of rubidium salts, but purer samples, because cesium was absent in this mineral.^{15b} Lepidolite has the typical formula $\text{KLi}_2\text{AlSi}_4\text{O}_{10}\text{F}_2$, with substitution of potassium by rubidium approaching 4% in extreme cases.¹⁶ Bunsen observed 0.2 wt. % rubidium,^{15b} corresponding to a substitution rate of K by Rb of about 1%. Bunsen was able to prepare metallic rubidium by using the "common procedure" of the mid-1800s to procure quantities of potassium: heating a mixture of charcoal and the alkali tartrate (or carbonate) to redness in an iron retort to yield carbon monoxide and the metal which was distilled directly into oil to avoid reaction with oxygen or moisture.¹⁷ In spite of these forcing and crude reaction conditions, Bunsen incredibly was able to procure a sample of rubidium which was

pure enough to give an accurate melting point of 38.5° (today's value, 38.89°).^{15b} The more electropositive cesium would not yield to this procedure; only an amalgam could be prepared. The preparation of pure cesium had to wait another 20 years, when in the same laboratory of Bunsen the more refined procedure of electrolysis was successful, using cesium cyanide.¹⁸ Modern methods of producing both metallic rubidium and cesium involve electrolysis techniques.¹⁹

The first mineral in which cesium was observed was pollucite (a zeolite) from La Spertza quarry, San Piero in Campo, Elba Island, Italy (N $42^\circ 44.83$ E $10^\circ 12.55$);²⁰ these deposits have since been depleted. Fifteen years before Bunsen's work, a sample of Elba pollucite had been analyzed by Carl Friedrich Plattner (1800–1858)²¹ who was puzzled by its "high alkali content" (at that time no alkali elements were known heavier than potassium). He died at the same time Bunsen and Kirchhoff were developing their spectroscopic techniques, never realizing that he had been dealing with a new element. Pollucite is now known to have the typical formula $(\text{Cs},\text{Na})\text{AlSi}_2\text{O}_6(\text{H}_2\text{O})$.¹⁶

Rubidium (but not cesium) salts are absorbed readily by plants. For example, analysis of tobacco, coffee, tea, oak, and beach show substantial quantities of rubidium. However, rubidium cannot replace potassium in plants, and in a potassium-free/rubidium-rich environment plants cannot live.¹⁷

Bunsen's career. Bunsen was the son of a professor of modern languages and librarian at the University of Göttingen (their home still exists and can be identified by a plaque at Untere-Masch-Strasse 30; (N $51^\circ 32.10$ E $09^\circ 55.76$). He matriculated there and received his Ph.D. in 1830, writing a dissertation on hygrometers. After traveling and studying in Paris, Berlin, and Vienna (1832–1834), he returned to Göttingen (1834–1835), where he made the significant discovery that ferric hydroxide absorbed arsenic trioxide and could serve as an antidote. After a short period at Cassel (1836–1837), he moved on to Marburg (1838–1851), where he established his reputation with cacodyl compounds (organic arsenic chemistry; named for their horrible odor). With this research, he established that organic radicals have a reality.^{2a} Berzelius, who tenaciously held the dualistic theory,^{1d} praised Bunsen's work and declared that it proved that the organic world and inorganic world abide by the same chemistry. Cacodyl was later found to have the formula $(\text{CH}_3)_4\text{As}_2$, consistent with Bunsen's vapor pressure results. Working with these compounds was extremely dangerous; in one explosion Bunsen lost an eye. After leaving



Figure 4. The Gradierbau ("graduation works") at Bad Dürkheim (N $49^\circ 27.87$ E $08^\circ 10.49$). Beginning in 1847, salt was mined here. Soon "free air inhalation rooms" were built, where hot salt water was poured over bundles of wood, creating a curative atmosphere for patients with respiratory ailments. The entrance straight ahead allows one to visit a museum and the historic sanatorium. Today Bad Dürkheim is known for its convalescence centers (Kurzentrens), as well as its specialty Riesling wines. Inset: Dürkheimer Maxquelle available for purchase in the 1800s ("Quelle" = "spring"). Bunsen and Kirchhoff could detect the presence of two new elements spectroscopically in only a few drops of the mineral water.

Marburg he no longer dealt with organic compounds.^{3a}

After a short stint at Breslau (1851–1852), where he initiated electrochemical preparation of metals (leading to his development of new batteries), Bunsen moved on to Heidelberg in 1852 where he found his true "Heimat" (home). In 1855 he initiated photochemical studies^{3b} with British student Henry Enfield Roscoe (1813–1915). This significant research involved the photochemical union of hydrogen and chlorine, quantifying the catalytic effect of light. This work required a clean, steady, colorless flame for calibration, and Bunsen decided to design a new burner.

The Bunsen burner. When Bunsen moved to Heidelberg, the laboratory was the refectory of an old monastery. There was no gas or water; instead alcohol lamps and charcoal fires, and water from an outside pump, were used. Fortunately, Bunsen had been promised a new laboratory and adjoining house which were completed in 1855. These new buildings still exist and appear remarkably the same as they did one and one-half centuries ago (Figure 7).

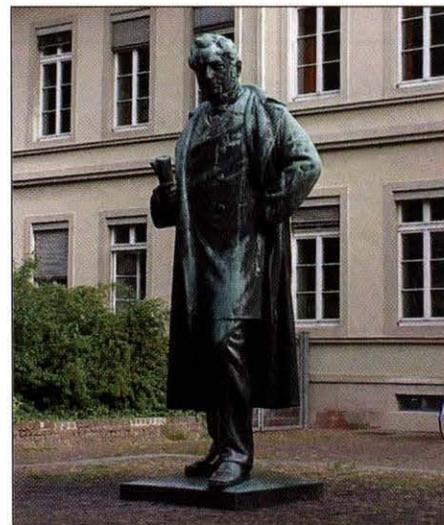


Figure 5. Statue of Bunsen in the Altstadt (Hauptstrasse 51, N $49^\circ 24.64$ E $08^\circ 41.88$). Bunsen was "fully six feet in height and built like Hercules."¹³ He could handle hot objects with total disregard, picking up the lid of a glowing porcelain crucible with his bare fingers.³ When Bunsen was blowing glass, sometimes one could smell burnt flesh.^{5a} The building in the background is the Institute of Psychology, once housing the physical sciences; Kirchhoff lived on the third floor.

When Bunsen moved into his new laboratory Easter of 1855, he decided to install piping of the new city gas (which had been lighting Heidelberg streets since 1852) into his workplace²² and began his quest for a burner that would solve the problem of luminous, smoky flames. Roscoe suggested the idea of a "gauze burner" which was used at the University College, London. The "gauze burner" was an adaptation of Davy's safety lamp, which took advantage of the fact that a metal gauze held between the source of the fuel and the flame would prevent the flame from backflashing into the fuel. This invention had been gratefully and immediately adapted by the Cornish miners, who previously had been in constant fear that their lamps would detonate explosive mixtures of gases in the mines.^{5a}

It was true that Roscoe's burner was colorless and there was no flashing and flickering caused by microscopic particles of soot; but the flame was cool and weak, and frequently would self-extinguish. Bunsen wanted to remove the gauze and pre-mix air with the fuel. This idea was greeted with alarm by his colleagues who feared accidental explosions,^{5a} but with the enlisted help of the Heidelberg University mechanic, Peter Desaga, a redesign of the tube and air intake openings yielded in 1854 an appliance which worked beautifully.²³ This burner was an essential tool for the photochemical work of Bunsen and Roscoe, and then



Figure 6. Across Hauptstraße from Bunsen's statue is this building dating from 1707, (Hauptstraße 52, N 49° 24.62 E 08° 41.87), which originally housed the inn "Zum Riesen" ("At the Ogre's"), a brewery and a schnapps distillery. In the mid-1800s it became part of the University, where Kirchhoff developed his method and theory of spectroscopy. Bunsen and Kirchhoff performed their spectroscopic discoveries on rubidium and cesium here. On the far right of this building is a plaque [see inset] that simply but profoundly describes the significance of his work: "In this building Kirchhoff turned his spectral analysis that he developed with Bunsen to the sun and the stars, thereby unlocking the chemistry of the cosmos." The building now houses the Institut für Übersetzen und Dolmetschen (Translation and Interpreter's Institute).



Figure 7. Bunsen's home and laboratory. Bunsen House/Lab, Plöck 55 (N 49° 24.62 E 08° 41.87). This house is one block south of the Hauptstraße 52 building of Figure 6. Bunsen's laboratory, built in 1855 and extending the entire block north (along Akademiestrasse, N 49° 24.59 E 08° 41.87) reaching to the "Zum Riesen" building. Bunsen's chemical work was done in this large complex. The appearance of the Bunsen home and laboratory remains virtually unchanged since his days here in the 1800s. His home is now used for the Institut für Deutsch als Fremdsprachen-philologie (German as a second language, paralleling American's ESL system).

for the flame source of the spectroscope of Bunsen and Kirchhoff.

The exhibit at the New Campus. In the Hörsaal of the Chemistry Department at the New Campus, 2 km to the west of the Altstadt (see map, Figure 2), stands a long parade of display cases (Figure 8) which hold the history of Bunsen and Kirchhoff's work at the University of Heidelberg. The original spectroscope (Figure 9) and Bunsen burner (Figure 10) are presented. Original preparations of rubidium and cesium are shown (Figure 11). Other showcases include his chromic acid battery (he found chromic acid was better than nitric acid for an electrolyte), other instruments used in his laboratory, chemical preparations, historic letters, and even his death mask. At the end of the hallway is a life-size enlargement of the famous photograph of Kirchhoff, Bunsen, and Roscoe (Figure 12). Roscoe moved in 1857 to Owens College in Manchester, England, where he gained fame with his research on vanadium compounds: he was the first to isolate the element in metallic form (Note 1). Roscoe and Bunsen remained close friends throughout their lives.

The legacy of Bunsen. Bunsen was a modest man. His "manners were simple but dignified, and his expression one of rare intelligence and great kindness."^{5a} He was quiet and helpful, always in the laboratory with his students, making sure that the beginners were helped



Figure 8. In the hallway of the Hörsaal Zentrum Chemie (Lecture Hall, Chemistry; Im Neuenheimer Feld 252) on the new campus of the University of Heidelberg (N 49° 25.11 E 08° 40.38) is this consummate display of chemical and spectroscopic equipment utilized by Bunsen and Kirchhoff.

and encouraged as well as the experienced.^{5a} Once when praised for his honors and awards, he said, "These things were valuable only because they pleased my mother, but she is no longer alive."²⁴ He is reported never to have used the word "I" ("ich") when referring to his work; instead, he always said, "Man hat gefunden. . . ." ("It has been observed. . ."). To others for their discoveries, however, he always gave full credit.¹³

Bunsen was solely occupied with experimentation and facts and resisted being drawn into theories: "One irrefragable and important act was worth an ocean of theories."¹³ In his last lectures of 1889, he did not even refer to the Periodic Law of Dmitri Mendeleev and Lothar Meyer, both of whom had worked with him in Heidelberg.^{3a}

In spite of his modesty, the name "Bunsen" is probably more familiar to the layman or begin-

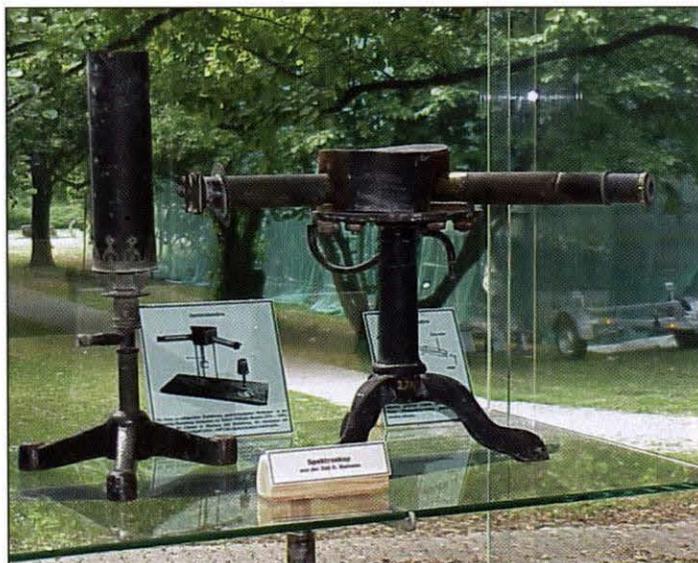


Figure 9. This is an original spectroscope developed by Bunsen and Kirchhoff. The “Bunsen” burner is to the left, with added screen and nebulizer; a collimating tube leads to the prism assembly in the middle, and a telescope tube on the right allows the eye to view the line spectrum directly.



Figure 10. Bunsen burner, “constructed by R. Bunsen himself.”

ning student than any other 19th century chemist, because of the eponymous burner. After its invention, it soon became the standard heating device in all laboratories. Beatrix Potter, the niece of Sir Henry Roscoe, has prepared a fitting tribute to the fame and historic charm of the Bunsen burner (Figure 13, the cover of this issue; and the accompanying article, page 47).

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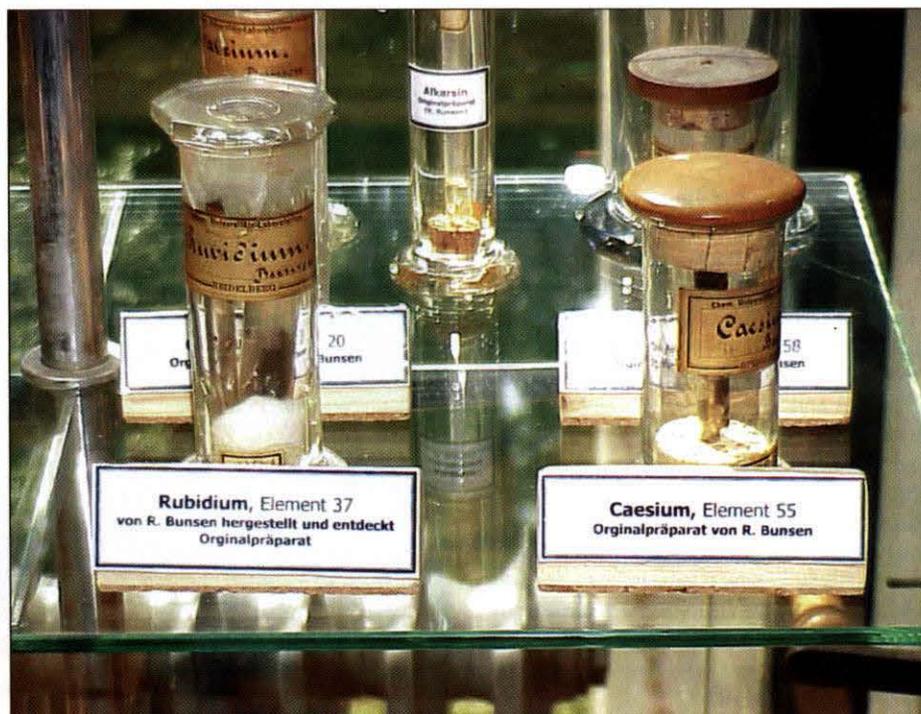


Figure 11. Original samples of rubidium and cesium.

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(continued on page 48)

Figure 12. Photograph of Kirchhoff, Bunsen, and Roscoe (left to right), with an author to show scale. This famous photograph was taken in Manchester (where Roscoe was professor; Note 1) while the two Germans were visiting England for the 1862 London Exhibition. Roscoe was involved with photochemical studies in Heidelberg and contributed the idea of the "gauze burner," the precursor to the Bunsen burner. Bunsen and Roscoe remained close friends throughout their lives despite the geographical separation across the English Channel.



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Notes.

Note 1. Sir Henry Enfield Roscoe (1824–1887) studied at the University College, London (1848–1853) and then with Bunsen at the University of Heidelberg (1855–1856). He succeeded Edward Frankland (1825–1899, noted for his introduction of the theory of valence) at Owens College in Manchester in 1857. The building comprising Owens College still stands (19 Quay Street, N 53° 28.72 W 02° 15.12). For several years Roscoe would return to Heidelberg during the summers to continue collaboration with Bunsen.^{3c,5a} His most noted work at Owens College was the first preparation of metallic vanadium in 1869 and the recognition of the many oxidation states (with associated vivid colors) of that element. His dedication to society was exemplified by his service to the unemployed textile workers of Manchester during the early 1860s during the blockade of America's cotton throughout the War Between the States. Roscoe wrote an interesting autobiography which conveys a realistic portrayal of the times in which he lived.⁶ Many of his chemical samples may be viewed in the archives of the Museum of Science and Industry (as well as exhibits on John Dalton), Liverpool Road, Castlefield (a SW suburb of Manchester), N 53° 28.63 W 02° 15.25. The Roscoe Building (Brunswick St., N 53° 28.02 W 02° 13.89) at the modern University of Manchester is named for him. ☉



Swedish scholar Bengt Hogrelius (left) translates an ancient text published in 1758 by Cronstedt, the discoverer of nickel.



Led by Alf Olaf Larsen (right), the leading mineralogist of the Langesundfjord area in Norway, the original site for the discovery of hafnium is sought in the mine area near Kragero.

March 28, 2008

Dear Jim and Virginia,

I enjoyed reading your article about Yttrium and Johan Gadolin in the spring issue of *Hexagon*. Thanks, it was well done.

The photographs and maps provide a good connection with the reality of the times. I suppose they came from Professor Pekko Pyykkö in Helsinki.

I am an organic chemist and missed getting much background on the rare earths. I joined the Alpha Phi Chapter of Alpha Chi Sigma when I was a grad student at the University of Tennessee in Knoxville in 1947.

Frank MacArtor
Wilmington, Delaware