Rediscovery of the Elements

Aluminum

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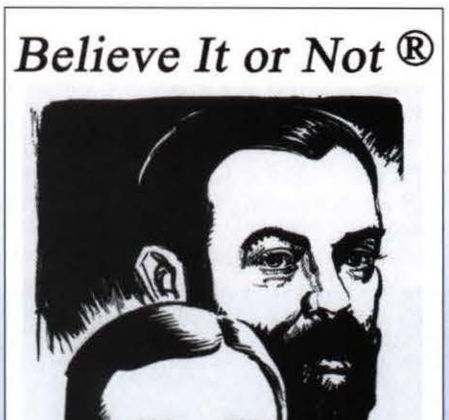

Figure 1. This Robert L. Ripley's cartoon headlines the possibility of simultaneous discovery in the sciences and reminds us that discovery will occur "when the time is ripe." Héroult's discovery is documented in his French patent application dated April 23, 1886, Hall's in a letter dated February 24, 1886, which established priority in the U.S. Patent Office. In the original cartoon published in the (London) Sunday Express, June 12, 1938, Hall and Héroult were heralded "The Aluminium Twins." (Photo, courtesy of Ripley Entertainment Inc.).

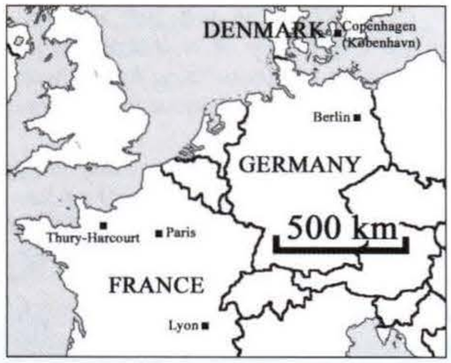

Figure 2. During the 18th and 19th centuries, the important research on aluminum was done by scientists in Denmark, Germany, and France, and in the United States (Ohio—not shown).

Aluminum, even though it is the most common metal in the earth's crust, was not isolated in elemental form until the early 1800s, and its commercial production did not commence until half a century later with the development of the Hall-Héroult process (see Figure 1).

Alum (potassium aluminum sulfate, $AlK(SO_4)_2 \cdot 12H_2O$) has been used as a mordant (fixer of dyes) for centuries.[1] Ancient mines of alum were located at volcanic sites where the alum crystallized out from hydrothermal waters rich in sulfates produced by the oxidation of extruded sulfur. By the 17th century, alum was commonly used in the paper industry, and also as an antiseptic, medicine, and a "preserver of organic bodies" (embalmer). Stahl, whom we met earlier in the *HEXAGON*[2] as the proponent of phlogiston, believed it contained lime (calcium). He showed that alum could be leached from clay, but he could not prepare it by reacting lime with various acids. There continued to be much confusion in the scientific world regarding chalk (calcium carbonate), gypsum (calcium sulfate), Epsom salts (magnesium sulfate), alum, and other "earths" until the middle of the 1700s.

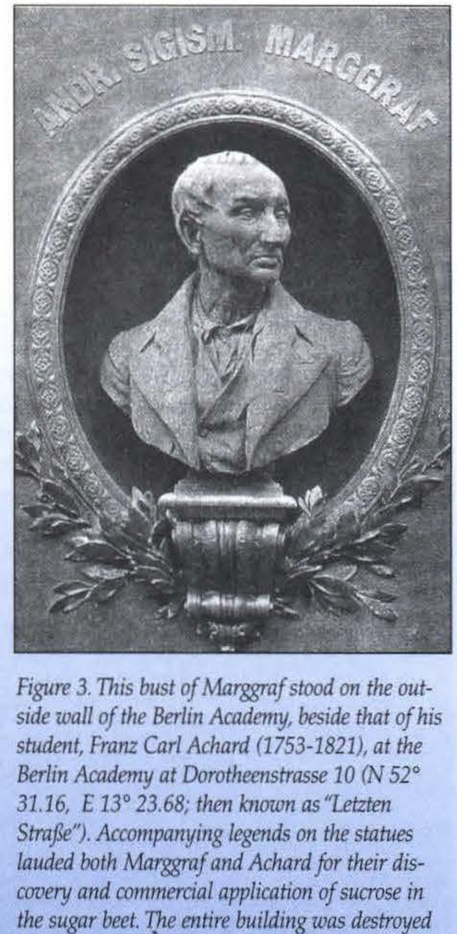

Figure 3. This bust of Marggraf stood on the outside wall of the Berlin Academy, beside that of his student, Franz Carl Achard (1753-1821), at the Berlin Academy at Dorotheenstrasse 10 (N 52° 31.16, E 13° 23.68; then known as "Letzten Straße"). Accompanying legends on the statues lauded both Marggraf and Achard for their discovery and commercial application of sucrose in the sugar beet. The entire building was destroyed in the Second World War. The site is now a vacant lot in back of the Humboldt University.

The earliest definitive work on alum (Figure 2) was done in 1754 by Andreas Sigismund Marggraf (1709–1782) of Berlin[1] (Figure 3), who distinguished the respective earths of alum and lime.[3] When he reacted lime with oil of vitriol (sulfuric acid), he obtained only selenite (a transparent form of calcium sulfate). He dissolved alum in alkali and precipitated "Alun-Erde" ("earth of alum," aluminum hydroxide). He then dissolved this earth in nitric acid and showed that calcium compounds (e.g., lime) could not be generated. By very carefully adding the correct amount of oil of vitriol and fixed alkali (KOH), he was able to regenerate the original alum.[3]

Marggraf performed his aluminum work at the Berlin Academy (Figure 4), where he began working in 1754 after leaving his father's apothecary (Note 1). Marggraf was perhaps the first modern analytical chemist.[3] The chemical biographer Thompson described him so: "His papers have a greater resemblance to those of Scheele than of any other chemist to whom we can compare them. He may be considered as in some measure the beginner of chemical analysis; for, before his time, the chemical analysis of bodies had hardly been attempted."[3] Even though his career preceeded Lavoisier's, he appeared to ignore the theory of phlogiston and instead used facts and logic to produce work that appears amazingly modern today.[3] Other important work by Marggraf at the Berlin Academy included the first careful characterization of sodium and potassium, where he clearly differentiated these two alkalis for the first time.[3,4]

Figure 4. The Humboldt-Universität zu Berlin is the former Berlin Academie. At this main entrance on the historic boulevard dressed with linden trees stands the statue of Alexander von Humboldt (Unter den Linden 6, N 52° 31.06 E 13° 23.64). Forty meters to the left sits a statue of his brother Wilhelm, the founder of the university. Straight ahead 200 meters to the north, on the other side of this building, is the old site of the Berlin Academy at Dorotheenstrasse 10. In the other direction, to the rear of the viewer, 100 meters to the south, is Bebelplatz, the site of the Nazi book burnings in 1933.

Figure 5. Portrait of Ørsted (Drawing of I.V. Gertner; courtesy of the Niels Bohr Archive).

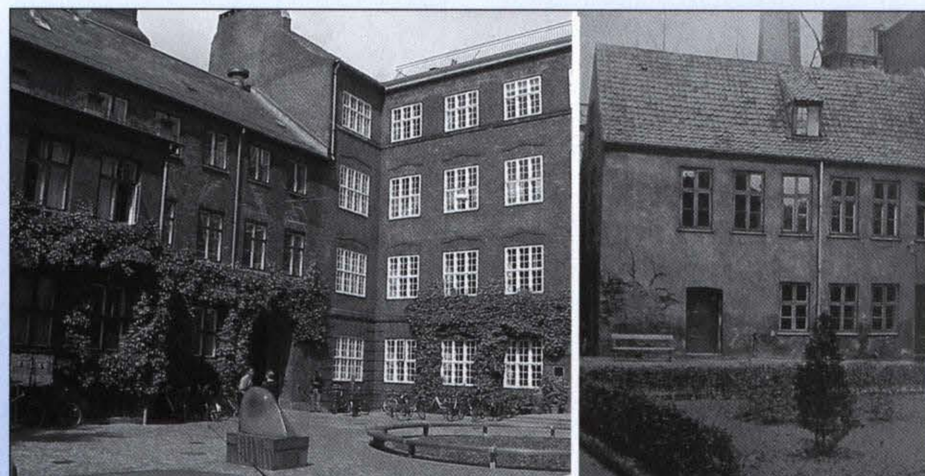

Figure 6. Right. Ørsted's chemical laboratory where he discovered metallic aluminum in 1825 (Studiostræde 6, N 55° 40.75 E 12° 34.24). This is not where Ørsted made his famous electromagnetism discoveries (Note 2). This building was taken down in 1914. Left. The appearance of the courtyard today where the old chemical laboratory stood. Outside the courtyard on the main street, a plaque (in Danish) translates: "Hans Christian Ørsted lived here from October 1824 until the day of his death 9 March 1851."

Sir Humphrey Davy at the Royal Institution in London from 1807–1808 was able to separate for the first time several alkali and alkaline earths into elemental (metallic) form,[3,5] but he was unsuccessful in isolating metallic aluminum. This first person to accomplish this task was Hans Christian Ørsted (1777–1851), (Figure 5) the discoverer of electromagnetism (Note 2). Ørsted's work in chemistry was ignored for years—it has only been recently established that he should be credited with the first isolation of elemental aluminum.[6] Although mainly interested in physics, Ørsted persuaded the University of Copenhagen in 1823 to set up a chemical laboratory; accordingly, a two-story stable was converted to a professor's residence, which included not only the university physics collection but also the requested facilities. Here he prepared elemental aluminum in 1825 (Figure 6). Ørsted passed elemental chlorine over a mixture of alum and charcoal to prepare aluminum chloride (the classical method of producing volatile metal chlorides), which he then treated with a potassium amalgam to prepare a few chips of metal "resembling tin." Ørsted did not attempt to purify the metal or to characterize it fully, and his attention turned to other scientific matters.

Friedrich Wöhler (1800–1882) visited Ørsted in Copenhagen, and hearing that the Danish scientist planned not to pursue the aluminum studies, then took up the task himself of preparing larger and purer quantities of aluminum.[7] The laboratory in Berlin where Wöhler performed his work was the same as where he prepared elemental yttrium and beryllium, and verified the presence of the new element vanadium. (In a previous *HEXAGON* we visited Wöhler at this Berlin site[8].) Wöhler has often been credited with the "first" isolation of metallic aluminum, whereas he should more accu-

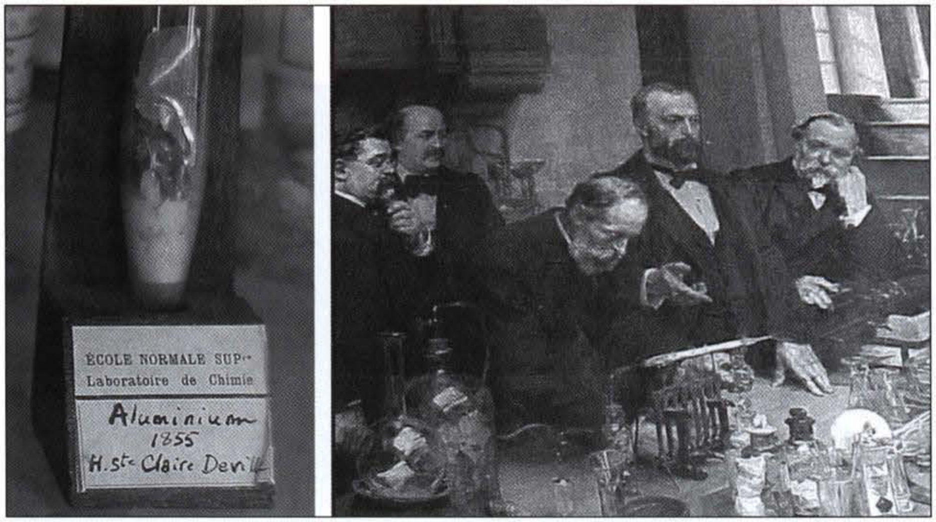

Figure 7. On display in the library of École Normale Supérieure Physique (24, rue l'Homond, N 48° 50.57 E 02° 20.82) are (left) an original Deville sample of aluminum and (right) a painting of Deville (second from right) demonstrating in the Sorbonne the preparation of aluminum "surrounded by his assistants" (Note 5). This library resides 200 meters to the northeast of the laboratory of Deville (see next figure).

Figure 8. École Normale Supérieure was the site of Deville's work on aluminum (45, rue d'Ulm, Paris, N 48° 50.52 E 02° 20.67). Two hundred meters to the southeast is the site where the Curies discovered radium.

rately be recognized as the one who first prepared a pure sample of metallic aluminum and described its chemical and physical properties.

The preparation of large quantities of metallic aluminum eluded chemists for many years until Henri-Étienne Sainte-Claire Deville (1818–1881) (Figure 7) showed that the more expensive metallic sodium could be used to advantage. The son of a French consul, Deville was born at St. Thomas Island, (then Danish) West Indies; he moved to France for his education. He was made professor and dean of the new faculty of science in Besançson (1845–1851), and then was appointed professor at the École Normale Supérieure (1851–1880) (Figure 8). At the École Normale, Deville soon was producing sizeable quantities of "l'argent d'argile" (silver of clay). Devillle's "bijoux d'aluminium" ("jewels of aluminum"),[9] including broaches, pins, and bracelets, were a hit at the Paris Exposition (L'Exposition universelle) of 1855 at the Palais d'Industrie on the Champs Elysées,[10] which was erected in an attempt to rival the Crystal Palace at London's Great Exhibition four years earlier. Emperor Napoleon III commissioned Deville to make dishes and eating utensils for the banquet dining table, much to the envy of the dignitaries who did not sit at the head table and who were relegated to using mere gold- and silverware. Deville went into production at the Javel works on the Seine River (Note 3) where he prepared other metal curiosities for the emperor, including opera glasses, cigarette cases, belt buckles, and even a baby rattle.[9,10,11] Napoleon also ordered several sets of armor, but these were never produced.

Despite Deville's success and the excited curiosity aroused by his magic metal, the expense of aluminum kept it beyond the reach of the general public. "There is aluminum in every bank of clay," rued Deville.[12] Since kaolin (chemically pure clay) is hydrous aluminum silicate ($Al_2Si_5O_5(OH)_4$),[13] it was clear that there was a huge amount of aluminum available, if only chemists could discover a way to extract it economically (Note 4).

Finally, in 1886 a breakthrough was found independently by an American and a Frenchman (Figure 9)—Charles Martin Hall (1863–1914) and Paul-Louis-Toussaint Héroult (1863–1914).[12] Soon Hall had procured patent rights for the U.S., Héroult for Europe.[14] The success of each depended upon the electrolysis of aluminum oxide (mp 2072°C) in molten cryolite (Na_3AlF_6, mp 1025°C), allowing the preparation of the metallic aluminum under much milder conditions. Hall entered Oberlin College with the intent of working on the problem of producing aluminum; he was further inspired by his professor, Frank J. Jewett (1844–1926), who had studied under Wöhler in Göttingen (1874–1875) and who had an ingot of aluminum from his stay in Göttingen.[15] The independent Hall[16] produced buttons of aluminum in a woodshed behind his house in Oberlin, Ohio,[17] which he excitedly showed to his Oberlin mentor. Hall's process led to the formation in 1888 of the Pittsburgh Reduction Company, renamed in 1907 the Aluminum Company of America (now Alcoa Inc., which proudly owns the original "buttons"). The house in which Hall lived and carried out this landmark experiment still stands (Figure 10).

Héroult's birthplace in Thury-Harcourt, Normandy, France, also still exists (Figure 11) on the banks of a river where his father ran a tannery. While a teenager, his father moved to Gentilly (now a suburb in South Paris) to set up larger facilities. Young Paul was enrolled in a liberal Paris school where he became enthralled by Jules Verne's stories and other scientific tales. One day he read Deville's description of aluminum and was immediately obsessed with the challenge posed by Deville: the problem of producing "silver from clay" economically. At the age of 19, Héroult entered the École des mines,[18] but preoccupied with his dreams, he failed his first year. Back at his father's tannery he attacked the problem of aluminum with vigor and discovered a process essentially identical to Hall's.[1] Today this neighborhood in

Figure 9. An aluminum bust of Héroult (left) stands in the center of Thury-Harcourt, Normandy, in the Champ de Foire (park) (N 48° 59.06 W 00° 28.54), 100 meters west of the École Paul Héroult, a progressive elementary school. An aluminum statue of Hall (right) resides in the Oberlin College Science Center in the chemistry and biochemistry department (119 Woodland St., N 41° 17.88 W 82° 13.33). Plaques have been erected at Oberlin College establishing this as a historic landmark by both the American Society for Metals and the American Chemical Society.[14]

Figure 10. Hall's house, 64 East College St., Oberlin, Ohio (N 41° 17.51 W 82° 12.94). In a back woodshed, the critical experiment was performed where metallic aluminum was produced by the electrolysis of aluminum oxide in molten cryolite. This house is within walking distance, 800 meters southeast of Oberlin College.

Gentilly—known as "Avenue des les Tanneurs" ("Avenue of the tanners")—has been pulled down and high-rise apartments have replaced the original buildings, with no trace or memory of the original site.

Discovery of cryolite. Cryolite (Na_3AlF_6) was first described by Europeans in the beginning of the 18th century; the native people of Western Greenland used it for fishing sinkers because it was soft and could be easily bored. Danish missionaries brought samples to Europe, and the mineral was studied in Copenhagen and was named "kriolit" (1799) after its icelike appearance (Greek: ice + stone).[13] A sample dating prior to 1795 is on display at the Geologisk Museum, Københavns Universitet, Voldgade 5–7, Copenhagen, Denmark (N 55° 41.24 E 12° 34.64), originating from the classical locality "Ivigtut, Arsuk Fjord, Grønland" (N 61° 12 W 48° 12) and bearing the original label "Sauerspath" ("acid spar"). Cryolite was mined by Denmark from this site principally as a source of sodium (to produce sodium carbonate) until its use in the electrolytic production of aluminum was developed. In the instructional classroom, pieces of cryolite immersed in water become almost invisible, owing to the two identical respective refractive indices (viz., 1.33).[13]

Acknowledgments

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Notes

Note 1. Marggraff worked at his father's apothecary ("Zum goldenen Bären") during 1738-1753 before he moved to the Berlin Academy. At this earlier address, Marggraf isolated elemental zinc. The site of this apothecary is known and is marked by a plaque tucked in an archway beside the St. Nicholas Church (corner of Probststrasse and Nikolaikirchplatz, N 52° 31.04 E 13° 24.46). The plaque does not mention Marggraf, but instead Klaproth, who assumed ownership of "Zum Bären" in 1780 and who discovered uranium there in 1789.

Note 2. Ørsted taught at the University of Copenhagen 1800–1816, and he was appointed professor of physics in 1817. The electromagnetic discoveries were made in the physics lecture hall at Nørregade 21 (N 55° 40.84 E 12° 34.26) in April, 1820.[19] The building has been razed and replaced by the modern "Telefonhuset," marked with a plaque commemorating this research. Ørsted lived in this building from 1819–1824. Ørsted's new home and chemical laboratory were built in 1824 at a new site 180 meters south, at Studiostræde 6, where Ørsted lived from 1824 until his death in 1851. Ørsted discovered metallic aluminum here in 1825. A full description of Ørsted's

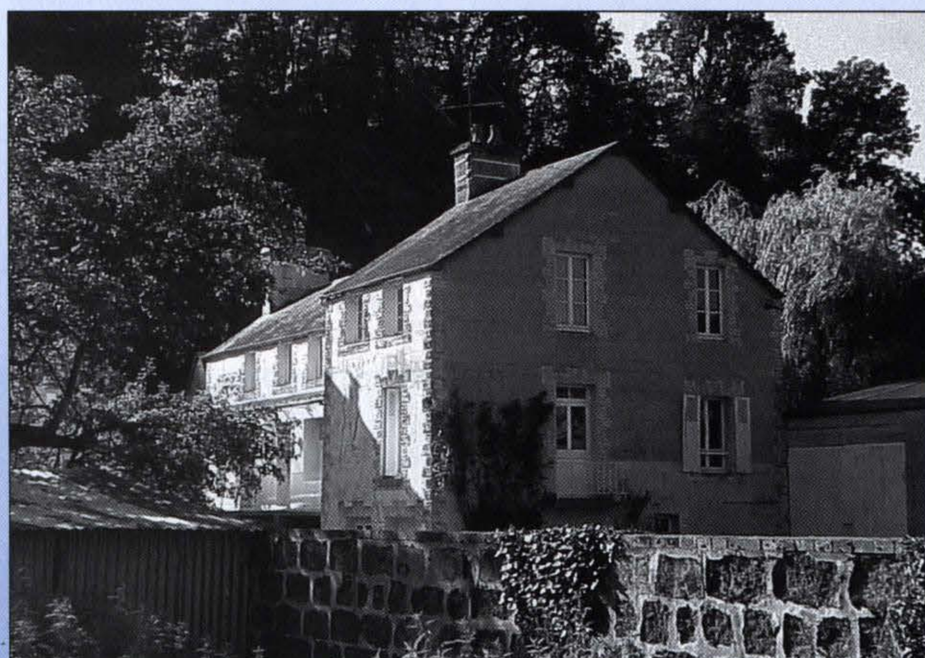

Figure 11. The house where Héroult was born is marked by a plaque (23 rue Saint-Bénin, Route D166), N 48° 59.27 W 00° 29.04), in the middle of a beautiful valley named "Swiss Normandy" in Saint-Bénin, an outlying village from Thury-Harcourt. On the banks of l'Orne River, this is where his father ran a tannery. Héroult's bust (Figure 9) is 800 meters to the southeast, across the river.

chemical procedure in 1825 has been published, and the equipment was reconstructed in Copenhagen in 1932 to reproduce Ørsted's original procedure.[6] Ørsted was made director of the Polyteknisk Læranstalt (College of Advanced Technology) in 1829 when it was constructed at the site on Studiostræde.[19]

Note 3. Originally a fishing village on the banks of the Seine, Javel began its manufacturing days in 1789 when Bertholet started producing chlorine bleach, shortly after the discovery of chlorine by Scheele. Today the French equivalent of Clorox® is "l'eau de Javel" and can be purchased at any neighborhood market. The Javel site became the factory site for the Citroën automobile industry during the World Wars and now is an expansive park (Parc André Citroën, N 48° 50.50 E 02° 16.44). The Javel manufactury was the site of Boisbaudran's ingots of gallium.[20] It is alleged[21] that the first ingot of aluminum produced by Deville was actually cast at the Chateau de la Damette in Irigny, near Lyons. When the authors visited this mansion, it was subdivided and leased into separate apartments (47 rue de la Damette, N 45° 40.45 E 04° 49.76). This chateau was the site where the dye fuchsine (also called magenta) was first synthesized in 1858–59 by François Emmanuel Verguin, important in the silk industry of which Lyons was a principal center. The Chateau de la Damette was a popular gathering site for French chemists to share recent chemical findings. The Museum of Textiles in Lyon (Musée des Tissus et des Arts décoratifs, 34 rue de la Charité; N 45° 45.14 E 04° 49.87) devotes particular attention to the history of the silk industry from the Renaissance to the present.

Note 4. Despite claims by patriotic Frenchmen that Deville should be credited with the discovery of metallic aluminum, he prepared an aluminum medal to recognize the "original" discovery of Wöhler (the importance of Ørsted's work was not known to him at the time).[1] This medal is today on exhibit at the Deutsches Museum in München (Munich; Museuminsel 1; N 48° 07.82 E 11° 34.97) and is accompanied by the following label "von Napoleon III, zur Ehrung von Friedrich Wöhler angefertigt, 1854." [by Napoleon III, prepared in honor of Friedrich Wöhler, 1854]. In the same museum cabinet, beside the aluminum medal, lies the original sample of urea (Harnstoff) prepared from ammonium isocyanate by Wöhler to disprove the theory of "vitalism."

Note 5. The library painting is a copy of the original by Léon Lhermitte at the Sorbonne. The persons are (left to right) Alfred Ditte (1843–1908, a professor of inorganic chemistry at the Sorbonne); Henri Jules Debray (1827–1888, a collaborator of Deville at the École Normale in the area of dissociation of gaseous dissociation and the platinum metals); Paul Gabriel Hauteville (1836–1902, an assistant to Deville at the École Normale); Deville; and Louis Joseph Troost (1825–1911, a professor in inorganic chemistry at the Sorbonne). Interestingly, the original painting in the Sorbonne places Debray in a less prominent position behind Troost. The date of the original painting is 1878 and the copy is 1890. Also in the library of École Normale Supérieure Physique are a bust of Deville cast in aluminum, and other chemical preparations including the original thallium compounds of Lamy and the racemic acid of Pasteur. Another aluminum bust of Deville resides at the Deutsches Museum in Munich, Germany.

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