Rediscovery of the Elements

Aluminum

Believe It or Not®

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(SO₄)₂·12H₂O) has been used as a mordant (fixer of dyes) for centuries. 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 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 (Figure 3), who distinguished the respective earths of alum and lime. 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

James L. Marshall, Beta Eta 1971
Virginia R. Marshall, Beta Eta 2003
Department of Chemistry, University of North Texas, Denton, TX 76203-5070, jimm@unt.edu
fixed alkali (KOH), he was able to regenerate the original alum.

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. 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." Even though his career preceded Lavoisier's, he appeared to ignore the theory of phlogiston and instead used facts and logic to produce work that appears amazingly modern today.

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.

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, 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. 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. 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.) Wöhler has often been credited with the "first" isolation of metallic aluminum, whereas he should more accu-
broschés, pins, and bracelets, were a hit at the kitchen 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. “There is aluminum in every bank of clay,” rued Deville. Since kaolin (chemically pure clay) is hydrous aluminum silicate (Al₄Si₂O₇(OH)₄), 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). Soon Hall had procured patent rights for the U.S., Héroult for Europe. The success of each depended upon the electrolysis of aluminum oxide (mp 2072°C) in molten cryolite ([Na₃AlF₆], 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. The independent Hall** produced buttons of aluminum in a woodshed behind his house in Oberlin, Ohio,** 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,** 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.** Today this neighborhood in 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 stands in the center of Thury-Harcourt, Normandy, and a plaque in the Oberlin College Science Center in the chemistry and biochemistry department (119 Woodland St., N 41° 17.88' W 82° 13.33') commemorates the establishment of both the American Society for Metals and the American Chemical Society.
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 (Na₃AlF₆) 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). 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, Gronland” (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).

**Acknowledgments**

The authors are indebted to Felicity Pors, Niels Bohr Archive, Blemdagsvej 17, Copenhagen, Denmark, for much information and many photographs regarding the scientific life of Hans Christian Ørsted. For information and photographs concerning Andreas Sigismund Marggraf and the Berlin Academy, the authors acknowledge the gracious assistance of Dr. Wolfgang Knobloch, Berlin-Brandenburgische Akademie der Wissenschaften, Jägerstr. 22/23, Berlin, Germany. The authors are especially grateful to Emeritus Professor Norman C. Craig of Oberlin College who made numerous perceptive observations and suggestions regarding the history of aluminum.

**Notes**

**Note 1.** Marggraf 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 Norregade 21 (N 55° 40.84 E 12° 34.26) in April, 1820. 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 Studiostredet 6, where Ørsted lived from 1824 until his death in 1851. Ørsted discovered metallic aluminum here in 1825. A full description of Ørsted's chemical laboratory is given in a recent article by Hollaender and Mertens. 20

**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.

**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 Thierry-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 constructed in Copenhagen in 1932 to reproduce Ørsted's original procedure." Ørsted was made director of the Polyteknisk Læreranstalt (College of Advanced Technology) in 1829 when it was constructed at the site on Studierade.31

**Note 3.** Originally a fishing village on the banks of the Seine, Javel began its manufacturing days in 1789 when Berthollet 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 Citroen, 40.45 E 04°49.76). This Javel was the site where the dye fuchsin (also called magenta) was first produced from ammonium isocyanate by Wöhler prepared an aluminum medal to recognize the importance of Ørsted at the Château 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 Javel was the site where the dye fuchsin (also called magenta) was first synthesized in 1858-59 by François Emmanuel. It was subdivided and leased into separate apartments (47 rue de la Damette, N 45° 40.45 E 04°49.76). This Javel was the site where the dye fuchsin (also called magenta) was first synthesized in 1858-59 by François Emmanuel.

**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).31 This medal is today on exhibit at the Deutsches Museum in 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 Hautville (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.

### Alpha Chi Sigma luncheon at the Atlanta ACS Meeting

On Tuesday, March 28, 2006, 29 brothers and guests enjoyed a brief break from the usually hectic schedule of the national meetings of the American Chemical Society. Announcements and reminders about this year's Conclave were among the topics of conversation, and a sneaky little preview that some new Chapter charters were just around the corner. The following people attended a lovely luncheon held at the Westin Peachtree Plaza, Sun Dial Restaurant: Gary D. Anderson (GMA, Alpha Eta 1962), Howard L. McLean (GPA, Iota 1969), Paul Jones (OA, Beta Eta 1970), Jian Cheng Wang (Beta Eta 1994), John E. Adams (GV, OA, Beta Delta 1971), Carol A. Deakyne (Delta 1994), Howard Mayne (DC NE, Mu 2001), Michael Heilman (DC SEDC, Epsilon 1991), Stacy Blake (guest), James A. Walsh (Beta Nu 1957), Frank Guthrie (Iota 1984), Bassam Shakhbash (Zeta 1970), Michael Sheldon (Grand Webmaster, Alpha Omega 1996), James A. Hammond (Pi 1947), Chuck Carroll (Zeta 1990), Adair Blakely (guest), Niny Rao (Gamma Beta 1999), Robert Pett (Beta Lambda 1962), James Boughton (Alpha Sigma 1991), Laura Sugarman (guest), Joseph Sardone (Alpha Omega 2004), Andrew Marin (Alpha Omega 2005), Chien Lai (Alpha Omega 2004), Harmon J. Davis III (Alpha Omega 2004), Carrie Kelley (Alpha Omega 2005), Jeffrey Hart (MA, Alpha Omega 2004), Sarah Black (Alpha Omega, pledge 2006), Jessica Swearingen (Alpha Omega, pledge 2006), (Matthew) Clay Hampton (Alpha Omega 2002).

### Fond Recollections from the University of Illinois

In a recent issue of Journal of the American Society for Mass Spectrometry (Volume 16, Number 7), Mike Bowers (recipient of the 2004 Award for Distinguished Contribution in Mass Spectrometry) recounts his early years in science. He recalls moving into the Alpha Chi Sigma house at the University of Illinois in mid-September 1962. Mike credits the house brothers with helping him to study organic chemistry so that he could pass the entrance exam in that area for incoming graduate students. Later on in the article, Mike mentions a "Pat Boone" Award given to him by his cohabitants in the house. Anyone out there care to recount the nature of this award?

### Welcome to the Brothers of Gamma Sigma Chapter at Kent State University

A petition having been approved by unanimous vote of the active subordinate chapters, the Supreme Council issues a charter to the Kent State University Colony of Gamma Sigma Chapter at Kent State University in Kent, Ohio as the Gamma Sigma Chapter of Alpha Chi Sigma Fraternity, effective May 8, 2006. Congratulations to the brothers of Gamma Sigma and Gamma for a job well done.

### Welcome to the Brothers of Gamma Tau Chapter at Indiana University of Pennsylvania

A petition having been approved by unanimous vote of the active subordinate Chapters, the Supreme Council issues a charter to the Indiana University of Pennsylvania Colony of Nu Chapter at Indiana University of Pennsylvania in Indiana, Pennsylvania, as the Gamma Tau Chapter of Alpha Chi Sigma Fraternity, effective May 8, 2006. Congratulations to the brothers of Gamma Tau and Nu for a job well done.
CARAGOL, Wilfrid John, Alpha Nu 1933
COCHRAN, Robert L., Sigma 1942
FENNER, Otto H., Alpha Epsilon 1941
JUPPENLATZ Jr., John W., Nu 1952
LEMLEY, James D., Nu 1950
MASTIN, Thomas G., Beta Gamma 1937
MOUNTJOY, Charles Paul, Nu 1950
NETTLETON Jr., Donald E., Nu 1950
LEMLEY, James D., Nu 1950
RAMBO, William S., Alpha Omega 1940
SAAATHOFF, George T., Alpha Zeta 1940
SARVADI Jr., George, Alpha Psi 1944
TOWNLEY, Robert John, Eta 1937
VERNOOY, Malcolm B., Chi 1943
STEWART, Warren Earl, Alpha 1945, 81, died unexpectedly from a heart attack on March 9, 2006. He was the McFarland-Bascom Professor Emeritus of Chemical Engineering at the University of Wisconsin-Madison. Warren was born on July 3, 1924, on a farm in Whitewater, Wisconsin, to Earl and Avis Stewart. Growing up as a boy in Delavan, Wis., he played the trombone in the Wild Cat Band, directed and acted in school plays, enjoyed archery with his own hand-made bows and arrows, attended school enthusiastically, and graduated from Delavan High School in 1942. During his time there he won the naming contest for the high school athletic teams, which are called the Comets to this day. Warren met Jean Durham Potter the first week of orientation, freshman year at the University of Wisconsin-Madison. Their romance continued and they were married on May 24, 1947, and had 58 happy years together. While at the UW, Warren enjoyed playing the trombone in the band, the marching band and the orchestra. He majored in chemical engineering and graduated with a B.S. in 1945. He became famous as the first undergraduate student in the history of the College of Engineering to graduate with a straight A academic record. Warren continued at UW-Madison and received his MS in 1947. During World War II, Warren enlisted in the U.S. Navy (1944–1946) under the V-12 program, and after graduation served as a communications officer (ensign) on the aircraft carrier USS Midway. Warren graduated from Massachusetts Institute of Technology in 1951 with a doctor of science (ScD) degree in chemical engineering. His MIT experience proved valuable in many ways, introducing him to numerical analysis and computational techniques that were essential to his research at the dawn of the electronic computing age. Warren worked for Sinclair Research Laboratories from 1950 to 1956 as a research engineer. He joined the faculty in the Department of Chemical Engineering at UW-Madison in 1956, where he was an active faculty member for 40 years and continued his research following retirement in 1997. While serving as chairman of the Department (1973–1978), Warren recruited and nurtured several young faculty, who went on to become international leaders in their field. He supervised many PhD students and postdoctoral fellows, many of whom hold distinguished positions in universities and industrial research laboratories around the world. Warren was an inspiring teacher and valuable consultant. Although he was a quiet and modest person, Warren received many awards for his work, including the Benjamin Smith Reynolds teaching award, and the Byron Bird research award. Warren was a member of the Fellow of the American Institute of Chemical Engineers, Phi Beta Kappa, Tau Beta Pi, and was elected to the National Academy of Engineering, which awards those who have demonstrated “unusual accomplishment in the pioneering of new and developing fields of technology.” He is survived by his wife, Jean, their six children, and 18 grandchildren.

IKAWA, Miyoshi (Mike), 87, co-discoverer of warfarin and professor emeritus of biochemistry at the University of New Hampshire, died of heart failure on March 7. The only son of Japanese immigrant parents, Ikawa was born in California. In 1941, he earned a B.S. from California Institute of Technology. During his first year of graduate school, the U.S. declared war on Japan and after its attack on Pearl Harbor, Linus Pauling, Ikawa’s graduate adviser at Caltech, arranged for him to work with Karl Paul Link at the University of Wisconsin before Japanese people living on the West Coast were sent to relocation camps. Ikawa completed an M.S. in 1945 and a Ph.D. in biochemistry in 1948 at Wisconsin. During that time, Ikawa, Link, and Mark A. Stahrsmann synthesized warfarin, so named for the Wisconsin Alumni Research Foundation. In 1948, the patent issued for warfarin listed its use as a rat poison. Two years later, warfarin (Coumadin) was introduced as an anticoagulant in clinical treatment for thrombosis and other blood clotting disorders. Fluent in Japanese, Ikawa served in occupied Japan for the Army Military Intelligence Service. Ikawa returned to Caltech as a postdoc and continued postdoctoral research at the University of Texas and the University of California, Berkeley. When Ikawa joined the University of New Hampshire faculty in the early 1960s, his research shifted to the chemical nature of marine biotoxins. Responding to the first red tide in the southern Gulf of Maine in 1972, he and his colleagues initiated the Paralytic Shellfish Monitoring Program for the state. For the next 40 years, Ikawa served on numerous technical panels and peer review committees for federal research grants and scientific journals. His first wife, Norma, died in 1969. Ikawa is survived by his wife of 26 years, Sayoko; two children; and one grandson. An emeritus member, he joined ACS in 1947.

(GE Note: Although Mike Ikawa was never a brother of Alpha Chi Sigma, the GE exercises a little editorial prerogative to note the passing of someone whose discovery has impacted so many lives... including that of the GE, as you might recall, and whose life also eerily intersects that of the GE, who earned his B.S. at UNH and his Ph.D. at UW.)