Rediscovery of the Elements

Gallium

Paul Émile (François) Lecoq de Boisbaudran 1838–1912

James L. Marshall, *Beta Eta '71*, and Virginia R. Marshall
Department of Chemistry, University of North Texas, Denton TX 76203-5070, *jimm@unt.edu*; Computer Technology, Denton ISD, Denton TX 76201

The Cognac Region in southwestern France (Figure 1) has been historically blessed with a rich, sweet soil well-suited for supporting a wine culture. With a navigable river allowing active commerce, Cognac for a thousand years traded its famous wines, as well as salt, to those who would sail up the River Charente. Frequent visitors were the Dutch, procuring wine for their ships engaged in world explorations. Because of low-alcohol content, wines deteriorated during long ocean voyages, and because space was at a premium on the cramped ships, the Dutch lent to the French the idea of concentrating their potables to a "brandywine" ("brandwijn" or "burnt wine"). So, in the 1600s, the distilled spirits of the region became known as "cognac" (Figure 2).

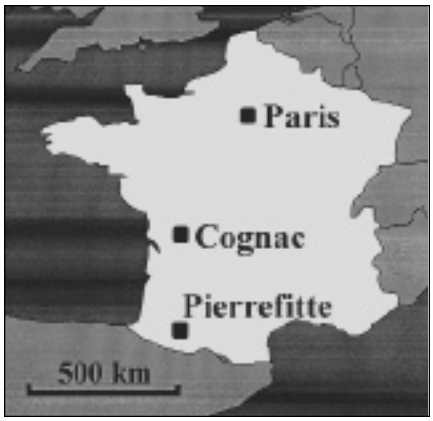

Figure 1. Map of France, highlighting the history of gallium: Cognac (where Boisbaudran conducted his spectral investigations and first detected gallium),Pierrefitte-Nestalas (the source of the gallium ore), and Paris (where Boisbaudran prepared metallic gallium).

Figure 2. The Martell distillery, at the time of Boisbaudran's researches in Cognac. His home would have been located off this illustration, a few hundred meters to the upper right (northeast).

Figure 3. Home of Paul Émile (François) Lecoq de Boisbaudran in Cognac with his parents (1, rue de Lusignan, N 45° 41.692, W 00° 19.848). The Boisbaudran family prospered with a wine business in Cognac. This back view is of the courtyard, showing the sumptuous carriage and stable facilities.

In the early 1800s, the family of Paul Lecoq de Boisbaudran (1801–1870) and his wife Anne Louise, of ancient Protestant nobility, embarked on a wine business that eventually prospered through perseverance of the whole family (Figure 3). One of the sons, Paul Émile (François) Lecoq de Boisbaudran (1838–1912), was particularly gifted; his mother taught him history, the classics, and foreign languages.[1] Paul Émile did not attend a formal university, but he followed the syllabi of classes taught at École polytechnique in Paris. His uncle, Scevola Lecoq de Boisbaudran (1802–1878), who had attended the École polytechnique, encouraged François and even funded a laboratory in the home (Figure 4). In this laboratory, François conducted sophisticated experiments involving solution chemistry and crystallization processes. His most famous work dealt with spectroscopy, resulting in the discovery of several elements. Although Bunsen and Kirchhoff (who discovered rubidium and cesium, 1860–1)

Figure 4. Front view of the Boisbaudran home. The laboratory of François was on the second floor. Inset: street sign of rue de Lusignan.

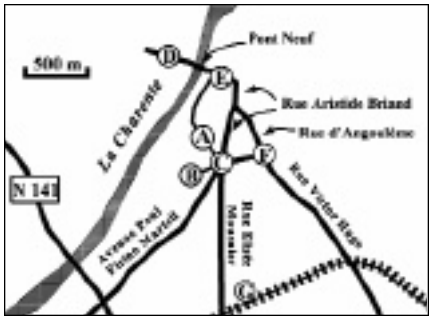

Figure 5. Map of Cognac. There are many interesting sites to visit, but noteworthy are the home of Boisbaudran (A), the castle where François I was born (E), the statue of François I (F), and cognac distilleries such as Martell (B). The home of Boisbaudran (A) at 1, rue de Lusignan resides in the middle of a complicated maze of narrow, winding streets (not detailed in the map), and is most easily reached by proceeding north from Place Martell (C). The rue Lecoq de Boisbaudran (D) may reached by crossing the River Charente. All are within walking distance of the train station (G).

and Crookes (thallium, 1861) pioneered spectral analysis,[2] Boisbaudran brought the art to a sophisticated level in Spectres Lumineux,[3] an 1874 landmark reference book on the spectroscopy of thirty-five elements, including the rare earths.

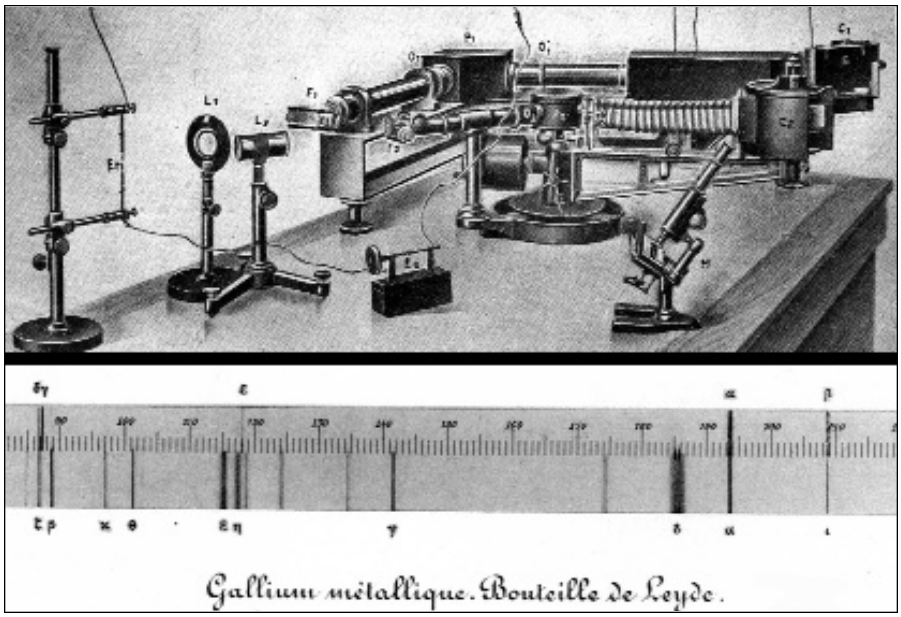

Figure 6. The spectroscope of Boisbaudran, with which he studied gallium, the rare earths, and other elements.[3] His spectrum of gallium appears at the bottom.

Figure 7. Map of the Argelès region of France. By France's bullet train, the TGV (Train Grand Vitesse), one can travel in six hours from Paris to Lourdes, famous for its Roman Catholic shrine where the Virgin Mary is said to have appeared to Saint Bernadette in 1858. By automobile one can travel south into the Pyrénées, visiting Pierrefitte or driving further south to Gavarnie and the famous Parc National des Pyrénées, famous for its wildlife, notably migrating butterflies and raptors.[15]

Cognac, a small town which may be explored easily by foot, has a number of interesting sites to visit, (Figure 5) including several cognac distilleries and the castle where Francis I, the king of France who battled the Holy Roman Emperor Charles, was born. One may reach Boisbaudran's home in the old section of town amidst narrow, winding streets. Today this home is a private residence, and contains none of the original possessions of the Boisbaudran family.

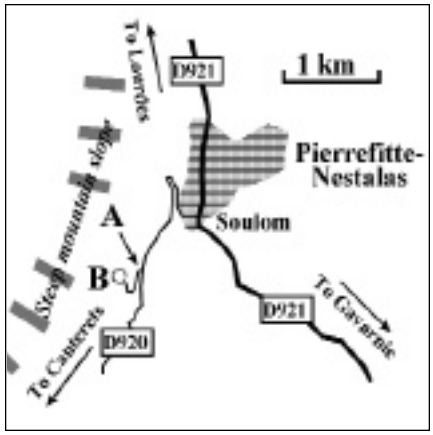

Figure 8. Map of the Pierrefitte-Nestalas region, showing the location of the mines, which have been shut down and filled in. The mines are reached by driving south from Pierrefitte on the main highway D921, taking the mountainous paved road D920 in Soulom (N 42°57.495, W 00° 04.530), and turning off a steep dirt road (A, N 42° 57.120, W 00° 04.945), and driving up to the mine region (B, N42° 56.818, W 00° 05.201), which now boasts the "La Galène" cottage vacation area at an altitude of 700 meters.

François Boisbaudran developed a theory of spectroscopy based on atomic vibrations and was able to recognize spectral trends based on atomic masses. Thus, Boisbaudran knew where to look for new spectral emissions. When he observed the new lines, he knew exactly what he found, namely, a new element (Figure 6). We know the exact day when he made his discovery: on August 27, 1875 between 3 and 4 in the afternoon [he wrote],[4] "I found indications of the probable existence of a new elementary

Figure 9. The road D921, extending from Soulom to the mine region of Pierrefitte,where the blende was obtained whence Boisbaudran procured gallium. This geographical region is typically foggy and the towering peaks of the Pyrénées are obscured.

body in the products of the chemical examination of a blende [sulfide ore] from the mine of Pierrefitte. The oxide…is thrown down by [precipitated with] metallic zinc in a solution containing chlorides and sulfates…The chloride is precipitated by a small quantity of ammonia. . . The few drops of zinc chloride in which I concentrated the new substance gave under the action of the electric spark a spectrum composed chiefly of a violet ray…" He later named the new element "gallium" in honor of his homeland—although some supposed that the name proceeded from his family name (coq=gallus,'rooster').[5]

The ores that Boisbaudran procured to obtain his gallium were from the Pierrefitte Mine (Figure 7) in the valley of Argelès of the Pyrénées, which supplied lead ore. When we visited this region (Figure 8), we found the mines on a steep slope that could be reached by a dirt road (Figure 9). Today the mines are closed and sealed over, and the only traces remaining were thin sandy debris and slag scattered on the slopes. The only physical memory of this historical activity is a village of summer cottages named "La Galène" [from the mineral galena,PbS].

The material which Boisbaudran investigated was a mixed iron-zinc-gallium sulfide with no specific chemical composition - gallium has a tendency to disperse through other minerals and is rarely found in specific composition.[6] The minerals of Pierrefitte Mine are found in an Ordovician formation, about 400 millions years old.[7] This formation, along with the rest of the Pyrénées, was uplifted and exposed as Africa smashed into Europe 80 million years ago[8] (as were the Apennines in Italy, where barium was discovered.[9]

To produce elemental gallium, Boisbaudran journeyed to Paris to work with Adolphe Wurtz (Figure 10), who at that time possessed the most sophisticated laboratory in that city[10] (Figure 11). By electrolysis of the hydroxide,in November of 1875, only two months after his original discovery, Boisbaudran was able to produce observable quantities of metallic gallium .He demonstrated to the Parisian scientific elite that indeed here was a new element,[11] and in December he presented 3.4 mg to the Académie des Sciences in Paris.[11] By this time he was producing enough of the metallic gallium to recognize its unusually low melting point.He remarked that this metal "could melt in the fingers."[12] This phenomenon puzzled him; he thought that possibly the liquid properties of electrolytic gallium might be due to some special effect of the electrolysis process, perhaps by imparting an impurity of potassium to the gallium,or by some unknown modification caused by contact with the humid air.[12] However, after extensive investigation he finally concluded: "Je pense donc que le gallium pur est réellement liquide..." ("I think pure gallium is really liquid. . ").[12] Today this unusual property of gallium is know to all educators in chemistry, that gallium is the only element that will (safely) melt (30°) in the unprotected hand.

By 1878 Boisbaudran was producing gram quantities, utilizing the facilities of"la manufacture de Javel"(Javel chemical works of Paris),[13] requiring 10 hours of electrolysis to produce 1 gram of metallic gallium. The blende used for this larger scale operation was obtained from Bensberg, about 10 kilometers east of Cologne. [Note 1]

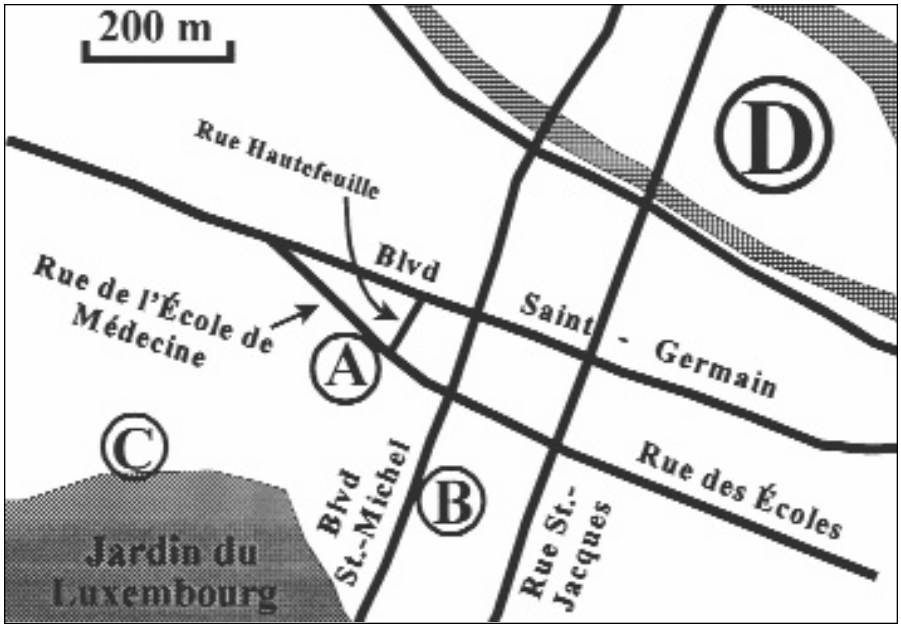

Figure 10. Map of Paris, region of rue École de médecine, where Adolphe Wurtz possessed the finest Parisian chemistry laboratory of the time (A). It was in this laboratory that Boisbaudran first prepared metallic gallium by electrolysis. To orient the tourist, other sites are identified: (B) courtyard of the Sorbonne; (C) meter stick on rue de Vaugirard, across the street from the Luxembourg castle (this is the only public meter measuring stick still remaining in Paris), (D) the Notre Dame cathedral.

Figure 11. Wurtz's original laboratory was in the attic of this building, the couvent [convent] de Cordelier, now set aside as a Historic Landmark by the city of Paris (N 48° 51.050, E 02° 20.460). The specific laboratory where the gallium work was done, was a few meters away, across the courtyard from the couvent de Cordelier. It has since been taken down and its site is now occupied by medical administration buildings.

Upon the initial announcement of the discovery, Mendeleev was exuberant [Note 2]; Boisbaudran was the first chemist to discover one of his predicted elements, in this case,"eka-aluminum." Mendeleev immediately proclaimed that his Periodic Table was vindicated, because he had foretold the physical and chemical properties of gallium.[14] Boisbaudran politely but forcefully affirmed that it was his special spectroscopic technique, and not Mendeleev's theories, that led to the discovery of gallium.[11] Today, the museum of Mendeleev in St. Petersburg displays the portrait of Boisbaudran (Figure 12), along with those of the other chemists whose work figured into Mendeleev's prophecies.

Boisbaudran, with his spectral technique, later discovered the elements samarium (1889), dysprosium (1886), and with de Marignac (independent discovery) of gadolinium (1886).[2] He could also be given partial credit for observing lines of terbium and europium before they were formally isolated. His many honors included the"Legion d'Honneur"and the Davy Medal.[1] He was a member of the Académie des Sciences and an honorary member of the Chemical Society of London.[5] What is quite remarkable about his spectral research is that it was his own theory of spectra - that spectral frequencies are a function of atomic weight—that led him to his discoveries, not Mendeleev's predictions.[11] Boisbaudran had indeed developed spectral analysis to a very high level of sophistication. And, most impressive of all, Boisbaudran had achieved all of this without a University diploma and without a University post![5]

Boisbaudran, who was educated by his mother, learned flawless English, which enabled him to travel to Great Britain in the 1860s, where he met with various famous scientists. Upon his death in 1912, Sir William Ramsay, discoverer of the inert gases at University College (London), wrote a fitting tribute to Boisbaudran,[1] lauding not only his scientific discoveries but also recognizing the character of the man. Ramsay related how Boisbaudran grew up in a supportive family with active encouragement from all, with a moral code of"justice, kindness, and the sense of personal responsibility,"[1] Upon his passing in Paris, Boisbaudran was returned from Paris to Cognac to be buried with his beloved family.[5]

Acknowledgments.

The authors gratefully acknowledge Pascal Pierre, Archiviste Municipal, Hôtel de Ville, 16108 Cognac Cedex, France, who furnished a great deal of information regarding the Boisbaudran family and their role in the wine industry of Cognac. Also helpful were the Offices du Tourisme of Cognac, Pitous-Charentes, France, and of Pierrefitte-Nestalas, Haute Pyrénées, France, who furnished information about the history of Cognac and the Pierrefitte Mining Region, respectively. For important information regarding the exact location of the laboratories of Adolphe Wurtz in Paris, the authors are indebted to Dr. Alan Rocke, Henry Eldridge Bourne Professor of History, Case Western Reserve University, Cleveland OH (also see ref 10).

Figure 12. Paul Émile (dit François) Lecoq de Boisbaudran,discoverer of gallium and three rare earth elements. This portrait hangs in the Museum of Mendeleev, in the St. Petersburg University (N 59° 56.491, E 30° 17.975).

Notes

1. The Javel works, on the left (south) bank of the Seine, 2.5 km downstream (southwest)from the Eiffel Tower, is known today for the Citroën automobile works. Historically it was an important source of sulfuric acid and hydrochloric acid, and was the French birthplace of chlorine bleach. Today no household in Paris would be found without its "l'eau de Javel," or sodium hypochlorite solution.

2. The rapid dissemination of scientific information in Paris during the latter 1800s was due to the publication, Comptes rendus hebdomadaires des séances de la Académie des sciences, in which current research was promptly reported in weekly readings. In the space of four months (September-December, 1875),this periodical reported the original spectroscopic findings of Boisbaudran in Cognac, then the production of metallic gallium by Boisbaudran in Paris, next the report of Mendeleev claiming his predicted eka-aluminum had been discovered, followed by Boisbaudran's response to Mendeleev, and finally Boisbaudran's further detailed spectroscopic and chemical description of gallium.

Literature Cited

1. W. Ramsay,"Obituary notices. Paul Émile (dit François) Lecoq de Boisbaudran,"J. Chem.Soc. Trans.,1913,103, Part 1, 742–746.
2. Weeks,M.E.Discovery of the Elements, 7th ed, *Journal of Chemical Education*, 1968.
3. de Boisbaudran, P.-E.L.,Spectres lumineux, 1874,Gauthier-Villars, Paris.
4. de Boisbaudran, P.-E.L.,Compt. rendu.,1875, 81 (Sept 20), 493-495; Amer. Chemist,1875, 146.
5. Pierre, Pascal (Archiviste Municipal), Hôtel de Ville, 16108 Cognac, France, personal communication.
6. Marshall, J. L., and Page,L., *Chemical Heritage, 2000*, 18,No. 2 (Summer), 6–7,36–37.
7. Johan, Z.; Oudin, E.; and Picot, P; Tschermaks Min. Petr. Mitt.,1983,31,97–119.
8. Osborne,R., and Tauling, D., *The Historical Atlas of the Earth*, 1996,Henry Holt and Co., N.Y.,140–141.
9. Marshall, J. L., and Marshall, V. R., *The Hexagon of Alpha Chi Sigma*, 2002,93,No. 2 (Summer),24–26.
10. Rocke,A. J., *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry, 2001*, MIT Press, Cambridge MA.
11. de Boisbaudran, P.-E.L.,Compt. rendu.,1875, 81 (Dec 6), 1100–1105.
12. de Boisbaudran, P.-E.L.,Compt. rendu.,1876, 82 (May 1), 1036–1039.
13. de Boisbaudran, P.-E., and Jungfleisch,E., Compt. rendu.,1878, 86 (Feb 18), 475–478.
14. Mendeleeff, D.,Compt. rendu.,1875, 81 (Nov 22), 969–972.
15. Botting, D.,ed., *Wild France*, 1994,Sierra Club Books, San Francisco,121–124.