Rediscovery of the Elements

The "Undiscovery" of Vanadium

Figure 1. Don Fausto Delhuyar, the director of the Mining Academy in Mexico, and his brother Don Juan José Elhuyar isolated metallic tungsten in the Laboratorium Chemicum, Bergarako Errege Seminarioa (Bergara Royal Seminary), Martin Agirre Deunaren Enparantza (St. Martin Agirre Plaza), Bergara, Gipuzkoa, Spain (N 43° 07.06, W 02° 24.80). The building now houses a children's school. During the authors' visit, a science fair was being held in the building—with all signs in Basque language. This site may be reached by automobile, 54 kilometers southwest from Irún, the Atlantic seacoast town on the France-Spain border.

Figure 2. The Belhazy House (N 48° 27.50, E 18° 53.46), 1 Sladkovicoca, in the Mining Academy, Banská Štiavnica, Slovakia, was the site where many famous chemists trained, including Müller von Reichenstein, who discovered tellurium in Romania[26] and Manuel del Río, who discovered vanadium in Mexico.[1] The original name (city and school) was Schmenitz, and the language was German. Later the city and school assumed the Hungarian name of Selmeczbánya, and after WWI the city became part of Czechoslovakia. Banská Štiavnica, which has been designated a United Nations World Heritage Site, may be reached by driving 107 kilometers north from Budapest.

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This follows the previous "Rediscovery" article in Hexagon[1], "Vanadium."

Humboldt's Return to France. When Alexander von Humboldt returned to Europe in 1804 following his five-year expedition to the Americas, he brought with him 19 boxes of mineralogical specimens.[2] One of these samples was *plomo pardo de Zimapán* (brown lead of Zimapán), which Manuel del Río had claimed contained a new element which he had named "erythronium," named for the red color of its compounds. Manuel del Río worked under Don Fausto Delhuyar (1755–1833), the director of the School of Mines in Mexico, who with his brother Don Juan José Elhuyar (1754–1796) had first isolated metallic tungsten in Bergara, Spain (Figure 1). Manuel del Río had gained his education in Freiberg, Germany[3] and in Schemnitz, Hungary (now Banská Štiavnica, Slovakia) (Figure 2), and he had an expert knowledge of lead ores, which he put to good use in his analysis of his *plomo pardo* (known today as vanadinite, $Pb_5(VO_4)_3Cl$)[2].

Humboldt delivered his specimen of *plomo pardo* to the Institut de France (Figure 3), which housed the elite French scientists of the day. The mineralogical sample was accompanied by a letter from del Río and was addressed to the "Citizens" Haüy, Vauquelin, Chaptal, Berthollet, Guyton, and Fourcroy.[4] France was at the height of her power and Paris was the European center in fashion, literature and science. Lavoisier in 1789 had announced[5] his recognition of the true elements and had dethroned the principle of phlogiston; at the Jardin du Roi, Lamarck and Buffon[6] were proposing that the earth was a much older place than previously imagined and that life forms had *evolved* in the long history of the planet. What better place than progressive Paris to authenticate del Río's discovery? Particularly appropriate for the analysis was Nicolas-Louis Vauquelin (1763–1829), considered one of the two foremost chemical analysts in the world (the other being the Berlin chemist Martin Heinrich Klaproth, 1743–1817). Vauquelin was riding a reputation of expert ability and meticulous analysis that had corrected many faulty analyses in the past; he had just discovered chromium and beryllium (Figure 4).

Laboratory Utilized in Analysis: l'École des Mines. Louix XVI established the French Mining Academy, l'École des Mines, at the Royal Mint in Paris (l'Hôtel de la Monnaie), in 1783 (Figure 5). During the French Revolution, in 1794, the academy was moved to l'Hôtel de Mouchy in Paris, which served as the location

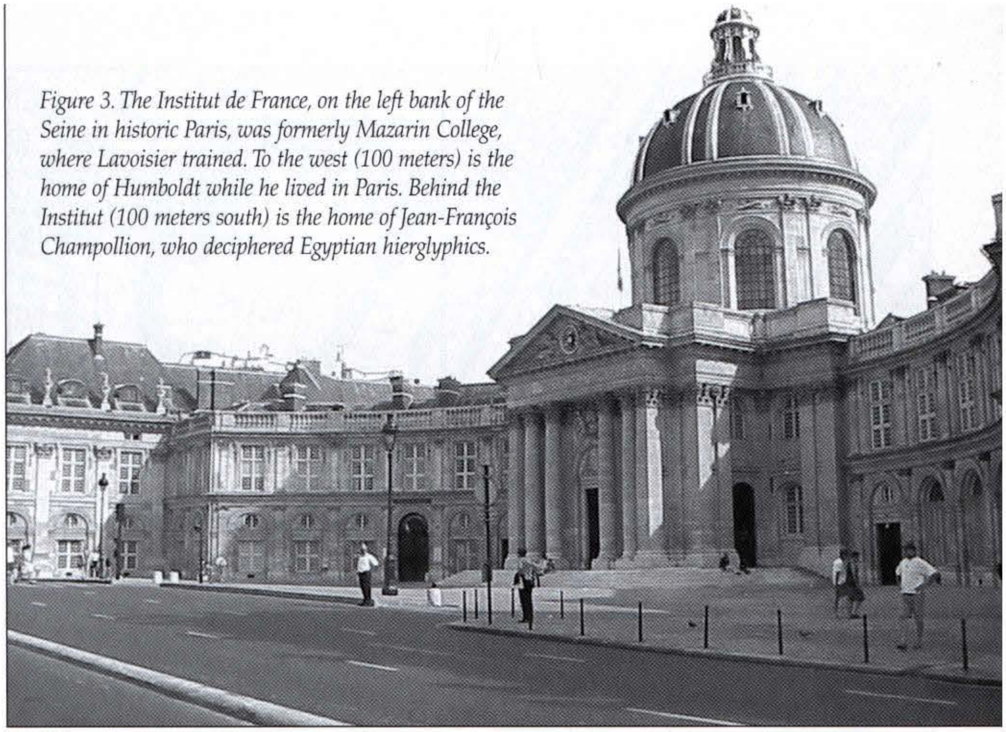


Figure 3. The Institut de France, on the left bank of the Seine in historic Paris, was formerly Mazarin College, where Lavoisier trained. To the west (100 meters) is the home of Humboldt while he lived in Paris. Behind the Institut (100 meters south) is the home of Jean-François Champollion, who deciphered Egyptian hierglyphics.

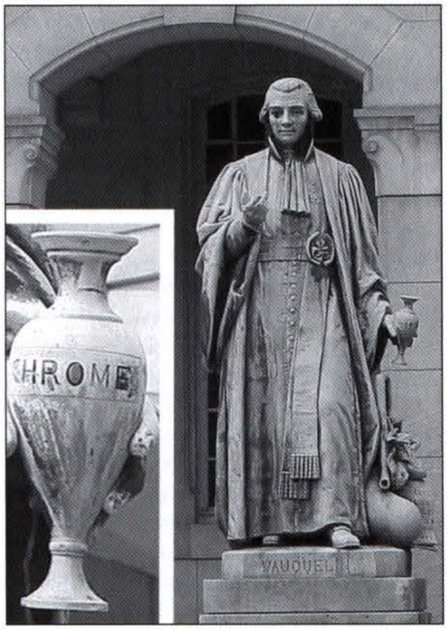


Figure 4. This statue of Vauquelin stands in front of the Faculté de Pharmacie in Paris. Although Vauquelin was at heart a pharmaceutical chemist, he is probably best known for his discoveries of beryllium and chromium in 1798-1799 before he became director of the Faculté de Pharmacie. Inset: closeup of the "chrome" vase.

for the entire school during 1794–1802, and for the laboratory and mineral collections during 1802–1816 when Napoleon temporarily moved the school to Mont Blanc. The Academy was permanently returned to Paris in 1816, when it was established at its present site on Boulevard Saint-Michel (Figure 6).[7]

It was at the second site, at Hôtel Mouchy, that Vauquelin in 1797–1798 performed his celebrated work on beryllium and chromium. (Note 1) Vauquelin analyzed various specimens given to him by René-Just Haüy (1743–1822), director of l'École des Mines. Haüy (Figure 7) thought that minerals could be identified by their crystallographic forms; and noticing that emerald and beryl had the same morphology, he suggested that Vauquelin compare them chemically. Vauquelin found the two had identical compositions, and in the process discovered beryllium.[8] (The formula for the mineral is $Be_3Al_2Si_6O_{18}$). He had previously studied emerald, finding only aluminum and silicon oxides, but now he looked at the composition more critically. Digesting and dissolving the mineral in acid, he neutralized with caustic potash and separated out a hydroxide that did *not* dissolve in an excess of alkali, thus recognizing a new earth and distinguishing it from alumina. The salts of the new earth had a sweet taste (and in fact, the element was first named *glucinium*).

In his discovery of chromium, Vauquelin investigated a sample of "red lead of Siberia" (crocoite, $PbCrO_4$). Many previous investigators

Figure 5. l'Hôtel de la Monnaie was the mint and the first site of l'École des Mines, the French Mining Academy. Almost simultaneously across Europe, five mining academies were established; at Freiberg (1767), Schemnitz (1770), St. Petersburg (1773), Almadén (1777), and Paris (1778). (7) "La Monnaie" is presently a museum of the history of French currency.

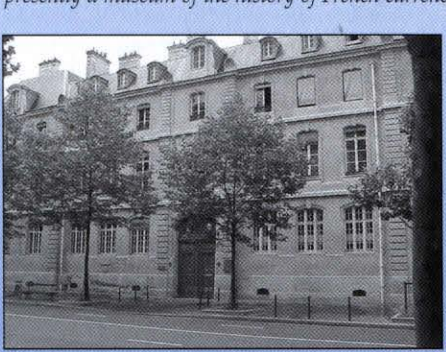


Figure 6. The present site of l'École des Mines on Boulevard Saint-Michel was the third location. Here an interesting museum, located in the historic Hôtel Vendôme, outlines the historical of French mining and mineralogy, emphasizing the pioneering work of Haüy.

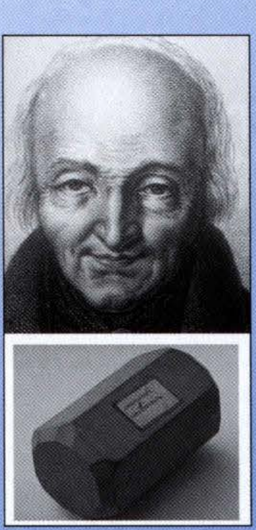
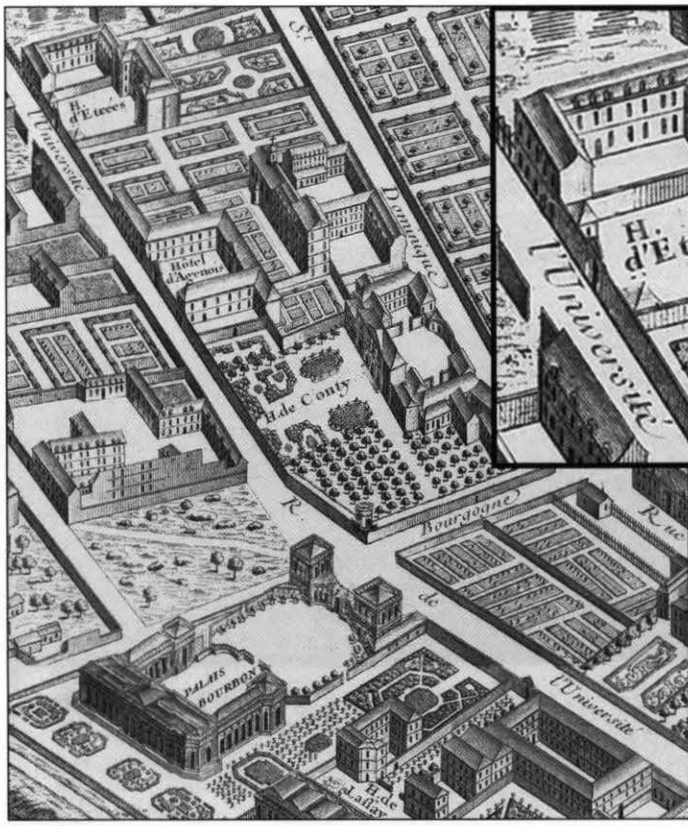


Figure 7. René-Just Haüy, the "father of crystallography," carefully measured crystal angles and characterized minerals on the basis of definite crystalline forms. Inset: One of his wooden models of a crystal of emerald, which he noticed was identical to that of beryl.



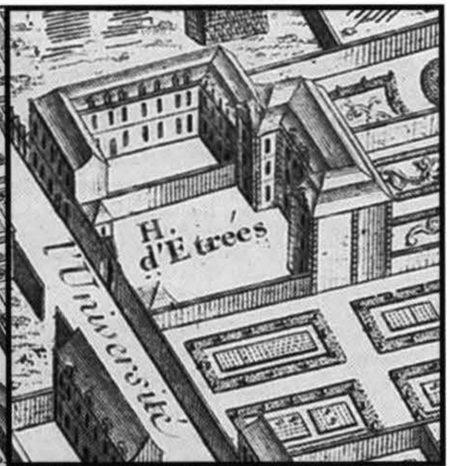


Figure 10. A close-up of the Hôtel d'Estrées, showing the incredible detail of this original work of Turgot. The Turgot project lasted during the period 1734-1739. Copies of the entire Turgot map[20] may be obtained in the Louvre and the Musée Carnavalet (City Historical Museum) in Paris.

Figure 9. In this figure, a portion is taken from Turgot's Plan de Paris showing the portion of rue de l'Université stretching from the Hôtel d'Estrées to the Hôtel Bourbon. Hôtel d'Estrées was the original name of Hôtel Mouchy. Today the boulevard Saint-Germain cuts directly from the Hôtel Bourbon through the demolished Hôtel d'Estrées (about 400 meters). The view is southeast.

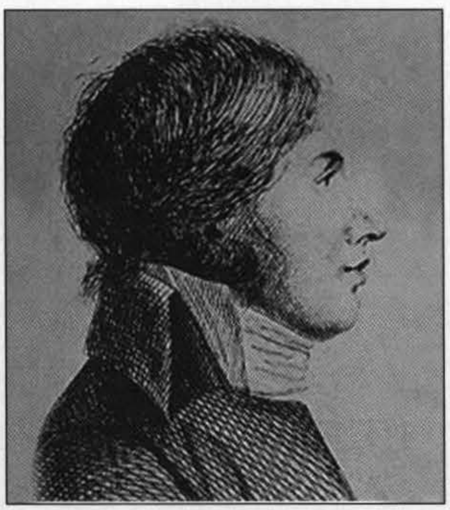


Figure 8. Hippolyte Victor Collet-Descotils, the director of the laboratory at l'École des Mines at the time the plomo pardo de Zimapán was analyzed in France.

had mis-analyzed the ore, finding varying amounts of arsenic, sulphur, iron, aluminum, molybdenum, nickel, cobalt, iron, and copper! In Vauquelin's expert and careful hands, however, he found only two ingredients: lead and the oxide of a new metal.[9] He reacted a portion of powdered mineral in potassium carbonate solution, obtaining precipitated lead carbonate and a yellow solution. This yellow solution was reacted with lead nitrate salts to give a "yellow-orange" precipitate, with mercuric salts to give a "deep cinnabar" precipitate, and with silver salts to give a "beautiful carmine" precipitate. He further characterized the new earth by reducing it with tin filings to chromic oxide (which he later exploited to produce a green glaze for ceramics). Vauquelin completed a full description by reacting the yellow solution with zinc, bismuth, antimony, nickel, gold, and platinum salts to obtain various products. (Note 2)

Unfortunately, when the *plomo pardo* was given by Humboldt to the Institut de France seven years later (in 1804), Vauquelin was no longer available to perform the analysis, because he had just left l'École des Mines to join the École de Pharmacie on rue l'Arbalète[10] (the school was moved in 1882 to its present site on avenue de l'Observatoire, where his statue now stands). For his replacement, Vauquelin dubbed Hippolyte Victor Collet-Descotils (1773–1815) (Figure 8), who had accompanied Napoleon during the Egyptian campaign.[11] Upon his return to France, Collet-Descotils became one of Vauquelin's students and his chief assistant at l'École des Mines at Hôtel Mouchy. It was upon Collet-Descotils' shoulders that the analysis of *plomo pardo* fell. It is not recorded exactly what instructions were given by Vauquelin to Collet-Descotils, but it is clear that general suspicion reined that the "new metal" was actually chromium.[2,4] One can only speculate that Vauquelin, at heart a pharmaceutical chemist,[12] displayed little interest in the analysis of del Río's sample. In any case, we know that Collet-Descotils dashed off three quick analyses[4] and promptly pronounced his conclusion that indeed there was no new element—just chromium.[13] This analysis in 1805 was performed by Collet-Descotils in Hôtel Mouchy, where he had remained as director of the laboratory.[7]

Close inspection of Collet-Descotils' laboratory analysis of *plomo pardo* demonstrates not only brief and superficial work, but also reveals clear errors—at least one of his three tests was unequivocally *negative* for chromium.[13] To a digested sample of ore whose lead had been removed (by precipitation of lead sulfate with sulfuric acid) and then neutralized, lead nitrate was added to give a "yellow" precipitate "resembling lead chromate," silver nitrate gave a "magnificent red" precipitate, but mercury nitrate gave a "*yellowish*" precipitate instead of the expected *deep red* precipitate that Vauquelin had observed for chromium. Some French scientists questioned the analysis,[4] but others rationalized the incongruity on the basis that the "test was not always consistent."[4] A further question was raised when Collet-Descotils reported an initial reddish precipitate that he "afterwards identified as iron oxide" but did not characterize—it could have been a vanadium oxide.[2] Collet-Descotils had the full repertoire of Vauquelin's previous experiments at his disposal, but did nothing further. Typically reserved in his judgments, James R. Partington, the renowned chemical historian, himself wrote "the reactions for chromium were not quite satisfactory."[14] Nevertheless, the case was considered closed by the French scientists; del Río lost his claim on the discovery of the new element, and the true nature of vanadium was not recognized for another twenty-six years. (Note 3)

History of Hôtel Mouchy. Because of a fire that destroyed archival records in 1871, much information on Hôtel Mouchy has unfortunately been lost.[15] Nevertheless, one can piece together a fascinating history of this mansion. The Hôtel was built in 1699[16] in the Fauberg St. Germain, a fashionable new community during the reign of Louis XIV located across the Seine and downstream from the Louvre, to which the elite and nobility were then drifting. The mansion, originally called Hôtel d'Estrées after the designer,[16] was erected on rue de l'Université (Note 4) for a widow marquise of the Noailles family (Marguerite-Thérèse de Rouillé de Meslay, 1660–1729),[17] who in 1702 married the 2nd Duc de Richelieu, formally known as Armand-Jean de Vignerot du Plessis (1629–1715), a nephew of the famous Cardinal de Richelieu (1585–1642), chief minister for Louis XIII (18). Marguerite-Thérèse, accompanied by her two daughters aged eight and eleven, married the 2nd Duc, now a debauched septuagenarian, in a bid to advance her social standing.[18] He moved into this mansion, now called "Hotel de Richelieu," accompanied by his six-year-old son, the 3rd Duc de Richelieu, Louis François Armand de Vignerot du Plessis (1696–1788). The 3rd Duc would soon gain notoriety in elite society as the "champion adulterer and model of fashion" of Paris.[19] In this age where the nobility of France was "so intricately linked by marriage and adultery,"[18] it was natural for the 3rd Duc to be married off in 1711 to his housemate stepsister Anne-Catherine (1694–1716), and the wedding feast was held in their Hôtel on rue de l'Université.[18]

Today, the 3rd Duc de Richelieu is probably best known in the annals of culinary art—during a military campaign on the island of Minorca, his cook celebrated a victory by concocting a tasty salad dressing from egg yolks and vinegar which soon became the rage in France cuisine.[18] This new condiment was named *mahonnaise* for the Minorca city (Mahón) captured by Richelieu, and is today known under the corrupted name "mayonnaise."

When Richelieu's wife died of smallpox after five years of marriage,[18] the Hôtel reverted to the Mouchy branch of the Noailles family,[15] and Richelieu moved on to other marriages and lodgings, dying one year before the French Revolution.[18] During the Reign of Terror in 1794, the occupants Philippe Count de Noailles and Anne Claudine Louise d'Arpajon were guillotined,[17] and the property was transferred to l'Agence des Mines. In 1816, when the École moved to its 3rd site, the property was returned to the Noailles family, but was condemned in 1866 and taken down in 1870 to make way for the present boulevard Saint-Germain and given to the Département de Défense.[7,15] Today the area is occupied by the Ministére de la Défense, and the location of the historic building can be identified by the intersection of boulevard Saint-Germain and rue de l'Université.

Apparently, the only likeness of Hôtel Mouchy (Note 5) lies embedded in the famous 1739 Plan de Paris by Turgot[20] (Figure 9). This Plan was a multi-year project recording the visual appearance of Paris so that future construction (principally by Louis XV) could be planned efficiently.[21] Turgot's "bird's eye view" encompasses some 20 square kilometers with incredible detail (with a resolution sometimes of a meter!) (Figure 10).

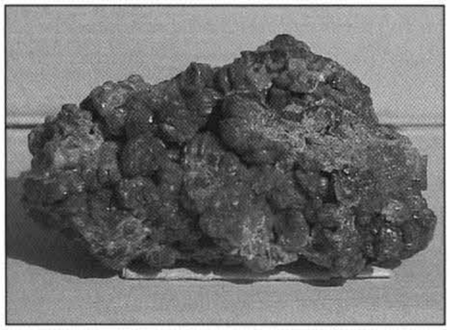


Figure 11. The original sample of plomo pardo Zimapán is on display in the Museum für Naturkunde, Invalidenstraße 43, Berlin, Germany.

The Ultimate Fate of the *Plomo Pardo* Sample. The original specimen of plomo pardo delivered by Humboldt to the Institut de France still exists; it was transported to the collections of Humboldt University in Berlin and is presently on exhibit at the Berlin Museum of Natural History (Figure 11). In the original handwriting of Humboldt (Figure 12), the label reads [translated] "Brown lead ore from a vein of Zimapán in north Mexico. Chromate of lead. M. del Rio believed that he had discovered a new metal which he named erythronium, then panchromium, finally recognized it as ordinary chromium," At the top of the label is written by Gustav Rose decades later, [translated] "vanadium lead ore," This correct identification of the mineral as that of a new element was possible only after accurate chemical analysis by Niels Sefström in Sweden and Friedrich Wöhler in Germany, whom we will visit in the next issue of *THE HEXAGON*.

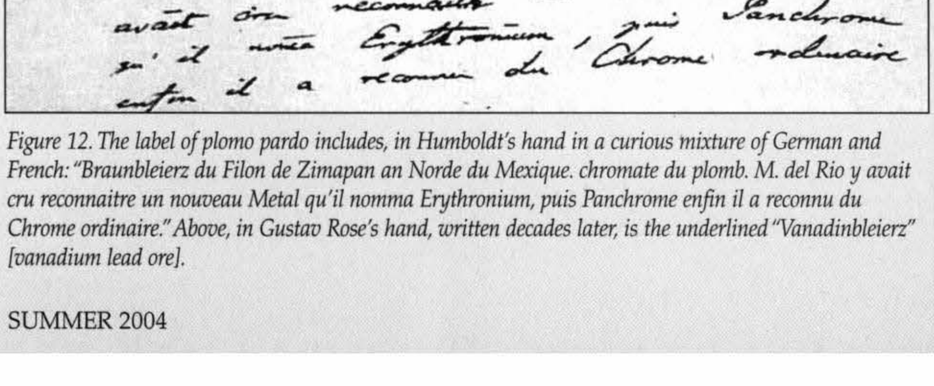


Figure 12. The label of plomo pardo includes, in Humboldt's hand in a curious mixture of German and French: "Braunbleierz du Filon de Zimapan an Norde du Mexique. chromate du plomb. M. del Rio y avait cru reconnaitre un nouveau Metal qu'il nomma Erythronium, puis Panchrome enfin il a reconnu du Chrome ordinaire." Above, in Gustav Rose's hand, written decades later, is the underlined "Vanadinbleierz" [vanadium lead ore].

Acknowledgments.

The authors are indebted to Francine Masson, Directeur de la bibliothèque, École des Mines de Paris, 60, boulevard Saint-Michel, Paris, who made available the resources of her library to us. Dr. Lyman Caswell, Professor Emeritus of Texas Woman's University, Denton TX, who has thoroughly studied the available scientific literature on del Río, is gratefully acknowledged, for his assistance in furnishing important information and useful suggestions.

Literature Cited.

1. J. L. and V. R. Marshall, "Rediscovery of the Elements: Vanadium" *THE HEXAGON of Alpha Chi Sigma*, **2003**, *94*(4), 60–62, 65.

2. L. R. Caswell, "Andrés del Río, Alexander von Humboldt, and the Twice-discovered Element," *Bull. Hist. Chem.*, **2003**, *28*(1), 35–41.

3. J. L. and V. R. Marshall, "Germanium and Freiberg," *THE HEXAGON of Alpha Chi Sigma*, **2001**, *92*(2), 20–22.

4. E. L. Wittich, "El descubrimiento del Vanadio," *Boletin minero*, **1922**, *13*(1), 4–15.

5. A. L. Lavoisier, *Traité Élémentaire de Chimie*, **1789**, Paris.

6. E. C. Spary, *Utopia's Garden*, The University of Chicago Press, Chicago: R. W. Burkhardt, Jr., **2000**; and *The Spirit of System. Lamarck and Evolutionary Biology* Cambridge: Harvard University Press, **1977**.

7. Archival information from Francine Masson, Directeur de la bibliothèque, École des Mines de Paris, 60, boulevard Saint-Michel, Paris 75272.

8. N.-L. Vauqelin, "Analyse de l'aigue marine ou beril; et decouverte d'une terre nouvelle dans cette pierre," *Ann. Chim.*, **1798**, *26*, May, 155-177; N.-L. Vauquelin, "De l'Émeraude de Pérou," *Ann. Chim.*, **1798**, *26*, June, 259–265.

9. N.-L. Vauquelin, "Sur une nouvelle substance métallique contenue dans le plomb rouge de Sibérie, et qu'on propose d'appeler Chrôme," *Ann. Chim.*, **1798**, *25*, pp 21–31; N.-L. Vauquelin, "Sur le métal contenu dans le plomb rouge de Sibérie," *Ann. Chim.*, **1798**, *25*, 194–205.

10. A. Queruel, *Vauquelin et son temps* (1763–1829) Paris: Éditions L'Harmattan, **1994**; 132.

11. J. R. Partington, *A History of Chemistry*, Vol. 3, London: Macmillan & Co., Ltd, **1961**, 105.

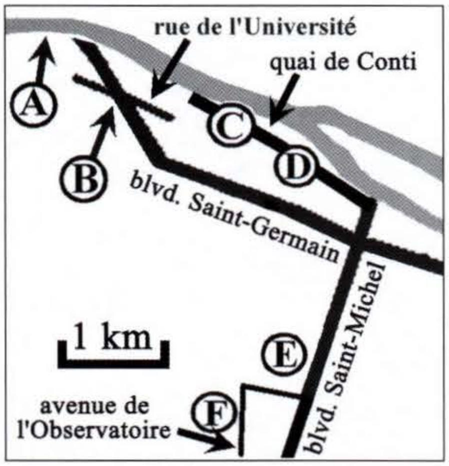


Figure 14. Sites mentioned in this article include (A) Palais Bourbon, now the Assemblée Nationale, quai Anatole France (N 48° 51.75 E 02° 19.14); (B) site of Hôtel Mouchy (now demolished; N 48° 51.60, E 02° 19.30); (C) Institut de France (23, quai de Conti, N 48° 51.44, E 02° 20.24); (D) Hôtel de la Monnaie (11, quai de Conti, N 48° 51.39, E 02° 20.34); (E) present l'École des Mines (60, Boulevard Saint-Michel, N 48° 50.73, E 02° 20.39); (F) Faculté de Pharmacie (4, avenue de l'Observatoire, N 48° 50.58, E 02° 20.18).

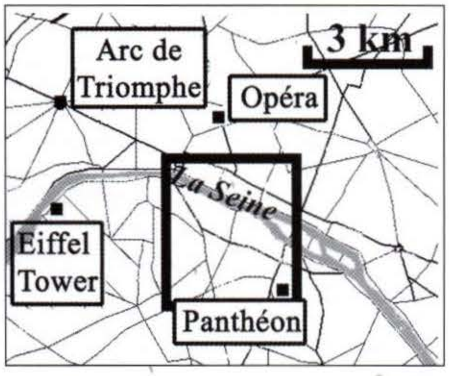


Figure 13. The left bank (south side) of the Seine in Paris holds the historical locations of interest to the chemist during the Revolutionary days of France. The inset is expanded in Figure 14.

12. P. Jaussaud, *Pharmaciens au Muséum*, Paris: Muséum national d'Histoire naturelle, **1997**, 128–131.

13. H.-V. Collet-Descotils, "Analyse de la mine brune de plomb de Zimapan," **1805**, *Ann. Chim.*, 53, 268–271.

14. Ref 11, Vol. 4, 153.

15. J. Vacquier, *Les Vieux Hôtels de Paris. Le Faubourg Saint-Germain*, Paris: Tome VI, F. Contet, **1924**, 3–4.

16. L. Hautecoeur, *Histoire de l'Architecture classique en France*, Paris: Tome III, Éditions A. et J. Picard et Cie., **1950**, 107.

17. The name of Noailles occurs with almost confusing reiteration throughout the 18th century, but with careful study one may sort out the genealogy of this high pedigree family, e.g., *http://pages.prodigy.net/ptheroff/gotha/noailles.html*

18. H. Cole, *First Gentleman of the Bedchamber. The life of Louis-François-Armand, maréchal duc de Richelieu*, New York: The Viking Press, **1965**.

19. W. and A. Durant, *The Story of Civilization. Part IX. The Age of Voltaire*, New York: Simon and Schuster, **1965**; 291.

20. *Le Plan de Paris de Louis Bretez dit Plan de Turgot*, **1739**. Many copies of this famous work are available, e.g., **1989**, Verlag Dr. Alfons UHL, Nördlingen, Germany; and wall maps may be purchased from various sources in Paris.

21. R. Blomfield, *A History of French Architecture, from the death of Mazarin till the death of Louis XV 1661–1774*, Vol. 2, London: G. Bells and Sons, **1921**; 183–184.

22. A. J. Rocke, *Nationalizing Science. Adolfe Wurtz and the Battle for French Chemistry, Cambridge*: MIT Press, **2001**.

23. Private communication, E.V. Bourlakov, Director, Geological Museum, Ekaterinburg, Russia; A. F. Bushurakin, "Crocoite from the Berezovsk Gold Mines," *World of Stones (Mir Kamya*, English Translation), **1966**, No. 10, 28–31; J. A. Polenov, V. A. Avdonin, and J. V. Burlakov, "Beresowsk," *Lapis*, **1997**, No. 7/8, 31–43.

24. W. H. Wollaston, "On the identity of columbium and tantalum," *Phil. trans.* Roy. Soc. London, **1809**, *99*, 246–252.

25. J. Vacquier, *Les Vieux Hôtels de Paris. Le Faubourg Saint-Germain*, Paris: Tome III, F. Contet, **1924**; 7.

26. J. L. and V. R. Marshall, "Tellurium and Romania," *THE HEXAGON of Alpha Chi Sigma*, **2000**, *91*(3), 43–45.

Notes.

Note 1. As A. Rocke has pointed out,[22] it can be very confusing when attempting to trace the constantly changing laboratories and academic positions of the French, who engaged in the system of *cumulard*, wherein they would hold simultaneous and fluctuating positions. Fortunately, several sources clarify[7,10,12] that Vauquelin worked in the laboratory with Antoine-François de Fourcroy at the 1st site of École Polytechnique at Hôtel Bourbon (see Figure 9) until 1797, when he had leave his "dear laboratory"[10] to commence work full-time in l'École des Mines; he had become a professor at l'École in 1794 when it moved to its second site on rue de l'Université. After 1802 he left l'École des Mines and became engaged mainly in organic chemistry, taking successive/simultaneous positions at École de Pharmacie, Faculté de Medicine, Jardin du Roi, etc.[10]

Note 2. The exact locations of the sources of the emerald and "white beryl" investigated by Vauquelin are unknown. Records suggest the emeralds analyzed were from Peru[8] and Limoges, France,[12] and the beryl from Saxony.[12] It is known that the crocoite was obtained at a site (N 56° 51.8 E 60° 48.2) about 2.5 kilometers north of Beresov, which is 14 kilometers northeast of Ekaterinburg, in the Urals Mountains, Russia.[23] Beresov was a famous gold producing area for many years; Ekaterinburg was the location of the assassination of the seven Romanovs in 1918.

Note 3. In an effort to be fair in our assessment of the faulty analysis of plomo pardo by Descotils, it may be useful to compare the misidentification of vanadium with another element of the same period. William Hyde Wollaston (1766–1828) in London studied samples of niobium (discovered by Charles Hatchett in 1801) and tantalum (discovered by Anders Gustaf Ekeberg in 1802) and he concluded in 1809 they were the same elements.[24] In his study more than twenty chemical tests were performed, with every one exhibiting indistinguishable behavior for the two. Wollaston can hardly be criticized for not anticipating the lanthanide contraction, which makes the chemical behavior of the two elements virtually identical. Furthermore, Wollaston's caution was clear when he emphasized that the different specific gravities of the two minerals raised certain questions of identity. It took over half a century before Heinrich Rose (1847), C. W. Blomstrand (1864), and Jean-Charles Galissard de Marignac (1865) were able to distinguish clearly the different chemistries of niobium and tantalum. No such excuse should have been entertained in 1805 for the confusion between chromium and vanadium, which have unmistakable chemical differences. It should be recalled that del Río was a master of assay and an expert of the analysis of lead ores; Descotils had scant such experience.

Note 4. The listed street numbers vary from 67 to 71 rue l'Université[7,15,16] but the mansion's location can be located with precision.[20,25] Throughout its colorful history, the edifice has been known as Hôtel d'Estrées,[16] Hôtel de Richelieu,[25] Hôtel Noailles,[18] Hôtel Noailles-Mouchy,[15] and finally Hôtel Mouchy.[7]

Note 5. In *Les Vieux Hôtels de Paris*,[15] only three photographs exist of the interior of the building, and no renditions of the exterior. These photographs include the elaborate remodeling by the Noailles-Mouchy family shortly before the demolition of the mansion in 1870.