A Travelogue of Rediscovery Sites

Part 5



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Figure 1. Oliver Sacks (right) and the author are standing before the "Living Periodic Table" in the home of the Marshalls. Oliver is holding a willow blue cup of hot tea, which has melted an ingot of gallium! YouTube videos of "disappearing" gallium spoons may be viewed on the internet.[5]



Figure 2. This specimen is gallium-rich sphalerite ("le blende" in French, ZnS) from the Pyrenees in southern France. This sphalerite was found in conjunction with lead sulfide (galena, PbS) in the local mines called La Galène (N42° 56.82 W00° 05.20), 2 km southwest of the village of Pierrefitte-Nestalas. Collection, J. Marshall.

This is a continuation of a review of "Rediscovery" episodes, initiated in the Spring 2017 issue of The HEXAGON. *This series includes the visits to mine sites taken by Jim and Jenny Marshall over the ten-year period of 1999–2008 in their successful search for the actual original source for the elements. The present issue is devoted to England and France.*

Gallium.[1b] This element was memorialized by the well-known science writer Sam Kean in his *The Disappearing Spoon*.[2] After it was discovered in 1875, gallium's low melting point (30°C) could be used to advantage in scientific parlor tricks. Gallium could be cast into dining utensils appearing as aluminum (the two elements are in the same chemical family of the Periodic Table). A gallium spoon when used to stir hot tea, would mysteriously melt and drip away like cooking oil.[2] Oliver Sacks, the acclaimed author of *Uncle Tungsten*,[3] said this unusual behavior rendered this metal his favorite element.[4] In his book he described how he became acquainted with it in his Uncle Dave's light bulb factory in Farringdon, England. Gallium had the widest temperature of any metal in the liquid state and could be used conveniently as the carrier liquid in thermometers in the furnaces of the factory. While viewing the Marshall element collection during his trip to UNT in 2001 (Figure 1), Oliver exhibited his supreme sense of humor by dropping an ingot of solid gallium into a warm cup of his favorite English tea. The gallium quickly melted, forming a metallic pool resembling mercury. After drinking his tea (gallium is not poisonous), Oliver then dropped an ice cube into the cup, quickly freezing the gallium. The specimen, now appearing like a shiny blob of frozen solder, was then was returned to the element collection.

The element gallium was discovered by Paul Emile (Francois) Lecoq de Boisbaudran (1838–1912), who set up his own laboratory in Cognac, France.[1b] Boisbaudran was a master of spectroscopy and originally identified gallium by its spectral lines before procuring it in quan-



Figure 3. This is route D920, reaching from Lourdes to Gavarnie. A side route reaches up to La Galène. Lourdes (15 km north of Pierrefitte) is famous for its 14-year-old peasant girl named Bernadette Soubirous who had visions of the Virgin Mary in 1858, leading to its shrines and pilgrimages by those who wish to share in the healing powers of the local spring waters. Gavarnie (30 km south of Pierrefitte) is a popular tourist site in the Parc National des Pyrénées (see Figure 4).



Figure 4. The "cirque" (circle), a famous panoramic scene in the National Park of the Pyrenees (Parc National des Pyrénées). The Pyrenees were formed 80–20 million years ago, when the Iberian Peninsula (Spain and Portugal) collided with Europe—a separate event from the creation of the Alps 34–23 million years ago, but nevertheless related as being part of the extensive mountain building when the African plate and Eurasian tectonic plates collided.



Figure 5. The abandoned mine region of La Galène, the historic lead mining region of Pierrefitte. The mines were originally simply large holes in the ground, allowing entry down deep shafts, but have been filled in and can be identified only by rocky patches on the wooded slopes. The Pierrefitte-Nestalas minerals, including the gallium-rich sphalerite, are found in an Ordovician formation, about 400 million years old.



*Figure 6. Seaweed (*Fucus*) on the coast of Normandy, France. In the 16th century, seaweed was burned in pits or kilns to form varec, the potassium-rich ashes used in the manufacture of saltpeter. Bernard Courtois discovered iodine when he accidentally reacted varec with sulfuric acid.*

tity. Boisbaudran isolated the gallium from a specimen of sphalerite (zinc sulfide) taken from lead mines near Pierrefitte in southern France (Figure 2).

The Pierrefitte lead-mining region can be reached via the sinuous roads winding through the slopes of the Pyrenees (Figure 3). (Continuing further south on this route, one can reach the famous National Park of the Pyrenees (Figure 4)). The historic mines themselves where the gallium-rich ore was found was called *La Galène*, the French word for the mineral galena (lead sulfide, PbS), from the Latin word for lead ore (not to be confused with the name "gallium" which was taken from the Latin word *Gallia* for France). *La Galène* can be visited by taking an unimproved road up a steep hillside. Mining in this area began in Roman times, with the extraction of lead and silver. In the 16th century, mining was resumed, with extensive extraction of lead and silver, as well as copper and zinc and other metals. By the end of the 19th century, the rich reserves were depleted. Limited mining continued until all activity ceased in 1969. Today, all that remains are slag heaps, talus slides, and filled-in mine shafts. (Figure 5).

Iodine.[1d] Although metal iodides are commonly found in minerals, this element was not discovered in a mine. Instead, it was found in seaweed! (Figure 6) Bernard Courtois (1777–1838) accidentally observed a purple vapor when he reacted varec (the ashes of seaweed) with sulfuric acid at his nitrary in Paris, France. A nitrary



Figure 7. This is the birthplace of Bernard Courtois (78, Rue Monge, N47 19.121 E5 02.018). On the plaque is the inscription (translated) "In this house was born on 8 February 1777 the pharmacist Bernard Courtois who discovered iodine in 1811."

("Nitrière" in French, "Nitriary" in German) was a manufactory of potassium nitrate (saltpeter). This product was mixed with sulfur and charcoal to manufacture gunpowder, used in Europe beginning in the 1300s. At the nitrary, rows of hills were filled with manure, garbage, blood, ash, and lime and were periodically soaked with urine. The nitrogenous compounds organically produced over a year's time released ammonia, which was air-oxidized to nitrates. After a year or so the "ripened" saltpeter beds were processed in the refinery (French "le Raffinerie") by leaching with water to extract calcium nitrate. Then the ashes of seaweed (varec) were used to produce the *potassium* salt of nitrate (calcium nitrate, being hygroscopic, does not allow an explosive chemical reaction). Unsurprisingly, raffineries were found in the countryside, and not in the cities, because of their awful stench. Raffineries were particularly critical for the war effort in France because of the British blockade which prevented nitrates from being imported from India.

Bernard Courtois was born in Dijon, France, (Figure 7) where there were a number of nitraries. (Today Dijon is famous for its boutique mustard shops). Across the street from Courtois' home was the historic Academie de Dijon, where his father was chemistry demonstrator, hired by Guyton de Morveau (1737–1816) who founded the chemistry department at the Academie. Morveau is best known for being one of the authors of the modern system of chemical nomenclature (along with Lavoisier, Berthollet, and Fourcroy).

In 1798 Courtois moved to Paris, where he became laboratory assistant at the École Polytechnique, arranged by Morveau who had become professor there. In 1802 he began assisting his father who had set up a nitrary in the countryside, northeast of Paris. It was here that he made his iodine discoveries. On old maps of the region, the site of the Courtois raffinerie can be located near the "Wall of the Farmer's General," built for tax purposes and used to enforce the collection of tolls on goods brought into the city.



Figure 8. This is what remains of the largest and oldest (1582) saltpeter raffinerie in Dijon (N47° 19.01 E 05° 03.25), now a residential area. The street sign says: "Rue [street] de la Raffinerie."



Figure 9. Viewing south on Rue Saint Ambroise in the 11th arrondissement of northeast Paris. On the right down the street is an apartment complex (N48 51.76 E02 22.70, 31 street number) which was the original site of Courtois' raffinerie. The steeple in the distance is the St. Ambroise church on Boulevard Voltaire, built in 1868. In the times of Courtois, this was countryside, 2 kilometers northeast of the Notre Dame Cathedral.



Figure 10. This is Joseph Black's house where he lived in his final years. It was located on Nicolson Street, near the College. When he died, the house became a blind asylum. The present address has different buildings now, composing a row of shops.[1e]



Figure 11. This exhibit on Joseph Black can be viewed in the Royal Museum, Chambers Street, Edinburgh, Scotland. (N55° 56.81 W03° 11.44). The various bottles and flasks were used to store and study fixed air (carbon dioxide). Black was the first to distinguish magnesium from calcium.

Lavoisier, the famous French scientist who was the first to recognize the true elements, played a critical role in overseeing the production of gunpowder during the latter part of the 18th century. He was also a "farmer-general" ("ferme general"), essentially a tax collector on goods entering Paris. This highly lucrative employment was how Lavoisier made his money to pay for the high quality scientific instruments in his laboratory. As were all tax-collectors, he was very unpopular. Unfortunately, he was caught up in the politics of the Revolution and was guillotined in 1794.

The wall that ensured taxation on all incoming goods to Paris is now gone. It ran along the present Boulevard de Ménilmontant, 600 meters northeast of Courtois' raffinerie. Today nothing remains of the raffineries in Dijon and Paris, whose original countryside areas have been overrun by urban sprawl (Figures 8,9).

Magnesium.[1e] The "discovery date" of an element sometimes can be straightforward—that is, by a single recorded research date of a solitary effort. For example, the platinum metals iridium and osmium were discovered by Smithson Tennant (1761–1815) in 1803, and palladium and rhodium were discovered by William Hyde Wollaston (1766–1828) in 1804, in "one-step" events. These British chemists obtained samples of crude Old World platinum (Russian platinum had not been discovered yet) and isolated these new elements and characterized chemical properties and their elemental (metallic) form. Other elements may be "two-step," such as chromium, whose mineral—"red lead of Siberia" (lead chromate)—was discovered in a gold mine in the Urals. Later, chromium was isolated and characterized (both compound and metallic forms) by the French chemist Nicolas-Louis Vauquelin (1763–1829) in his Paris laboratory during 1797–1798. Other elements can be multi-step, such as strontium,[1a, f] which has a tortuous history—its mineral (strontium carbonate) was discovered in a Scottish lead mine; these crude salts found their way to the historic St. Thomas Hospital in London (mentioned in *The Canterbury Tales*) where they were administered to patients in a London hospital as a variant of barium salts, a good "evacuant, deobstruent and tonic." Then the salts were chemically analyzed at the chemical laboratory at Woolich Arsenal on the Thames River and found to be similar but distinctly different from barium. Next, the salts were purified by Thomas Charles Hope (1766–1844) in Edinburgh who fully recognized it as a separate element (and gave it its present name). Finally, the metal itself was prepared by Humphry Davy (1778–1829), using his technique of electrolysis, in the Royal Institution in London.

Magnesium is another such example of a "multi-step discovery."[1e] Magnesia (magnesium oxide) was named for its original discovery site, Magnesia, Thessaly, Greece. This mineral providing magnesia was called *magnesia alba* (magnesium carbonate), i.e., white magnesia. (Another mineral from this site was called magnesia niger, black magnesia (MnO), which is the etymological origin of the element manganese, discovered by Johan Gottlieb Gahn (1745–1818).[1c]). Magnesia (today's "milk of magnesia") was used as an antacid and routinely prescribed for stomach maladies. Magnesia was considered as a variant form of calcia (calcium oxide), used as mortar in building construction.

Magnesia (MgO) could be easily produced from magnesia alba by heating, expelling carbon dioxide, $MgCO_3 \rightarrow MgO + CO_2$. Magnesia was investigated by Joseph Black (1728–1799) of Edinburgh (Figure 10) and was shown by him to have similar (but definitely different) chemistry to calcia. Black's investigations of calcium and magnesium compounds led to his discovery of "fixed air," (carbon dioxide), as he showed calcia and magnesia could absorb atmospheric carbon dioxide (to "fix" it in solid form) to form the carbonates, $CaO + CO_2 \rightarrow CaCO_3$ and $MgO + CO_2 \rightarrow MgCO_3$. The carbonates in turn could be heated, regenerating the oxide and expelling carbon dioxide which could be collected in laboratory bottles. (Figure 11).

RIGHT: Figure 12. This is the original well of Epsom, source of the "curative waters," discovered in 1618 during a severe drought—now known to be heavily laden with magnesium sulfate (eventually to be known as Epsom salt). This drawing was by the Dutch artist Willem Schellinks (1632–1678) in 1662, three years before the Great Plague. Courtesy, Bourne Museum of Ewell Library, Epsom, England.





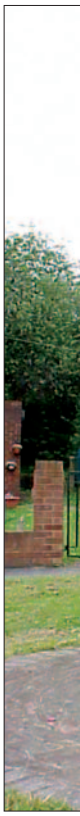


Figure 13. By the early 1700s, Epsom had become commercialized with many inns and pubs; timber-framed cottages were being replaced by brick shops. Courtesy, Bourne Museum.



Figure 14. In the 19th century, the Epsom Derby (better known as simply "The Derby") was prime entertainment; the wells were closed and the original reason for the resort area (the "curative waters") had been forgotten. Courtesy, Windmill Inn, Clapham Common, England.

Although magnesium compounds could be conveniently available in abundance from a multitude of mines and quarries, Black found that a purer source was the medicative well water of Epsom, 20 km southwest of London. Black found that pure magnesia alba could be easily prepared from Epsom salts (magnesium sulfate), the primary salt in the "curative waters" of the Epsom well. A shed was built over the well, and visitors would lounge about the well (Figure 12), imbibing the Epsom waters and then "take to the bushes" for digestive relief from the resulting laxative powers of the tonic. Samuel Pepys, the famous diarist (1633–1703), visited this area in 1663 and described it in detail.

By the early 1700s, the village of Epsom had developed into a bustling community with abundant innkeepers. In the summer, young fellows would come down from London ostensibly to "drink the waters" but were really there for the "entertainment"—betting on horse races, gambling, playing bowls outside, or taking advantage of the music inside of pubs while drinking German wine or local beer. (Figure 13). In the 1800s, the Epson Derby at Epsom Downs had become a popular event (Figure 14), and "The Derby" survives to this day as the premier thoroughbred horse races for 3-year-old colts and fillies. Today all that remains of the Epsom well site is a modest brick memorial (Figure 15) in front of a retirement home.

The preparation of metallic magnesium was accomplished by Humphry Davy at the Royal Institution in 1808, half a century after Black's pioneering work, along with his preparation of the other "reactive" elements (potassium, sodium, lithium, boron calcium, strontium, and barium).

NEXT: Discoveries in Eastern Europe

The July 1, 2019, issue of *Chemical and Engineering News* featured two articles on Jim and Jenny Marshall's work on the Periodic Table.

https://cen.acs.org/magazine/97/09726.html



Figure 15. All that remains today of the original Epsom well is a retirement home with a memorial well located at Well Way (N51° 19.63 W00° 17.41) at the center of a spiraling inward road. The Epsom Downs racetrack is 3 kilometers to the southeast.

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