A Travelogue of Rediscovery Sites

Part 7



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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 the world outside of Europe.*



Figure 1. This is a view of the Temple of the Oracle area in Siwa, situated on a hilltop (N29° 12.33 E25° 32.60). The temple area itself is at the left (north) end of the hill; the prominent structure to the right is the Oracle Tower. (Courtesy, David M. Lewis)



Figure 2. This is a Greek tetradrachm, minted 323-281 B.C. The obverse depicts Alexander the Great with the ram horns of the Egyptian God Amun (Ammon). The name of the extinct cephalopod "ammonite" is derived from its appearance of a tightly-coiled ram horn. (Private collection of J. L. Marshall)

Egypt—the origin of "ammonium." Ancient Egypt flourished along the Nile River, but several outposts of Egyptian culture existed further west. One such community was Siwa, an oasis in the Libyan desert, 550 kilometers west of present Cairo. Alexander the Great made a pilgrimage to this thriving community in AD 332, where he conferred with the oracle of Amun (sometimes spelled "Ammon") (Figures 1, 2). He was told he was the son of Amun (the Egyptian god of the sun and air) and was proclaimed Pharaoh.

After the Egyptian dynasties waned and the Roman Empire expanded, Roman visitors collected a volatile white crystalline material from the ceiling and walls of the Amun temple deposited from the smoke of burning of "natural fuels" (camel dung). (Old timers of the Southwest United States can attest to value of cow dung during the Great Depression, which served as a cheap but reliable fuel for their campfires, hot and long-lasting for both cooking and cattle branding.) This white crystalline material (NH_4Cl, ammonium chloride) was called "sal ammoniac" ("salt of Ammon") by the Romans. The deposition of sal ammoniac on stone walls of old stables and houses is fairly common, and burning coal mines produce this sublimate frequently.

In the 1700s, Joseph Priestley (1733–1804) found that sal ammoniac, when reacted with lime, produced a gas that he collected over mercury. It was suggested, from the name of "sal ammoniac" that the vapor be called "ammonia." The role of ammonium salts later was critical for further discoveries. For example, Lord Rayleigh (John William Strutt, 1842–1919) in 1894 in his home laboratory at Terling, England, noticed the density of nitro-

gen obtained from the atmosphere (after the oxygen had been removed) was slightly heavier (2.3102 g/1800 mL) than the nitrogen synthesized from ammonium salts (2.2990 g/1800 mL). This was a a tipoff that the inert portion of the atmosphere included an unknown gas. Further study by Lord Rayleigh and Sir William Ramsay (1852–1916) involved removing the nitrogen (by passing over hot magnesium metal) to reveal the new element argon.[1a]

Although nitrogen itself was simultaneously discovered in 1772 by Daniel Rutherford (1749–1819) in Edinburgh, Scotland (he identified it as "dephlogisticated air"),[1i] and by Carl Wilhelm Scheele (1742–1786) in Uppsala, Sweden (he called it "skämp luft" = "spoiled air."),[1e] sal ammoniac was known much earlier to the Arabian chemists.[2] The chemical culture of the Arabians was kept alive during the Dark Ages of Europe, and was eventually transferred along with the Greek tradition of logic and philosophy to Europe during the Renaissance. Representative of this Arabian science was Abū Mūsā Jābir ibn Hayyān (721–815)—called "Geber" in European literature. The Arabian chemists invented various chemical devices and refined distillation and crystallization techniques. Many words in chemistry are derived from Arabian; for example, from "al-Qili" ("the ashes" of a wooden fire, principally sodium carbonate) is derived "alkali"; from "al-cool vini" ("the essence of wine") is derived "alcohol." The Arabians were the first to utilize caustic soda (sodium hydroxide), which they derived from reacting al-Qili with slaked lime—$CaO + Na_2CO_3 \rightarrow 2\ NaOH$ (aqueous solution) + $CaCO_3$ (precipitate). The slaked lime, in turn, was produced by heating limestone (calcium carbonate)—a long-standing technology for producing mortar from ancient to modern times: $CaCO_3 \rightarrow CaO + CO_2$. In addition to caustic soda, sal ammoniac, and distilled alcohol, the Arabians were pioneers in organic chemistry, perfecting destructive distillation, thereby producing many essences and organic compounds. "Chemistry owes the Arabian alchemists far more than has been recognized, and their contribution to the development of science was a major one."[2]

Vanadium—Mexico. In the rich silver-mining region of Mexico north of Mexico City, a peculiar mineral—plomo pardo ("brownish gray lead")—was found in Purísima del Cardonal Mine near Zimapán. (Figures 3, 4) This mineral was investigated by Don Andrès Manuel del Río (1764–1849), a professor of mineralogy at the University of Mexico.[1b] In 1801, del Río thought he had discovered a new element in plomo pardo which he called "panchromium" from the various shades of colors of its compounds; he later called it "erythronium." He gave a sample to Alexander Humboldt (1769–1859), the famous German naturalist who was making a tour of the New World, who brought it back to Europe to be analyzed and to confirm the claim of a new element. The analysis was



Figure 3. The author (right) with the head of the Lomo de Toro mines, Oscar Fernando Nieto de la Mora, deep in the silver mining district near Zimapán, Mexico. These mines, 150 kilometers north of Mexico City, bear silver-rich galena (lead sulfide).



Figure 4. The actual mine from which del Río's sample was procured was the Purísima del Cardonal Mine, near Cardonal, Hidalgo, Mexico (N20° 37.16 W99° 06.76). The author is approaching the entrance and is dwarfed by the large cavity in the side of the mountain. Hiking about the area is treacherous, with dangerous shafts hidden by vegetation.

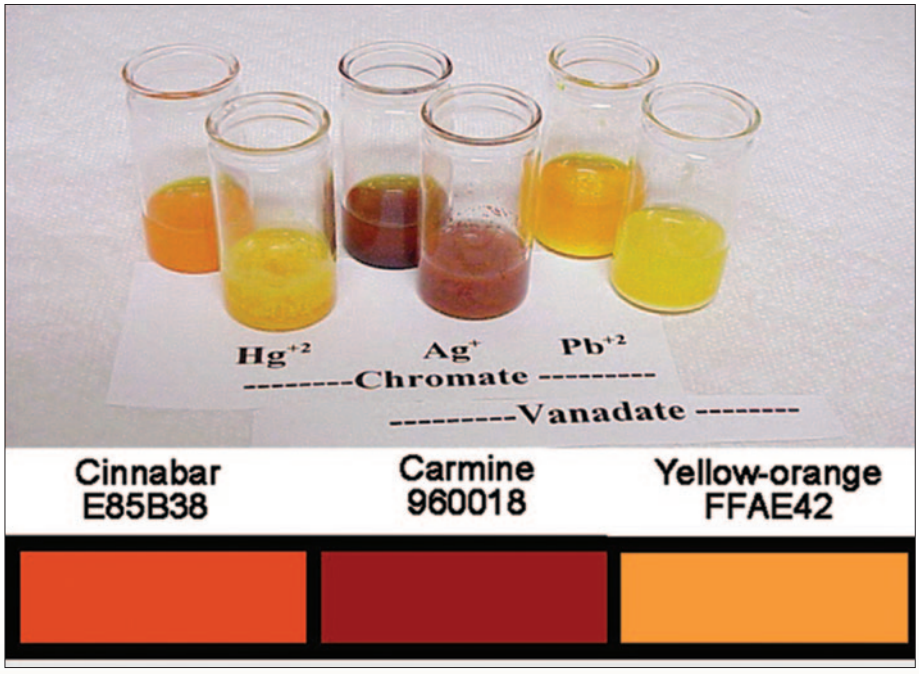


Figure 5. The authors repeat Descotils experiments in their "kitchen chemistry," comparing the reactions of chromate (back row) and vanadate (front row) with Pb^{+2}, Ag^{+}, and Hg^{+2}. Vauquelin described the reactions of chromate to give the colors, respectively, of cinnabar, carmine, and yellow-orange (see color code at bottom). The authors' results for chromate agree with Vauquelin's descriptions. However, the colors observed with vanadate are not the same and beg for further tests, which regrettably Descotils never performed (see text).

supposed to be performed by Louis Nicolas Vauquelin (1763–1829), who was recognized as one of the two best analytical chemists in the world (the other being Martin Heinrich Klaproth, 1743–1817, of Berlin). However, the responsibility was delegated to his student Hippolyte Victor Collet-Descotils (1773–1815), who had accompanied Napoleon during his Egyptian campaign. Descotils dashed off three quick chemical tests in 1805 and concluded the new metal was merely chromium, previously discovered by Vauquelin himself eight years previously.[1c] This error was not recognized until 26 years later, when the element was "rediscovered" in Swedish magnetite in 1831 by Nils Gabriel Sefström (1787–1845). He named it "vanadium" after Vanadis, a Scandinavian goddess.[1d]

The historian James Partington in his discussion of the Descotils experiments on the vanadium ore remarked that "…the reactions for chromium were not quite satisfactory..."[3] The authors decided to repeat the three experiments of the French chemist—reacting nitric acid solutions of the ore with lead, silver, and mercuric nitrates,[4] and the results corroborated Partington's suspicions—the results didn't "look quite right." (Figure 5) What Descotils should have done was to perform additional chemical tests which Vauquelin had done in his chromium studies. Descotils would have been surprised to observed that:

vanadate + tin → blue solution… however, chromate + tin → green precipitate

vanadate + HCl → orange solution… however, chromate + HCl → green solution

vanadate + heat → red solution… however, chromate + heat → green solution

Descotils' experiments were indeed folly, because they were incomplete. Probably he had already made a conclusion regarding the unknown's identity. Today del Río is recognized as the true discoverer of vanadium.

The platinum metals—South America.[1f] Platinum was first reported by the Spanish explorer Antonio de Ulloa (1716–1795), who was given samples collected from the river sediments of the rivers of New Granada, South America (area including today's Colombia, Ecuador, Panama, and Venezuela).

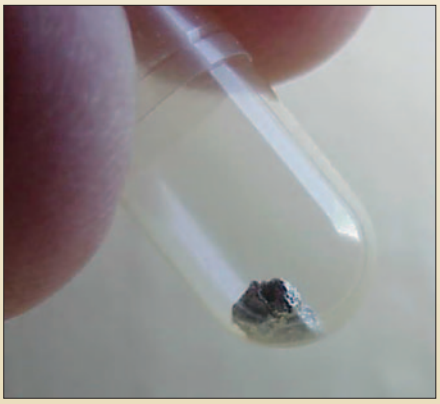


Figure 6. This tiny nugget of platinum from the San Juan River is typical of the original platinum found in that area. (Private collection of J. Marshall)



Figure 7. This is the Condoto River, tributary of the San Juan River, typical of the lush tropical jungles and meandering shallow rivers which afforded rich gravel beds of platinum. The San Juan River system is in the westernmost province of Colombia (Chocó Department), South America. (Courtesy, Christian Castro)

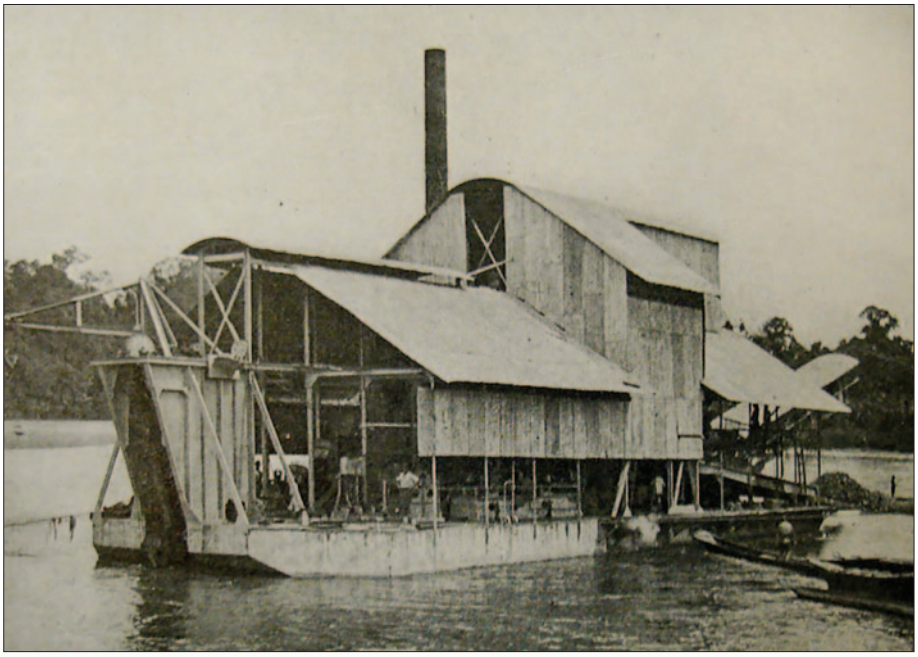


Figure 8. Dredge operation near Andagoya in the Condoto River intended to recover tons of platinum eroded by nature from the mountains, as well as intentionally dumped by gold workers in the 1800s.[5]

(The metal had been known to the native population, who used it in jewelry.) de Ulloa brought back samples to Europe for scientific study. A paper delivered to the Royal Society in London by William Brownrigg (1712–1800) recognized platinum as a new metal (1750), and platinum was recognized as one of the 31 principal elements by Antoine Lavoisier in his monumental *Traité Élémentaire de Chimie* (1789).

From New World samples of platinum, minor amounts of four additional elements were found and characterized in 1803 in London by William Wollaston (1659–1724) and Smithson Tennant (1761–1815). The remaining platinum member, ruthenium, was discovered in 1844 by Carl Claus (1796–1864) in Kazan, Russia; he obtained the element as an impurity in Russian platinum, which had been discovered in the Ural Mountains in 1819.

It is impossible to ascertain the exact location of de Ulloa's platinum granules, but was somewhere in the San Juan River system of present day Colombia. (Figures 6,7) The new metal was originally called "Platina di Pinto." The "Pinto" tributary of the San Juan cannot be located today. The original gravel from the river beds was gathered for its gold, but later platinum was also recognized as a valuable commodity, e.g., in nonreactive vessels used in chemical reactions. East of the San Juan river basin looms the Cordillera Occidental, a rugged western mountain range of the Andes Mountains. These mountains boast several important national parks. These peaks have been eroded down over the ages and furnish the gold/platinum-rich gravels. In Figure 8 is shown a dredge operation in the San Juan River in the early years of the 20th century, intended to retrieve tons of platinum eroded from the mountains, as well as that intentionally dumped by gold workers in the 1800s, who did not yet appreciate the value of the metal.

Niobium aka Columbium — Connecticut, U.S.A. Niobium was discovered in a specimen of columbite from the U.S.A., while the analysis itself was performed in London, England.[18] There is general agreement among mineralogists that the columbite (iron-manganese niobate, $(Fe,Mn)Nb_2O_6$) was from the Haddam, Connecticut, area, near Middletown. (Figure 9) The story of how the original sample was collected and then transported to the British Museum in London is an intriguing one and makes for a good detective story. Most probably, Native Americans brought the sample to John Winthrop II (1606–1676), who was governor of Connecticut (1657–1676). From time to time, gifts were sent from the colonies to Hans Sloane (1660–1753), an Irish physician and naturalist. Late in life, he bequeathed his entire collection to the British Museum (as well as to the London Library and the Natural History Museum), where the sample lay dormant until found by Charles Hatchett who analyzed it and found a new element, which he named "columbium." Hatchett, a fellow of the Royal Society, was a British chemist whose wealth was accrued by means of a stagecoach manufactory of his family in London (his business even extend-



Figure 9. Outcrops of rocks still protrude from a filled-in quarry near Middletown, Connecticut (N41° 30.85 W72° 31.12). Columbite is a common mineral embedded in the pegmatite quarry, which once furnished quantities of lepidolite (source of lithium).

ed to Catherine the Great, Empress of Russia, to whom Hatchett delivered a special carriage in 1790). The actual specimen of columbite Hatchett analyzed resides in the Natural History Museum in London (Figure 10, found on page 60).

The story of columbium/niobium continues to provide an interesting history.[1h] After tantalum was discovered in Scandinavia by Anders Gustaf Ekeberg (1767–1813) in 1802, it was recognized that Hatchett's columbium and Ekeberg's element were surprisingly similar in chemical and physical properties. Wollaston argued that they were the same, even though their densities were vastly different. (He was not yet aware of the lanthanide contraction, which renders the two elements the same size in spite of their different atomic masses.) It is now recognized by mineralogists that columbite and/or tantalite found in nature all have varying ratios of niobium: tantalum, and it is virtually impossible to find in the field a specimen that is 100 percent one or the other. Today their chemical similarities are understandable, both being in the same chemical family (below vanadium in the Periodic Table).

Heinrich Rose (1795–1864) in Berlin studied the matter and announced in 1847 that there was more than one element, but was originally confused about how many—he initially thought that there were three, which he called niobium, pelopium, and tantalum. Rose was misled by the similar chemistry of niobium and tantalum—for example, he was unaware that these two elements give three different products when the minerals are reacted with chlorine: $NbCl_5$, $NbOCl_3$, and $TaCl_5$ (but not $TaOCl_3$). For some reason, he did not analyze for oxygen, and merely assumed he had three different chlorides from three different metals. It took several years before it was recognized that in fact there were only two elements, and the "niobium" of Rose and the "columbium" of Hatchett were the same. A debate ensued across the Atlantic about the naming of columbium/niobium; for a good portion of the 20th century American scientific literature maintained the correct name was columbium. Today, the official name universally is niobium, even though Hatchett has been given credit for the original discovery.



Figure 10. Columbite from Middletown, Connecticut, exhibited in the London Natural History Museum, essentially identical to the specimen collected by the author from the same geographical area (not shown). (The actual sample analyzed by Hatchett is archived in the special collections of the museum and not available for general view.) All three specimens have been analyzed and prove to contain a ca. 2:1 ratio of niobium:tantalum.[1h] The chemical properties of niobium and tantalum are so similar that columbite always contains a mixture of the two elements, a fact not recognized for decades after the original discovery.

Next: Rediscovery visits to the cities.

A Note for Contributors

We certainly appreciate the added appeal of pictures in *The HEXAGON*. When taking photos for submission, please:

- Always use a flash indoors.
- Do not edit or alter your images. *The HEXAGON* production staff can and will determine if an image needs color correcting or additional processing.
- Set your digital camera quality to its highest setting with the least compression. Photos that are less than 8 inches wide at 72 dpi, or that have a file size of under 1 megabyte, may be too small for print production.
- Please send us the image file that is directly from the camera. Photos that are extracted from iPhoto albums, Facebook pages or Word documents have file sizes that have been compromised.
- Even print photos are welcome!

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