ANDRÉS del RÍO, ALEXANDER von HUMBOLDT, AND THE TWICE-DISCOVERED ELEMENT

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The Spanish-Mexican mineralogist Andrés del Río is today acknowledged as the discoverer of Element 23, although its accepted name, *vanadium*, was given to it by Swedish chemist Nils Sefström some 30 years after del Río's discovery. The initial failure to recognize del Río's work, and to assign his name, *erythronium*, to the element, was the result of poor communications, reliance on a friend, German naturalist Alexander von Humboldt, and, possibly, to prejudice. In this paper these effects will be examined, along with a misinterpreted analysis that also contributed to that failure.

Andrés Manuel del Río y Fernández was born in Madrid, Spain on November 10, 1764 (1). His early education, in classical subjects, resulted in a bachelor's degree at the age of 15 from the University of Alcalá de Henares. His scientific education began two years later with private instruction in physics. Thereafter, he concentrated his studies on mineral chemistry, analytical chemistry, and, especially, mineralogy.

In June 1782 Del Río enrolled in the Royal Academy of Mines at Almadén, Spain, with a scholarship from the Spanish Crown. At Almadén he studied chemistry, geology, mineralogy, and mining engineering. In 1783 the Spanish Ministry of Mines provided him with a grant for travel and advanced study elsewhere in Europe. He went to Paris, where he spent four years studying mineral chemistry with Jean d'Arcet, professor of chemistry at the Collège de France and director of the porcelain factory at Sèvres.

In 1789 Del Río enrolled in the Mining Academy at Freiberg in Saxony. The director of the Freiberg Academy, Abraham Gottlob Werner, was an outstanding mineralogist and one of Europe's most influential geologists. The academy was a leading institution for instruction in geology and mining engineering, as well as in *oryctognosy*, Werner's cumbersome term for "practical" mineralogy as applied to the needs of the mining technologist. Werner was a leading proponent of the *Neptunian hypothesis*, which held that most geological structures were deposited from materials dispersed or dissolved in water, and which minimized the importance of volcanic activity (2).

While Del Río was at Freiberg, Alexander von Humboldt enrolled in the mining academy. Baron Friedrich Wilhelm Karl Alexander von Humboldt was born in Berlin on September 14, 1769, the son of a retired Prussian army officer and an heiress (3). A brilliant but restless young man, Humboldt had attended several institutions without taking a degree, until he found inspiration from Werner's instruction at Freiberg. Del Río and Humboldt went in separate directions after graduation from Freiberg, to meet again several years later in Mexico.

After leaving Freiberg, Del Río went to the Austrian Imperial-Royal Mining Academy at Schemnitz (4) in Hungary to study analytical chemistry. The director of the Schemnitz academy, Anton von Rupprecht, had made the academy a leading center for instruction in the chemical analysis of minerals (5). From Schemnitz, Del Río went to England to study new developments in iron metallurgy. Late in 1791 he returned to France to become an assistant to Lavoisier. When Lavoisier was arrested during the Reign of Terror, November 8, 1793, Del Río returned to England. It is said that Del Río, fearing that he might also be arrested, fled from Paris disguised as a water-carrier (6).

In February, 1793 Fausto Delhuyar offered Del Río the chair of chemistry at the newly organized Royal College of Mines in Mexico City. Delhuyar, the codiscoverer of tungsten, had come to Mexico in 1788 as the Director-General of Mines of New Spain. Under his direction, the College of Mines, the first technical college in the Western Hemisphere, was organized on the model of the Freiberg mining academy and inaugurated on January 1, 1792 (7).

Andrés del Río

Del Río declined the offer of the chair of chemistry and requested the chair of mineralogy, which Delhuyar granted. He arrived in Mexico City in December, 1794, bringing a supply of laboratory equipment and accompanied by a servant. He initiated his course in oryctognosy on April 27, 1795, with a class of ten students. In order to provide his students with a text in their native language, Del Río published the *Elementos de Orictognosía*, "organized according to the principles of A. G. Werner." The first volume of the *Elementos*, "comprising earths, stones and salts," was printed in Mexico City in 1795, and the second volume, "comprising combustibles, metals and rocks," was published in 1805 (8).

The Twice-Discovered Element

In addition to his teaching duties, Del Río had the tasks of organizing the large mineral collection that had already been accumulated at the College of Mines and of carrying out chemical analyses of newly discovered minerals. In 1801 with two assistants, he analyzed the "brown lead" (*plomo pardo*) from the Purísima del Cardonal mine near Zimapán in the present state of Hidalgo, initially following the procedure for analyzing lead ores that he had learned at Schemnitz. The only surviving complete description of these experiments is a lengthy footnote in Del Río's Spanish translation of the *Tables of Karsten* (9). Treatment of a half ounce of the pulverized ore with hot, dilute sulfuric acid yielded a precipitate of lead sulfate and a green solution, which was neutralized with ammonia. White crystals were deposited from this solution in the course of a few days. Acidification of the ammoniacal solution with nitric acid yielded "aurora red" crystals, which formed a yellow salt with potash. Thermal decomposition of the white crystals gave "an opaque mass of color between the brown of liver and the gray of lead." A portion of this residue was dissolved in hot, concentrated nitric acid. The nitric acid was evaporated from this solution and the residue was diluted with cold water, giving an emulsion which gradually cleared. This solution gave yellow precipitates with silver, mercury and lead nitrates. The borax bead test on the residue that settled from the emulsion gave a green glass. An attempt to reduce a portion of the "opaque mass" with charcoal was unsuccessful.

The observed chemistry was unlike that of any element known to Del Río. Deciding that he had discovered a new element (9):

> I called it 'panchromium' (*pancromo*, from the Greek, "all colors") for the universality of colors of its oxides, solutions, salts, and precipitates, and then 'erythronium' (*eritrono*, from the Greek, "red") on account of the red color formed by its salts with the alkalis and the earths, on treatment with heat and with acids.

The first published notice of the new element appeared in a Spanish journal in 1802 (10):

> Panchromium. New metallic substance announced by Don Manuel del Río in a report sent from Mexico to Sr. Don Antonio Cavanilles, dated September 26, 1802.

Del Río's first complete paper describing his experiments and their conclusions was addressed to French chemist Jean-Antoine Chaptal. It was lost when the ship carrying it wrecked off Pernambuco, Brazil.

Alexander von Humboldt arrived in Mexico City in April, 1803. After graduating from the Freiberg Mining Academy in 1792, Humboldt had been certified an inspector of mines. He rose rapidly in the Prussian mining bureaucracy, partly through his ability and partly through influence. Upon the death of his mother in 1796, he inherited a large fortune and resigned from all of his official positions, hoping to fulfill an ambition to be a scientific explorer, inspired by the model of Captain James Cook. Frustrated in his attempt to follow Napoleon to Egypt, he went to Spain, where King Charles IV granted him permission to explore and evaluate the resources of the Spanish possessions in the Americas, provided Humboldt paid all the expenses of the expedition. Humboldt and French botanist Aimé Bonpland arrived in South America in July, 1799. Mexico was the last Spanish colony that they visited.

Humboldt and his companions remained in Mexico from March, 1803 until March, 1804. In Mexico City he visited the Royal College of Mines several times, giving lectures, participating in oral examinations, and ultimately selling his scientific instruments to the college. In addition, he spent nearly six months in the mining districts of Mexico, inspecting the mines, mining technology then in use, and the methods for processing silver ores. He reported all this information and much more concerning Mexico, its resources, its products, and its people, in his comprehensive *Political Essay on the Kingdom of New Spain* (11). He renewed his friendship with Del Río, whom he praised as a "distinguished chemist" in the *Political Essay*. Humboldt wrote an "Introducción a la Pasigrafía Geológica," which was included in the second volume of the *Elementos de Orictognosía.*

Del Río told Humboldt about his newly discovered element. Humboldt was skeptical, noting that the behavior of the element sounded like that of chromium, which had been discovered by Vauquelin in 1797, or uranium, discovered by Klaproth in 1789. In those times of slow communication, a detailed description of chromium did not reach Mexico until after Humboldt's arrival, when the College of Mines received Volume V of Fourcroy's *Système des Connaissances Chimiques* at the end of 1803 (12). The new information convinced Del Río that his discovery was actually chromium. A lecture on mineral veins published in Mexico by Del Río in 1802 (13), which briefly described the brown lead of Zimapán, but made no mention of its analysis, was republished in lengthened form in Spain in 1804 with an added footnote, which read, in part (14):

> From this brown lead I obtained 14.80% of a metal that appeared new to me...but having seen in Fourcroy that chromic acid also gives red and yellow salts on evaporation, I believe that the brown lead is a chromate of lead with an excess of base in the state of yellow oxide.

A similar statement was appended to Del Río's description of the analysis of the brown lead in his translation of the *Tables of Karsten*, which was also published in 1804. The latter reference gave his full analysis, "...80.72% yellow lead oxide, 14.80% of 'this new substance,' the rest being a little arsenic, iron oxide, and muriatic acid."

Humboldt had agreed to take Del Río's new paper, describing the discovery of erythronium in more detail than the one lost at sea, on his return to Europe, as well as samples of the brown lead. In a communication to the Museum of Natural History in Paris, Humboldt described the contents of 19 boxes of rocks and mineral samples that he had shipped. Box No. 14 contained (15):

> [B]rown lead of Zimapán...It is in this lead mine...that Mr. Delrio...has discovered a metallic substance very different from chromium and from uranium...Mr. Delrio believes it to be new, and the name erythronium has been proposed for it because the erythronate salts take a beautiful red color on heating and with acids. The ore contains 80.72% yellow lead oxide, 14.80% erythronium, a little arsenic and iron oxide.

Since Humboldt, although skeptical ("Mr. Delrio *believes*..."), nevertheless allowed for the possibility of a new element in this description, it is probable that his note was written and the samples shipped before Del Río discovered the description of chromium in Fourcroy's text and decided that his conclusions were in error.

Alexander von Humboldt

Following his arrival in Paris in August 1804, Humboldt gave a sample of the brown lead to Hippolyte-Victor Collet-Descotils at the Institut de France. Collet-Descotils (16) began his analysis by treating 25 decigrams of the pulverized ore with hot, dilute nitric acid, obtaining a greenish-yellow solution and a red precipitate, "...that I afterward recognized as iron oxide." He acidified the solution with concentrated sulfuric acid, precipitating lead sulfate. The filtrate was evaporated to dryness and the residue dissolved completely in an ammonia solution. After boiling off the excess ammonia, he added lead nitrate, obtaining a yellow precipitate. Silver nitrate gave a "magnificent orange" precipitate, but mercury nitrate gave a "yellowish" precipitate instead of the expected red one (17). To Collet-Descotils, these observations confirmed the presence of chromium. His completed analysis reported 69% metallic lead, 5.2% "presumed oxygen," 3.5% iron oxide insoluble in nitric acid, 1.5% "dry muriatic acid", 16% chromic acid, and a loss of 4.8%. At the conclusion of his report, Collet-Descotils' wrote (16):

> The experiments that I have reported appear to me sufficient to prove that this ore contains nothing of new metal.

Many of the chromates and vanadates of metals are known today to have similar, but not identical colors. Collet-Descotils may have been influenced by Humboldt's expectation that erythronium was actually chromium, leading him to conclude that he had proven this element, even though the color of at least one of the precipitates was not quite right. Humboldt had not shown him Del Río's paper to provide a basis for comparison of results. It is also possible that Collet-Descotils' initial red precipitate was misidentified. Ferric oxide, vanadium pentoxide, and vanadic acid are similar in color; and all three of these compounds have low solubility in dilute nitric acid. Collet-Descotils did not explain how he "afterward recognized" that the initial red precipitate was iron oxide.

Humboldt accepted Collet-Descotils' conclusion that erythronium was chromium, and Del Río's paper was never published. Humboldt forwarded Collet-Descotils' paper on the analysis, published in 1805, to Del Río; but it was apparently several years before it was received in Mexico, a result, no doubt, of the tight British blockade on Napoleonic France at the time. The paper produced an annoyed response from Del Río (18), published in 1811, in which he pointed out that he had already, in 1804, published his conclusion that the element in the brown lead was chromium (9,15). "[T]hese foreigners," he said, "do not deign to read even our most celebrated periodicals."

Del Río's annoyance at the lack of recognition for his priority in the conclusion that the brown lead contained chromium festered into bitterness as time went on. In 1817 he addressed a letter to Humboldt that was published in 1819 (19), in which he protested against Humboldt's turning over to Collet-Descotils for analysis not only the brown lead, but a number of other mineral specimens as well, all of which Del Río had already analyzed to his own satisfaction, and whose results he had published. Referring to the brown lead, he said (19):

> [You] saw fit to give it to your friend doubtless for the reason that we Spaniards should not make any discovery, no matter how small, either in chemistry or mineralogy, these being a foreign monopoly.

After reviewing in detail the history of his and Collet-Descotils' analyses, and emphasizing his priority, he asked (19):

> [D]id I lose all credit for it for not having known in 1802 all the properties of chromium in a country so lacking in books, where for the same reason the sciences are so little cultivated?

In a final slightly conciliatory note, he added:

> I believe that in compensation for your injuries to me, you have showered me with praise in your *Political Essay*, most of it excessive, and some of it qualified... Speaking frankly, I would have appreciated less praise and more accuracy.

Swedish chemist Nils Gabriel Sefström in 1831 found a new element in a sample of cast iron prepared from an ore mined at Taberg, Småland, Sweden. He gave the element the name *vanadium*, after Vanadis, one of the names of Freya, the Norse goddess of love and beauty. Friedrich Wöhler simultaneously was reinvestigating the composition of the brown lead of Zimapán, working with a sample that Humboldt had given him. Sefström gave some vanadium pentoxide to J. J. Berzelius, who demonstrated that the new element was not uranium. Berzelius sent some of the vanadium pentoxide to Wöhler, who conclusively showed that vanadium was identical to Del Río's erythronium, not to chromium. In a communication to *Poggendorffs Annalen* Berzelius described these developments (20):

> This metal, recently discovered by Professor Sefström...has also been found in a mineral of Zimapán, in Mexico...Del Río had already analyzed this mineral in the year 1801, and had at first claimed to have discovered in it a new metal, called by him "erythronium"; but later the chemist Collet-Descotils analyzed the same mineral, affirming that the supposed metal was not new but only chromium. Del Río became convinced that he had believed in something that was an error...until Sefström had the luck to discover it again in a surprising fashion. The recognition that the mineral of Zimapán is a vanadate and not a chromate was made by Professor Dr. Fr. Wöhler in Berlin.

Wöhler, who was on the track of the same metal, was disappointed, first by Sefström's prior announcement of the new element, and because (21):

> ..[e]ven if I had charmed her out of the lead mineral, I would have had only half the honor of discovery, because of the earlier results of Del Río on erythronium.

Although Wöhler recognized Del Río's earlier work, he supported Sefström's priority in the discovery, "because he succeeded by an entirely different method (21)."

Humboldt described the discovery of vanadium, giving equal credit to Sefström, Wöhler, and Del Río, at the session of the French Academy of Science on February 28, 1831 (20). He also sent a copy of Berzelius' report to Del Río. Del Río remained unmollified. In the second edition of the *Elementos de Orictognosía*, published in 1832, he wrote (22):

> When [Humboldt] left Mexico, I gave him...a copy in French of my experiments in order that he might publish them. If he had judged them worthy of public attention...*the discovery of a new metal would not have been delayed for thirty years*, which is the objection now unjustly made against me.

The brown lead of Zimapán now bears the mineralogical name *vanadinite*. Chemically it is lead chlorovanadate, $Pb_5Cl(VO_4)_3$. Vanadinite is found not only in Mexico, but also in South Africa, where it is mined commercially as a source of vanadium.

Vanadinite

Two Personalities: Analysis and Conclusions

After his return to Europe, Humboldt lived first in Paris, and then, after his expedition to Russia and Siberia in 1829, in his native Berlin, punctuated by frequent trips to Paris. He died in Berlin in 1859. Del Río remained in Mexico after that country became independent in 1821, unlike his Spanish-born colleagues at the College of Mines, who returned to Spain. He had married a Mexican woman and adopted Mexico as his home. Except for a sojourn in the United States in 1829-1833, Del Río remained in Mexico for the rest of his life, teaching at the College of Mines and ultimately becoming its director. He died in Mexico City in 1849.

Andrés del Río and Alexander von Humboldt lived in an era of rapid change in the style in which science advanced. Humboldt was a polymath, one of the last of the scientific amateurs who supported their investigations either with inherited wealth or by employment in one of the traditional professions. By the time of his death, Humboldt was probably the last such scientist on the European continent, although a few, notably Charles Darwin, remained in England. Del Río, on the other hand, was one of the new, more specialized breed of scientists who made their living as professors of their sciences in academic institutions. The French scientists with whom Humboldt associated upon his return to Europe in 1804 were already mostly of this new kind. This trend, beginning in the technical schools like those of Freiberg and Schemnitz, and amplified by the École Polytechnique in Paris, spread with the introduction of science departments or institutes into the traditional universities in the first half of the nineteenth century (5, 23). Although Humboldt had a general knowledge of chemistry and kept himself up-to-date on the latest advances, his knowledge was not sufficiently specialized for him to critique the analyses of Del Río or of Collet-Descotils.

The education and personalities of Humboldt and Del Río may also be contrasted. Humboldt, educated in the broad outlook of the eighteenth-century Enlightenment, retained the social and political views of a man of the Enlightenment throughout his life. On the other hand, Del Río moved from a purely classical education in languages and literature, mathematics and philosophy, to the narrow specialization of the mining academies. Whatever social and political views he may have had he kept to himself, which, realistically, may have been the safest thing to do in colonial Mexico. We know him mostly through his works in mineralogy and chemistry.

Del Río and Humboldt differed in their ability to accept new theoretical developments in the sciences. Humboldt was quick to accept the "new chemistry" of Lavoisier and Fourcroy, seeing the advantages of the oxygen theory of combustion and the binomial nomenclature. Del Río, more conservative, gave up the older nomenclature and the phlogiston theory only after his chemist colleagues, Fausto Delhuyar and Luis Lindner, had adopted their Spanish translation of Lavoisier's *Traité Élémentaire de Chimie* as the chemistry text for use at the College of Mines (24). Humboldt's study of volcanoes in South America and Mexico led him to abandon Werner's Neptunian hypothesis of geology; but Del Río clung to it despite the evidence around him in Mexico.

Both men were diligent workers with a capacity for long, detailed and enthusiastic activity. Humboldt was a compulsive collector of data and specimens and a prolific writer. Humboldt was also a brilliant speaker, a very social person, whose company was enjoyed by most of the leading intellectuals of the Americas and of Europe (25) and who had a talent for being accepted into their society in each country he visited. Much less is known about Del Río's personality, since there are no contemporary accounts; and Ramírez' biography of Del Río (1) is more laudatory than objective. We know that Del Río was an effective teacher, dedicated to the College of Mines and to its students. He was probably less out-going than Humboldt. He did have an Iberian sensitivity to a perceived slight, as shown by his responses to Collet-Descotils' analyses; but he was likely right in his accusation of prejudice on the part of the European scientific establishment.

There is no evidence that Del Río ever forgave Humboldt, or was willing to accept the name that another gave to the element he had originally discovered. Humboldt was occasionally sharp in expressing his opinion of persons whose intellectual abilities did not, in his opinion, match their pretensions; but Del Río was not one of those persons. He was always friendly toward Del Río and kind in his responses to him; and if he took offense at Del Río's complaints, he kept it to himself. Indeed, Humboldt may never have been fully convinced of Collet-Descotils' conclusion that the element in the brown lead was chromium. If he had been, why would he have given a sample of the brown lead to Wöhler to re-analyze? Wöhler could have learned of Del Río's erythronium only from Humboldt, who may even have shown him Del Río's unpublished paper.

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4. Selmec in Hungarian. Now Banská _tiavnica in Slovakia.
5. F. Szabadváry, "Die Gründung der Bergakademie Selmec (Schemnitz) und ihre bahnbrechende Bedeutung für den chemischen Unterricht in der Welt," *Periodica Polytech., Chem. Eng.*, **1963**, *7*, 127-133.
6. Some sources state that he was disguised as a woman. In Ramírez's words, "...y con el disfraz de aguador salió de ese país...," the word for "water-carrier," *aguador*, is in the masculine form. (Ref. 1, p 14)
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25. For example, the poet Johann Wolfgang von Goethe was a life-long friend of Humboldt, and greatly admired his intellect. On the other hand, Goethe’s neighbor in Weimar, the poet Friedrich von Schiller, said about Humboldt that “There is a little too much vanity in all his doings...I experience through him, with all due respect for the wealth of his subject matter, a poverty of meaning...” (Ref. 3, p 74).

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