Rediscovery of the Elements

Platinum Group: Ruthenium

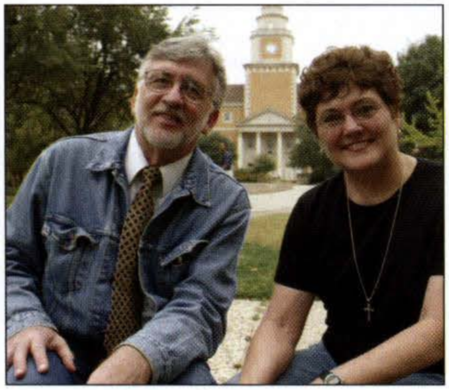

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Figure 1. "Rediscovery" sites in Russia and environs. The first Russian platinum strikes in the 1820s were in the Nizhniy Tagil area on the east slope of the Urals. Platinum was used in coins minted in St. Petersburg 1828–1844, and the platinum residues were important in the discovery of ruthenium, discovered in Kazan by Klaus in 1844. Earlier work on Russian platinum in a search for additional elements was done in 1828 by Osann in Dorpat (now Tartu), Estonia, and in 1808 by Sniadecki in Vilnius, Lithuania. Other sites for reference are included: Beresov was the source of crocoite (lead chromate) for Vauquelin's discovery of chromium; Tobolsk was the birthplace of Mendeleev; Dubna is the site of Russia's super heavy nuclei research, for which dubnium was named.

In an earlier issue of *The HEXAGON*, we witnessed the discovery in South America of platinum and in London of four of its associated elements—palladium, rhodium, osmium, and iridium. In the present issue, we shall learn of the discovery of the rich deposits of platinum in Russia and the history of ruthenium, the last of the platinum-group elements. (Figure 1).

The discovery of Russian platinum. At the end of the 16th century, the Russian Empire began its expansion eastward. The Cossack explorer Ermak (pronounced Yermak) Timofeyevich (?-1585) is familiar to Russians in heroic ballads of the Siberian chronicles as the leader who marked the beginning of colonization beyond the Urals.[1b] (Figure 1) In 1580, he crossed the Urals and rafted down the Barancha River to the Tagil River (the site of the future Russian platinum discoveries, Figure 2), and eventually went as far as the Ob and Irtysh rivers deep in Siberia.[1b] The Pacific Ocean was finally reached during the reign of Alexei Mikhailovich Romanov (1629–1676), the father of Peter the Great (1672–1725), the founder of St. Petersburg.[1a] This eastward expansion of hunters and settlers was in many ways analogous to the American westward migration during the 1700s and 1800s.

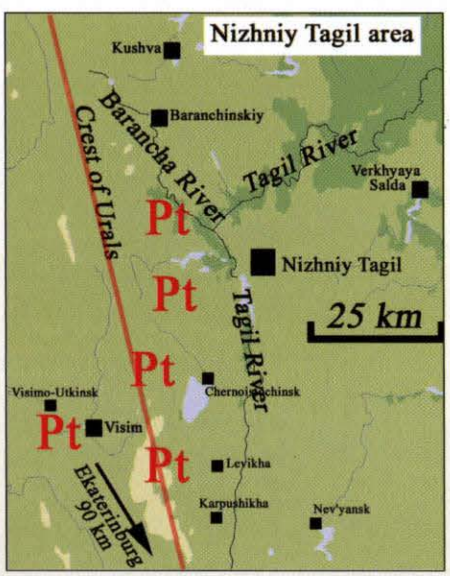

Figure 2. Urals north of Ekaterinburg. Platinum grains were originally discovered in placers washed from the Urals eastward toward Nizhniy Tagil. Today, the area about Visim affords the richest platinum mining.

The Urals were a vast source of mineral riches, ready to be exploited. This chain of mountains was created 250–300 million years ago when the supercontinent islands Siberia and Baltica collided, creating geological hydrothermal processes for mineral separation and concentration.[2] A particularly bountiful area was just west of Nizhniy Tagil (Figure 2), 125 kilometers north of Ekaterinburg. Iron, copper, and gold mining rapidly developed in Nizhniy Tagil in the 17th century. The famous malachite (basic copper carbonate) used in the Hermitage and the Peter and Paul Fortress in St. Petersburg was procured here[1c]; steel and copper production was developed; and later, Stalin would choose this area for maximum production of steel and the manufacture of tanks for WWII.[1d]

In the early 1800s, rumors began to circulate that platinum—previously known only from the New World—could be found in the Nizhniy Tagil area.[3] The first documented Russian platinum was in the form of placer grains in 1819, washed down from the Urals; five years later, the first commissioned platinum mine was established on the banks of the Barancha River,[4] northwest of Nizhniy Tagil (Figure 3). By 1840, dozens of platinum mines had been developed about Nizhniy Tagil, and later, additional discoveries were made north and south along the Urals.[3]

Soon there was a glut of platinum in Russia. Count Frantsevich Krankin (1775–1845) of the St. Petersburg Mint (Figure 4) proposed to use this metal in coinage,[5] and during 1828–1844, 1.4 million coins were struck from 485,000 ounces of platinum.[5] To mint these coins, the powder metallurgy (pioneered by Chabaneau and used by Wollaston to produce laboratory equipment)[6c] was independently developed by Peter Grigorievich Sobolevsky (1781–1841) in St. Petersburg.[7]

Figure 3. Reka Barancha (Barancha River), a tributary flowing into the Tagil River at Nizhniy Tagil, must have looked much like this when Ermak Timofeyevich, the first explorer beyond the Urals, rafted down this stream during the beginning of his exploration of the trans-Urals in 1580. Two and a half centuries later, platinum was discovered in this region. Notice the alluvial deposits in the foreground, which were the source of the original discovery of platinum in the early 1820s in the Nizhniy Tagil region. The view is south, with the city of Baranchinsky just behind the viewer (N 58° 09.27 E 59° 43.04). Courtesy, Konstantin Lopachak.

Initial analyses of Russian platinum. Gottfried Wilhelm Osann (1796–1866) of the University of Dorpat (now Tartu, Figure 5), who had studied with Döbereiner[6c] and received his degree in 1821 from the University of Jena,[8] became acquainted with the peculiar properties of platinum to catalyze and ignite a stream of hydrogen, and he sought a quantity of the platinum wastes to search for additional elements which might have unusual properties and uses.[8] Krankin, who was sending samples of platinum ore to prominent scientists for further study, gave Osann four pounds.[8]

In his sample, Osann observed, in 1827, the metals previously discovered by Wollaston and Tennant[6c]—palladium, rhodium, iridium, and osmium, in small quantities, just as in South American material.[9a] His analysis was typical for crude platinum, showing 1% or less for each of these minor constituents, as well as the normally alloyed iron (5–10%) and small amounts of copper and other metallic elements.[9a] Osann continued with a confusing series of publications in which he claimed four new elements. First, in 1828, he reported "reddish needles,"[9b] which he called "ruthenium." Later the same year, not being able to repeat this preparation, he transferred the name "ruthenium" to a crystal with "a golden luster."[9c] He simultaneously claimed two new elements as well, which he named pluranium ("long crystals") and polinium ("gray metal"). His hopes for the discovery of a new element were dashed by his inability to reproduce his results, by Berzelius' negative reports of samples Osann had sent to him, and by the frustratingly minute amounts of material that he was able to prepare. Of his pluranium, polinium, and "first ruthenium," two were observed only once and, in any case, only a few milligrams could be prepared, and then, with only incomplete descriptions. Osann agreed with Berzelius that his "second ruthenium" was a mixture of zirconium, iron, silicon, and titanium oxides,[9d] and that, perhaps, polinium was impure iridium. More modern assessments of Osann's claims by scholars in platinum chemistry conclude that polinium was impure iridium with perhaps some ruthenium, pluranium was an unknown mixture with possibly some ruthenium, and that the "first ruthenium" (reddish crystals) may have been an impure mixture of osmium and ruthenium tetroxides.[3]

The discovery of ruthenium. Karl Karlovich Klaus (1796–1864), a native of Dorpat and a student of its famed university, was originally trained as a pharmacist, and in 1826, he moved to Kazan to open up his own pharmacy there. (Klaus is sometimes known by his German name Carl Ernst Claus; "Karlovich" is the Russian patronym).[10] Throughout his life, he frequently visited the steppes of Russia and made extensive studies of the flora around the Volga. During some of his travels, he became acquainted with the Ural placer deposits and became interested in platinum chemistry. In 1831 he sold his pharmacy and returned to Dorpat to study chemistry; in 1837 he won his Master's degree. While at Dorpat, he become acquainted with Osann's research and the question of further platinum elements. He took an appointment in the pharmacy department at the University of Kazan, but soon was given responsibilities in the chemistry department and soon was moving up the ranks in that department (Figures 6 and 7).

At the University of Kazan, Klaus began research on the platinum problem, along with his favorite pastime of traveling about the Siberian steppes and preparing painted illustra-

Figure 4. This is the St. Petersburg Mint, next to the St. Peter and Paul Cathedral on the fortress island which Peter the Great built as a precaution against Swedish attack shortly after he founded St. Petersburg in 1703. In the St.Peter and Paul Cathedral, all of the Russian czars and families are buried, including the remains of the assassinated (1918) family of the last Czar Nicholas II, which were excavated after 1998 from a field near Ekaterinburg. The Mint was founded in 1724; the present building itself was built 1798–1806. The residues from the platinum coinage 1828–1844 were stored here, which were eventually used by Klaus in his platinum-group research. The inscription at the top is "Monetniy Gvor" = "Money Yard." The location is N 59° 57.00 E 30° 18.87.

tions of plants of the region. Klaus consulted directly with Krankin of the St. Petersburg Mint, which, by then, had accumulated a large waste pile of platinum residues, and he was blessed to receive the sumptuous quantity of 18 pounds of processed ore from which the platinum had already been extracted.[10]

The methodical and careful Klaus was able to isolate a new element with a complete characterization.[11] Klaus' procedure for preparing ruthenium was straightforward:[10] First repeat Wollaston/Tennant's procedure of dissolving crude platinum in aqua regia to remove the rhodium, palladium, residual platinum, iron, and other metallic ions; take the remaining black residue (which Tennant had recognized held osmium and iridium) and heat with potash and saltpeter to redness for an hour to produce the oxides of Os, Ir, and Ru. Add aqueous acid to the cooled melt and heat to distill off the osmium tetroxide (OsO_4) (Klaus realized the oxide of ruthenium was volatile, but that, in acid, it reverts to the nonvolatile ruthenium chloride). Then add potassium chloride, and then ammonium chloride to precipitate the ammonium chlororuthenate, $(NH_4)_2RuCl_6$. Upon ignition, the metallic ruthenium is returned. Klaus was able to prepare the prodigious amount of 6 grams of metallic ruthenium in such a manner:[10] "I named the new body, in honour of my Motherland, ruthenium. I had every right to call it by this name because Mr. Osann relinquished his ruthenium and the word does not yet exist in chemistry."[10b] (Figures 8 and 9).

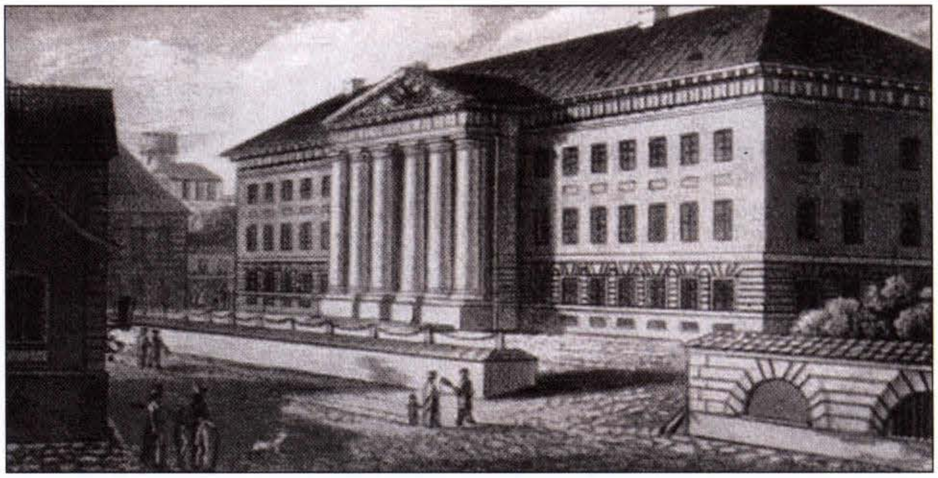

Figure 5. The main university building of Dorpat in 1827-1828, contemporaneous with Osann who researched crude platinum residues in an unsuccessful attempt to discover the sixth platinum-group element. Osann's laboratory was in the right wing. The university was founded in 1632 by Gustavus Adolphus II as the second university in the Swedish empire (after Uppsala). Today, the name of the university and the city is Tartu, in the modern country of Estonia. The building looks the same today, located at Ülikooli 18 (N 58° 22.87 E 26° 43.21).

Figure 6. This is the appearance of the main university building of the University of Kazan on Voskresenskaya (today's Kremlevskaya), about the time of Klaus. The university building dates from 1822. The building in which Klaus worked (presently Butlerov Institute) was located behind this main building. The view is westward.

Osann immediately claimed prior discovery,[12] asserting his polinium was, in fact, ruthenium.[9e] Klaus calmly refuted the argument, showing that, at best, polinium was a crude mixture of iridium and ruthenium. James Lewis Howe, the leading authority of platinum chemistry in the U.S. and an expert in ruthenium chemistry,[13] assessed the situation thusly: "Claus announces the discovery of a new metal, which he calls ruthenium, for the purpose of honoring Osann, whose ruthenium had failed to prove itself an element.... Osann hardly appreciated the compliment, for he attacked Claus with considerable asperity, accusing him of claiming to discover what Osann himself had discovered. To an impartial critic, Osann wholly fails to make out his case."[3]

Figure 7. This is the main university building today (Ul. Kremlevskaya 18, N 55° 47.45 E 49° 07.31). The Russian name of the university is "Kazanskiy Gosudarstvennyi Universitet"—abbreviated at the top as KGU. To the right (out of view) is a statue of young Vladimir Ilyich Ulyanov (1870–1924)—better known as Lenin— who was a student at Kazan for three months in 1887 (he was expelled for his political activities).

The frustrated Osann had simply been cursed with having to work with such a meager amount of material, and he was unaware of the problem of the "... close analogy of the platinum metals [which]. . . . give rise to many difficulties,"[14] which led to cumbersome multi-step analytical schemes—plus the occasional problem of a redox reaction with the solvent itself (such as alcohol).[14] Klaus' success resulted not only because of the the large quantity of material he had been given, but also because of his recognition of the mutual interferences of the chemically similar platinum metals which might prevent quantitative separations, and he was able to work out simple, efficient separation schemes for their various combinations.[10b]

Klaus wrote a 200-page treatise on platinum chemistry published in Kazan.[15] Previous to

Figure 8. The Buterlov Chemical Institute at Kazan State University (100 meters south of the main university building), where Klaus discovered ruthenium, presently holds a chemical museum (N 55° 47.40 E 49° 07.31). Aleksandr Mikhailovich Butlerov (1828–1886) was professor at Kazan 1857, then at the University of St. Petersburg 1868. Butlerov was a pioneer in the study of the structure of organic molecules, such as using double bonds in structural formulas. He also discovered formaldehyde. Kazan was also known for Nikolai Ivanovich Lobachevsky (1792–1856), famous for his development of non-Euclidean geometry, or hyperbolic geometry, which is today used in such fields as Einstein's relativity, and Vladimir Vasilevich Markovnikov, who formulated his eponymous rule for organic chemistry in 1870. Courtesy, Renat Zagretdinov

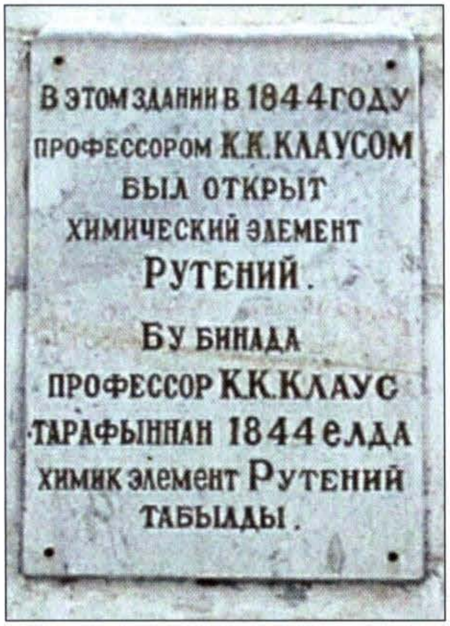

Figure 9. Plaque on the Butlerov Institute in two languages — Russian (top) and Tatar (bottom). It reads: "In this building in 1844 Professor K. K. Klaus discovered the chemical element ruthenium." Tatar is a Turkish language and is the official language of Tatarstan, of which Kazan is the capital. The Tatar language was for centuries written in Arabic, but in 1920, the alphabet was changed to a Latin base, and then, in 1939, to the Cyrillic alphabet. Also on the building are plaques honoring Butlerov, Markownikoff, Zinin, Arbuzov, and Boris. Courtesy, Alexander Bednekoff.

Klaus, perceived chemical relationships among the platinum group elements included the natural pairings of platinum with gold and palladium with silver.[3] Klaus accumulated a vast body of knowledge that allowed him instead to discern two corresponding natural series of triades—Ru-Rh-Pd and Os-Ir-Pt, with chemically similar pairs Ru-Os, Rh-Ir, and Pd-Pt. These triades presaged the Periodic Table by two decades. Klaus also introduced the concept of structure of double salts (e.g., K_2PtCl_6), which was developed and refined by Alfred Werner almost 40 years later into his coordination chemistry.[10b]

Berzelius was sent samples of ruthenium (Figure 10) and gave the new element his official sanction.[16] Klaus continued to work on ruthenium and published his 20-year work on the platinum group in celebration of the 50-year Jubilee at Kazan University.[17] For a century, this served as the standard textbook for the platinum metals.[10b]

In 1852, Klaus had moved back to his beloved Dorpat to assume the Chair of Pharmacy at his Alma Mater. By now, he was a celebrity as he visited Berlin, Paris, London, and Switzerland. In February, 1864, after giving a lecture to a group of Russian pharmacists at St. Petersburg, he caught a winter chill; when he returned to Dorpat, he died of pneumonia a month later.

Figure 10. Chemical samples in the chemical museum of the Butlerov Institute, including original ruthenium samples of Klaus.

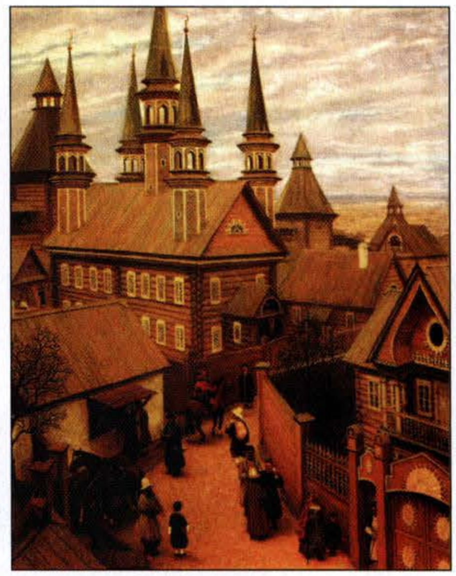

Figure 11. Kazan is the capital of Tartarstan (Qazan in Tartar). Kazan was founded by either the Volga Bulgars or the Taters (Tarters) of the Golden Horde. In the mid-15th century, Kazan became an important city in trading routes. In 1552, the city was conquered by Ivan the Terrible. A revival of the Tatar culture has occurred in the 20th century, with public signs written in both Russian and Tatar. This painting, by modern artist Ravil Zagidullin, appears in the National Kazan Cultural Center (Nationalniy Kazanskiy Kulturniy Tsentr; Ul. Ol'kenitskogo and Ul. Pushkina, N 55° 48.09 E 49° 7.56).

James Lewis Howe, in 1900, in ultimate tribute, summarized Klaus' contributions thusly: ". . . there appears at the University of Kazan, almost on the far eastern frontier of Russia (Figure 11), a chemist, Claus, who is destined to make greater contributions to the chemistry of platinum metals, not only those who had preceded him, but than any one of those who have lived in the nearly forty years since his death."[3]

Acknowledgments.

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