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 Ural mountains. In 1580, he crossed the Ural mountains 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 Irtish rivers deep in Siberia. 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. This eastward expansion of hunters and settlers was in many ways analogous to the American westward migration during the 1700s and 1800s.

The Ural mountains were a vast source of mineral richness, ready to be exploited. This chain of mountains was created 250–300 million years ago when the supercontinent Siberia and Baltica collided, creating geological hydrothermal processes for mineral separation and concentration. 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; 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.

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. 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, northwest of Nizhniy Tagil (Figure 3). By 1840, dozens of platinum mines had been developed about Nizhniy Tagil, and later, addi-
tional discoveries were made north and south along the Ural's. Soon there was a glut of platinum in Russia. Count Frantsevich Krankin (1775–1845) of the St. Petersburig Mint (Figure 4) proposed to use this metal in coinage, and during 1828–1844, 1.4 million coins were struck from 485,000 ounces of platinum. To mint these coins, the powder metallurgy (pioneered by Chabaneau and used by Wollaston to produce laboratory equipment) was independently developed by Peter Grigorievich Sobolevsky (1781–1841) in St. Petersburg.  

Initial analyses of Russian platinum. Gottfried Wilhelm Osann (1796–1866) of the University of Dorpat (now Tartu, Figure 5), who had studied with Döbereiner and received his degree in 1821 from the University of Jena, 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. Krankin, who was sending samples of platinum ore to prominent scientists for further study, gave Osann four pounds. In his sample, Osann observed, in 1827, the metals previously discovered by Wollaston and Tennant—palladium, rhodium, iridium, and osmium, in small quantities, just as in South American material. 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. Osann continued with a confusing series of publications in which he claimed four new elements. First, in 1828, he reported “reddish needles,” 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.” 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, 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.  

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. 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 became 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-
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: 12 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 (OsO₄) (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, (NH₄)₂RuCl₆. 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: 13 "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." 14a (Figures 8 and 9).

Osann immediately claimed prior discovery, 15 asserting his polinium was, in fact, ruthenium. 16 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, 17 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." 18

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," 19 which led to cumbersome multi-step analytical schemes—plus the occasional problem of a redox reaction with the solvent itself (such as alcohol). 20 Klaus' success resulted not only because of 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. 21

Klaus wrote a 200-page treatise on platinum chemistry published in Kazan. 22 Previous to
Klaus, perceived chemical relationships among the platinum group elements included the natural pairings of platinum with gold and palladium with silver. Klaus accumulated a vast body of knowledge that allowed him instead to discern two corresponding natural series of triads—Ru-Rh-Pd and Os-Ir-Pt, with chemically similar pairs Ru-Os, Rh-Ir, and Pd-Pt. These triads presaged the Periodic Table by two decades. Klaus also introduced the concept of structure of double salts (e.g., K₂PtCl₆), which was developed and refined by Alfred Werner almost 40 years later into his coordination chemistry.¹⁰

Bekelius was sent samples of ruthenium (Figure 10) and gave the new element his official sanction.¹¹ 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.¹² For a century, this served as the standard textbook for the platinum metals.¹³

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.

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, Klaus, 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.

For information and photographs pertaining to Klaus and Kazan, the authors are indebted to Dr. Renat Zagretdinov, Professor of Astronomy, Kazan State University; and to Dr. Alexander Bednekoff, Professor Emeritus of Pittsburgh State University, Pittsburgh, Kansas, who is fluent in Russian and who visited his parents' homeland in Kazan and Ekaterinburg. For much valuable information used in the writing of this report, gratitude is extended to Dr. William P. Griffith, Imperial College, London, scholar of platinum chemistry and chemical history, who furnished many archival Russian documents.

(continued on page 31)
Rediscovery of the Elements

(continued from page 23)

References.

1. A. M. Prokhorov, ed. Great Soviet Encyclopedia, 3rd ed. Eng. trans., 1973, Macmillan, (a) 1, 415; (b) 9, 130; (c) 15, 352; (d) 17, 580–581.
3. J. L. Howe, Science, 1900, 11(287) [June 29], 1012–1021.
7. B. N. Menschutkin, J. Chem. Ed., 1934, 11(4), 226–229. The site where Sobelevsky analyzed platinum and developed the procedures for producing malleable platinum was actually the Saint Petersburg Mining Institute (address: Leitenanta Schmidt’s Nab. at intersection of Lin. 21; coordinates: N 59° 55.75 E 30° 16.15), on Vasily Island, about 2 km southwest of the Mendeleev Museum (at St. Petersburg University). The Mining Institute still exists and presently houses a splendid mineralogical museum.
9. G. W. Osann, [Poggendorf’s] Ann. Phys. Chem., (a) 1827, 11, 311–322; (b) 1828, 13, 283–297; (c) 1828, 14, 329–357; (d) 1829, 15, 158; (e) 1845, 64, 197–208.
10. (a) D. McDonald, Platinum Metals Rev., 1964, 8(2), 67–69; (b) V. N. Pitchkov, op. cit., 1996, 40(4), 181–188.