

# Bicentenary of Four Platinum Group Metals

## PART I: RHODIUM AND PALLADIUM – EVENTS SURROUNDING THEIR DISCOVERIES

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*The years 2002 to 2004 mark the bicentenaries of the discoveries of rhodium, palladium, iridium and osmium. Two remarkable people were responsible for their discoveries – William Hyde Wollaston (1766–1828) the discoverer of rhodium and palladium, and his friend Smithson Tennant (1761–1815) the discoverer of iridium and osmium. This and a subsequent paper will seek to retell the stories of their discoveries, and to indicate the growing usefulness of the metals throughout the nineteenth century to their importance today. In this first part we will discuss Wollaston and his discoveries. Part II, to be published in a later issue, will complete the story with Tennant's discoveries of the more intractable elements iridium and osmium.*

In 1789, Lavoisier defined the element as:

*du dernier terme auquel parvient l'analyse*

(the last point that analysis can reach). He listed thirty-three 'simple substances', of which we would now recognise twenty-three as elements. Ten of these had been known since antiquity and seventeen more were discovered before 1789, but the golden age of discovery and isolation of the elements followed after Lavoisier's definition. Fourteen years later, the first four of what we now know as the six platinum group metals (pgms) were discovered in England: rhodium and palladium by Wollaston, and iridium and osmium by his close friend and collaborator, Smithson Tennant. By the end of the nineteenth century, forty-seven more elements were known (the remaining elements and some synthetic elements (1) were discovered in the twentieth century). While platinum had been known about in the fifteenth century and perhaps even earlier (2), the last of the six pgms, ruthenium, was not discovered until 1844 by Karl Karlovich Klaus (1796–1864) (3).

### Platinum Group Metal Chronology

It is something of a simplification to claim the years 2003 and 2004 as the bicentenaries of the discoveries of palladium and rhodium, respectively. There is evidence from Wollaston's notebooks that he had discovered palladium (which he first called Ceresium) as early as 1802 (2, 4). He first

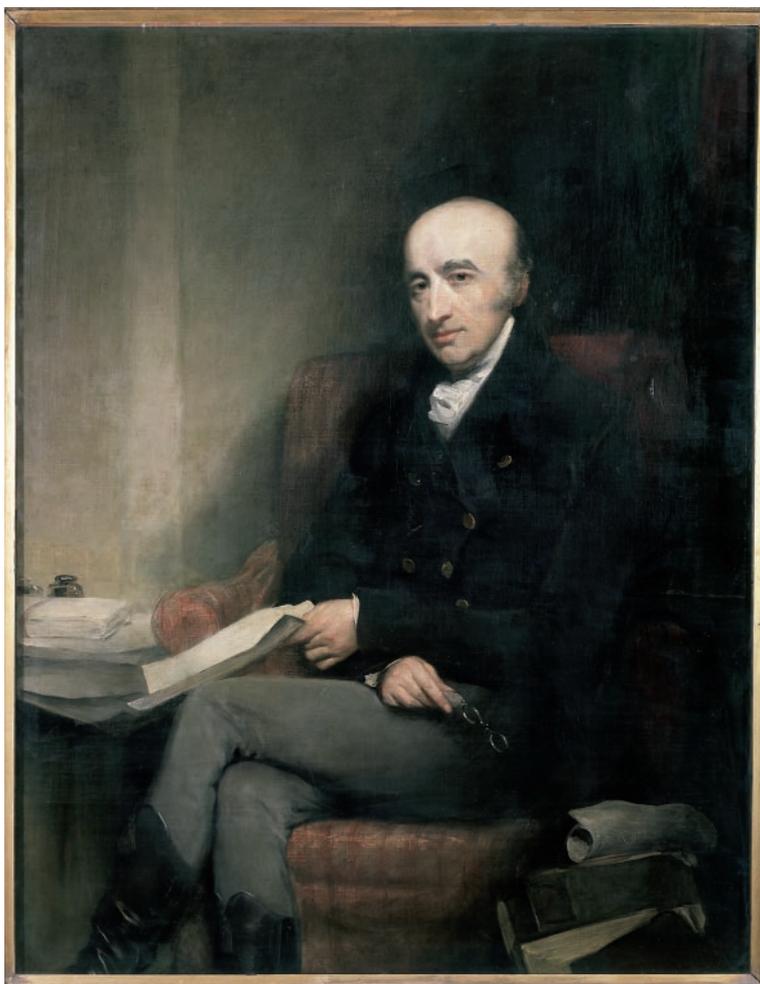
described it in an anonymous handbill in April 1803. Later that year Wollaston, still anonymously, published the information in *Nicholson's Journal* (5). In November 1803 he confided its discovery to his friend, Sir Joseph Banks, the President of the Royal Society (6, 7). Eventually he commented on it in the *Philosophical Transactions of the Royal Society* in 1804 (8) and finally published it openly in 1805 (9), so the year 2003 is thus reasonable to claim for the bicentenary of its publication if not for its discovery.

In 1804, Wollaston published a paper on the discovery of rhodium (8), but it is likely that preliminary work had occurred in the previous year. By contrast, iridium and osmium pose few problems as Smithson Tennant announced their discovery in 1804 (10).

### William Hyde Wollaston FRS

In this Journal in 1966, the bicentenary of the birth of Wollaston was commemorated (11). However, although Wollaston was a remarkable man and an important figure in many branches of science, as yet no full-scale biography of him has been published. Curiously, the perhaps rather less eminent Smithson Tennant has fared better in this respect. This summary is drawn from a number of accounts of Wollaston's life (2, 4, 6, 11, 12, 13).

Wollaston was born in East Dereham, Norfolk, on 6th August 1766, and educated at Charterhouse School, London. He went to Caius College,



**William Hyde Wollaston  
FRS**

**1766–1828**

*Discoverer of palladium and rhodium, and the first to produce malleable platinum. Born in Norfolk, Wollaston lived most of his adult life in London. In 1793 he obtained a doctorate in medicine from Cambridge University. While practicing medicine, he became interested in metallurgy, chemistry, physics and crystallography which from 1800 onward occupied him fully. Wollaston also invented various optical instruments. He was the first to observe (but incomprehendingly) the dark lines in the solar spectrum....he demonstrated the identity of frictional and voltaic electricity...he made important contributions to the design of voltaic batteries (6). The scale and variety of his research made him one of the most influential scientists of his time*

*From a portrait by John Jackson, by courtesy of The Royal Society*

Cambridge in 1782, and at this time his very productive friendship with Smithson Tennant began, as did their joint experiments on platinum concentrates. In 1787 he was elected a Senior Fellow of Caius College and held this position until his death on 22nd December 1828. In 1789 he became a physician in Huntingdon, and two years later he set up a practice in London at 18 Cecil Street (now Ivy Bridge Lane), off the Strand. In 1793 he was awarded an M.D., and on 6th March 1794 he was elected a Fellow of The Royal Society. Those proposing him included Henry Cavendish and Sir William Herschel.

In 1797, Wollaston entered into a partnership with Smithson Tennant. Tennant had substantial private means, and they collaborated in the pro-

duction of malleable platinum, in the isolation of the four metals which concern us here, and in some organic chemistry. On Christmas Eve in 1800 they bought 5959 Troy ounces of alluvial platinum ore containing some 80 per cent of platinum, from Nueva Granada (now Colombia), South America, which had been smuggled into the country via Kingston, Jamaica, at the then considerable cost of £795. During their experiments on the preparation of malleable platinum Wollaston noted that preliminary treatment of the crude ore with *aqua regia* dissolved most of the material, but small quantities of a black, insoluble component remained. Wollaston investigated the soluble part, which he was later to show contained rhodium and palladium in addition to platinum, while Tennant

examined the insoluble portion, which contained iridium and osmium.

In 1800 Wollaston retired from medicine, perhaps because he failed to obtain a position at St. George's Hospital. In 1801 he bought a house at 14 Buckingham Street (now Greenwell Street) and set up a laboratory in his back garden. Within five years he had developed a process for rendering platinum metal malleable, and this is said to have ultimately made him a fortune of £30,000. Wollaston's process for producing malleable platinum has been well described (2), including the interesting finances of this venture (14–16).

In November 1802 he was awarded the Copley Medal, the highest honour of the Royal Society, and for a short period in 1820 he was President of the Royal Society, bridging the gap between the long-serving President, Sir Joseph Banks and Sir Humphry Davy.

In all, Wollaston published over 50 papers on various aspects of chemistry, optics, physiology, pathology, mineralogy, crystallography, electricity, astronomy, mechanics and botany. Prominent among his many innovations was invention of a camera lucida and the development of the concept of equivalent weights. In 1809 he invented a reflecting goniometer which permitted very accu-

rate measurements of the positions of crystal faces in minerals. This and his other contributions to mineralogy are commemorated, not only in the inosilicate minerals wollastonite  $\text{CaSiO}_3$  (named in his honour by F. Léman in 1818) and another form of it, pseudowollastonite, again formulated as  $\text{CaSiO}_3$ , but also in the Wollaston Medal, awarded annually by the Geological Society (Geological Society of London, see Appendix).

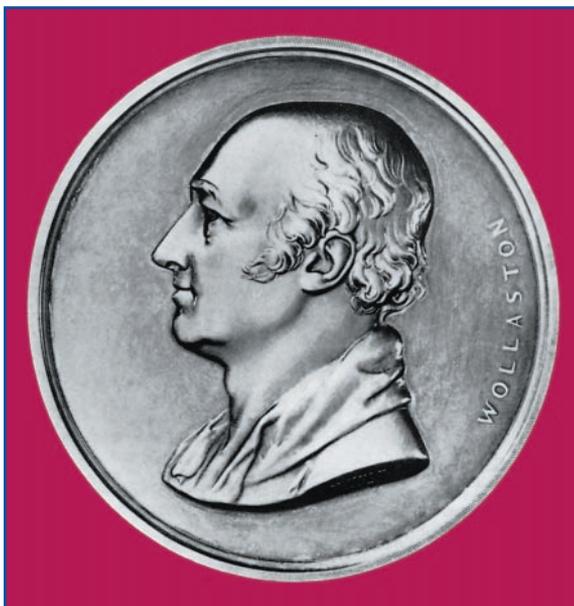
Sir Joseph Barrow provided, in his "Sketches of the Royal Society", a longer and more affectionate sketch of Wollaston than he did of the rather more remote figure Smithson Tennant, saying that he was one of the most remarkable men of his day (17). It was also said, admittedly some time after Wollaston's death, that:

*He led a solitary life, and was never married .... He was however a just and most honourable man, candid, open and free from envy with perfect straightforwardness; (his) relish for acquiring money with the generosity in parting with it when it could be generously bestowed; the clear intellect, the self-reliance, the aversion to interference on the part of strangers seem to merit Wollaston as, par excellence, the true English philosopher (13).*

It is perhaps a measure of him that after the bitter

*In 1831, the Geological Society of London, the world's oldest geological society, instituted the Wollaston Medal, its highest honour; and possibly the most prestigious award for any geologist to receive. It is awarded each year for outstanding achievement in geology. The first Wollaston Medal, made of gold, was awarded to William Smith, see Appendix. While made of gold for some years, the medal was made of palladium from 1846–1860 and again since 1930*

*Reproduced by courtesy of The Geological Society of London*



controversy with Richard Chenevix on the nature of palladium, recounted below, Wollaston seemed to retain no rancour, and entertained him several times in 1810 in the Royal Society Dining Club (4, 6).

## The Discovery of Rhodium

The first official announcement that Wollaston made of his discovery of rhodium was read to the Royal Society on 24th June 1804, and published in that year, when he described the discovery of:

*another metal, hitherto unknown, which may not be improperly distinguished by the name of Rhodium, from the rose-red colour of a dilute solution of the metal containing it (8).*

The metal was named after the Greek  $\rho\acute{o}\delta\omicron\nu$  (a rose), although in undated notebooks (4) he refers to it as “N-nov<sup>m</sup>” (perhaps Novum).

Platina (a concentrated form of platinum ore) was dissolved in *aqua regia* and most of the platinum removed (as  $(\text{NH}_4)_2[\text{PtCl}_6]$ ) by addition of  $\text{NH}_4\text{Cl}$ . Zinc was then added to the filtrate; this resulted in the precipitation of any residual platinum, some palladium, rhodium, copper and lead. The latter two were removed by dissolution in

dilute nitric acid, and the residue was then dissolved in more *aqua regia*;  $\text{NaCl}$  was added and the solution was evaporated to give the rose-red  $\text{Na}_3[\text{RhCl}_6] \cdot n\text{H}_2\text{O}$ . After extraction of this with hot alcohol, zinc was added to precipitate the rhodium metal (8).

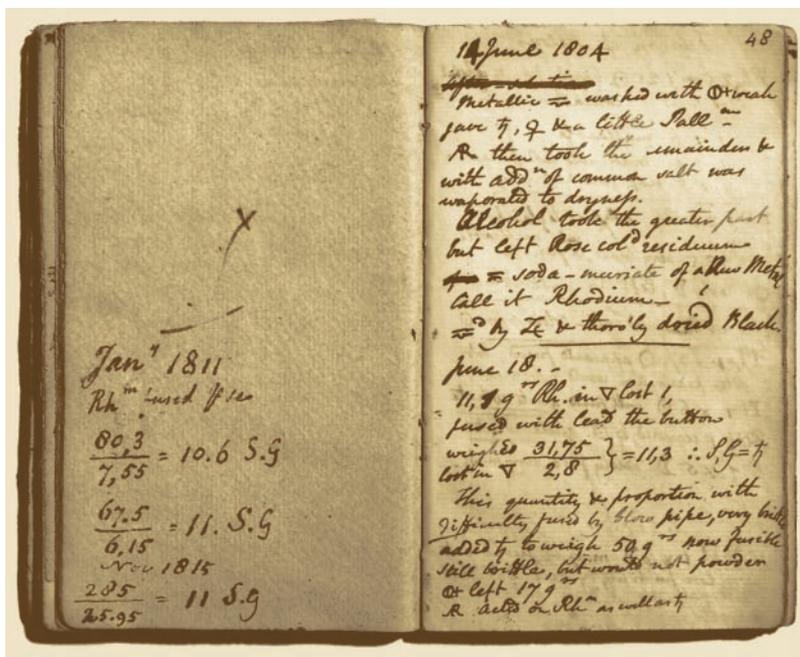
## The Discovery of Palladium

However, Wollaston’s prior discovery of palladium is a colourful story (2, 4, 7, 18, 19). Wollaston first mentions his discovery in his notebook for July 1802 calling the new element simply “C” (2, 4). In a later notebook he recalled that this probably stood for *Ceresium*, after the recently discovered asteroid Ceres. By August 1802 he had renamed it Palladium

*from a planet that had been discovered nearly at the same time by Dr. Olbers...*

and mentions this in his subsequent full paper on the element (9). This ‘planet’ would be Pallas, later shown to be an asteroid (2).

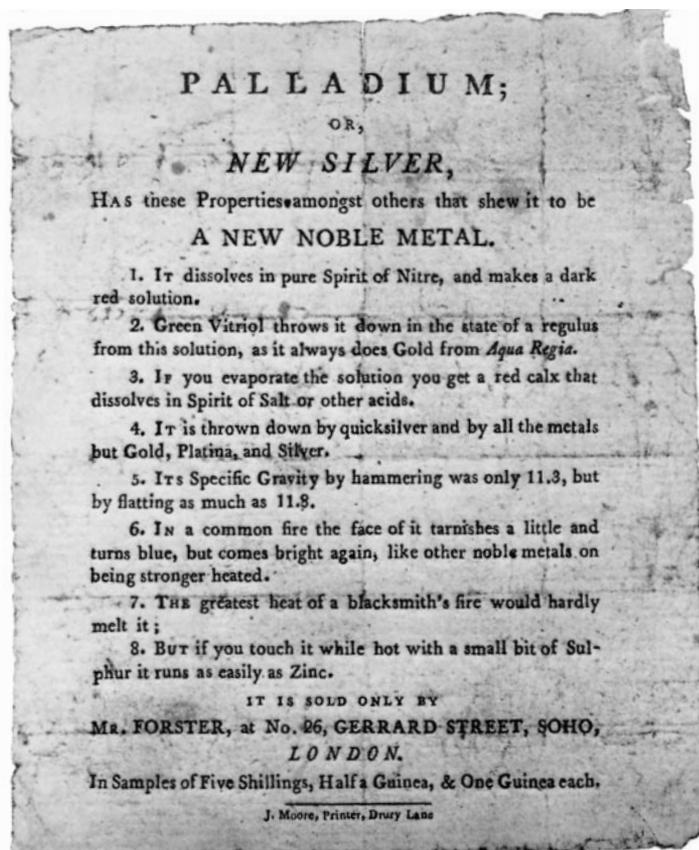
To establish the priority of his work – perhaps because he was aware that, in particular, the French chemists Collet-Descotils, Fourcroy and



One of Wollaston’s notebooks showing the page for 14 June 1804, on which he describes the new metal rhodium. Using common salt he evaporated to dryness the remainder of a metallic precipitate after it was washed. Following treatment with alcohol, a rose coloured residue remained. The metal he isolated from this he called Rhodium

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The handbill describing palladium which Wollaston published and distributed anonymously in April 1803. It offered for sale "Palladium; or, New Silver...a New Noble Metal". This handbill was later published in *Nicholson's Journal* by permission of the Syndics of Cambridge University Library



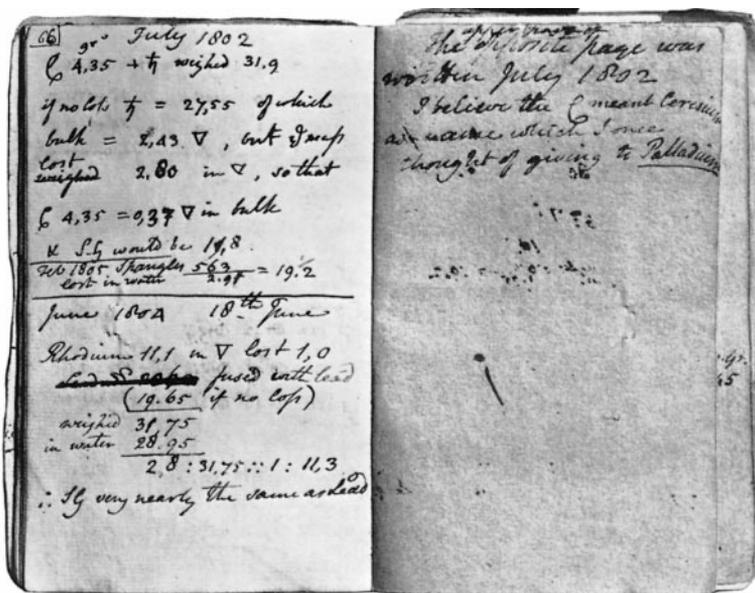
Vauquelin were pursuing research along similar lines – he adopted an unusual and, in the history of inorganic elemental discovery, unique stratagem. In April 1803 anonymous advertisements or handbills were distributed in London offering for sale at a shop in Gerrard Street, Soho, "Palladium, or, New Silver...a new Noble Metal". The handbill was later published in *Nicholson's Journal* (5).

Suspecting a fraud, the entire stock of the material was bought from the shop by an Irish chemist, Richard Chenevix (1774–1830), for some 15 guineas. He claimed that it was an alloy of platinum and mercury (20). A number of eminent chemists, including Vauquelin, Klaproth and Gehlen, investigated the material but did not agree that the "palladium" was an alloy. An anonymous letter was sent in December 1803, almost certainly by Wollaston, to the editor of *Nicholson's Journal* (21), offering a reward of £20 to anyone who could "make" palladium in public before three eminent chemists (Charles Hatchett, the discoverer of ni-

bium, was to be one of these). However, prior to this, in November 1803, Wollaston had privately confided his discovery of palladium to Sir Joseph Banks, apparently for fear that he would be blamed if Chenevix received the Copley Medal (6, 7).

The challenge to make palladium was not taken up, and in 1805 Wollaston provided an 'official' announcement of his discovery in a paper which he read to the Royal Society on 4th July 1805 (9), although he had made a number of references to palladium in his 1804 paper on rhodium (8). After the 1805 paper (9) it was generally accepted that palladium was indeed a true element.

In Wollaston's optimised procedure for the isolation of palladium he took the solution of platina in *aqua regia* and removed platinum, as described above. The filtrate from this was neutralised and then treated with mercuric cyanide,  $\text{Hg}(\text{CN})_2$ , to give a pale yellow-white precipitate of "prussiate of palladium",  $\text{Pd}(\text{CN})_2$ , which on ignition gave palladium metal (9).



The Wollaston notebook in which he records, probably for the first time, (left page) in July 1802, of palladium as “C”.

The right page states: “The upper part of opposite page was written July 1802. I believe the C meant Ceresium a name which I once thought of giving to Palladium”

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In his penultimate paper, read as the Bakerian Lecture to the Royal Society on 20th November 1828, just one month before his death, Wollaston described the method by which he rendered platinum malleable and, in a final section, he described his method of making malleable palladium. This involved heating  $\text{Pd}(\text{CN})_2$  with sulfur, followed by cupellation in an open crucible with nitre and borax; the residue was subjected to a low red heat whereupon a malleable ingot of palladium metal resulted (22).

Over the period 1803 to 1821 it has been calculated that Wollaston isolated some 255 Troy ounces of rhodium and 302 Troy ounces of palladium from 47,000 ounces of “ore of platina”. Analyses were recently carried out on samples of Wollaston’s palladium and rhodium held by the Science Museum in London. These were two samples from “Faraday’s Chemical Cabinet” labelled “Palladium from Dr. Woolaston” (*sic*) and four rhodium-containing samples labelled “Wollaston Relics, My Property, LFG”. The samples of palladium were 89.3 per cent pure (impurities included platinum, copper and rhodium), while the rhodium content in the last four varied from 67.4 to 99.3 per cent (impurities were platinum, palladium and iron) (7).

Although Wollaston gave the names rhodium and palladium (and these names have been used

ever since) he did not assign symbols to the elements. Berzelius originally suggested R for rhodium but later revised this to Rh; palladium first became Pl, then Pa and finally Pd (2). In his remarkable book “Exotic Mineralogy”, published in 1811, Sowerby illustrates three small specimens given to him by Wollaston of:

*Native Palladium, nearly pure.....(from) the Brazilian Platinum (23).*

From 1825 until his death in 1828 Wollaston lived at No. 1 Dorset Street, in London.

## Rhodium and Palladium in the Nineteenth Century

Wollaston recorded two industrial applications of rhodium and palladium. He used a palladium-gold alloy to make corrosion-resistant graduation plates for scientific instruments, including the mural circle at the Royal Observatory Greenwich erected by Troughton in 1812. Such alloys were also used in sextants. He also used a rhodium-tin alloy to achieve durable tips to pen nibs in the 1820s and these were sold for sixpence per tip (7). This market was later largely supplanted by the much harder osmiridium alloys (an osmium-iridium alloy). The Science Museum, London, keeps samples of Wollaston’s rhodium-tin alloy pen nibs.

During Wollaston's lifetime a "Mr. Johnson of 79 Hatton Garden" (the metallurgist Percival Norton Johnson (1792–1866), a founder of Johnson Matthey) supplied to a Sheffield steel firm material from which two rhodium-iridium-silver-steel razors were made. These were presented to Michael Faraday (6). Johnson later supplied the Geological Society with palladium for the Wollaston Medal (see Appendix). Johnson mentions the use of palladium alloys in chronometer bearings and in steels in 1837, and of 80% palladium-20% silver alloys in dentistry (24). The use of palladium in dental alloys continues to this day.

In 1866, Thomas Graham (1805–1869), who from 1837 to 1854 was Professor of Chemistry at University College, London, resigning this post to become Master of the Mint, noted that palladium could absorb up to six hundred times its own volume of hydrogen. At the Royal Mint he cast some medallions of hydrogen-containing palladium which he circulated to his friends. He considered hydrogen-containing palladium to be an alloy – which in a sense it is – and called it "palladium-hydrogenium" (2).

In 1908, Sir William Crookes (1832–1919) persuaded Johnson Matthey to 'fashion' crucibles of rhodium, iridium, ruthenium and osmium; Crookes does not record if they succeeded with the latter two metals, but he found rhodium to be almost as durable a material as iridium for this purpose (25).

In the late nineteenth century palladium salts (generally  $\text{Na}_2[\text{PdCl}_4]$ ) were used, often but not always in conjunction with  $\text{K}_2[\text{PtCl}_4]$ , for the production of palladium or palladium-platinum photographic prints. These have richer tones and more permanence than silver images. Such processes are still used occasionally (26).

The catalytic properties of the pgms were first noted in the nineteenth century. Humphry Davy first observed heterogeneous catalysis in 1817, with platinum, when he found that a mixture of coal gas and air over platinum wire caused the wire to glow. Later, Thénard showed that powdered rhodium, palladium and iridium catalysed the combination of hydrogen and oxygen (2).

In the twentieth century catalysis became an

important use of palladium and rhodium, and remains so today. Indeed, the industrial uses of all the pgms increased tremendously during the twentieth century, especially in the latter half and this continues today.

## Conclusions

Of the two elements palladium and rhodium, palladium in particular has a remarkable history and is surely the only element of the 114 we now know that was isolated and then, instead of its discovery being announced and published in a learned journal, was advertised for sale, causing the furore outlined above. Wollaston's motives in doing this, and the way that he conducted the whole affair, still remain obscure.

The two metals and their compounds and complexes are, of course, of absorbing scientific interest, and this has long been recognised (thus the Nobel Prize in Chemistry for 2001 was won by William S. Knowles and Ryoji Noyori for their work on rhodium-catalysed chiral hydrogenation reactions (and by K. Barry Sharpless for his chiral oxidation work, including *cis*-hydroxylations catalysed by osmium tetroxide (27))).

## Appendix

(a) **Iconography.** Walker's excellent "Regency Portraits" gives information on prints, engravings, busts and painting of Wollaston (28). The painting by John Jackson of 1820 is in the Royal Society (see also (2)). The National Portrait Gallery has drawings by John Jackson (1820) and William Brockenden (1830) (see also (4)) and holds two camera lucida sketches by Chantrey for Wollaston's bust. The bust itself (1830), in marble, by Francis Chantrey, is in the Royal Institution, and the plaster model is kept in the Ashmolean Museum, Oxford, the source of the portrait on the obverse of the Wollaston Medal. The Royal Society, Royal Institution, and the Geological Society all have engravings or drawings of him.

(b) **The Wollaston Medal.** Wollaston became a member of the Geological Society in 1812. Two weeks before his death in 1828 he left the Society £1,000 for research in geology. The Council of the Geological Society used the income for the purchase of a die for a medal to be called after him. At first it was cast in gold but later

(1846–1860) in palladium. The palladium was acquired by Percival Norton Johnson of Hatton Garden, also a Fellow of the Society. The palladium however damaged the dies, and in 1880 new dies were made, after which using gold was resumed. In 1930 the Society reverted to using palladium for this most prestigious award in geology. The Medal is awarded annually for outstanding geological research. It was first awarded on 20 June 1832 (the official award was made on 18 February 1831 but the medal was not ready) to William Smith, the ‘Father of English Geology’, who made the first reliable geological map of Britain, using the principles of fossil succession. Other early holders were Sir Henry de la Beche (1855), Charles Darwin (1859), Sir Roderick Murchison (1864) and T. H. Huxley (1876) (29). Wollaston’s profile, taken from the Chantry bust, is on the obverse, while the reverse is inscribed “Geological Society of London” with the recipient’s name enclosed between laurel and palm branches (29).

(c) Residences. Wollaston lived much of his life in London. Despite the demolition of many old buildings in London, streets tend to retain their names. It is therefore rather sad that the names of the first two streets in which Wollaston lived have been changed, and his houses lost. From 1797 to 1801 he lived at 18 Cecil Street, where he perfected some of his platinum purification procedures; Cecil Street is now Ivy Bridge Lane, a narrow private road leading from the Strand down to the Savoy at Savoy Place. He moved in 1801 to 14 Buckingham Street, not the charming Buckingham Street close to Ivy Bridge Lane, but a small street near Park Crescent, Regents Park, now called Greenwell Street: here his rhodium and palladium work was probably done. On July 4 1934 a

plaque was erected on that house by the Geological Society inscribed “William Hyde Wollaston (1766–1828 Natural Philosopher, lived here 1801–1825”); see reference (6) for a photograph. This site of the building is now a car park; and the plaque is housed in the archives of the Geological Society.

From 1825 until his death in 1828 he lived at No. 1 Dorset Street, near Manchester Square. Charles Babbage, the inventor of the forerunner of the computer, also lived in the house from 1829 to his death in 1871. The house (which is not the original) carries a plaque to Babbage.

## Bibliographies

The magisterial bibliographies by J. L. Howe cover the period 1748 to 1950 (30). The author wrote a survey of the chemistry of rhodium, covering the literature up to 1967 (31), and on the non-organometallic chemistry of rhodium (32) and palladium (33). F. R. Hartley wrote a book on the chemistry of palladium and platinum (34).

More up-to-date, though less comprehensive is a short book on the six platinum group metals by Cotton (35), and the “Encyclopedia of Inorganic Chemistry” has useful articles on the coordination and organometallic chemistry of rhodium (36) and palladium (37).

## Acknowledgements

Andrew Mussell, the archivist of the Geological Society and his colleague Gordon Herries-Davies; Professor Mel Usselman, University of Western Ontario, for a preprint of reference 14; and Professor J. Marshall, Duke University, Texas, for help in tracing Wollaston’s London residences.

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#### The Author

Bill Griffith is Professor of Inorganic Chemistry at Imperial College, London. He has considerable experience of the pgms, particularly of ruthenium and osmium. He has published over 250 research papers, many describing complexes of these metals as catalysts for specific organic oxidations. He has written seven books on the platinum metals, and is the Secretary of the Historical Group of the Royal Society of Chemistry.

## Magnetic Field Effects on Benzene Photodegradation

Since nuclear and electronic spin polarisation phenomena during chemical reactions were discovered, magnetic field effects on the kinetics of chemical reactions, especially those with free radicals, have been examined. As heterogeneous photocatalytic reactions in the presence of O<sub>2</sub> produce free radicals and radical ions the reactions may be affected by magnetic fields.

Scientists from Fuzhou University, P. R. China, have now reported the effects of magnetic fields on the UV photocatalytic degradation at 65°C, of benzene using a synthesised 0.5% Pt/TiO<sub>2</sub> catalyst (W. Zhang, X. Wang and X. Fu, *Chem. Commun.*, 2003, (17), 2196–2197).

The catalyst was placed in a quartz tube, surrounded by an electromagnetic field vertical to the axes in the photoreactor, and benzene was supplied at 20 ml min<sup>-1</sup>.

Benzene conversion and CO<sub>2</sub> production were monitored. On application of magnetic field (59.42 mT) benzene conversion increased from 15.5 to 18%, and CO<sub>2</sub> production increased from 52 to 175 ppm. On removing the field benzene conversion fell to 4%, and CO<sub>2</sub> production fell to its initial value. Low field intensities suppressed benzene conversion, but at fields > 52 mT benzene conversion increased rapidly. CO<sub>2</sub> production increased over the whole field range.

Removal and reapplication of the field produced a similar result, but putting fresh catalyst into a field produced little improvement. Without UV, Pt or catalyst, no reaction occurred. The results may be linked to decomposition of intermediate species on Pt. Reasons for the phenomena are unknown; further studies are in progress.