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ARTICLE

Limitations to elemental substitution as exemplified by the platinum-group metals†

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Substitution is often touted as a potential solution to concerns regarding material supply restrictions, yet the degree to which substitution can abate these concerns has not been fully explored. This article examines the issue of elemental substitution by identifying potential substitutes for the platinum-group metals (PGMs) and highlighting factors that may limit substitution in each of their major commercial applications. The findings suggest that substitution is often not possible or impractical due to various technical and economic reasons. When suitable substitutes are available they are often other PGMs or elements in close proximity to the PGMs on the periodic table, namely Ni, Co, and Au. In several cases, however, substitution has already occurred and further substitution may not be possible. Furthermore, the co-production of PGMs and their most promising potential substitutes from the same mineral deposits limits their ability to substitute for one another in the event of a supply disruption. The combination of these factors suggests that PGM substitution potential for current high-volume applications is limited and that further efforts are needed to develop new technologies that avoid the use of PGMs in order to significantly decrease our reliance on them in the future.

1. Introduction

Today, chemists, materials scientists, engineers, designers, and industrialists have the prerogative of selecting virtually any chemical element to perform the specific function of their desire. As a result, modern technology makes use of practically the entire periodic table of elements.¹ Increasing use and lack of end-of-life recycling² of some of the more “critical” elements has raised concerns regarding their long-term availability.³⁻⁷ As is often the case, these concerns have reinforced interest in finding substitute materials.^{8,9} While substitution appears to be a reasonable course of action, the extent to which it can abate these concerns has yet to be thoroughly examined. To explore these issues, this article investigates the substitution potential (and lack thereof) for the six platinum-group metals (PGMs): platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh), iridium (Ir), and osmium (Os).

PGMs possess an incredible array of physical and chemical properties that make them uniquely suited for a multitude of applications. Antoine Baumé put it best in his 1773 characterization of Pt: “So many excellent properties united in a single metal make it desirable that it should be introduced into commerce.”¹⁰ These excellent properties include high melting point, superior catalytic activity, and exceptional resistance to corrosive attack and high temperature oxidation, to name a few.¹¹ It is these and other exceptional properties that have allowed PGMs to be employed in a number of sectors including automotive (catalytic converters, spark plugs, oxygen sensors), chemical and petroleum (catalysts and laboratory equipment), electrochemical (anode coatings), electrical and electronics (hard disk drives and multilayer ceramic capacitors),

medical and dental (dental alloys, biomedical devices, and anti-cancer drugs), glass manufacturing equipment, as well as jewellery and investment.

The use of PGMs in such a wide range of applications coupled with their relatively high prices has led to various attempts to substitute them for less expensive metals. Indeed, finding suitable substitutes for the PGMs has been an ongoing concern (e.g., ref. 12). These concerns have recently been amplified in light of the recent Pt mine strikes in South Africa,¹³ the largest producer of PGMs.

While potential alternatives are generally known within an industry, such knowledge is typically absent across industries. Moreover, while substitution may be technically feasible there may be overriding factors that make implementation impractical. By combining information from a variety of sources, this article provides a comprehensive overview of the potential for and limitations of substitution for the six PGMs across all relevant industries. Because of the wide range of applications in which PGMs are used, only high-volume commercial applications are examined and discussed.

It is important to note that the evaluation conducted in this work is focused primarily on elemental substitution: substitution of one element (or one alloy composition) for another within a specific product or technology. Substitution can, of course, also occur across technologies (e.g., substituting hard disk drives that use PGMs for solid-state drives that do not), as well as at the system-level (e.g., transportation via motor vehicle versus telecommuting). Technology- and system-level substitutions are typically more difficult to implement and may require significant investment if solutions do not already exist.¹⁴ Nonetheless, these higher levels of substitution are undoubtedly important and should be considered in any long-term assessment of substitutability. They are for the most part, however, outside the scope of this study with the exception of price elasticity analyses, which account for substitution potential at all levels.

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2. Results and discussion

A summary of the potential substitutes that have been identified for each of the PGMs by major application is provided in Fig. 1 and Table 1, with more details in the electronic supplementary information. Overall, these results indicate that PGMs often make the best substitutes for each other. This is not surprising given the similarity in chemical and physical properties among this naturally co-occurring group of elements. Aside from other PGMs, Ni, Co, and Au are the elements most likely to substitute for PGMs in certain applications. Again, this is not surprising given their proximity on the periodic table. While there are important similarities among the PGMs and their neighbouring elements, there are important differences as well. These differences obviously limit the potential for substitution, but there are often other considerations that also make substitution unfeasible. The following sections will therefore discuss these and other important challenges that may impede substitution.

2.1. Lower substitute performance

As highlighted by Graedel, et al.⁹ potential substitutes often exhibit lower performance in one or more key attributes as compared to the target element. A classic example is the use of Al alloys in place of Cu in electrical applications, with the former exhibiting lower electrical conductivity. Lower performance is likely the greatest inhibitor of the adoption of substitutes in place of the PGMs. Consider, for example, the use of Pt (promoted by Re, Ir, or Sn) in petroleum reforming. Mo oxide catalysts were previously used in the hydroforming process, but were not as active or selective and required frequent regeneration.¹² The markedly lower performance of this alternative and the efficient recycling of the Pt catalysts make substitution impractical. Demand for this category thus exhibits extremely low price elasticity and then only after substantial time lags.¹⁵ In the chemical industry, an Ir catalyst (promoted by Ru) is used in the manufacture of acetic acid via the carbonylation of methanol (the Cativa™ process). Rh is an alternative as it is used in the production of acetic acid via the Monsanto process. However, the Cativa™ technology provides higher reaction rates, allows for a wider range of process conditions, and increases production capacity.^{11,16} The Rh-based Monsanto process itself was a replacement for the significantly less-active process that utilized a Co/iodine catalyst.¹¹ Similarly, the KBR Advanced Ammonia Process (KAAP™), which utilizes a Ru catalyst, is thought to be 20 times more active than the process that utilizes a magnetite-based catalyst.¹⁷ In general, there is often little incentive to substitute base metals for PGMs in catalytic applications because PGMs are often more catalytically active, operate under milder reaction conditions, are non-toxic and non-pyrophoric, and do not require pre-treatment.¹¹ PGMs are also recovered and recycled with high efficiency^{18,19} making substitution desirable only in applications in which significant PGM losses occur (e.g., the use of Pt in the cross-linking of silicones and nitric acid production). That being said, there has been some success in identifying alternatives using non-precious metal catalysts. For example, Studt, et al.²⁰ identified catalysts based on Ni-Zn alloys as an alternative to the commercial Pd-Ag catalyst used for the selective hydrogenation of acetylene. Other studies (e.g., refs²¹⁻²⁴) have also reported varying degrees of success at utilising alternatives to precious metal catalysts.

In certain applications, however, no suitable substitutes exist. This is the case for the three PGMs (Pt, Pd, and Rh) used in automotive catalytic converters. Thousands of catalyst compositions were investigated during the research and development effort that ultimately led to the use of PGMs in catalytic converters, and research into viable alternatives continues to this day.^{12, 15, 25, 26}

Although base metal oxide catalysts (e.g., CuO and Co₃O₄) exhibit comparable activity in the oxidation of CO, they are typically less active than PGMs in the oxidation of hydrocarbons and tend to react with the alumina support to form less active species.^{15, 25} Catalysts based on Ag and Au were also eliminated as potential candidates due to their limited activity and durability.⁸ Moreover, both Ag and Au have a Tamman temperature that is below that of the average exhaust gas resulting in lower thermal stability.²⁷ A recent review suggests that there are various approaches that may overcome the problems of low-temperature activity and thermal stability associated with using Au-nanoparticle catalysts, especially in lean-burning (i.e., those designed to operate in the presence of air in excess of stoichiometric ratios) compression-ignition (diesel) engines whose exhausts have lower temperatures than those produced by spark-ignition (petrol or gasoline) engines.²⁶ Indeed, a catalyst based on Au-nanoparticles, NS Gold™, has recently become commercially available for use in European diesel vehicles.²⁶ This catalyst does, however, utilise both Pt and Pd in addition to Au.²⁶

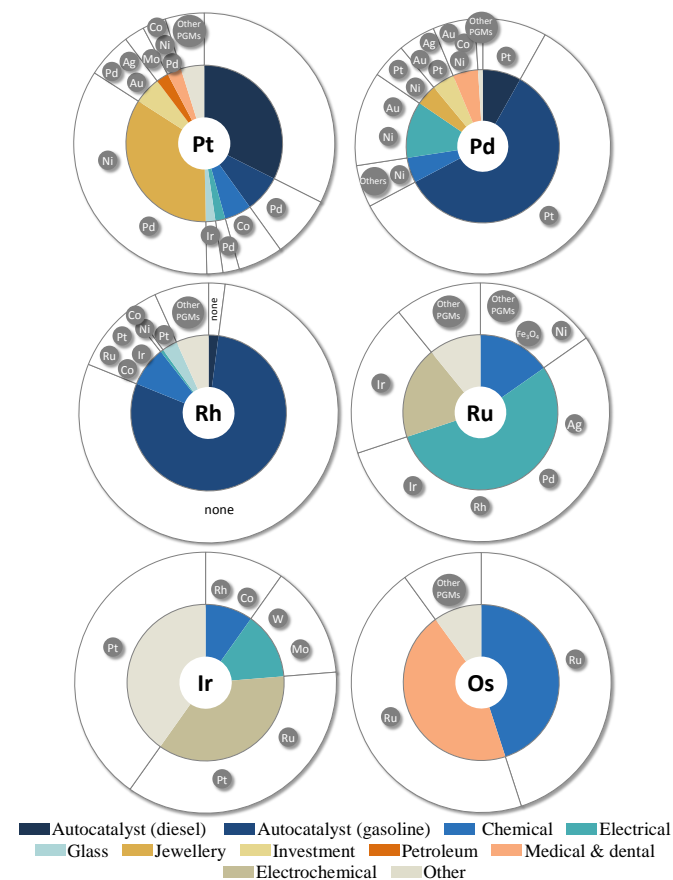


Fig. 1 Potential PGM substitutes (outer ring) by major application (inner ring). Global market share data obtained from Johnson Matthey²⁸. Market shares for Os applications are approximated due to lack of data. Not all potential substitutes displayed.

Being equally effective at oxidizing CO and hydrocarbon emissions, Pt and Pd can substitute for each other in catalytic converters used in spark-ignition vehicles.²⁷ Pt is, however, less susceptible to poisoning by Pb and sulfur, while Pd has a higher resistance to high-temperature ageing, especially in oxygen-rich conditions, and better performance at lean cold starts.²⁵ With the lowering of sulfur levels in diesel fuel and the increased use of diesel particulate filters, the use of Pd has become possible in diesel oxidation catalysts.²⁸ Today, up to 25% of Pt can routinely be

substituted for by Pd, with new technologies allowing for an increase of that portion to as much as 50% in certain applications.²⁹ The highly oxidizing environment of the diesel exhaust does, however, convert Pd into a catalytically less-active oxide state, thereby requiring the use of Pt which remains in its catalytically-active metallic form.²⁸ Research efforts exploring alternatives to PGMs in autocatalysts of lean-burning engines have yielded some promising results with regards to the reduction of nitrogen oxides (NO_x) utilising catalysts based on perovskite oxides.³⁰ These catalysts are, however, prone to deactivation via sulfur and require the addition of Pd for the effective oxidation of hydrocarbons and CO.³⁰ At this time there does not seem to be a viable alternative that completely eliminates the use of Pt and Pd in catalytic converters. Similarly, despite various efforts,³¹ no viable alternative to Rh in catalytic converters has been found.^{3, 8}

Where adequately performing substitutes are available it is often the case that the substitution has already taken place. Consider the use of Pd in multilayer ceramic capacitors (MLCC), one of its main uses in electronic applications. The introduction of Ni- and Cu-based MLCC in the mid-1990s has steadily eroded the market share of Pd-based MLCC from approximately 85% in 1997 to 10-15% in the late 2000s.²⁸ In recent years, an overall increase in MLCC demand has not been sufficient to offset the decrease of Pd use due to this substitution and “thrifting” via miniaturization.²⁸ Pd-based MLCC have thus been largely confined to niche areas that require superior performance, such as military and aerospace applications.²⁸ Because substitution has already occurred, further substitution of Pd for base metals, while still possible, will likely be considerably slower.

2.2. Economic considerations

Substitution can also be limited by various economic factors, the simplest of which is the price differential between the element and its potential substitute. For example, the utilisation of Ag in place of Cu in electrical applications is generally not feasible because of Ag's higher price despite its superior electrical conductivity. This is typically not a concern for the high-priced PGMs and is actually often a motivating factor for substituting them with the lower-priced base metals. It can also be a motivating factor for substituting one PGM for another. As previously discussed, Pt and Pd are noted as being equally effective at oxidizing CO and hydrocarbon emissions in spark-ignition vehicles.²⁷ The choice between the two metals is thus often based on the relative prices of the metals involved.²⁷ Similarly, in glass manufacturing equipment, the amount of Rh used as an alloying element with Pt is partly dependent on the relative prices of the two metals.³² In certain applications, however, material costs are relatively small and thus not a determining factor for substitution. This is the case in the pharmaceutical industry where the cost of the catalyst is small compared to the price of the drug.⁸

Beyond price differentials, there may be other economic considerations that can disincentivise substitution. In catalysis, for example, substitution may require plant or process modifications thereby resulting in significant capital expenditures.³³ Unlike other alternatives to the Pt-catalysed hydrosilylation reactions, the Pt-free radical-initiated technology does not have the advantage of being a drop-in replacement for existing coating systems.³⁴ Similarly, in addition to being less active and less selective, the previously used Mo-based catalysts cannot be used in the existing Pt-based petroleum reforming units.¹² Another example is the previously discussed Cativa™ process which allows for significant savings on capital expenditure that would otherwise be required to build new plants or to expand existing operations with the Rh-based Monsanto process.¹⁶

Table 1 Overview of PGM uses and potential substitutes

Element	Application	Application details	2012 market share (%)	Potential substitutes
Ru	Electrical	Thick film pastes, hard disk drives, electroplated reed contacts, and electrode coating in fuel cell stacks	55.5	Ir, Rh, Pd, Ag
	Electro-chemical	Coating of dimensionally stable anodes (DSA) used by the chlor-alkali industry	18.7	Ir
	Chemical	Process catalyst used in hydrogenation, oxidation, hydrogenolysis, synthesis of ammonia, synthesis of hydrocarbons, and hydroformylation	14.9	Fe ₃ O ₄ , Ni, other PGMs
	Other	Alloying agent in corrosion resistant piping, spark plugs, jewellery, and dentistry	10.9	Other PGMs
Rh	Autocatalyst	Catalyst used to control vehicle NO _x emissions	81.0	None
	Chemical	Process catalyst in hydroformylation, carbonylation of methanol to acetic acid, carbonylation of methyl acetate or dimethyl ether to acetic anhydride, and Pt-Rh gauzes in the catalytic oxidation of ammonia	8.4	Co, Ir, Pt, Ru
	Glass	Alloying agent with Pt fabrications used in the production of technical and specialty glass	3.2	Pt alone, or with Au or Ir
	Electrical	Alloying agent with Pt in thermocouples, sliding and pressure contacts, and jet engine glow plugs	0.6	Ni-Cr, Co-Cr
	Other	Various uses including electroplating onto metal surfaces, especially for jewellery	6.8	Other PGMs
Pd	Autocatalyst	Catalyst used to control vehicle exhaust emissions	66.9	Pt
	Electrical	Multilayer ceramic capacitors (MLCC), hybrid integrated circuits, plating connectors, and lead-frames	12.1	Ni, Au
	Chemical	Process catalyst used in the production of hydrogen peroxide, acetaldehyde, vinyl acetate monomer, purified terephthalic acid, and as a catchment gauze in nitric acid production	5.4	Ni, other precious metals
	Dental	Fabrication metal and alloying agent in dental restorations including crowns, bridges, and replacement teeth	5.4	Ni-Cr, Co-Cr, high-Au alloys, ceramics
	Investment	Coins and exchange traded funds (ETFs)	4.7	Au, Ag, Pt
	Jewellery	Fabricated Pd jewellery and alloy agent in Pt and white-Au jewellery	4.5	Other Pt alloys, Ni-based white Au
	Other	Various uses including industrial emissions control, oxygen sensors, as well as petroleum refining	1.1	Other PGMs
Os	Medical	Staining agent in electron microscopy		Ru
	Chemical	Process catalyst used in a limited number of processes including syn-dihydroxylation	No recent data available	Ru
	Other	Alloying agent for various uses including surgical implants, electrical contacts, jewellery, fountain pen points, instrument pivots, phonograph needles, and light filaments		Other PGMs
Ir	Electro-chemical	Coating of dimensionally stable anodes (DSA), cathodic protection, electrogalvanizing, and electrowinning	39.3	Ru, Pt
	Electrical	Crucibles used for growing high purity single crystals of metal oxides	23.6	Mo, W
	Chemical	Process catalyst used in hydrogenation, acetic acid synthesis, and hydroformylation	10.7	Rh, Co
	Other	Alloying agent in spark plug tips, jewellery, pacemakers, and catheters	26.4	Pt
Pt	Autocatalyst (diesel)	Catalyst used to control vehicle exhaust emissions	32.6	None
	Autocatalyst (gasoline)		7.7	Pd
	Jewellery	Jewellery fabrication	34.6	Pd- or Ni-based white Au
	Investment	Small and large bars, coins, and exchange traded funds (ETFs)	5.7	Au, Ag, Pd
	Chemical	Process catalyst used in the production of a variety of bulk and specialty chemicals, gauzes for catalytic production of nitric acid, and laboratory equipment	5.6	Co, other PGMs
	Medical & biomedical	Dental alloys, biomedical devices, and anti-cancer drugs	2.9	Pd alloys, Ni-Cr, Co-Cr alloys
	Petroleum	Catalyst used in petroleum refining processes including reforming and isomerization	2.5	Mo
	Glass	Fabrications of self-supporting parts, linings, and thin layer coatings used to manufacture various technical, specialty, and optical glass	2.2	Ir
	Electrical	Hard disk drives, thermocouples, contact materials, varistors, bond wires, and fuel cells	2.1	FePd alloys, Co/Pd multilayers
	Other	Spark plugs, oxygen sensors, stationary pollution control, corrosion resistant coatings on turbine blades, marine vessels, and deep-sea oil-drilling platforms	4.2	Other PGMs

Furthermore, a change in catalyst may require the use of a more expensive ligand thereby making substitution uneconomical.⁸ More generally, because PGM catalysts allow for milder operating conditions, operating costs can often be lower. For example, the use of Rh in place of a Co-based catalyst in the oxo process allows for operation at lower pressures, which reduces operating costs.³⁵

Financial incentives in the form of subsidies can also limit substitution. In Japan, for example, government subsidies for dental work stipulate the use of a specific Pd-Au alloy (kinpala),²⁸ thereby limiting the incentive for utilizing alternative alloys.

2.3. Limited substitute availability

Even if a substitute of adequate performance and positive economic attributes is identified, it may not be a suitable substitute due to its limited availability to fulfil that role. A substitute may, for example, be at a higher risk of supply restriction than the target element. Such considerations are often taken into account in various "criticality assessments" (e.g., ref. ⁶), with the substitution of Ag for Au as a prime example.³⁶ Moreover, sufficient supplies of the substitute may not be available due to the large quantities required for the application in question. While Ir-based spark plugs can substitute for Pt-based spark plugs, it is unlikely (even if technical hurdles are overcome) that Ir can completely substitute for Pt in the glass manufacturing sector due to the large volumes of metal required in this application. These limitations are more likely to occur when attempting to substitute a high-volume metal (e.g., Fe, Cu, or Al) with a minor (or by-product) metal.

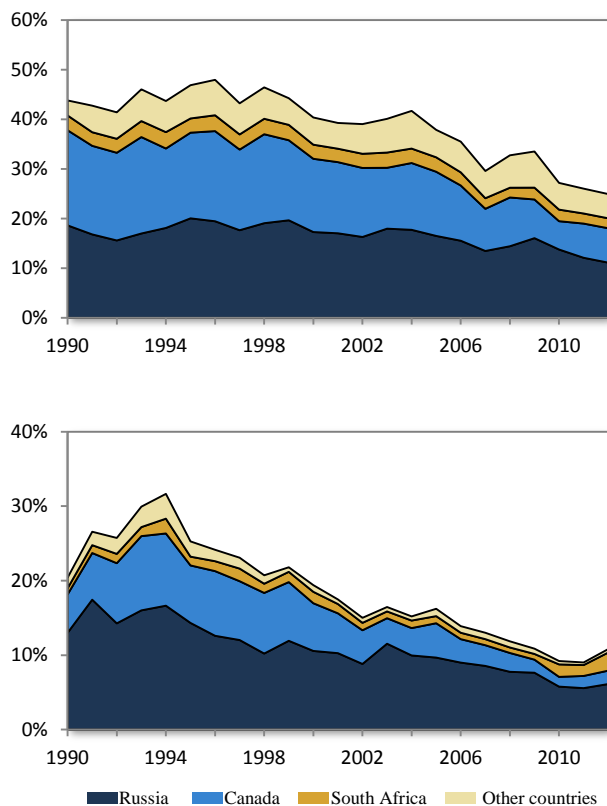


Fig. 2 Percentage of Ni (top) and Co (bottom) global mine production that is co-produced with PGMs. Data sources: refs. ³⁷⁻⁴⁸

More fundamentally, elements that share similar properties (and are thus good potential substitutes) are often found in the same ore

bodies. The co-production of PGMs from the same mineral deposits limits their ability to substitute for one another in the event of a supply disruption. This is also a concern for the other elements identified as potential substitutes, namely Ni, Cu, Co, and Au, but to a lesser degree because only a portion of those elements' supplies are co-produced with PGMs. The degree to which the fates of these metals are linked can be approximated by the quantity that is co-produced with PGMs.

As illustrated in Fig. 2, a sizable portion of global Ni and Co mine production is co-produced with PGMs. Au, Ag, and Cu are also co-produced with PGMs, but the quantities are small relative to those metals' global mine production. It is interesting to note that the percentage of Ni and Co mined with PGMs has decreased over the last two decades, mainly due to an increase in production from sources that are not directly associated with PGM production (e.g., laterite ores for Ni and D. R. Congo production for Co). This suggests that the supplies of Ni and Co today are less linked to those of PGMs than they were twenty years ago.

The issue of co-production of substitutes is perhaps most crucial for applications that have the largest market shares. Fig. 3 illustrates how the market shares of the various applications in which Pd is co-produced with its potential substitutes have evolved over the past two decades.

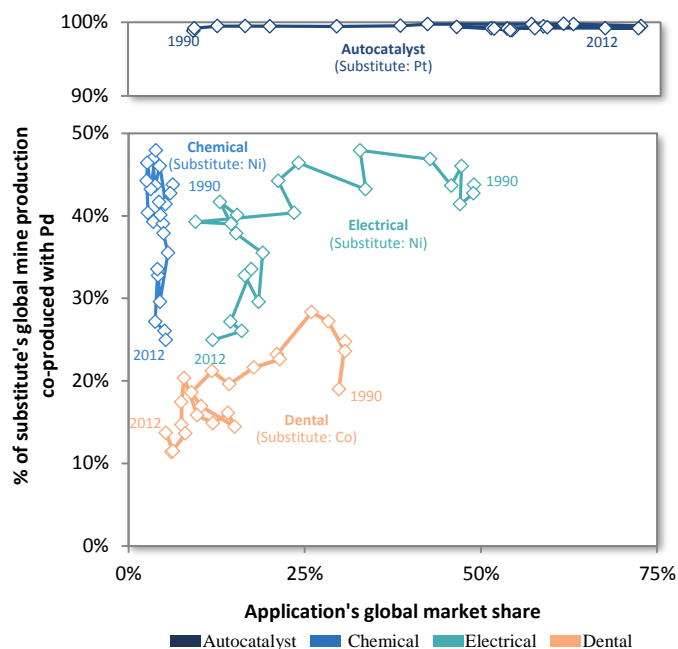


Fig. 3 Changes in the market shares and co-production values of Pd and its potential substitutes (Ni, Co, and Pt) in several of its main applications from 1990 to 2012. Market share data from Johnson Matthey²⁸.

Over the time period examined, both the market shares and the substitutes' co-production values have decline for Pd's use in electrical, chemical, and dental applications. All else being equal, this suggests a lower risk of not being able to substitute in the event of a supply disruption for these applications. However, the reduction in market shares for these applications is partly attributable to the increased market share of Pd's use in autocatalysts. Because Pt is Pd's substitute in autocatalysts and because Pd and Pt are co-produced in virtually all mines, the overall risk of not being able to substitute Pd in the event of a supply restriction has likely increased over this time period.

The co-production of elements and their potential substitutes is not restricted to the PGMs. Other examples of co-produced substitutes include Se and Te in pigments, rubber, free-machining alloys, Pb-free brasses and photoreceptors,^{29, 36} Ag and Pb in electronics,⁴⁹ and the rare earth elements substituting for each other in various applications,⁵⁰ to name a few.

2.4. Other considerations

In addition to performance, economic, and availability considerations, there may be other factors that limit the potential for substitution. For example, it is generally assumed that precious metal alloys can readily substitute for each other in jewellery applications. Aside from differences in physical properties and workability,⁵¹ there are various cultural and historical factors that influence a metal's selection in jewellery applications and limit its substitutability.³² Gold jewellery, for example, has important social and cultural significance in countries like India.⁵² Similarly for Pt, there is a resistance to substitution that is reflected in the relative price inelasticity of Pt jewellery demand.^{53, 54} There may also be resistance to substitution for industrial users due to an inherent aversion to change. This may be the case in the release liner industry where it is suggested that the conventional Pt-based technology is not expected to be replaced due in part to the industry's aversion to change.³⁴

Substitution can also lead to greater environmental burdens. As previously mentioned, PGM catalysts are often more active, operate under milder conditions, and are recovered and recycled with high efficiency as compared to their base metal counterparts. Substituting a PGM catalyst for a lower-performing base metal catalyst may, for example, result in increased operational energy consumption. Environmental burdens are also associated with the production of the metals themselves, with PGMs typically being allocated higher environmental impacts than base metals (mainly due to their higher prices).⁵⁵ Any environmental comparisons should therefore be conducted on a life cycle basis with the appropriate functional unit. Such an analysis was conducted by Xie and Subramaniam⁵⁶ in which they compared the gate-to-gate and cradle-to-gate life cycle impacts of a Rh-catalysed, 1-octene hydroformylation process in CO₂-expanded liquid (CXL) medium to the conventional Co-catalysed process. Their results suggest that the CXL process has potentially lower gate-to-gate life cycle impacts with respect to ecotoxicity, greenhouse gas emissions, and smog formation as compared to the conventional Co-catalysed process.⁵⁶

In certain cases, environmental factors have been a driving force that has resulted in materials substitution. For example, the phasing out of Hg-based cells in favour of the membrane technology in the chlor-alkali industry is largely driven by environmental regulations.⁵⁷ Among other things, this technological change has resulted in a partial substitution of Ru for Ir, as the Hg-based technology utilise RuO₂ coated titanium dimensionally stable anodes (DSA), while the membrane technology uses a coating mixture of both RuO₂ and IrO₂.²⁸ Another example of environmental considerations driving material substitution is the utilisation of Pb-free solders in electronics,⁵⁸ which in addition to phasing out the use of Pb has furthered the use of Pd where it helps maintain reliability at the high temperatures required for Pb-free soldering.²⁸

2.5. Price elasticity of demand

All of these limitations to substitution are inherently captured by a metal's price elasticity of demand (i.e., its demand's sensitivity to price changes). Applications in which demand is relatively elastic infer the availability of an adequate substitute (i.e., if the price of the metal increases its demand in that application decreases at a greater rate because its users are able to switch to a substitute), while

price inelastic demand suggests a lack of suitable substitute (i.e., if the price of the metal increases its demand in that application decreases at a lower rate due to the lack of adequate substitute or the existence of other impediments, such as those previously discussed, that makes substitution unfeasible). The results from price elasticity of demand analyses are described in detail in the electronic supplementary information and the results for Pt are summarized in Fig. 4.

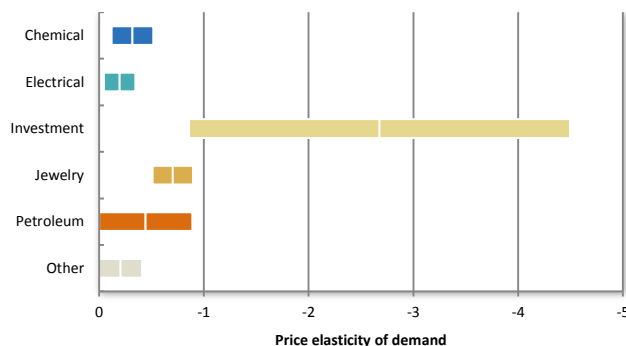


Fig. 4 Estimated price elasticity of demand for several Pt applications. Bars indicate the 95% confidence intervals of the price elasticity of demand's estimated value (white vertical line within each bar).

The results indicate that demand is price inelastic for all major applications of Pt, with the exception of the investment category. It was not possible to obtain price elasticity values for Pt's use in autocatalysts (which are required by regulation) and glass manufacturing, but previous studies^{15, 53} indicate that demand for those categories are price inelastic as well. As illustrated in Fig. 5, these results suggest that a doubling of the price of Pt (in real terms) is expected to decrease its demand in the chemical industry by only 8–30% (95% confidence interval) and that a 10-fold price increase would be needed to decrease that demand by 24–70%. Some applications are more price sensitive (e.g., jewellery) than others (e.g., electrical), but demand for all applications (except investment) display a relative inelasticity to price.

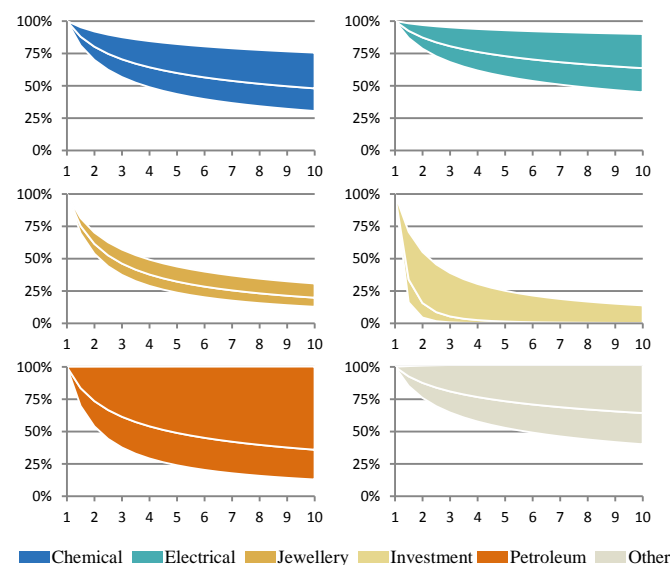


Fig. 5 Estimated relative decrease in Pt demand for various applications (vertical axis) that would result from a relative increase in Pt price (horizontal axis). Shaded region depicts the 95% confidence interval of the estimated value (white line).

One can infer from these results that substitution for these applications is often undesirable or unfeasible given the estimated modest decrease in demand despite significant increases in Pt's price. These results therefore support the conclusions of the literature review. However, should prices remain elevated for extended periods of time, one would expect that suitable substitute will eventually be developed. Indeed, some models suggest that, over the long-run, overall Pt demand is price elastic.⁵⁴

3. Conclusions

Concerns regarding the stability of PGM supply have reinforced interest in finding substitute materials. This article has sought to identify potential PGM alternatives and to highlight factors that may constrain substitution in each of the major commercial applications for all six PGMs. In some cases, suitable substitutes are not available due to technical reasons. In other cases, substitution is not pursued due to economic considerations. This lack of substitutability is highlighted by the relative price inelasticity of demand. When a suitable substitute exists it is typically an element that is in close proximity on the periodic table. However, one often finds that if substitution is viable it is likely to have already occurred and that further substitution is limited.

In addition to performance and economic considerations there may be issues regarding the availability of a substitute. A substitute's availability may be limited due to its higher risk of supply restriction, insufficient supply, or its co-production with the target element in the same mineral deposits. Finally, there are other considerations including historical, cultural, and environmental factors that may also constrain substitution.

All of these factors suggest that PGM substitution potential for current high-volume applications is limited. These obstacles to substitution should not, however, be interpreted as a call to curtailed or abandon research into PGM alternatives. Indeed, continued and expanded efforts are needed to develop alternatives wherever possible. To be most effective, these efforts should ideally take place in the early stages of research and development rather than after commercialisation where, as highlighted in this work, substitution is difficult to implement.

While this study has focused on PGM use in high-volume commercial application, there are countless applications that require small, but indispensable, quantities of PGMs. These applications, which include the use of PGMs in fine and specialty chemical catalysis, often face the added concern of being driven out of the market in the event of a prolonged supply restriction if they are unwilling or unable to pay for higher PGM prices.

In light of the limitations to substitution, more effort is needed to minimize losses of PGMs throughout their life cycle and increase recycling rates so that demand for virgin PGMs is minimized. As indicated by Nassar¹⁹, some 30 – 45% of PGM demand is lost or not recovered after use. While recovery and recycling is extremely efficient in some applications, such as glass manufacturing equipment, other applications, such as electronics, often have very low recovery rates at the end-of-life mainly due to lack of collection. Decreasing these losses and improving recycling rates can thus make significant reductions in the need for new PGMs. Furthermore, an equally significant portion of PGM supply is lost to mine tailings during the early beneficiation stages of comminution and concentration.¹⁹ Recovering these PGMs via hyperaccumulating plants (i.e., phytoextraction) is currently being investigated as a potential means of improving supply reliability and decreasing the associated environmental impacts.⁵⁹

Finally, it would be remiss to not mention the fact that much of current PGM demand is coupled with our use of fossil fuels. Autocatalysts are, of course, an end-of-pipe solution to a problem

caused by the combustion of fossil fuels. In addition to PGM catalysts used in petroleum reforming and isomerisation, many PGM catalysts are utilised in reactions where fossil fuels are the feedstock. Decreasing our dependence on fossil fuels by switching to alternative feedstocks and technologies is thus perhaps the most strategic long-term solution to reducing our reliance on PGMs.

4. Methods

To begin, the main application categories for each metal were identified and their respective market shares were determined using data from Johnson Matthey.²⁸ These categories include automotive catalytic converters (autocatalysts), jewellery and investment, chemical and petroleum catalysts, glass manufacturing equipment, dental, medical and biomedical devices, electrical and electronic components, electrochemical applications, and other miscellaneous uses. Contemporary global market share data for Os were not available and were thus approximated based on anecdotal evidence. Substitute determination was conducted via a systematic review of the scientific literature, technical reports, and expert opinion for each of these categories. For certain applications (e.g., chemical catalysts), it was necessary to delineate the categories further into subcategories in order to determine the most appropriate potential substitute(s). In most cases substitute identification was straightforward due to the previous or concurrent use of the substitute. In other cases, however, appropriate substitutes were more difficult to determine due to the lack of information (or lack of appropriate substitute). Details of this review are provided in the electronic supplementary information.

While the substitution assessment was largely qualitative and based on a comparison of a single desirable attribute, it was possible to perform a more quantitative assessment for certain applications. This was done using two different methods. The first method focused on the technical attributes of the potential substitutes in which more than one attribute plays an important role in determining their suitability. Consider, for example, the various potential substitutes for Pt jewellery. In the 1920s, white-Au alloys were developed to substitute for Pt-based alloys in the jewellery industry.^{18, 60} These white-Au alloys are based primarily on varying combinations of Au-Cu-Ni-Zn or Au-Pd-Ag alloys, with Ni and Pd providing the primary bleaching effect respectively.⁶⁰ Each alloy has both positive and negative attributes with regard to the most important properties of white-Au jewellery, namely colour and reflectivity, hardness, cold workability performance, liquidus temperature, amenability to soldering or brazing, recyclability, susceptibility to fire cracking, amenability to Rh plating for colour enhancement, resistance to tarnish and corrosion, allergy response, and cost.⁶¹ For example, while Ni-based white-Au alloys are generally characterized by adequate tarnishing resistance, amenability for Rh plating, a liquidus temperature less than 1100 °C, and inexpensive alloying constituents, they are typically plagued by poor workability, excessive hardness as cast, susceptibility to fire cracking, tendency to cause allergic reactions, and decreased recyclability for alloys with a high Zn content.⁶² In such cases where there are a number of competing attributes, it is necessary to simultaneously and quantitatively compare as many of these attributes as possible. One manner in which this can be done is to quantify the aggregated difference or Euclidean distance between a potential substitute and the target metal across a set of the most important attributes. To do this, the following metric, named multi-attribute vector distance (MAVD), was utilized:

$$MAVD = \sqrt{\sum_i \alpha_i (A_i - A_i^T)^2} \quad (1)$$

where A_i is the value of attribute i of the substitute under consideration, A_i^T is the target value of the same attribute, and α_i is a constant that can be set by the analyst to account for the importance of attribute i relative to the other attributes.

Several potential substitutes can thus be quantitatively compared across multiple attributes on the basis of MAVD, with the substitute exhibiting the smallest MAVD value being the “closest” substitute to the target. An example of how the MAVD was utilized in comparing a number of Ni- and Pd-based white-Au jewellery alloys across three attributes (colour difference, liquidus temperature, and Vickers hardness) is illustrated in Fig. 6, with details in the electronic supplementary information.

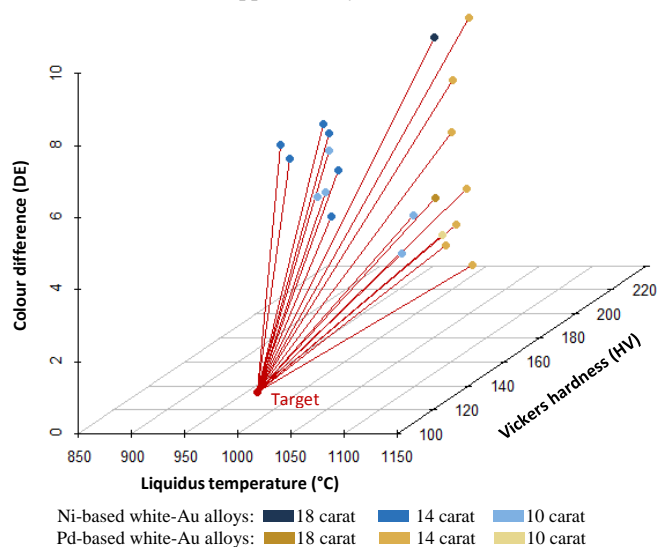


Fig. 6 Example illustrating the use of the MAVD metric for various Ni- and Pd-based white-Au jewellery alloys against a target along three attributes.

The second method of assessing substitutability examined the element's price elasticity of demand for the application in question and the cross-price elasticity of demand of the substitute in said application. As previously mentioned, applications in which demand is relatively elastic infers the availability of an adequate substitute, while inelastic demand suggests a lack of suitable substitute. Similarly, a positive cross-price elasticity suggests that the material is potentially a substitute, while a negative cross-price elasticity suggests that the material is possibly a complement.

Estimates for price elasticity of demand for some Pt applications are noted in the literature (e.g., refs.^{15, 53, 54}). To supplement and update these estimates, price elasticity values were derived for Pt and Pd applications using regression analyses of time-series data with the following generic equation:

$$\ln D_{t,i} = \alpha + \beta_{p,i} \ln P_t + \sum_j (\beta_{j,i} \ln X_{j,i}) + \varepsilon_t \quad (2)$$

where $D_{t,i}$ is the demand for a specific metal in application i during time period t , α is a constant representing demand for the metal in said application when all other parameters are zero, $\beta_{p,i}$ is the price elasticity of demand for application i , P_t is the price of the metal during time period t , $\sum_j (\beta_{j,i} \ln X_{j,i})$ is the sum of the contributions of all other statistically-significant explanatory variables, and ε_t is the error term. Details of the analyses are presented in the electronic supplementary information.

Both methods described here can potentially be utilized across most application for many of the elements (and alloys) of interest, assuming the availability of the necessary data.

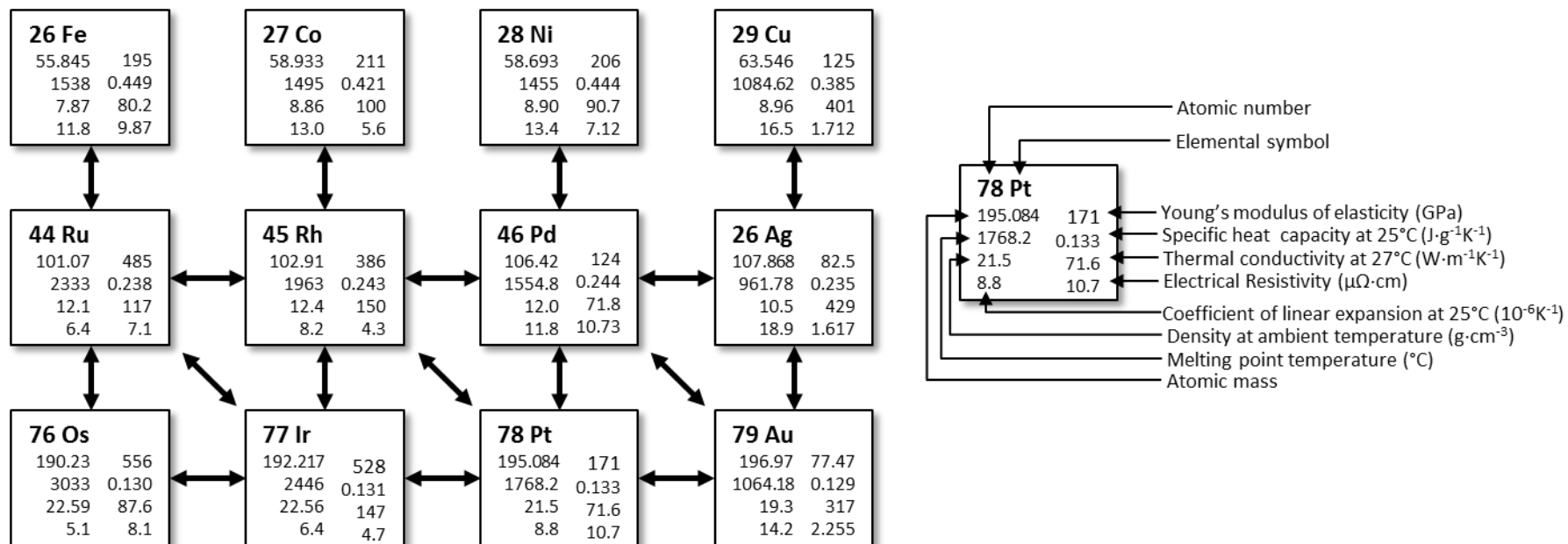
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A combination of factors suggests that PGM substitution is limited and further efforts are needed to decrease our reliance on them.