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COMMODITIES QUARTERLY

RHODIUM

EXECUTIVE SUMMARY

- Compared to Gold, Silver and the Platinum Group Metals Platinum and Palladium, Rhodium is relatively unknown in the investor community. However, it possesses some distinctive properties that set it apart from these better-known metals and make it worthy of consideration as an investment.
- The main use of Rhodium is in the automotive sector. However, demand from this industry is currently depressed as Rhodium has been replaced by Platinum and Palladium, which have been lately cheaper and have comparable pollutant reduction efficiency.
- High geographical concentration of supply and nascent investment demand, which could quickly swing the metal balance into deficit, could support higher prices in the future.
- Rhodium is currently undervalued compared to both its historical price range and Platinum and Palladium, and it offers an attractive risk / reward profile.

Eric SCHREIBER
Andrea GENTILINI
Cristiano MIGLIORINI

FOREWORD

From this issue onwards, our commodity research paper will appear quarterly rather than monthly, so it will be entitled *"Commodities Quarterly"*. As previously, we will continue to focus on interesting fundamental or technical themes that could affect precious metals in the weeks and months that lie ahead. During 2011, the *"Commodities Monthly"* has been one of the most downloaded documents on both UBP Intranet and Internet. We thank you for your trust and feel honored for the attention.

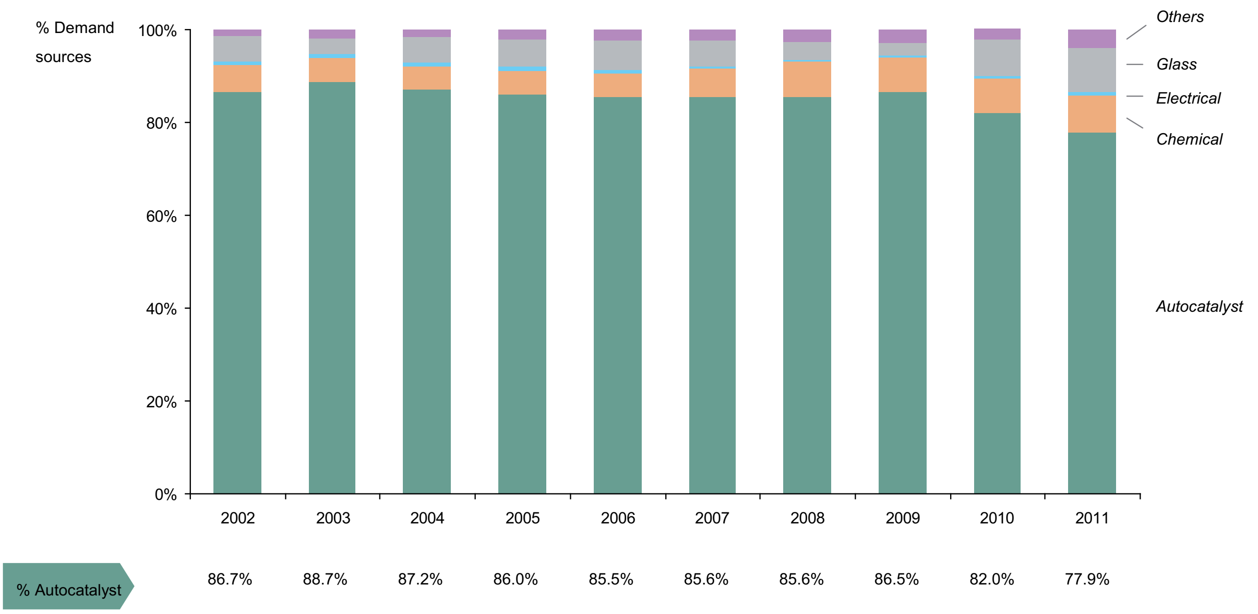
THIS QUARTER'S AGENDA

This quarter we take a look at Rhodium, a Platinum Group Metal (PGM) with many similarities to the better-known members of the group, Platinum and Palladium, but also with some unique features. We focus on the metal's fundamentals relative to those of Platinum and Palladium before reviewing Rhodium's main industrial applications and looking at future industrial demand for the metal. Finally, we review Rhodium from a technical perspective to highlight its current investment potential.

RHODIUM DEMAND – AN OVERVIEW

The automotive and glass manufacturing sectors are the main sources of demand for Rhodium, accounting for 78% and 9% of demand in 2011. The proportion of the various sources of demand has remained fairly stable over the past decade, as Figure 1 shows.

Figure 1 – Sources of Rhodium demand, 2002-11



Source: Bloomberg, UBP

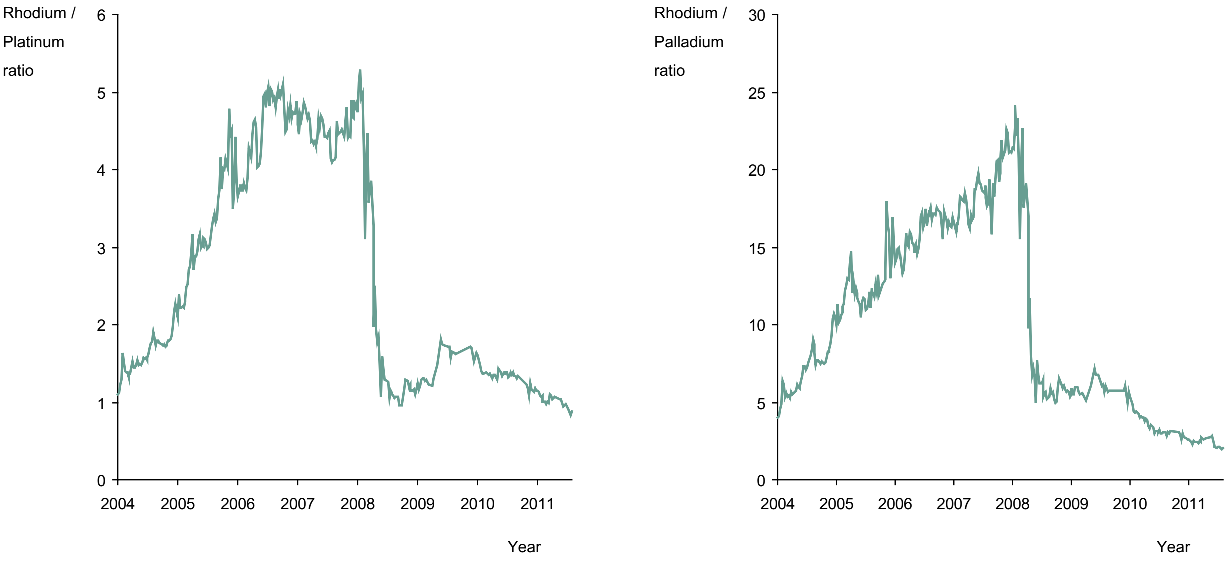
In 2011, the proportion of demand from the autocatalysis sector dropped significantly due to higher demand from the glass sector, which overtook chemicals as the second-biggest source of demand for Rhodium since 2010.

RHODIUM DEMAND IN THE AUTOCATALYST SECTOR

In its latest *"Platinum Review"* in November 2011, Johnson Matthey – the most authoritative research source on PGMs – noted that Rhodium demand from the automotive sector is poised to fall in 2012. With most of this demand coming from Japanese manufacturers, this is due to the ongoing disruption caused by last year's tsunami.

As Rhodium is effective in autocatalytic converters in place of Platinum and Palladium, price ratios are an important factor in anticipating which metal manufacturers will use. As Figure 2 shows, Rhodium is undervalued relative to Platinum and Palladium. New all-time lows for the Rhodium : Platinum and Rhodium : Palladium price ratios of 0.84 and 1.98 were hit near the end of January. By contrast, up until the mid-1990s, the Rhodium : Palladium ratio had oscillated between 8:1 and 20:1.

Figure 2 – Rhodium : Platinum and Rhodium : Palladium price ratios



Source: Bloomberg, UBP

Rhodium has some interesting chemical properties that set it apart from Platinum and Palladium. Its unique features had led the industry to consider the metal as the main PGM element in autocatalytic converters during the early stages of the technology. However, that was before Rhodium prices jumped to a high of USD 10'000 / oz in June 2008. Researchers ultimately managed to replace Rhodium with the cheaper Platinum and Palladium. Nowadays, though, Rhodium is cheaper than Platinum. Given that Rhodium is also better at removing nitrous oxides (NO and NO_2 – abbreviated to NO_X) from engine emissions and that NO_X will be the main focus of the next round of global emission standards, we believe there will always be a special place for Rhodium demand in this sector, especially now that it is trading at a discount to Platinum.

The main argument against Rhodium in this sector is the competing Selective Catalytic Reduction (SCR) technology, which does not use any PGM to reduce NO_X emissions. The use of SCR technology, however, is thus far limited to diesel engines and we expect this to remain the case for some years.

While in our view it makes sense for the automotive industry to use more Rhodium, there is limited transparency about whether the new emission standards are really prompting the industry to consider increasing its use of Rhodium. This will be the subject of future research. For the time being, we forecast Rhodium demand in the automotive industry to fall by -5% per year until 2014, in line with the trend of the past four years.

RHODIUM DEMAND FROM THE GLASS MANUFACTURING SECTOR

Platinum-Rhodium alloys are used in the manufacture of glass as a lining for the equipment involved in the processing of molten glass. The uptake of Thin Film Transistor Liquid Crystal Display (TFT- LCD) screens in flat-screen TVs, computer monitors and mobile phones has increased demand for Platinum and Rhodium from this sector. Consumer demand for such devices has been growing strongly for several years, but its impact on Platinum and Rhodium has not been felt until recently because until 2010 the PGMs need could be obtained by recycling them from cathode ray tube (CRT) plants. In 2010, Rhodium demand in this sector jumped 2.5 times from 19'000 oz in 2009 to 68'000 oz in 2012. In 2011, demand from this sector continued to grow, albeit at a slower pace of 25% year-on-year.

CRT plants that produce old-fashioned televisions are slowly being decommissioned – Johnson Matthey expects no new CRT devices to be produced after 2015[1]. In this sector, PGM recycling rates amount to 95-98%. As consumer demand for flat screens accelerates and CRT decommissioning comes to an end, a new wave of demand for PGMs is expected to come from this sector.

Another positive factor for Rhodium demand is that the proportion of Rhodium used in Rhodium-Platinum alloys has been increasing since September 2011, when Platinum prices surpassed those of Rhodium. In addition to its economic advantages, a 20% Rhodium alloy is increasingly being preferred to the traditional 10% Rhodium alloy due to its greater durability.

With the high cyclicality of this source of demand, we forecast Rhodium demand from the glass manufacturing industry to grow by a moderate 10% in 2012 and 5% in 2013 and 2014, significantly below the 2010 and 2011 levels of 258% and 25% respectively.

RHODIUM DEMAND FROM THE JEWELRY SECTOR

The jewelry sector makes extensive use of Rhodium but, due to its historically high prices and poor malleability, there is not as yet a Rhodium jewelry segment in its own right. Rather, Rhodium is 'flashed' onto white Gold and Platinum jewelry to increase its lustre, and it is coated around sterling Silver to increase the metal's resistance to tarnishing.

However, Rhodium has historically been used as the principal metal in high-prestige jewelry when not even Platinum was adequate enough to symbolize the uniqueness and prestige of the item. Rhodium is the main PGM metal in the word's most expensive pens, and has been used to plate the Queen of the United Kingdom's crown jewels. It was also used by Italian jewelry designer Giovanni Bosco to manufacture the USD 32'000 Harmony ring that President Obama gave his wife Michelle for putting up with years of uninterrupted political campaigns[2]. Meanwhile, Paul McCartney might be disappointed to hear that Rhodium is trading at a discount to Platinum given that in 1979 the Guinness Book of World Records awarded him a Rhodium-plated disc for his musical achievements. At today's prices, he might have preferred to receive a traditional Platinum-plated disc instead.

If precious metal demand were solely determined by jewelry preferences and rarity on the earth's surface, we would conclude that Rhodium's discount to Platinum is unjustified. While fundamentals indicate the opposite should hold, the lack of appreciation for Rhodium can last for a long time. We expect Rhodium demand from this sector to remain low in 2012.

RHODIUM DEMAND FROM OTHER INDUSTRIAL SECTORS

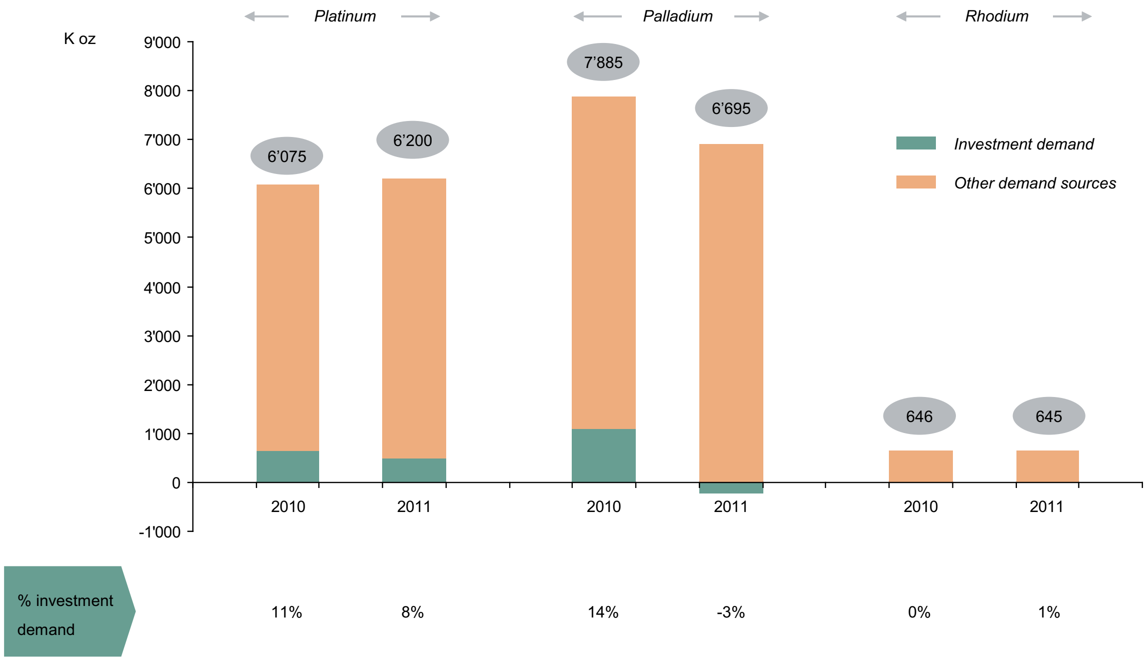
Rhodium is used as an electrical contact material due to its stable contact resistance and high resistance to corrosion in mammography instruments due to the X-rays the process produces and in detectors to measure neutron flux levels. Due to the highly variable nature of this source of demand and its relatively insignificant weight, we have assumed no growth in this sector through to 2014.

RHODIUM DEMAND FROM INVESTMENT

Like Platinum and Palladium, Rhodium is primarily used in autocatalytic converters. Unlike Platinum and Palladium, however, investment demand for Rhodium is in its infancy. Figure 3 shows the investment demand for the three metals as a proportion of total demand in 2010 and 2011. With no investment demand in 2010 and just 1% of total demand in 2011, Rhodium is clearly only just starting to be considered as an investment asset. It is interesting to note that while investment demand for Platinum as a proportion of total demand has remained fairly stable at around 10%, Palladium dramatically fell from favor in 2011. Since Exchange Traded Product investment demand is mostly down to inflows into ETPs, this suggests that Palladium investors are much more tactical in their allocations compared to the more *"buy-and-hold"* nature of Platinum investors. While Rhodium prices are likely to be as volatile as those of Palladium investor demand for Rhodium is likely to be of *"buy-and-hold"* nature given its nascent role as an investment asset. Moreover, the limited liquidity offered by the few Rhodium investment vehicles is not conducive to excessive trading.

[1] Source: Johnson Matthey 2011 Platinum Review.
[2] http://www.independent.co.uk/news/people/hit-and-run/hit--run-ring-the-changes-1044166.html

Figure 3 – Investment demand versus total demand for Platinum, Palladium and Rhodium

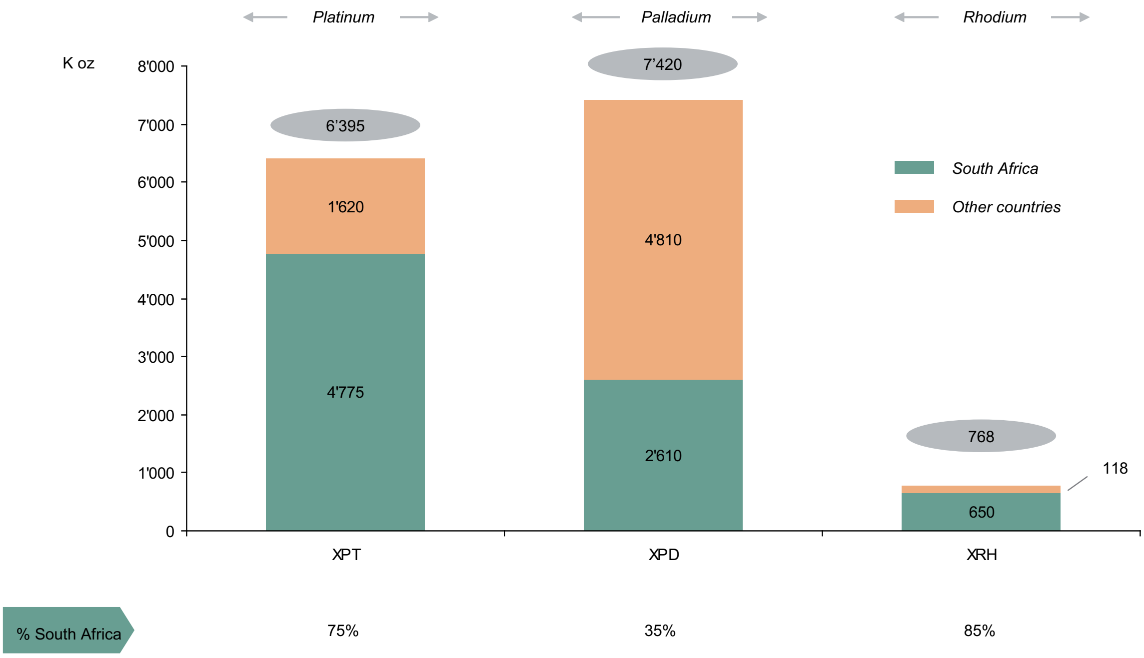


Source: Bloomberg, UBP

RHODIUM SUPPLY

Figure 4 shows the proportion of total Rhodium supply coming from South Africa, and that Rhodium has a greater link to the macroeconomic situation in South Africa than Platinum and Palladium. While South Africa accounts for 75% and 35% of Platinum and Palladium supply respectively, it accounts for 85% of Rhodium supply.

Figure 4 – South African supply relative to total supply in 2011



Source: Bloomberg, UBP

The information contained herein is based on sources deemed to be reliable, though UBP offers no guarantee of its accuracy or completeness

SUPPLY-DEMAND BALANCE

Figure 5 shows the actual supply-demand balance for Rhodium from 2007-11 and our expectations until 2014. As a result of the conservative assumptions we made above, we expect the market to be in surplus through to 2014. However, we expect the rate of stock accumulation to fall from its current levels over this period.

Figure 5 – Supply-demand for Rhodium for 2007-11 (in thousand ounces, actual[3]) and 2012-14 (UBP forecast)

	2007	2008	2009	2010	2011	2012 F	2013 F	2014 F
Supply	824	695	770	734	768	752	738	725
Total demand	844	670	529	646	645	657	639	623
Autocatalyst[4]	695	541	432	486	445	449	426	405
Chemical	63	68	54	67	72	72	72	72
Electrical	3	3	3	4	6	6	6	6
Glass	59	34	19	68	85	94	98	103
Other	24	24	21	21	37	37	37	37
Change in stock	-20	+25	+241	+88	+123	+95	+98	+102

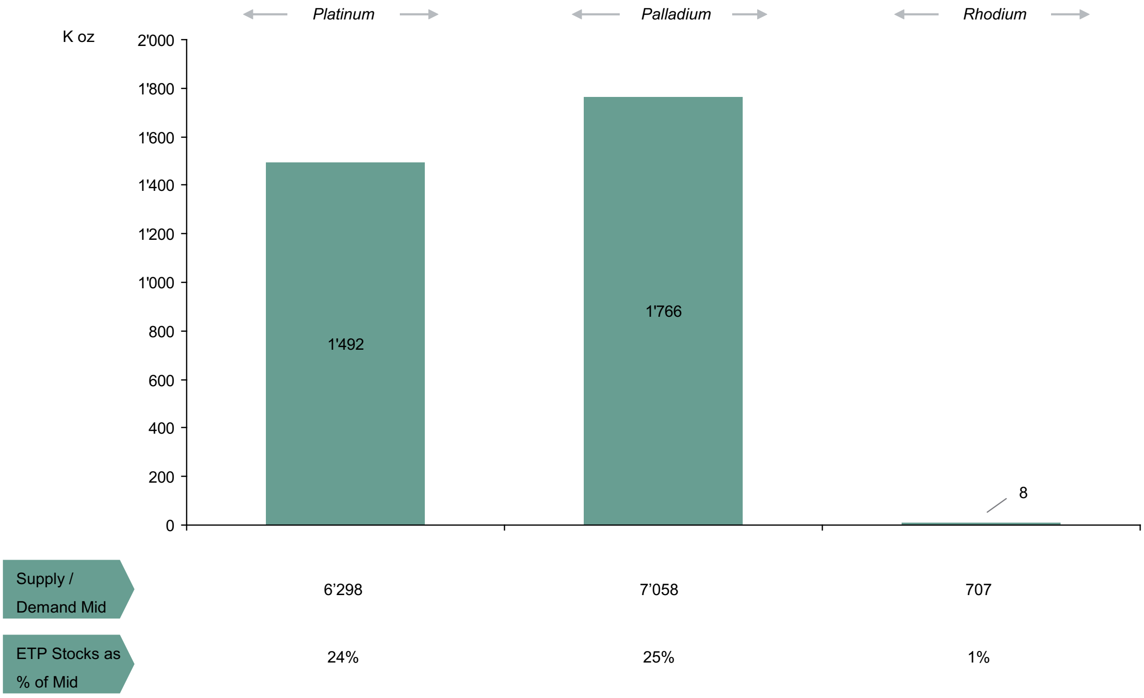
In these supply-demand models we are not trying to accurately predict the exact balance but rather to understand whether our estimation is for a net surplus or a deficit. In this respect, while our models predict declining mining output, our supply volumes remain optimistic. To be precise:

- We assume output from South Africa to fall by 3% per year through 2014. We believe that this is optimistic given that Impala – the world's largest Platinum and Rhodium miner based in South Africa's accounting for about 25% of total Platinum supply – has already suffered severe output disruptions due to illegal strikes at its mines in 2012. Moreover, while the country seems to be moving away from the radical aim of nationalizing its mining industry, a proposal has been made to introduce a super-profit tax on mining earnings, which is as likely to spook investors as nationalization. South African Rhodium output fell by -1.7% per year between 2007-11.
- We predict that output from Zimbabwe, which grew by 19% per year between 2007-11, will grow by 10% per year. While this may seem conservative, President Mugabe intends to nationalize the mining industry and expropriate the profits of precious metal mining conglomerates, as he has already done with agriculture and diamonds.
- We assume output from North America will keep growing by 15% per year until 2014. After falling by 33% in 2010, the supply of Rhodium doubled in 2011 and looks set to keep growing due to a renaissance in the US mining sector. Compared to virtually all other jurisdictions, the US offers a more stable legislative framework and body of regulation that – while being more expensive to comply with due to the multiple (and worthy) environmental constraints – at least gives corporations more stability in their cost projections and production forecasts. However, North America only accounts for 3% of global Rhodium production.

Note that we have not factored in investment demand to our calculations. While this is currently virtually non-existent, this could change quickly. For example, the overall surplus for Rhodium in 2011 was estimated by Johnson Matthey to be 123'000 oz and is likely to remain at around 100'000 oz according to our estimates until 2014. At a spot price of USD 1'500 / oz, this equates to USD 150 mn. Meanwhile, the average daily net inflow into Gold ETFs in 2011 was about USD 40 mn. If the one ETP (Rhodium Exchange-Traded Product) in existence saw just three days of such volumes, the whole metal balance would shift into deficit.

[3] Source: Johnson Matthey 2011 Platinum Review.
[4] Reported as demand net of recycling.

Figure 6 – Ounces held by ETPs versus average between supply and demand by metal in 2011



Source: Bloomberg, UBP

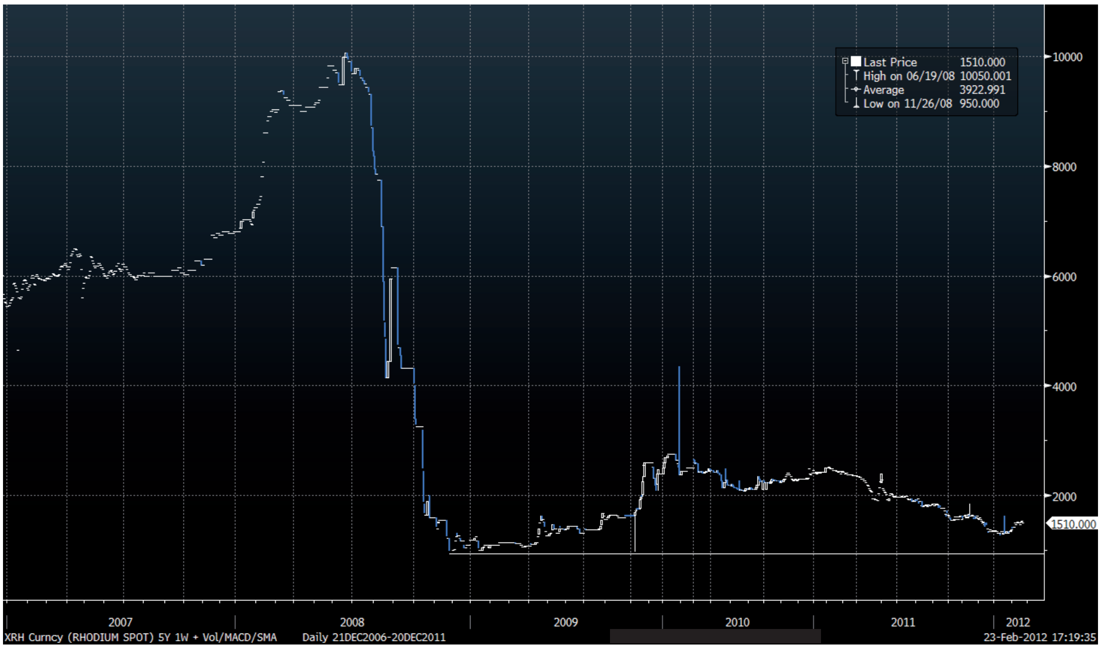
To consider in more depth how investment demand can affect price volatility, it is worth looking at the ratio between metal ounces held by ETPs and the average between supply and demand for each metal, as shown in Figure 6. The higher the ratio, the more important investment demand is as a driver of price and (more importantly) volatility. While Platinum and Palladium ETPs represent about a quarter of demand for these metals, they only represent 1% of total Rhodium demand. Also, while according to JP Morgan[5] there are 57, 35, 18 and 15 investable Gold , Silver, Platinum and Palladium ETP share classes, there is only one ETP for Rhodium.

TECHNICAL ANALYSIS

After an abrupt price fall in 2008, when Rhodium fell by 90% from a high of USD 10'000 / oz to a low of USD 950 / oz in about 20 weeks, a long consolidation period has acted as a much needed basing period for the market to trade normally again, as Figure 7 shows. After more than three years within a USD 950-2'700 / oz range, Rhodium has finally broken its 2011 upper resistance line at USD 1'550 / oz, as shown in Figure 8. This is bullish for Rhodium in our view.

[5] JP Morgan ETF Global Select Tool, February 2012.

Figure 7 – Rhodium prices, 2007-12

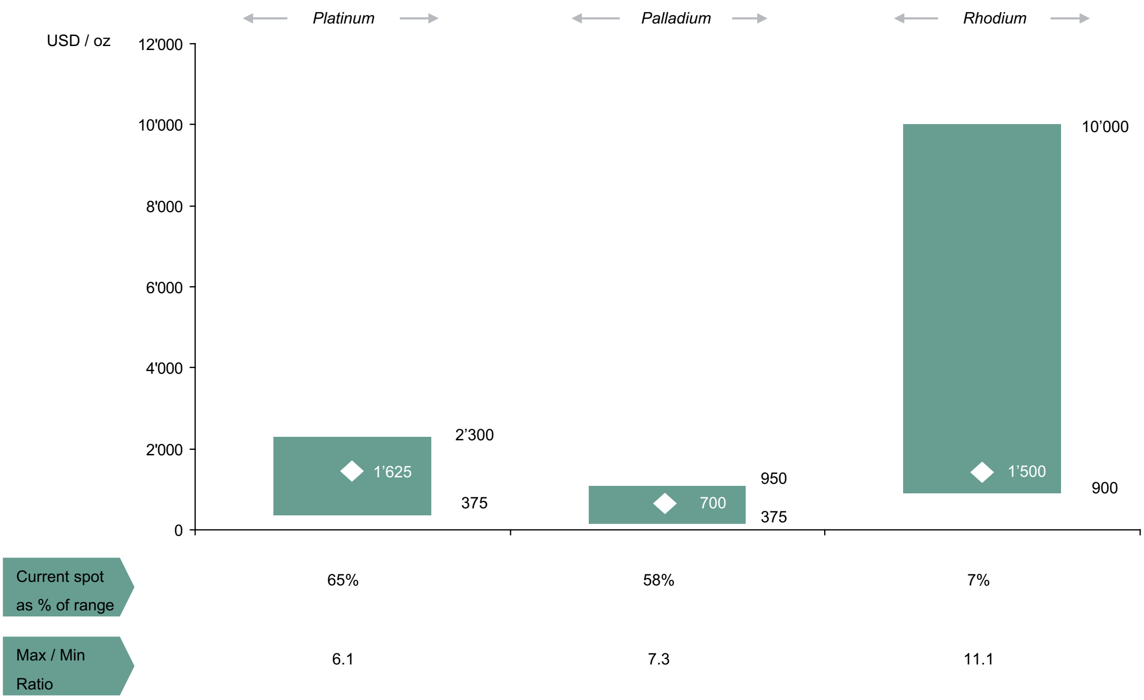


Source: Bloomberg

Figure 8 – Rhodium has broken its 2011 upper resistance trendline

Source: Bloomberg

Figure 9 – Current spot prices and min-max range between 2000-11



Source: Bloomberg

This may lead to the false impression of Rhodium trading in a narrower range than Platinum and Palladium, mostly due to the lack of investment demand and consequent dry liquidity in the spot market. However, Rhodium has in fact experienced a much wider trading range and much higher realised volatility during the past decade. Figure 9 shows current spot prices (mid-February 2012) and the range of prices between 2000-11. The chart shows that the min-max range for Rhodium is 16 and 5 times the corresponding range for Palladium and Platinum respectively.

Figure 9 also shows that if you are a believer in assets retesting their highs and lows, you may buy Rhodium rather than Platinum or Palladium, Rhodium is just 7% off its all-time lows compared to 65% and 58% for Platinum and Palladium respectively.

CONCLUSION

In a nutshell, we believe that Rhodium is undervalued both in absolute and relative terms. Given its unique properties in the autocatalytic sector and unmatched prestige as a jewelry component, Rhodium should trade at multiples of Platinum and Gold rather than at a discount to both. Nascent mainstream investor demand bodes well for Rhodium prices as it has the potential to unleash the same kind of demand that has been partially responsible for driving Gold , Platinum and Palladium prices to where they are today.

Should investor interest in Rhodium grow, we believe that the impact on prices will be much greater than on other precious metals, since the average value of supply demand figures is around USD 1 bn for Rhodium compared to USD 12 bn and USD 230 bn for Platinum and Gold respectively.

Moreover, the higher proportion of Rhodium supply coming from South Africa – a country we have analyzed in previous issues of this publication – than for Platinum and Palladium makes the case even more compelling as country-specific supply shocks could have a more pronounced effect on Rhodium than on Platinum or Palladium.

An investment in Rhodium at current prices is justified from the value perspective, since it trades at considerably low values with respect to Gold and Platinum. The catalyst to unlock the value and trigger a price increase could be coming from investment demand. Even a modest interest in this metal as an investment vehicle could tip the supply/demand balance into serious deficit.

In spite of all the above, we fail to see a fundamental that could unlock the realization of Rhodium's unique value at current prices. 'While lack of evidence is not evidence of a lack', we would recommend investors who wish to enter now to arm themselves with plenty of patience.

APPENDIX – A PRIMER ON PGM USAGE IN AUTOCATALYSIS

There are basically three gases coming out of a motor engine that you want to get rid of before they make it to the atmosphere: Carbon Monoxide (CO), Nitrous Oxides (NO and NO_2 , abbreviated as NO_X) and unburned hydrocarbons (HC). Although being a chemical substance that is naturally produced by living organisms and plays a useful role as a neurotransmitter, CO is accountable for the most fatal air poisoning causalities in many countries[6]. It's especially dangerous since it's tasteless, odorless and colorless. By binding to hemoglobin, CO prevents oxygen molecules from doing the same and being carried to internal organs. Concentrations of 667 parts per mn in volume (ppm) can cause about 50% of the body's hemoglobin to stop carrying its vital function[7] and is enough to cause seizure, coma and fatality. To put those levels in perspective, consider that the average level of CO in the whole atmosphere is around 0.1 ppm, the one measured close to car exhausts in Mexico City is around 100-200 ppm and that the exhaust from a home wood fire contains around 5'000 ppm.

Getting to cleaner exhaust gases is achieved by making undesired gases react in order to transform them in less poisonous substances. For CO and HC, an oxidation reaction is performed (also referred as combustion) in order to transform them in Carbon Dioxide (CO2) and water according to the scheme below.

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad (1)$$

$$C_xH_{2x+2} + [(3x+1)/2]\, O_2 \rightarrow x\, CO_2 + (x+1)\, H_2O \quad (2)$$

On the other hand, NO_X are 'reduced' into nitrogen and water.

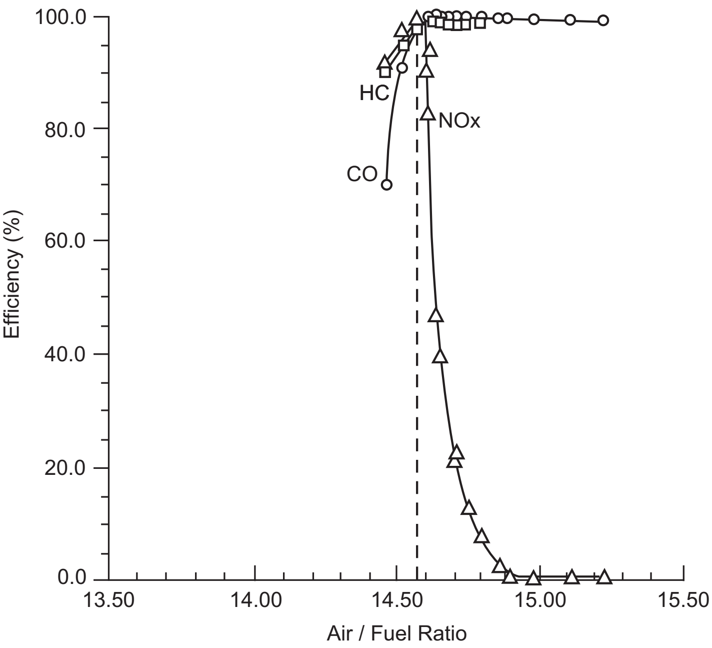
$$2NO_X \rightarrow xO_2 + N_2 \quad (3)$$

Oxidation and reduction reaction are opposite to each other. While during an oxidation the reactant is 'giving away' electrons to oxygen molecules, the opposite occurs during a reduction. Because of this, while oxygen is a product of a reduction reaction (i.e., stays on the right of the arrow in (3)), it is a reactant of a combustion reaction (i.e., it is needed for the reaction to occur and therefore stays to the left of the arrow in (1) and (2)). While an environment rich in oxygen stimulates reactions (1) and (2), it creates an obstacle for reaction (3) to occur. Fortunately, a patent filed in the 1960s proved that if the pollutants to be oxidized (CO and HC) are matched in exact quantities by the pollutants to be reduced (NO_X), the thermodynamic equilibrium foresees all CO and HC to be oxidized into CO_2 and $H_2$2 and all NO_X to be reduced to N_2[8]. The challenge thus became two-fold. First, how to ensure that the gas mixture contained the exact proportion required for the thermodynamic equilibrium to consist in the full completion of (1), (2) and (3). Second, how to ensure that – once the thermodynamically-desired equilibrium is theoretically achieved – reactions (1), (2) and (3) do indeed proceed towards such equilibrium at an adequate speed in order for all gases to be converted in satisfactory proportions before being released in the air.

To illustrate the delicacy of solving the first challenge, consider Figure 10 where the gas conversion efficiency (measuring the degree to which pollutants can be converted according to (1), (2) and (3)) is depicted as a function of the air to fuel ratio (A/F) in the exhaust mix. The measurements were taken by letting the engine run at constant levels of 2'000 rpm and load of 55 ft-lb. The graph was taken from a review article on Rhodium's role in the autocatalytic sector[9]. Small oscillations around the optimal point cause unacceptable declines in efficiency ratios. The commercial availability of oxygen sensor devices at affordable prices has allowed manufacturers to add closed-loop feedback controllers to regulate the A/F ratio in a very tight range around the optimal point. A series of factors can alter the A/F ratio coming into the exhaust. For example, hard accelerations are known to briskly reduce the A/F ratio as the proportion of unburned hydrocarbons suddenly increases.

[6] Omaye ST (2002), "*Metabolic modulation of carbon monoxide toxicity*", Toxicology 180 (2): 139–150.
[7] Tikuisis, P; Kane, DM; McLellan, TM; Buick, F; Fairburn, SM (1992), "*Rate of formation of carboxyhemoglobin in exercising humans exposed to carbon monoxide*", Journal of Applied Physiology 72 (4): 1311–9.
[8] G. P. Gross, W. F. Biller, D. F. Greene, and K. K. Kearby, U.S. Patent 3,370,914.
[9] Shelef, M.; Graham, G. W. (1994), "*Why Rhodium in Automotive Three-Way Catalysts?*", Catalysis Reviews 36 (3): 433–457.

Figure 10 – Gas conversion efficiency as a function of air / fuel ratio



Source: Bloomberg

To solve the second challenge a catalyst is used, which can accelerate the reaction speed towards equilibrium. By definition, catalysts do not alter thermodynamic equilibrium. They are simple accelerators that allow chemical reactions to occur faster.

All PGMs are used as catalysts to promote the speed of the aforementioned chemical reactions. While Rhodium is known to favor reduction reactions such as (3), Palladium selectively favors oxidations like (1) and (2). Platinum is used both for reduction and oxidation.

Rhodium offers distinctive properties as a catalyst. Around the optimal A/F ratio, Rhodium is highly selective in two respects. First, it allows NO to compete with O_2 as a reductant, which means that NO can act as the oxidizing agent for CO in (1) instead of O_2 according to the alternative pathway below

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad (4)$$

Second, it favors (3) as opposed to the undesired alternative

$$2NO + 3H_2 \rightarrow 2NH_2 + O_2 \qquad (5)$$

which would lead to ammonia (NH_3) being released in the atmosphere. Rhodium appears to be better at favoring (3) because of its dissociative absorption properties towards NO. That is, Rhodium – more so that Platinum and Palladium – is better at breaking N2 and O2 from NO. This occurs after NO (as a gas) desorbs from Rhodium (a solid) after having been temporarily retained in its close proximity. Rhodium-Platinum alloys were found to perform less well than their individual constituents. Infrared spectroscopy studies revealed that Platinum is much more affine in absorbing CO than NO, which ultimately prevents (4) from happening and reduces Platinum's effectiveness (compared to Rhodium) in promoting (3). In general, the addition of Platinum and Palladium to Rhodium favors oxidation but increases the amount of ammonia (NH_3) as a by-product, thus further narrowing the optimal operating window depicted in Figure 10.

Rhodium exhibits a higher resistance to sintering and sulfur poisoning than Platinum. Sintering is a physical degradation process that occurs after several hours of operation at high temperatures. Crystals start growing on the autocatalyst's washcoat surface and pores start collapsing, leading to an overall reduction in the catalytic surface. Sulfur particles in the exhaust form a permanent bound to the autocatalytic surface, thus deactivating their functionality. Sulfur poisoning is not an issue of the same magnitude as it used to be few years ago. First and foremost, sulfur can be removed from the active surface by subjecting the autocatalytic surface to very high temperatures. Second, commercially available fuels contain significantly less sulfur compared to 10 years ago.

Back in January 94, an oz of Rhodium was 3 times more expensive than an oz of Platinum. It is therefore understandable how back then a significant research effort had been unleashed to substitute the more expensive Rhodium with Platinum and Palladium. Palladium had seemed the most obvious candidate. Not only it is chemically more similar to Rhodium than Palladium, but it turned out that in order to maintain the same width in the operating window than pure Rhodium, about 2 to 5 times the weight of Rhodium was needed for comparable efficiency in using Palladium. Given that back then the Palladium to Rhodium price ratio had oscillated in the range 1/20 to 1/8, the substitution attempt had been deemed worthwhile. Higher levels of rare earth oxides such as ceria and lanthana were found to improve the catalyst efficiency since they act as oxygen buffers. Under low A/F ratios, such oxides release oxygen in the mixture, thus effectively widening the optimal operating window of Figure 11.

A reasonable idea on how to achieve the same pollutant reduction efficiency while striving to reduce total costs consists in finding base metal substitutes for some of the functions performed by noble PGM metals. While it has been demonstrated that 15-20% weight compositions of molybdenum oxide added to PGM metals can achieve the same efficiency of a PGM-only catalyst, two challenges existed, one of which has been removed. First, the oxides are easily inactivated by sulfur rich gasoline, a problem that has been completely removed by lowering the amount of sulfur that is tolerated in the mix. The second problem is more challenging and is due to the fact that under normal operating temperature molybdenum and tungsten (the other base metal utilized) react to become oxyhydroxides, which tend to vaporize and join exhaust gases, creating unacceptably toxic exhausts.

The advent of lean burn gasoline and diesel engines permanently impaired Rhodium demand. In both cases, the combustion cycle results in exhaust mixtures that are way leaner (i.e., richer in air) than normal gasoline engines. In lean burn gasoline engines this is due to the fact that such engines are fueled with an A/F mixture that is way leaner to start off in order to achieve a reduction in fuel consumption of around 15-20%. Diesel produces exhausts that are leaner than in gasoline engines due to the difference in the ignition process (compression for diesel, spark for gasoline) and combustion cycles.

In both circumstances, the exhaust is too rich in oxygen for (3) to be favored. Therefore, to solve for (3) manufacturers either add NO_X-traps or Selective Catalytic Reduction (SCR) elements to a classic oxidation catalyst that will in turn perform (1) and (2). Since the catalyst is not asked to achieve the balance that is necessary for NO_X reduction to occur, a simpler Platinum or Palladium based catalyst can be used.

Under normal operating conditions, NO_X traps absorb NO and NO_2 on their surface. Once the surface's empty pores are fully occupied, a rich mixture is injected onto the trap, which regenerates the surface by forcing the release of NO and NO_2 into the air and triggering (3). A purging cycle may last for about 10 sec every 5 km and is literally imperceptible by drivers. While NO_X-traps use PGMs (usually a mixture of Rhodium and Platinum) to selectively favor (3), the SCR approach uses ammonia to reduce NO_X according to the reaction below

$$NOx + NH_3 \rightarrow N_2 + 3/2\ H_2O + (x\text{-}3/2)\ ½\ O_2 \qquad (6)$$

Ammonia is not inserted directly, but is obtained by urea according to the reaction below

$$(NH_2)\ _2CO + H_2O \rightarrow 2\ NH_3 + CO_2 \qquad (7)$$

SCR techniques do not use PGMs. Given that (3) is taken care by alternative methods that do not required high catalytic selectivity for reduction reactions, Rhodium has been gradually substituted for Platinum and Palladium. While NO_X traps were common practice for lean burn gasoline engine, they were still second choice compared to the preferred SCR method in diesel engines[10].

Another phenomenon that happened over time is the substitution of Platinum with Palladium in gasoline engines. Historically Platinum had been preferred to Palladium due to its higher stability in high oxidizing environments, e.g., in diesel engines. In such environments Palladium was found to degrade to its less effective Palladium oxide form and was therefore disregarded for a long time. However, Palladium was a more cost effective solution in the more reducing environment of a gasoline engine, where the highly oxidizing environment does not threaten Palladium's role in the catalytic process. Platinum also has the advantage of being more resistant to organic sulfur compounds, which tend to deactivate the catalytic converters pores by binding to their surface. But when temperatures are high (as it is in the gasoline cycle), Palladium performs reasonably well as can be used instead of the more expensive Platinum because organic sulfur compounds find it more difficult to bind to pores. That also explains why Platinum remains to date the preferred component in autocatalytic converters for diesel engines, since Platinum engines (and their exhaust) operate at lower temperatures.

[10] Source: Johnson Matthey 2007 Platinum Review.

Small amounts of Palladium help stabilize Platinum in a diesel autocatalytic converter and delay the sintering process that is responsible for catalytic ageing over time. That is why Platinum-Palladium alloys are encountered way more frequently than Platinum-only catalyst despite Platinum's superior performance as the catalyst of choice in diesel engines.

Sulfur oxides in diesel emissions had historically prevented higher concentrations of Palladium to be used up until recently, since Palladium is easily de-activated by such substances. However, tighter regulations have gradually imposed lower sulfur content in diesel fuel, making the matter a non-issue. Consider that while about 500 ppm of sulfur content was tolerated around Europe in the 1990s, such limit is 10 ppm since February 2009.

A positive factor that stimulated higher Palladium usage in catalytic converters is also related to the need for Diesel Particulate Filters (DPFs) at the end of the diesel catalytic cycle. Since diesel engines operate at lower temperatures, a significant proportion of carbon particles (soot) are present in the exhaust. These particles are removed to comply with emission requirements by having the exhaust run through a DPF, whose cavities retain carbon-rich molecules. To prevent the DPF from accumulating an excessive amount of carbon – which will ultimately increase the engine back-pressure to intolerable levels – the engine is run for brief periods at higher temperatures, which lead to the oxidation of the unburned hydrocarbons retained in the DPFs. At these higher temperatures any sulfur oxide that had been retained by Palladium and threatened its efficiency is easily released. Diesel catalysts containing Palladium were first introduced in 2005. The Platinum : Palladium ratio currently used in diesel catalyst has decreased to current levels of 2:1 in weight terms. A lower limit on how far the ratio can go seems to be represented by the fact that Platinum remains superior to Palladium in favoring (2).

This means that if Rhodium prices stay below Platinum and the Palladium / Platinum ratio is not excessive, one might expect manufacturers will switch back to use Rhodium for reductions and Palladium for oxidations, thus removing the need for Platinum altogether. The Palladium to Platinum ratio must remain below 0.4 for this scenario to occur, because for every ounce of Platinum substituted, about 2.5 ounces of Palladium are needed to get the same results. The current Palladium / Platinum ratio trades at precisely 0.4 levels right now.

CONTACTS

Eric SCHREIBER	+41 (58) 819 2548	esc@ubp.ch
Andrea GENTILINI	+41 (58) 819 2519	gea@ubp.ch
Cristiano MIGLIORINI	+41 (58) 819 2541	mcr@ubp.ch
Anne MIKULOVIC	+41 (58) 819 2871	ami@ubp.ch

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UNION BANCAIRE PRIVÉE, UBP SA

Rue du Rhône 96-98 | CP 1320 | 1211 Geneva 1, Switzerland
ubp@ubp.ch | www.ubp.com