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The Solubility of Palladium (Pd) in Crude Oil at 150, 200 and 250 °C and its Application to Ore Genesis

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1. Abstract

Although most economic palladium deposits occur in mafic igneous rocks and are the products of magmatic processes, there are a number of polymetallic deposits hosted by organic-rich (bituminous) black shales in which the palladium reaches exploitable concentrations. Considering that palladium is rarely concentrated by hydrothermal processes, and as organic-rich black shales are the source beds for the production of hydrocarbons and bitumen commonly records the path taken by these hydrocarbons, it is reasonable to entertain the possibility that liquid hydrocarbons may act as an ore fluid for palladium. In order to test the potential of liquid hydrocarbons to act as ore fluids, Pd (0) metal wires were reacted with three crude oils, A, B and C (A being the lightest and C being the heaviest crude oil), at temperatures of 150, 200 and 250 ˚C. After reaction at 150 ˚C, the Pd concentrations in crude oils A, B and C were 60 ± 20 ppb, 19 ± 4 ppb, and 128 ± 29 ppb, respectively. The corresponding concentrations at 200 ˚C, were 18 ± 6 ppb, 17 ± 6 ppb, and 50 ± 15 ppb, respectively, and at 250˚C, were 16 ± 2 ppb, 11 ± 1 ppb and 26 ± 2 ppb, respectively (n = 3). The measured solubility of Pd was highest in the heaviest crude oil, C. All three oils reached their maximum Pd concentration at 150 ˚C, with Pd concentration decreasing progressively as temperature increased to 250 ˚C. To gain insights into the mechanism controlling the dissolution of Pd in crude oil, we analyzed the reacted Pd wires using X-ray Photoelectron Spectroscopy (XPS). The XPS spectrum displays a well-defined thiol (R-SH) peak at a binding energy of 163eV, which indicates that Pd has an affinity for reduced organosulfur compounds. Moreover, Pd concentrations were observed to increase with the total thiol content of the oil, thereby corroborating the results of the XPS analyses. Our results clearly show that Pd solubility in crude oil is promoted by the presence of thiols. As thiol-rich hydrocarbons usually develop in deep, high temperature (100 to 140 °C) carbonate sequences containing abundant sulfate mineralization, it is thought that the thiols are the products of thermochemical sulfate reduction (TSR) (Machel, 2001). We therefore propose that liquid hydrocarbons, which have interacted with sulfate at relatively high temperature, may serve as effective ore fluids for palladium.

2. Introduction

Platinum group elements (PGE) are intimately associated with hydrocarbons in a number of ore deposits. One such deposit is the Polish Kupferschiefer, in which palladium (Pd) and platinum (Pt) concentrations in the clay-organic matrix of the black shales reach 1,900 and 600 ppm, respectively (Kucha and Przybylowicz, 1999). In the Kupferschiefer, platinum group elements are particularly enriched in a variety of pyrobitumen known as a thucholite, which is composed primarily of thorium, uranium, carbon and hydrogen (Th, U, C, H; Barthauer et al., 1953). Palladium and platinum concentrations in the Kupferschiefer thucholite can be as high as 5,000 and 1,770 ppm, respectively (Vaughan et al., 1989; Kucha and Przybylowicz, 1999). Lower, but nevertheless significant concentrations of Pd and Pt have been reported for black-shale-hosted deposits in the Zunyi district, Guizhou province, China, namely 0.4 and 0.3 ppm, respectively (e.g., Coveney, 1991; Coveney et al., 1992; Lott et al., 1999). In a similar black shale-hosted deposit in the Yukon, Canada, the Nick Prospect, Pd and Pt concentrations reach 0.9 and 0.7 ppm, respectively (Jowitt and Keays, 2011). Both the Zunyi deposits and the Nick prospect also contain percentage levels of Ni, a metal that is sparingly soluble in hydrothermal fluids (Liu et. al., 2012) but is highly soluble in petroleum (Jones, 1975). It is therefore attractive to consider the possibility that instead of being transported in hydrothermal fluids, as has been generally assumed, the PGE (and Ni) in these deposits were concentrated by liquid hydrocarbons. Support for this idea, in the case of the Kupferschiefer deposit, comes from the fact that the ores formed at temperatures of 80 – 140 ^{o}C (Oszczepalski, 1999), which coincide with those of the oil window, and accumulations of polyaromatic sulfur hydrocarbons in the sulfide ore of the Polish Kupferschiefer (Püttmann and Goβel, 1990) suggest the influx of sulfur-rich crude oil into the ore zone from deeper Carboniferous sequences.

Arguably, the best evidence for the association of PGEs with hydrocarbons is provided by the Boss deposit in Nevada, U.S.A, which is hosted by bituminous dolomitic limestones (Knopf, 1915); the bitumen is interpreted to have formed from liquid hydrocarbons that are thought to have impregnated the limestones (Jedwab et al., 1999). Most of the PGE is concentrated in bitumen within fine-grained siliceous "ore shoots" that cut the limestone and contain an average of 660 ppm Pd, 150 ppm Pt and 1315 ppm Au. Transmitted Electron Microscopic (TEM) imaging showed that the PGEs are dispersed in the bitumen as nanoparticles of potarite, an alloy of Hg {(Pd_{81}, Au_{13}, Pt_{01}) Hg}, although they are also present in appreciable concentrations in bitumen that is apparently devoid of nanoparticles (Jedwab et al., 1999).

Despite the potential involvement of liquid hydrocarbons in the formation of the aforementioned PGE deposits, there have been no experimental studies of the solubility of these metals in this medium. Indeed, the only experimental study that bears on the topic is that of Plyusnina et al. (2000), who evaluated the capacity of organic matter to adsorb Pt from aqueous solutions. This study showed that at 200 and 400 °C, 0.02 and 1.95 g Pt was adsorbed per kg of organic matter (20 and 1950 ppm), respectively.

In this study, we report the results of experiments designed to determine the solubility of Pd in crude oils (Pd (0) wire) at temperatures of 150, 200 and 250 ˚C and saturated vapour pressure. Based on hard-soft-acid-base (HSAB) theory (Pearson, 1963), Pd is a soft acid and is expected to react with soft bases, such as reduced sulfur compounds. The oils were therefore selected to provide a range of compositions, particularly in respect to sulfur content. The results are encouraging and show that liquid hydrocarbons can dissolve Pd in concentrations sufficient for them to constitute ore fluids.

3. Crude Oil Characterization

Three crude oils, A, B, and C were supplied by Statoil for this study. The crude oils were selected so as to provide a range of properties and compositions, i.e., API gravity, total acid number (TAN), the proportions of paraffins, naphthenes, aromatics and asphaltenes, and the contents of sulfur (S) and nitrogen (N). These are reported in Table 1.

Table 1. The characteristics and compositions of three crude oils, A, B and C, employed in our current experimental study.

Parameters	Oil A	Oil B	Oil C
API Gravity	26.6	25	19
Specific Gravity	0.895	0.904	0.94
Sulfur (wt.%)	0.84	0.52	0.82
Thiols/sulfides (ppm)	44	0	52
Thiophenes/Disulfides (ppm)	1401	37	1052
Benzothiophenes (ppm)	3892	1884	3164
Dibenzothiophenes (ppm)	2575	2737	2024
Benzonaphtothiophenes (ppm)	490	549	109
Nitrogen (wt.%)	---	0.2	0.44
TAN (mgKOH/g)	0.2	2.9	2.3
Paraffins (wt.%)	---	37	19
Naphthenes (wt.%)	---	49	65
Aromatics (wt.%)	---	13	15
Asphaltenes (wt.%)	1.6	0.3	1.4

Crude oil is a complex mixture of organic and inorganic constituents, i.e., paraffins, naphthenes, aromatics and asphaltenes, together with inorganic constituents such as S, N, trace elements and silicate minerals (Manning and Gize, 1993). The proportions of the different organic constituents determine the API gravity, an inverse measure of the density of oil relative to that of water (Speight, 2001). Crude oils are most simply distinguished by their API gravity. In this study, A is the lightest (highest API number) and C the heaviest (lowest API number) crude oil that was considered (Table 1). A parameter that is important in controlling metal uptake by crude oil is the S content, as the thiol group (-SH) is known to be involved in the formation of organometallic complexes (Lewan, 1984; Giordano, 1994; Speight, 2001). The crude oil with the lowest S content is crude Oil B (0.52 wt.%) and that with the highest S content is crude Oil A (0.84 wt.%); crude Oil C has a S content very similar to that of crude Oil A (Table 1). The TAN (mgKOH/g) value, which is a measure of acidity, is also important to quantify because high acidity can lead to the demetallation of organometallic compounds via ion-exchange reactions (Falk, 1964; Buchler, 1978; Manning and Gize, 1993; Giordano, 1994). The TAN values for oils A, B and C are 0.2, 2.9 and 2.3 mg KOH/g respectively. Finally, the nitrogen content is important to know because it is a measure of the porphyrin content, although other nitrogen compounds also may be present, including amine, pyridine, quinolone, pyrrole and carbazole (Tissot and Welte, 1978). The crude oil with the lowest N content is crude Oil B (0.2 wt.%), and that with the highest N content crude is crude Oil C (0.44 wt.%; Table 1).

4. Methodology

4.1. Experimental Methods

The experiments were performed at 150, 200 and 250 °C and a pressure of approximately 12 bars in quartz reactors prepared by fusing quartz tubing (OD = 12 mm, ID = 10 mm) supplied by National Scientific Inc. (figure 1). Prior to being used, the quartz reactors were cleaned with nitric acid (~75% HNO_3) for 24 hours, neutralized with Milli-Q™ water and dried at 100°C for 2 hours. The palladium was introduced in the form Pd (0) wire, and was placed in a fused quartz ampoule (OD = 9 mm, ID = 7 mm) that had been cleaned using the method employed for the quartz reactors. The ampoule was then placed in the reactor. Aliquots (~0.5 ml) of the three different types of crude oil (A, B, and C) were placed in separate reactors, which were sealed using an oxyhydrogen flame. All weights, namely, those of the quartz reactor before and after introduction of the Pd (0) wire-bearing quartz ampoule and the crude oil, before and after an experiment, were carefully determined using a high precision Mettler M3 analytical balance. The reactors were then placed in a Thermo Scientific^{TM} Thermolyne^{TM} tabletop muffle furnace oven that had been preheated to the desired temperature. The temperature was controlled to ± 1 ˚C.

After an experiment, the reactor was quenched to room temperature in water, opened with a diamond cutter and the Pd (0) wire-bearing ampoule removed with disposable tweezers. The reactor was then prepared for analysis by being stoppered with clean quartz wool to prevent loss of material.

4.2.Analytical Method

The unreacted and reacted crude oils were analysed using a method similar to that described by Sugiyama and Williams-Jones (2018). The crude oils were ashed using a combination of thermal combustion and chemical oxidation, and the residues leached with HCl and analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Fig. 1). Refer to appendix A.1 for further details on the ICP-MS dilutions and data correction.

After an experiment, the Pd (0) wires were retrieved from their reactors, rinsed in toluene and vacuum-dried at room temperature for 24 hours (Fig. 1). The surface composition of the wires was characterized by X-ray Photoelectron Spectroscopy (XPS) on a Thermo Scientific Kα spectrometer, using Al Kα radiation (1486 eV) and an X-ray spot size of 200 μm. Scans were made with a pass energy of 50eV and a resolution of 0.1 eV. The curve fitting analysis was performed using Avantage software version 4.60 with Gaussian–Voigt curves functions and background removal through the Smart method (Castle and Salvi, 2001).

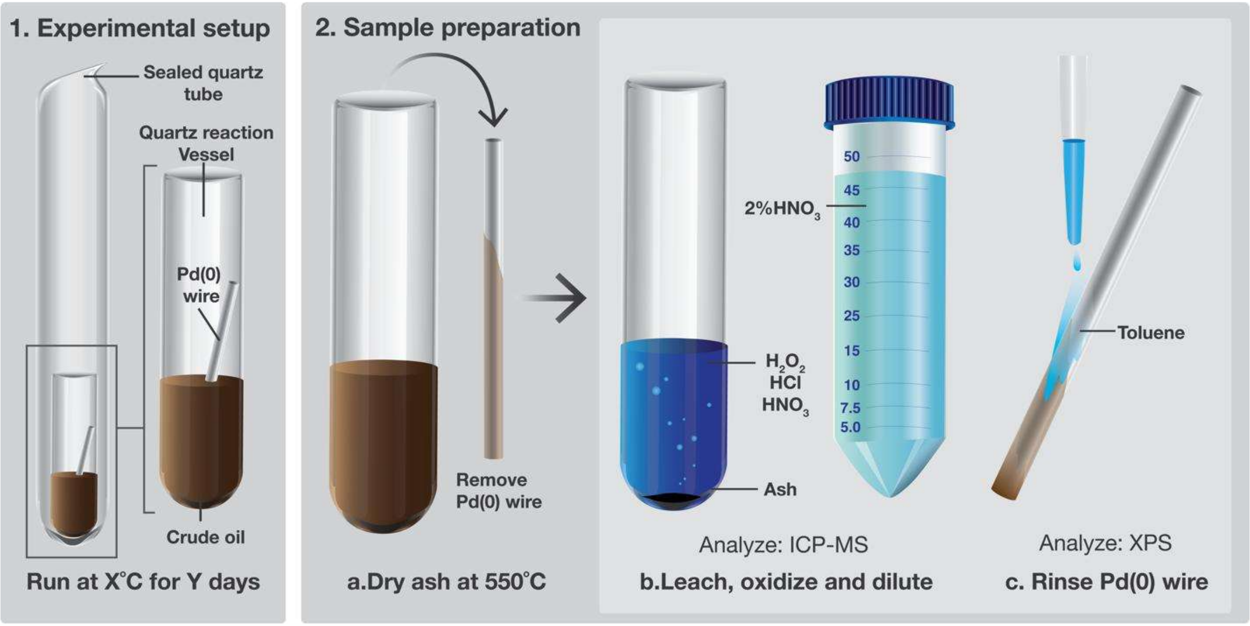

Figure 1. The experimental protocol employed for the investigation of Pd solubility and speciation in oils A, B, and C at 150, 200 and 250˚C.

5. Experimental Parameters

5.1 Temperatures of the experiments

Although the oil window extends from 80 to 160 ˚C (Peters et al., 2004), it is known from pyrolysis experiments (Price and Wenger, 1992), and the entrapment of liquid hydrocarbons in black smokers (Peter and Scott, 1988), that liquid hydrocarbons are stable for protracted periods of time at temperatures above 300 ˚C. We therefore elected to conduct the experiments at temperatures of 150, 200 and 250 ˚C. The lowest temperature of the range was chosen for kinetic reasons, i.e., to ensure that equilibrium was reached in a reasonable amount of time and the upper temperature limit to avoid any risk of thermal degradation of the crude oils.

5.2 Duration of the experiments

To establish the time required for the experiments to reach equilibrium, kinetic experiments were conducted at 150, 200 and 250 °C using crude oils A, B and C. Aliquots of these crude oils were reacted with Pd (0) wire for durations ranging from 1 to 30 days at 150 ˚C and 1 to 15 days at 200 and 250 ˚C, as discussed in Section 5.1, and the Pd concentrations in the crude oils were determined as described in Section 4.2. As is evident from Figure 2, Pd concentrations in the crude oils start to plateau after approximately 5 days. This steady state concentration is interpreted to indicate the attainment of equilibrium. Accordingly, experiments designed to determine the solubility of Pd in crude oils were conducted for durations of 10 or more days at temperatures of 150, 200 and 250 ˚C.

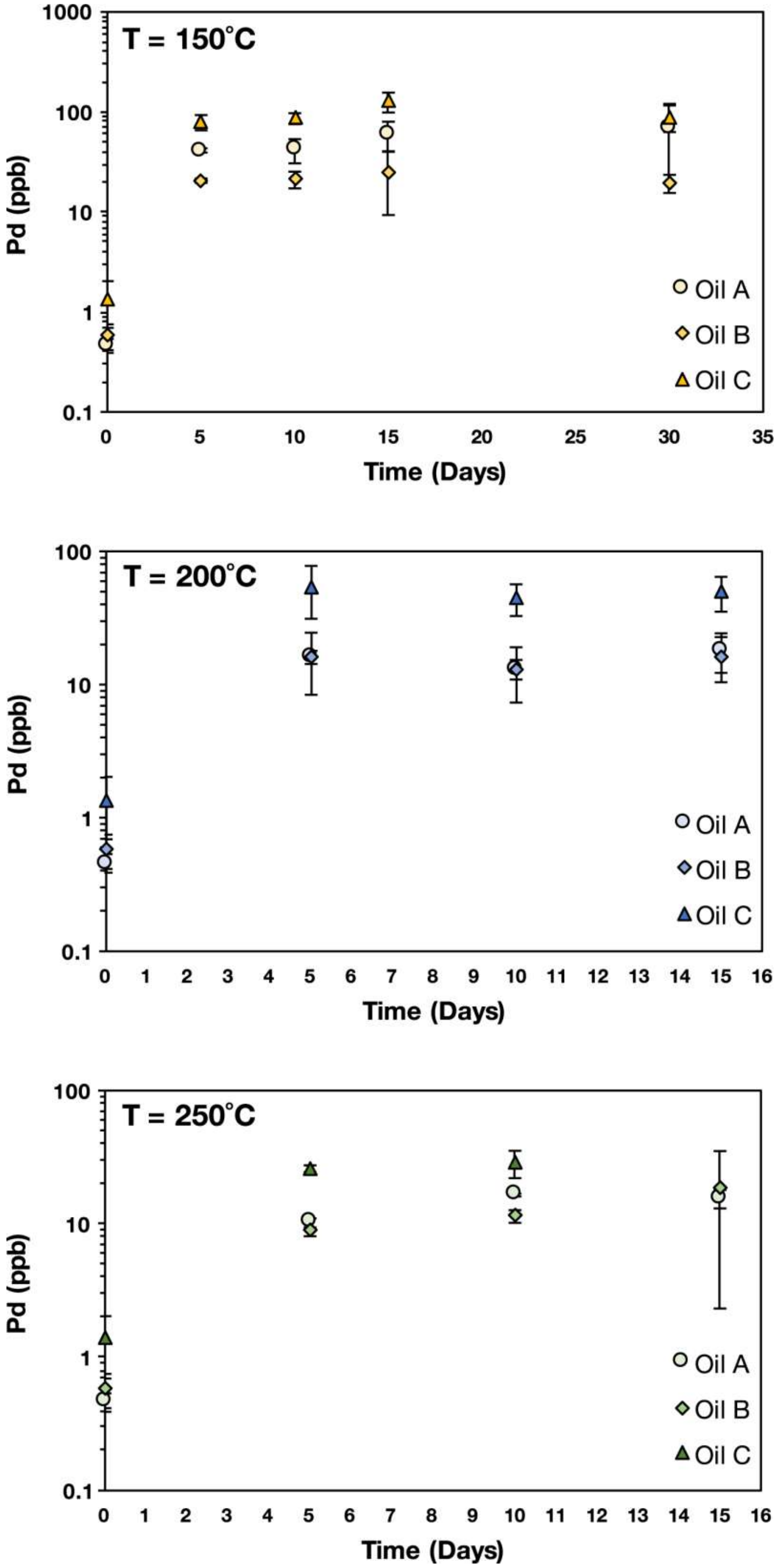

Figure 2. Concentration of Pd in oils A, B and C at 150, 200 and 250˚C as a function of the duration of the experiments.

6. Results

6.1 Results from the Palladium Solubility Experiments

From Table 2, it is evident that the Pd concentration in each crude oil decreased progressively with increasing temperature. It is also evident that the composition of the crude oil plays a key role in controlling Pd solubility. These differences in Pd concentration can be accounted for largely by differences in the thiol content and perhaps also the asphaltene content of the oils. Oil C has the highest thiol content of the all the oils and dissolved the highest concentration of Pd at each temperature tested followed by Oil A which has the second highest thiol content. Oil B, which has no detectable thiols dissolved a comparatively small yet still appreciable amount of Pd (19.5 ppb of Pd at 150 ˚C) relative to its counterparts, Oil A and Oil C, which means that Pd dissolution in crude oil is not determined solely by the thiol content (See Section 7.1 for more detail). Nevertheless, it is evident from Figure 3, which compares the maximum Pd concentration dissolved by each oil with its thiol content, that the decreasing trend in maximum Pd concentration is mirrored by a decreasing trend in thiol concentration. Of all the compositional parameters measured in our crude oils, only the sulfur content and more broadly the asphaltene content correlate positively with Pd concentration.

Table 2. A summary of the experimentally determined solubility of Pd in oils A, B and C at 150, 200 and 250˚C. The palladium concentration at 25˚C is the background concentration in the unreacted oils.

	Oil A			**Oil B**			**Oil C**		
Temp.	**n***	**Pd (ppb)**	**Error (%)**	**n***	**Pd (ppb)**	**Error (%)**	**n***	**Pd (ppb)**	**Error (%)**
25 ˚C	3	0.5 ± 0.1	15	3	0.6 ± 0.2	29	3	1.4 ± 0.7	49
150 ˚C	3	60.1 ± 19.7	32	3	19.5 ± 4.0	21	3	127.6 ± 28.7	22
200 ˚C	3	18.3 ± 6.0	33	3	16.6 ± 6.2	37	3	49.9 ± 14.6	29
250 ˚C	3	15.5 ± 2.5	16	3	11.4 ± 1.3	11	3	26.0 ± 1.5	5.8

n* is the number of experiments conducted

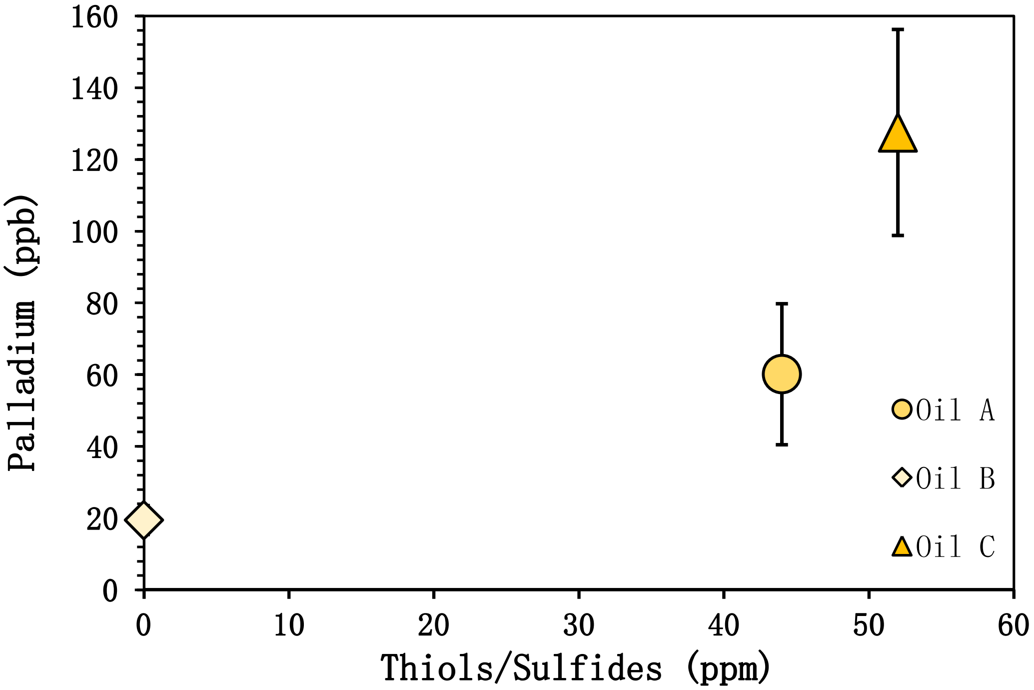

Figure 3. The maximum Pd solubility (ppb) in crude oils A, B and C versus the thiol content (ppm).

6.2 Results of XPS Analyses

X-ray Photoelectron Spectroscopy (XPS) was employed to determine the composition of the residual oil coating the surface of the palladium wire. Figure 4 illustrates an XPS spectrum for the sulfur compounds coating the Pd wire after reaction with Oil C at 150 ˚C; sulfur coats approximately 6 atom % of the wire surface. The prominent sulfur (S2p) peak, indicated by the dotted line, is centered at a binding energy of 163 eV corresponding to the thiol functional group (Castner et al., 1996). This indicates that most of the sulfur coating the wire is in the form of thiols, implying that palladium has a strong affinity for the reduced sulfur in oil.

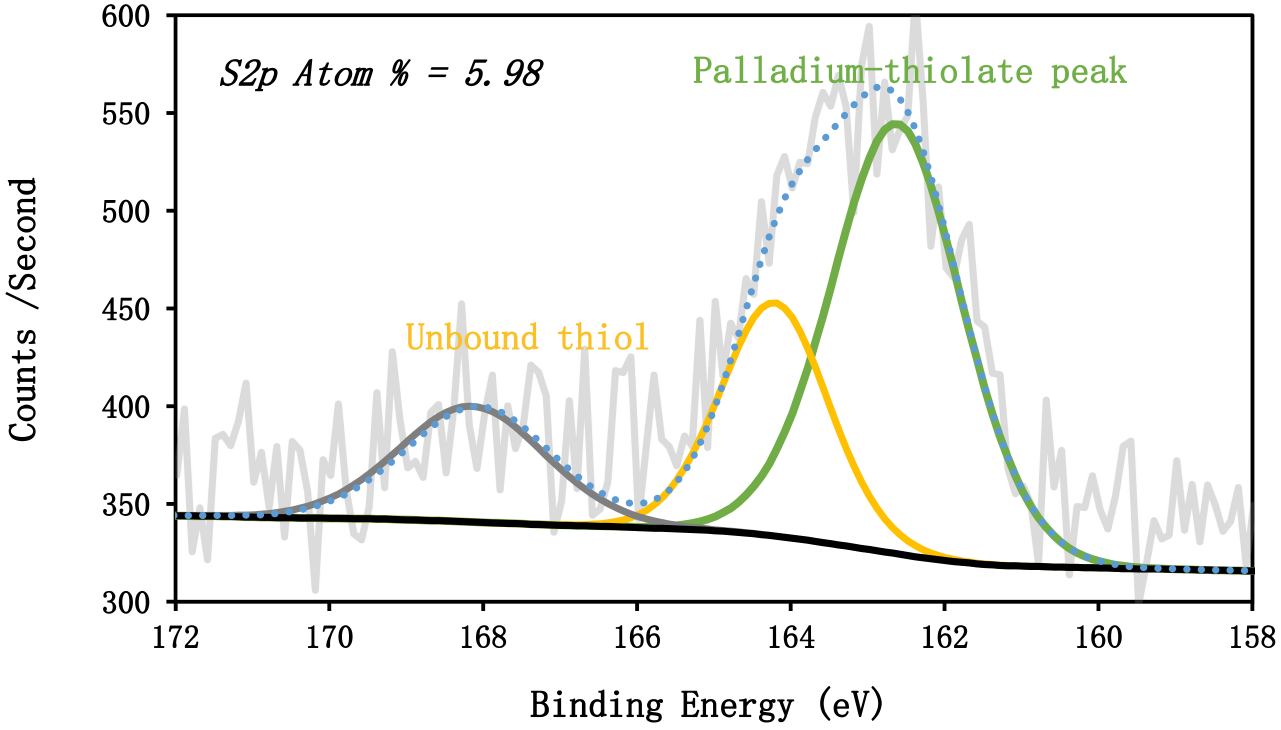

Figure 4. An XPS spectrum illustrating the sulfur speciation of residual oil on a palladium wire after reaction with oil C at 150°C. The thiol peak is resolved into an unbound thiol peak in yellow and a palladium-thiolate peak in green.

The thiol peak in Figure 4 is relatively broad and can be resolved into two separate peaks. The peak at 164.7 eV indicated by the yellow line represents free thiols, whereas the green peak located at 162.4 eV corresponds to palladium-thiolate. The latter interpretation assumes that the binding energy for gold-thiolate is similar to that for palladium-thiolate, for which there are no data (Castner et al., 1996). This means that, whereas some thiols remain unbound, a large proportion of the thiols are chemically bonded to the palladium wire. A less prominent sulfur peak at 168 eV corresponds to the sulfate functional group. The much smaller size of the sulfate peak relative to the thiol peaks provides evidence that oxidized sulfur is a much less important ligand for palladium, consistent with HSAB principles (Pearson, 1963); sulfate is a hard base and palladium a soft acid.

In Figure 5, we show a XPS spectrum for palladium after reaction with crude Oil C at 150 ˚C. Deconvolution of the spectrum reveals that the wire is coated in a mixture of native Pd metal and Pd(II). The XPS spectrum for the native Pd metal consists of a doublet (in green) with the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks centered at 335.7 and 340.9 eV, respectively. The Pd(II) doublet (in purple) is shifted to slightly higher binding energies than the doublet of its non-oxidized counterpart. Thus, the palladium wire was oxidized by reaction with the crude oil, whereas thiols in the oil were reduced to form palladium-thiolate. In this reaction the hydrogen atom of the thiol group is replaced by a Pd atom ($2\ RSH + Pd\ (0) \Rightarrow (RS)_2\text{-}Pd^{++}$). Palladium-thiolates are clearly stable in crude oil up to 150 ˚C and are evidently important in controlling palladium solubility in liquid hydrocarbons. This is consistent with the predictions of HSAB theory (Pearson, 1963).

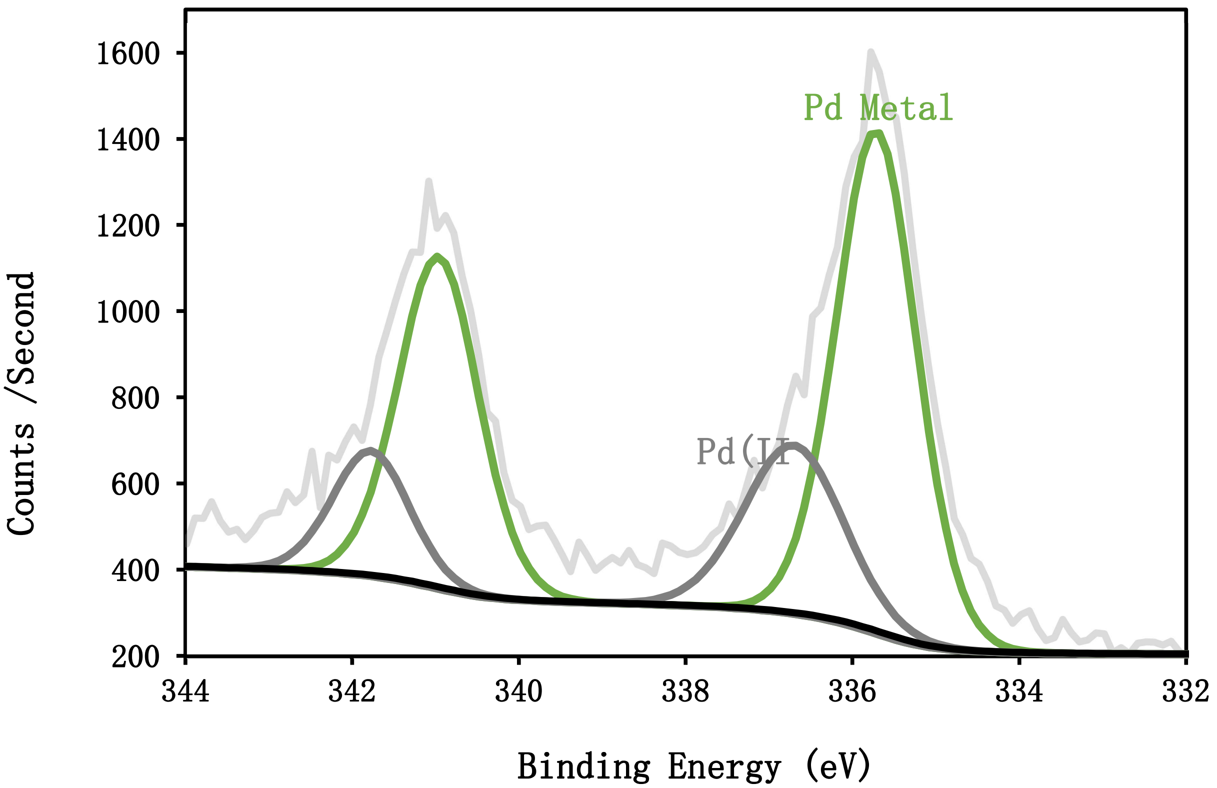

Figure 5. An XPS spectrum for palladium after reaction with crude oil C at 150˚C. The grey doublet correspond to the Pd(II) species whilst the green doublet corresponds to Pd(0).

7. Discussion

7.1. Factors determining Pd concentration and speciation in crude oil

Sulfur compounds in mature crude oils evolve during the mobilization of hydrocarbons through oil-rock interaction. Our results suggest that thiol-rich crude oils can dissolve appreciable concentrations of Pd, with Oil C, our most thiol-rich oil, dissolving up to 127 ppb Pd at 150˚C. This oil contains 52 ppm of thiols, which is a low concentration compared to that reported for some crude oils. For example, the "Rodney Crude" described in Ho et al. (1974) has a thiol content of 3179 ppm based on an API gravity of 32 and a mercaptan number of 275 (refer to

Electronic Supplement, Section B for a calculation of the thiol content of the Rodney Crude oil). Similarly, the “Light Mixed B.C.” oil, also described by Ho et al. (1974), has a thiol content of 1310 ppm. Based on the results of our experiments, an oil such as the Rodney Crude or the Light Mixed B.C. oil would be expected to dissolve substantial amounts of Pd. Mature thiol-rich crude oils of this type come from deep carbonate reservoirs, which contain elevated concentrations of hydrogen sulfide and are typically associated with sulfate-bearing carbonate sequences (Ho et al., 1974; Cai et al., 2003; Wei et al., 2011; Nguyen et al., 2013). Orr et al. (1974) proposed that thermochemical sulfate reduction (TSR) was responsible for the large concentrations of hydrogen sulfide and polysulfides in the oils hosted by carbonate reservoirs. Reactions between hydrogen sulfide and organic compounds from oil, gas or condensates can produce an elevated steady-state concentration of thiols, leading to thiol-enriched oils (Ho et al., 1974, Wei et al., 2011, Cai et al., 2003, Nguyen et al., 2013). In contrast, oils that mature in the absence of sulfate have low total sulfur and thiol contents (Ho et al., 1974; Orr et al., 1974).

Another compositional parameter that may control Pd dissolution in high viscocity crude oil is the asphaltene content; asphaltenes comprise a variety of very high molecular weight compounds including porphyrins, which are effective metal chelators (Filby and Berkel, 1987). As they form stable complexes with Pd (Kostas et al., 2007), porphyrins could play an important role in the dissolution of PGEs in crude oils. This is supported by the observation that the metalation of porphyrins during diagenesis by chalcophile elements such as Ni is promoted by ion transfer compounds like carboxylic acids (Lipiner et al., 1988). Since Pd is a d_{10} transition metal and a chalcophile element like Ni, it should display somewhat analogous chemical behavior. If we assume this to be the case, then an oil with a high carboxylic acid content has the potential to form Pd porphyrin complexes under diagenetic conditions. Interestingly, Oil B has the highest TAN (an indicator of high carboxylic acid content) of the three crude oils considered in this study (2.9 mg KOH/g). Furthermore, although Oil B contains no detectable thiols, it has an appreciable asphaltene content (0.3 wt.%). Thus, Oil B has the potential to form Pd porphyrins, which may explain why it was able to dissolve significant Pd despite the absence of thiols. Even so, Oil A and Oil C each have approximately 5-fold larger asphaltene fractions than Oil B (1.6 wt.% and 1.4 wt% respectively), and so their potential to form Pd porphyrins is correspondingly higher. However, despite sharing similar asphaltene contents, Oil C dissolved considerably more Pd at 150°C than Oil A. This difference is likely accounted for by the larger concentration of thiols found in Oil C (52 ppm thiol S) versus oil A (44ppm thiol S), a ligand which according to our XPS analyses, has a strong chemical affinity for Pd.

7.2. The environment of hydrocarbon-associated palladium ore formation

The Kupferschiefer, Zunyi and Boss deposits all exhibit notable Pd enrichment and lie in close spatial proximity to sulfate-bearing carbonate sequences. For example, the Permian Kupferschiefer is overlain by an anhydrite-rich carbonate sequence (Oszczepalski, 1999) and consequently, some researchers have suggested that TSR may have played a role in the mineralization of the Kupferschiefer deposit, although this continues to be debated (Bechtel and Püttmann, 1991; Jowett et al., 1991; Sun, 1998, Oszczepalski et. al., 2012). In contrast, the Zunyi deposit in Southern China consists of a thin layer of transition metal sulfides within a sequence of black shales. However, the black shales locally contain barite deposits and unconformably overlie a thick sequence of Precambrian dolomite (Lott et al., 1999; Mao et al., 2002). Moreover, barite is commonly observed in the Zunyi deposit (Murowchick et al., 1994), consistent with the production of the reduced sulfur by thermochemical sulfate reduction. Finally, it is noteworthy that sulfate-bearing minerals (plumbojarosite and hydronium jarosite) are also observed in close association with bitumen in the Boss deposit (Jedwab et al., 1999).

Although, there is no agreement on the genesis of black-shale-hosted PGE deposits, most researchers favor one of two models, a synsedimentary model, in which the metals precipitate from the seawater column and accumulate at the seawater-sediment interface, and a hydrothermal model in which the metals are deposited by sea-floor vent fluids (Jowitt and Keays, 2011; Kucha and Przybylowicz, 1999). These models, however, do not adequately account for the fact that a significant proportion of the Pd in black-shale-hosted deposits occurs as organometallic bituminous material (Kucha, 1993; Mitkin et al., 2000). Indeed, the currently favored genetic models do not consider this observation, proposing only that hydrocarbons act as chemical reduction fronts which aid in the precipitation of redox sensitive elements from a metalliferous hydrothermal fluid or from seawater (Disnar and Sureau, 1990). A hypothesis that therefore needs to be considered is that the metals were transported to the site of deposition in liquid hydrocarbons. In the case of the Zunyi deposit in southern China (Ni-Mo-PGE) support for liquid hydrocarbons as alternatives to a hydrothermal ore fluid is provided by the fact that the principal ore metal, Ni, is sparingly soluble in aqueous liquids. Indeed, chemical analyses of modern petroleum and bitumen from over mature reservoirs and analyses of petroleum in modern hydrothermal seafloor vents all indicate that the major metals that are concentrated in the ore zone at Zunyi are all very soluble in petroleum (Emsbo et al., 2005). This conclusion led

Emsbo et al. (2005) to propose that petroleum, rather than a hydrothermal fluid, was responsible for the metal enrichment of the Zunyi Deposit.

Platinum group element enrichment is associated with organic matter potentially derived from petroleum in a number of black-shale-hosted deposits, i.e., Zunyi, Nick, the Polish Kupferschiefer and the Boss deposit. At Zunyi, particles of migrabitumen, indicative of brecciation by petroleum, have been found in the ore zone (Kříbek et al, 2007). Large bituminous veins underlie the mineralized horizon of the Nick Prospect, potentially documenting the passage of a liquid hydrocarbon fluid into the black shales from below (Hulbert et al, 1992). Polyaromatic sulfur hydrocarbons (PASH), which are common constituents of crude oils, are abundant in organic matter associated with the sulfide ore of the Polish Kupferschiefer and are interpreted by Püttmann and Goβel (1990) to have been transported into the Kupferschiefer from the underlying Carboniferous strata. Finally, the PGE-ore of the Boss Deposit is hosted by bitumen in breccias that almost certainly represents the residues of petroleum (Jedwab et al., 1999).

The ability of a crude oil to dissolve Pd is dependent on the abundance of key ligands in the oil, of which thiols appear to be the most important (this study). Metals and thiols can be incorporated into hydrocarbon source rocks by sulfate reducing bacteria during sedimentation (Vairavamurthy and Mopper, 1987). As shales undergo diagenesis, the metal and sulfur content of the nascent oil will reflect that of the source rocks (Caumette et. al., 2009). The thiol content of the oil, however, may be increased to unusually high levels through catagenetic reactions like TSR which occur when the oil encounters sulfate minerals at temperatures in excess of 100°C

(Machel, 2001). These thiol-rich oils, of which the Rodney crude and Light Mixed B.C. oils (see above) are examples, in turn, would have greatly enhanced capacity to leach ‘soft’ metals like Pd from the surrounding sediments, potentially leading to orders of magnitude higher Pd concentrations than those of our experiments, which employed comparatively thiol-poor oils. We propose that such metalliferous, thiol-enriched oils eventually accumulate in traps, where through continued heating they form carbonaceous, PGE-rich sulfide seams exemplified by the deposits referred to in this paper.

7.3. Evaluation of the potential of crude oils to act as ore fluids for palladium

In the previous section, we discussed evidence for the association of petroleum with PGEs in several deposits, among which, the Kupferschiefer is the most important. Because of its location at the edge of the Carboniferous-Rotliegend petroleum system, which occupies a large part of the southern North Sea, and adjacent onshore parts of Europe (Gautier, 2003), it is therefore reasonable to propose that the Kupferschiefer was infiltrated by hydrocarbons from this source. Moreover, this hypothesis is supported by the observation that the source rocks (Carboniferous Coal Measures), reservoir rocks (Permian Rotliegend sandstones), and evaporite seals (Zechstein formation) of the Carboniferous-Rotliegend petroleum system (Gautier, 2003) are reproduced by the Kupferschiefer stratigraphy, i.e., the Kupferschiefer shales are overlain by the Zechstein evaporites and underlain by the Permian Rotliegend sandstones (Kucha and Przybylowicz, 1999).

A key question for the present discussion is whether the Carboniferous-Rotliegend petroleum system could have supplied sufficient petroleum to the Kupfershiefer shales to account for the mass of Pd that accumulated in this deposit. To answer this question, we calculated the size of the Pd resource in the Polish Kupferschiefer (Electronic Supplement; Section C) by integrating the annual production of Pd from the start of mining in 1995 to present and the projected annual production to 2054, when the last reserves are predicted to be exhausted. According to this calculation, the Polish Kupferschiefer initially contained ~ 1000 kg. Assuming that the putative petroleum ore fluid contained 100 ppb of Pd (Oil C dissolved a maximum of 127 ppb Pd), it follows that 10 billion kg of oil would have been required to form the Kupfershiefer resource of 1000 kg of Pd ore. By comparison, the Carboniferous-Rotliegend petroleum system in Western Europe has estimated mean undiscovered resources of 144 million barrels of oil which, given an oil density of 940 kg/m^3 (comparable to Oil C), is equivalent to 21.5 billion kg oil. Thus, the Carboniferous-Rotliegend petroleum system would have been more than sufficient to form the Pd resource of the Polish Kupferschiefer. We note also that our estimate of the amount of oil needed to form the Kupferschiefer is conservative, because of the relatively modest thiol content of Oil C compared to that reported for many other crude oils (Ho et al., 1974).

In assessing the potential of petroleum to act as an ore fluid, it is important to compare the Pd solubility in petroleum to its solubility in hydrothermal fluids, which as discussed earlier, also have been invoked to explain Pd enrichment in black shales. The solubility of Pd in hydrothermal fluids at temperatures comparable to those considered in this study is controlled mainly by the formation of chloride and bisulfide complexes and depends on the ligand concentration, oxygen fugacity and pH. As a chloride complex, the solubility of Pd exceeds 1 ppb only under highly oxidised conditions (above the magnetite-hematite oxygen buffer), at relatively low pH (< 4) and at unusually high salinity (> 3 m NaCleq.) (Gammons et. al., 1992). The solubility of Pd is similarly low as a bisulfide complex; for a geologically realistic reduced sulfur concentration of 0.01 m, the solubility at 200°C is < 1ppb (Gammons and Bloom, 1993). For comparison, the highest concentration of Pd that has been measured in a hydrothermal fluid is 2 ppb, which was for a geothermal fluid at 300 °C (McKibben et al., 1990), considered to be an analogue for epithermal ore-forming fluids (Clark and Willams-Jones, 1990). In summary, the solubility of Pd in Oil C at 150 °C (our thiol-rich oil) is at least two orders of magnitude higher than the solubility of Pd in hydrothermal fluids that might have been present during the formation of black shale-hosted Pd deposits, further strengthening the case that hydrocarbon liquids rather than aqueous fluids are the main agents of Pd transport for black-shale-hosted Pd deposits.

8. Conclusions

We have demonstrated that crude oils can serve as effective Pd ore fluids for black shale-hosted deposits. X-ray Photoelectron Spectroscopy analyses of Pd wires reacted in crude oil at 150 ˚C indicate that Pd has a strong chemical affinity for the reduced sulfur fraction of crude oil causing Pd to be preferentially dissolved as thiolate complexes. Heavy crude oils that mature in the presence of sulfate at the interface between a black shale and a carbonate sequence at temperatures between 100 and 140˚C are likely to undergo thermochemical sulfate reduction. This leads to hydrogen sulfide production and the formation of a thiol-rich oil. Palladium concentrations in our most thiol rich oil reached 127 ppb at 150˚C, which is considerably higher than the solubility of Pd in hydrothermal fluids of the type that have been invoked as possible ore fluids.

Despite the clear link between thiol and Pd concentrations in crude oil, one of our oils dissolved 19 ppb Pd at 150˚C yet contained no detectable thiols. This we attribute to the formation of Pd porphyrin complexes in the asphaltene fraction of the oil. Given that carboxylic acids promote the metalation of porphyrin complexes by metals such as Pd, we propose that the transport of Pd as Pd-porphyrins is likely to be important in heavy oils with a large asphaltene fraction and a high carboxylic acid to thiol ratio. Lastly, we note that in crude oils with truly anomalous thiol contents, Pd concentrations are expected to far exceed the concentrations reported in this study.

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Supplementary Materials

A. ICP-MS sample preparation and Data correction

The crude oils were ashed using reusable Pyrex™ culture tubes and glass wool that was cleaned with HNO_3 for 24 hrs, neutralized with Mili-Q® water for two hours, and then dried in an oven for one hour at 150 ˚C. Three mL aliquots of oil were placed in three separate culture tubes, which were capped with glass wool to prevent loss of ash. The capped culture tubes were then combusted at 550 ˚C in a muffle furnace for 12 hours. After combustion, 0.25 ml of 75% Optima^{TM} grade HNO_3, 0.5 ml of Optima^{TM} grade H_2O_2 and Trace metal grade 0.25 ml HCl was placed in each culture tube to oxidize the ash and leach the metals. The crude oils, acids, and culture tubes were weighed at each of the steps outlined above.

We measured ^{105}Pd and ^{89}Y counts in digested samples (crude oils from Table A), Pd standards (0.1, 0.5, 1, 5, 10, 15, 20 and 50 ppb standards diluted from 1000 ppm Pd aqueous standards supplied by SCP Science Ltd.) and a blank solution (1 ppb Yttrium (Y) diluted from 1000 ppm Y aqueous standards supplied by SCP Science, 2% Optima grade HNO_3, and Mili-Q® water). The blank solution was also used as a diluent for the digested acid samples and the standards. Digested acid samples were diluted ~80x in 50 ml centrifuge tubes, and then analysed with an ICP-MS using Y as an internal standard. To convert the counts to concentrations, we constructed calibration curves for each metal by plotting the corrected ^{105}Pd/^{89}Y ratios (^{105}Pd/^{89}Y ratios subtracted from the blank ^{105}Pd/^{89}Y ratios; Eq. A.1) with known standard concentrations (Eq. A.2). All the calibration curves regressed linearly through the origin with a $R^2 > 99.9\%$. Finally, the metal concentrations in the samples were determined by converting counts to concentrations using the slope from Eq. A.2, and then corrected by multiplying dilution factors and density factors to account for dilutions and acid-oil density differences between the digested acid samples and the original oil samples (Eq. A.3).

$$\left(\frac{^{105}Pd}{^{89}Y}\right)_{Corrected} = \left(\frac{^{105}Pd}{^{89}Y}\right)_{Sample} - \left(\frac{^{105}Pd}{^{89}Y}\right)_{blank} \quad \text{Equation A.1}$$

$$\left(\frac{^{105}Pd}{^{89}Y}\right)_{Corrected\ standard} = slope\ \times\ Known\ Pd\ Standard\ Concentration\ (C1) \quad \text{Equation A.2}$$

$$\text{Metal Concentration in Crude Oil} = \text{C1 x Dilution factor x } \frac{acid\ (in\ grams)}{oil\ (in\ grams)} \quad \text{Equation A.3}$$

B. Calculation of the thiol content of the Rodney Crude oil

$API = \frac{141.5}{SG} - 131.5$, where API is a measure of the weight of petroleum liquids and SG is the specific gravity of the oil.

Therefore, $SG = \frac{141.5}{API+131.5}$

The API value for the Rodney Crude is 32. (Ho et al., 1974)

$SG_{Rodney\ Crude} = \frac{141.5}{32+131.5} = 0.865$

$SG = \frac{\rho_{Oil}}{\rho_{H2O}}$ where ρ denotes density.

Assuming $\rho_{H2O} = 1.0$ g/mL

$\rho_{Rodney\ Crude} = SG_{Rodney\ Crude} = 0.865$ g/mL

Mercaptan Number= $\frac{mg\ of\ thiol\ S}{100mL}$ (Oswald, 1961)

The Mercaptan number for the Rodney Crude is 275 (Ho et al., 1974)

Mercaptan Number= $\frac{275\ mg\ of\ thiol\ S}{100mL} = \frac{275\ mg\ thiol\ S\ x\ \frac{1000\mu g}{mg}}{100mL\ x\ \rho_{Rodney\ Crude}} = \frac{275000\ \mu g}{100mL\ x\ \frac{0.865g}{mL}} = 3179\ ppm$

Thus, the Rodney Crude contains 3179 ppm of thiol S.

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C. Calculating size of the Pd resource at Polish Kupferschiefer and the petroleum reserves of the Carboniferous-Rotliegend petroleum system

Calculating Pd resource of the Polish Kupferschiefer

Pt and Pd are extracted together as a by-product of copper mining at the Polish Kupferschiefer.

Pd + Pt produced in 1995: 95 kg (Piestrzyński and Sawlowicz, 1999)

Pd + Pt produced in 2011 = $2505\ oz\ x\ 0.0284 kg/oz$ = 71kg (Bartlett et. al, 2013)

Working mines of polish Kupferschiefer have average concentrations of **0.2ppm Pt** and **0.1ppm Pd**. (Piestrzyński and Sawlowicz, 1999)

Pt:Pd = 2:1

We can use this ratio to estimate how much Pd was extracted in each year

Pd(1995) = 95kg/3 = **31.7 kg**

Pd(2011) = 71kg/3 = **23.7 kg**

The earliest available report of Pd production at the Polish Kupferschiefer that we could find dates to **1995 (**Piestrzyński and Sawlowicz, 1999) and mining is expected to last until **2054** at the latest (Speczik et. al, 2013).

Now we can use this data to linearly extrapolate the amount of Palladium mined in any given year.

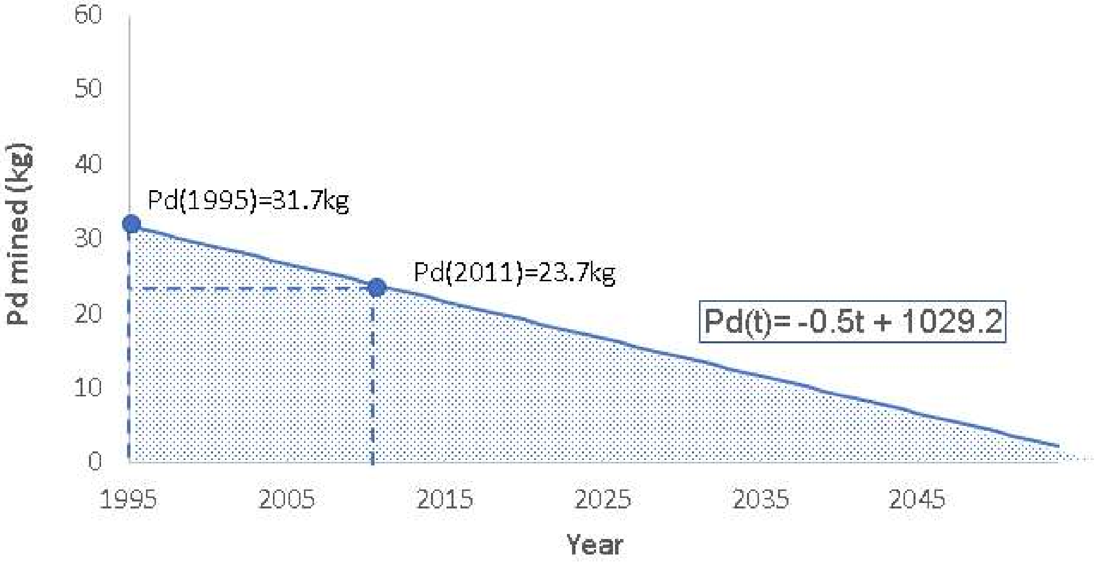

Figure S1. Linear extrapolation showing the amount of Pd extracted from the Polish Kupferschiefer every year.

Estimation of total Pd resource at the Polish Kupferschiefer

Total Pd = $\int_{1995}^{2054} 1029.2 - 0.5t\ dt$ = 1000kg

Quantity of oil required to form the Pd mineralization at the Polish Kupferschiefer

Assuming oil is transporting 127ppb Pd.

127ppb = $127x10^{-9}kg\ Pd/kg\ oil$ = $1.27x10^{-7}\ kg\ Pd/kg\ oil$

Amount of oil = $1000kg\ Pd/\frac{1.27x10^{-7}kg\ Pd}{kg\ oil}$ = **7.87 billion kg oil**

Mean undiscovered resources in Carboniferous Rotliegend petroleum stystem.

Mean undiscovered resources of Carboniferous-Rotliegend petroleum system: 144 million barrels of oil

Assuming oil density is equal to Oil C

Density oil C (ρ) = Specific Gravity Oil C x $\frac{1000kg}{m^3}$ = 0.94 x $\frac{1000kg}{m^3} = 940\,kg/m^3$

Volume of oil barrel= $0.159\,m^3/barrel$

Mass of oil in petroleum system = $144x10^6 barrels\ x\ \frac{0.159\,m^3}{barrel} x\ \frac{940\,kg}{m^3}$ = **21.5 billion kg oil**

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***Declaration of Interest Statement**

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: