METAL TRANSPORT BY OIL

APPLICATION TO ORE GENESIS

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THESIS ABSTRACT

This thesis describes the results of an experimental study designed to measure and interpret the solubility of palladium oxide in crude oil, and the modification of a method for analyzing metal concentrations in crude oils. An approach that has been employed previously in the analysis of crude oils is to combust (dry ash) them and then leach the residues with acids to prepare an aqueous solution that can be analysed instrumentally. This method of preparation, however, has been criticized as being inaccurate because it led to underestimates of the metal contents of crude oil standards to which it was applied. In this study, modifications were introduced that now permit its reliable application. The modifications involved the use of Pyrex^{TM} tubes instead of platinum crucibles and addition of nitric acid and hydrogen peroxide to ensure that any residues remaining after dry ashing were completely oxidized. This modified method was tested by analyzing the nickel and vanadium concentrations of certified crude oil standards using this dry-wet-ashing preparation, leaching the residues with concentrated HCl, diluting them in Milli-Q™ water and measuring the concentrations of Ni, V in the resulting solutions using ICP-MS. The results show that the concentrations of the standards can be reproduced to ± 5% for concentrations ≥ 100 ppm and ± 10 for concentrations down to 1 ppm Ni or V. These results are similar to or better than those using other more costly or less accessible methods of analysis. This suggests, that at least for Ni and V, and probably for most other metals, concentrations of metals in crude oils can be analyzed reliably using the modified dry ashing – ICP-MS method described in this thesis.

The solubility of palladium oxide was measured in three crude oils at temperatures of 150, 200 and 250 °C for a duration of seven days, which was shown by kinetic experiments to be sufficient to ensure equilibrium. The selected crude oils varied appreciably in their asphaltene, nitrogen and sulfur contents. Palladium concentration in the lightest crude oil (lowest asphaltene content) decreased systematically from 141 ± 34 ppb to 77 ± 17 ppb between 150 and 250 °C whereas in the other two crude oils, it reached a maximum at 200 °C. The concentration was highest in the heaviest crude oil, reaching 1183 ppb at 200 °C.

This suggests that palladium can be dissolved in appreciable concentrations in liquid hydrocarbons and that its solubility is controlled by the proportion of asphaltene macromolecules. The concentration of palladium also increases with increasing nitrogen content and decreasing acidity, suggesting, as has been demonstrated for Ni and V, that it may be dissolved as porphyrin species, which are known to concentrate in the asphaltene fraction. The results of this study show that liquid hydrocarbons have the potential to transport palladium in amounts sufficient to form ore deposits, and emphasize the need for studies of environments in which palladium and hydrocarbons have been shown to be spatially associated.

RÉSUMÉ

Cette thèse décrit les résultats d'une étude expérimentale visant à mesurer et à interpréter la solubilité de l'oxyde de palladium dans du pétrole brut, et la modification d'un procédé pour analyser les concentrations de métaux dans les pétrole bruts. Antérieurement, la méthode pour l'analyse des pétroles bruts comprennait premierement de brûler les Une approche qui a été utilisée précédemment dans l'analyse des huiles brutes est de brûler les échantillons de pétrole brut et par la suite de filtrer les résidus avec des acides afin de préparer une solution pour être analysé instrumentalement. Cette méthode de préparation, cependant, a été critiquée comme étant inexacte, car elle conduit à une sous-estimation de la concentration métallique des standards de pétrole brut à laquelle elle a été appliqué. Dans cette étude, des modifications ont été introduites, qui améliorent la méthodologie; par conséquence, les déterminations de contenus métalliques sont plus fiables. Les modifications incluaient l'utilisation de tubes Pyrex en place de creusets de platine et l/addition d'acide nitiric et de peroxyde d'hydrogène aux résidus pour assurer que tous les résidus soient oxydés. Cette méthode modifiée a été testée en analysant les concentrations de nickel et de vanadium dans des standards de pétrole brut certifiées après la préparation sec-humide-incinération des échantillons, la filtration des résidus avec du HCl concentré, et la dilution dans de l'eau Milli-Q™. La mesure des concentrations de Ni et V des solutions diluées a été faite pas ICP-MS et les résultats montrent que les concentrations des normes peuvent être reproduites à ± 5% pour des concentrations ≥ 100 ppm et ±

10% pour des concentrations jusqu'à 1 ppm Ni ou V. Ces résultats sont similaires ou encore meilleurs qu’en utilisant d'autres méthodes qui sont souvent plus coûteux ou moins accessibles que. Cela suggère, qu'au moins pour Ni et V, et probablement pour la plupart des autres métaux, que les concentrations de métaux dans les pétroles bruts peuvent être analysées avec meilleur confiance en utilisant la méthode préparation sec-humide-incinération décrit dans cette thèse. La solubilité de l'oxyde de palladium a été mesurée dans trois pétroles bruts à des températures de 150, 200 et 250 ° C pour une durée de sept jours, ce qui a été montré autrepart par des expériences cinétiques d'être suffisante pour assurer l'équilibre soit atteint. Les pétroles bruts sélectionnés avaient des concentrations d’asphaltène, d'azote et de soufre qui variaient considérablement. La concentration de palladium dans le pétrole brut le plus léger (celui qui contient le moins d’asphaltènes) a diminué systématiquement de 141 ± 34 ppb à 77 ppb ± 17 ppb entre 150 et 250 ° C alors que dans les deux autres pétroles bruts on, elle a atteint un maximum à 200 ° C. La concentration de palladium a été la plus élevée dans le pétrole brut lourd (celui avec le plus d’asphaltènes), en atteignant 1 183 ppb à 200 ° C.

Ceci suggère que le palladium peut être dissous dans des concentrations appréciables dans des hydrocarbures liquides et que sa solubilité est contrôlée principalement par la proportion des macromolécules d'asphaltènes. En plus, la concentration du palladium augmente avec l'augmentation de la concentration d’azote et la diminution de l'acidité, ce qui suggère que le palladium peut être dissout en tant qu'espèce de porphyrine, connus pour se concentrer dans la fraction d'asphaltène. Cela a été démontré dans cette thèse pour Ni et V. Les résultats de cette étude montrent que les hydrocarbures liquides ont le potentiel pour le transport de palladium dans des quantités suffisantes pour former des gisements, et affirment la nécessité pour plus d'études dans des environnements dans lesquels se trouvent ensemble le palladium et les hydrocarbures.

ACKNOWLEDGEMENT

I would like to extend my sincere gratitude and appreciation to my supervisor, Dr. A.E. Williams-Jones, whose encouragement, guidance, enthusiasm and above all passion in science has helped through this thesis for me to reach my full potential. I am also extremely in debt to Dr. A. A. Migdisov for his encouragement, guidance, and late night advice, which helped me to become a better experimentalist.

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Finally, I would like to thank every professor, graduate student, undergraduate and staff in the department of Earth and Planetary Sciences and in Geotop, who helped to see me through my thesis. Especially, Peter Crockford, Anna Jung, Anne Kosowski, Kristy Thornton, Angela Di Ninno, Brigitte Dionne, Jim Clark, Andre Poirier, Vincent Van Hinsberg, Alfonso Mucci, Christie Rowe, Boswell Wing, Jeanne Paquette, Andrew Hynes, Don Francis, Bjorn Sundby, Robert Martin, Melissa Maisonneuve, Brandon Bray, Karin Siegal, Kalina Malowany, Lucas Kavanagh, Jethro Sanz and Andy Mort (GSCC), for providing me with enthusiasm, inspiration, insightful ideas and loving support.

TABLE OF CONTENTS

LIST OF TABLES

CHAPTER 1 TABLES:

CHAPTER 2 TABLES:

CHAPTER 3 TABLES:

LIST OF FIGURES

CHAPTER 1 FIGURES:

CHAPTER 2 FIGURES:

CHAPTER 3 FIGURES:

PREFACE

The research presented in this thesis is a result of the collaboration of the author with her supervisor, Dr. A.E. Williams-Jones and his research associate, Dr. A.A. Migdisov. The thesis comprises four chapters: a general introduction, two stand alone manuscripts intended for publication, and a general conclusion. The two manuscripts are co-authored by Dr. A.E. Williams-Jones and A.A. Migdisov who provided guidance, scientific knowledge, help with the experiments and data interpretation, and critical reviews of the manuscripts. Dr. A.E. Williams-Jones also edited the thesis. Dr. Vincent Van Hinsberg (McGill University), A.A. Migdisov (McGill University), Dr. Anna Jung (McGill University), and Dr. Andre Poirier (Geotop-UQAM) provided assistance with inductively coupled mass spectrometry (ICP-MS). The author performed all of the experiments and analysis on her samples. The author also did all of the data analysis, much of the interpretation, and wrote the thesis. The French translation of the thesis abstract was made by Melissa Maissoneuve.

CHAPTER 1

GENERAL INTRODUCTION

1.1. INTRODUCTION

Although there is commonly a close spatial association between metallic mineralization and organic matter (e.g., pyrobitumen), with few exceptions (Manning and Gize, 1993; Fein and Williams-Jones, 1997) no consideration has been given to the possibility that liquid hydrocarbons could constitute ore fluids. Instead, where ores show a close spatial association with organic matter, this association is interpreted to be either coincidental or to provide evidence for redox-induced mineral deposition by the organic matter (e.g., Parnell, 1988; Püttmann et al., 1991; Disnar and Sureau, 1990; Nakashima et al., 1984; Jowett et al., 1987; Saxby, 1976; Krauskopf, 1955; Kucha and Przybylowicz, 1999; Oszczepalski, 1999). In this thesis, I report data on the metal concentrations of crude oils and present experimental evidence that palladium can dissolve in liquid hydrocarbons in concentrations sufficient for the latter to be agents of metal transport in nature.

1.1.1. CRUDE OIL CHARACTERIZATION

Crude oil is a variable mixture of organic and inorganic molecules (Table 1.1; Manning and Gize, 1993; Speight, 2001). The organic molecules in crude oil are paraffins, naphthenes, aromatics, resins and asphaltenes as shown in Figure 1.1. Paraffins (i.e., alkanes) are saturated hydrocarbons consisting of single bonded carbon (C) and hydrocarbon (H) compounds (the general formula is C_nH_{2n+2}, where n is the number of carbons). Naphthenes (i.e., cycloalkanes) are saturated cyclic hydrocarbons

Table 1.1. The average composition of the conventional crude oil (Speight, 2001).

Property	Conventional Crude Oil
Specific Gravity	0.89 - 0.90
Viscosity, cp	
38˚C/100˚F	$<$ 200
100˚C/212˚F	-
Pore point, ˚F	ca. -20
Elemental analysis (wt%):	
Carbon	86
Hydrogen	13.5
Nitrigen	0.3
Oxygen	$<$ 0.5
Sulfur	$<$ 2.0
Ash	0
Nickel (ppm)	1 - 200
Vanadium (ppm)	1 - 1000
Asphaltenes	$<$ 10.0
Resins	$<$ 20.0
Aromatics	$>$ 30.0
Saturates	$>$ 30.0
Carbon Residue (wt%)	
Conradson	$<$ 10.0

containing one or more rings with the general formula $C_nH_{2(n+1-g)}$, where n is the number of carbon atoms and g the number of rings). Aromatics are cyclic compounds containing delocalized electrons in the center of the ring. The aromatic rings are known to form sandwich complexes, in which the metals are bound by coordinate covalent bond, wherein two aromatic rings sandwich a metal (Tatsumi et al., 2006). The resins and asphaltenes are macromolecules containing functional groups (i.e., heteroatoms) involving nitrogen, sulfur and oxygen, which are thought to be the dominant ligands that participate in organometallic complexation, e.g., metalloporphyrins (Falk, 1964; Manning and Gize, 1993; Speight, 2001). Crude oil also contains trace elements and inorganic constituents such as silicate minerals (Yen, 1975). The most abundant elements in crude oil, apart from C and H are sulfur, nitrogen, oxygen, nickel, vanadium, molybdenum, zinc and copper (further information on the trace element composition of crude oil is provided in section 1.1.3). Different crude oils have different sulfur contents (<10% based on Tissot and Welte, 1978) and a variety of sulfur species (Table 1.2). The same can be said for nitrogen and oxygen compounds in crude oil (Table 1.3).

Crude oils are commonly described as sweet, sour, light, medium, and heavy, with the first two terms referring to the sulfur content and the latter three terms to the content of asphaltene macromolecules. The proportion of the latter is quantified by measurements of the American Petroleum Institute gravity (API gravity), which is the density of the crude oil relative to that of water (Diaz-real et al., 1993; Simanzhenkov and Idem, 2003). Light crude oil has a high API gravity (lighter than water) and low viscosity (Yen, 1975; Speight, 2001). By contrast, heavy crude oil, has low API gravity (sinks in water) and high viscosity (Yen, 1975; Speight, 2001). Sweet crude oils are oils that contain less than 0.5 wt.% total sulfur, and sour crude oils more than 0.5 wt.% total sulfur (Simanzhenkov and Idem, 2003).

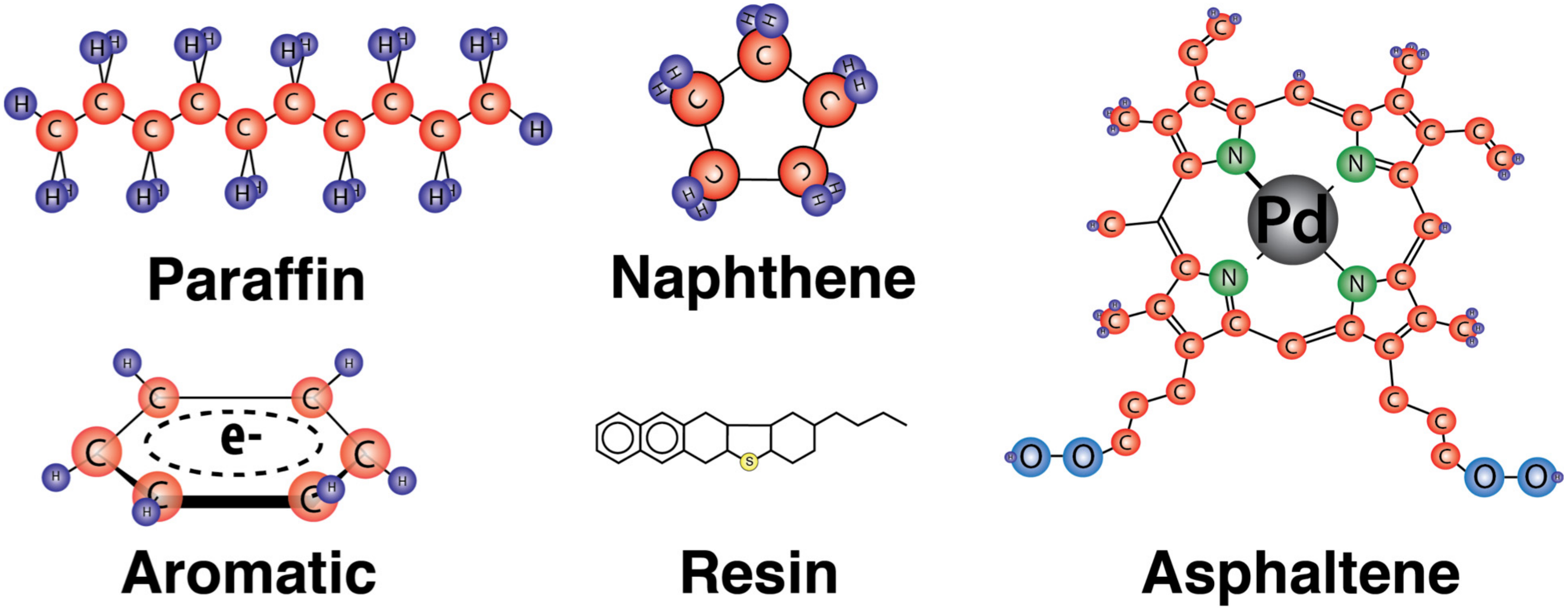


Figure 1.1. Crude oil is a complex mixture of organic molecules, characterized by paraffins, naphthenes, aromatics, resins and asphaltenes. Variable proportions of these molecules dictates the degree to which oil is light (more paraffins) or heavy (more asphaltenes and resins).

Table 1.2. Examples of sulfur compounds and their structures in crude oil (Ho et al. 1974; Tissot and Welte 1978). R represents carbon, S represents sulfur, a single line represents a single bond between two carbons unless specified, and a double line represents a double bond (again between two carbons unless specified).

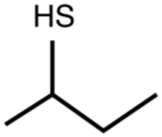
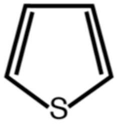
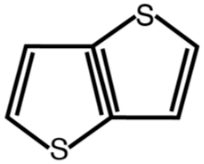
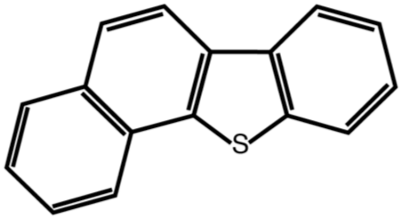
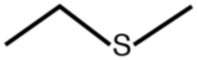
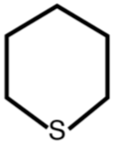
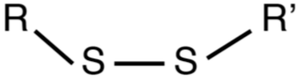
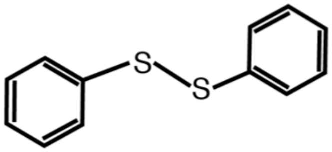
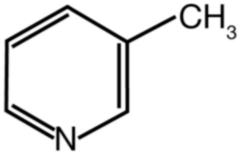
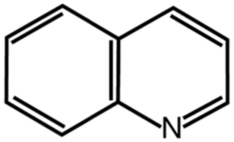
Types of Sulfur	General Structure	Examples
1.Thiols	R — SH	 Butanethiol
2. Thiophenes		 Thioenothiophenes  Benzonaphtothioenothiophenes
3. Thioether	R— S — R'	 Thiobutane  Thiocyclohexane
4. Disulfides		 Diphenyl Disulfide

Table 1.3. Examples of nitrogen and oxygen compounds in crude oil (Tissot and Welte 1978). N represents nitrogen, H represents hydrogen, O represents oxygen, C represents carbon, a single line represents a single bond between two carbons unless specified, and a double line represents double bond (again between two carbons unless specified).

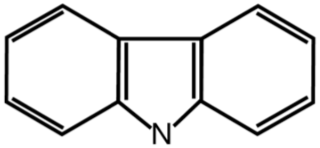
Nitrogen Compounds



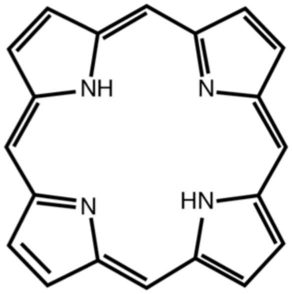
Methylpyridine



Quinoline

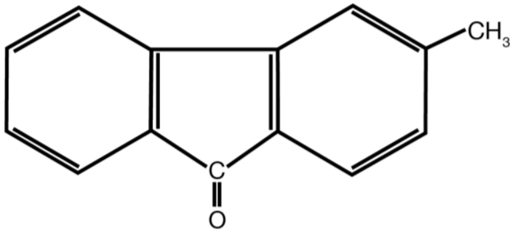


Carbazole

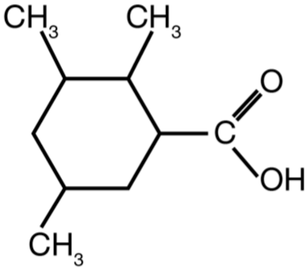


Porphyrins

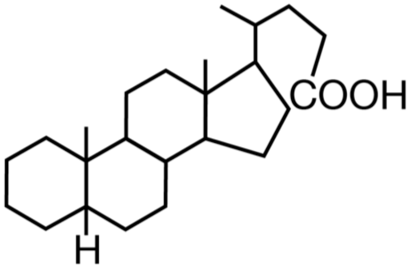
Oxygen Compounds



Methylfluorenone



Trimethylcyclohexane Carboxylic Acid



Steroid Carboxylic Acid

The chemical and physical properties of crude oil can vary significantly with location and even with difference in depth in a single well (Speight, 2001). However, the proportions of inorganic and organic constituents are controlled by the source rock and therefore vary mainly as a function of the variability of the source rocks (Peters et al., 2004).

Formation of crude oil is generally considered to be a biological phenomenon (e.g., Tissot and Welte, 1978; Peters et al., 2004; Gao et al., 2013) although an abiogenic origin has been proposed for some oils (Glasby, 2006). The biological formation of crude oil involves the decomposition or maturation of organic matter from living organisms in sediments that undergo diagenesis to form source rocks (containing kerogens). Accumulation of the sediments and organic matter is followed by catagenesis, a process in which the organic matter in the source rock is thermally altered by heating at temperatures in the oil window (50 - 150°C) during burial for durations of many millions of years (Peters et al., 2004). By contrast, the abiogenic formation of crude oil is thought to occur through a Fischer-Tropsch reaction in which carbon monoxide or dioxide released from the mantle reacts with hydrogen produced by serpentinization in the presence of iron oxide (also produced by serpentinization) to form alkanes and more complex hydrocarbons (Peabody and Einaudi, 1992; Glasby, 2006; Krylova et al., 2012). A biological origin is supported for most crude oils, however, based on the presence of biomarkers, which are molecules that retain the basic carbon skeletons of biological compounds from living organisms (e.g., porphyrins, pristine, phytane, steranes, triterpanes, etc.) after losing functional groups through the maturation process (Speight, 2001).

1.1.2. EVIDENCE FOR METAL TRANSPORT BY OIL FROM NATURAL SYSTEMS

Ores in a number of low-temperature metallic mineral deposits show a close spatial association with liquid hydrocarbons (Figure 1.2). For example, the presence of bituminous hydrocarbons has been reported from a number of Mississippi-Valley type (MVT) lead-zinc deposits (Parnell, 1988; Blasch and Coveney, 1988; Anderson and Macqueen, 1982; Macqueen and Powell, 1983; Kesler et al., 1994). Moreover, in some, the main zinc ore mineral, sphalerite, has been shown to contain primary oil inclusions together with brine inclusions, indicating that petroleum coexisted with brine at the time of ore formation (Blasch and Coveney, 1988; Kesler et al., 1994; England et al., 2002; Billström et al., 2012). These observations led Giordano and Barnes (1981) to propose that the metals are transported in hydrothermal fluids as organometallic complexes. Giordano and Barnes (1981), Giordano (1985), and Manning (1986) evaluated the stability of Pb and Zn complexes involving a number of potential organic ligands (carboxylate), and concluded that the highest concentration that can be reached with organic acids is at the ppb level (acetate), which is insufficient to form an ore deposit. This indicates that organic ligands are insignificant in metal transport. However, Giordano and Barnes (1981) and Giordano (1985) did not consider the possibility that the liquid hydrocarbons may have been the agents of metal transport.

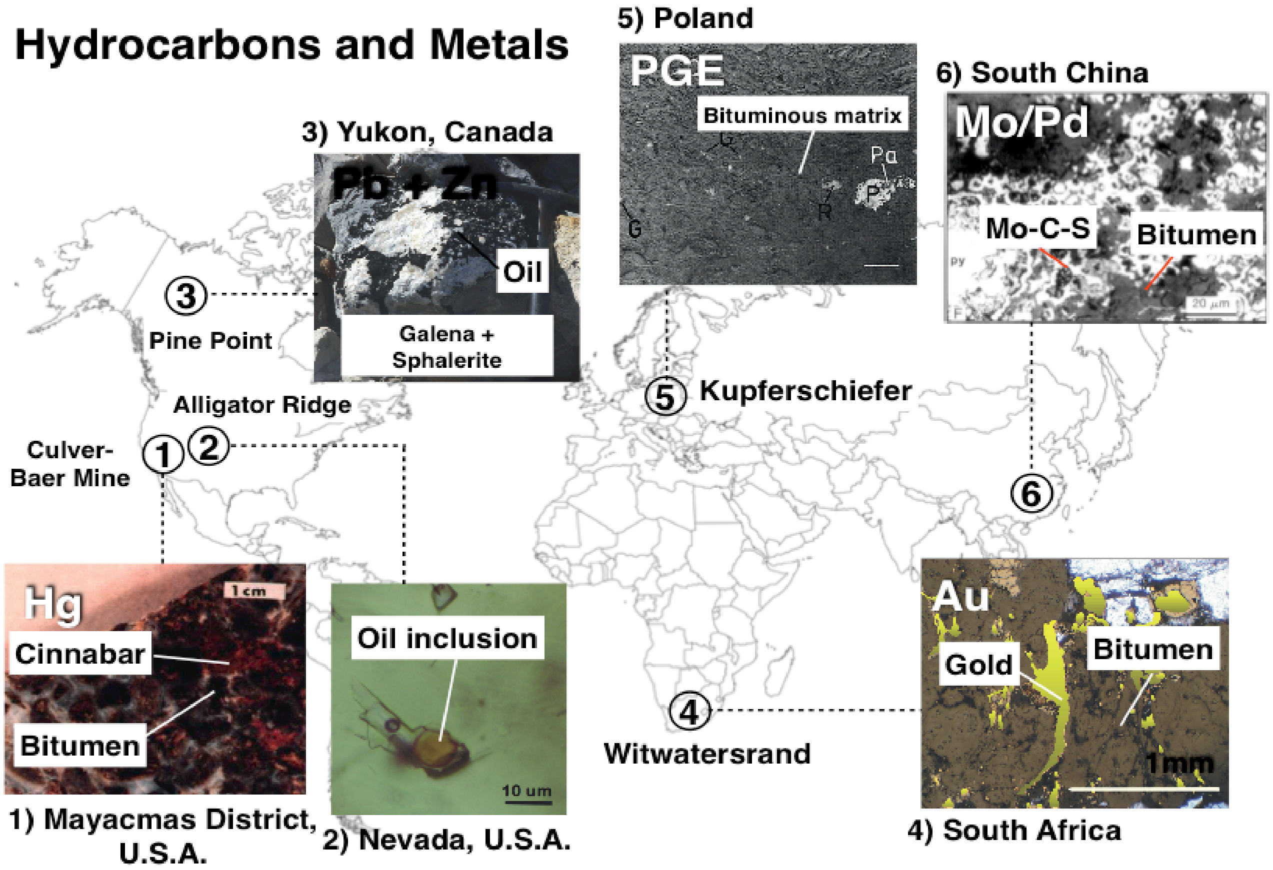


Figure 1.2. Metal-hydrocarbon textural associations in ore deposits. 1) The Culver Baer mine (Mayacmas District, California, U.S.A.) exhibits a close association of bitumen and cinnabar (Peabody and Einaudi, 1992); 2) Carlin-type gold deposits at Alligator Ridge, Nevada, U.S.A., host oil-bearing inclusions; 3) MVT-type Pb-Zn mineralization at Pine Point, Yukon, Canada is closely associated with liquid oil; 4) In the Witwatersrand area, South Africa, gold concentrations are often associated with bitumen; 5) In the Kupferschiefer of Poland, ~1000 ppm palladium occurs in bituminous shale (Kucha and Przybylowicz, 1999); 6) At Zunyi, China, black shales contain elevated concentrations of Ni, Mo and PGE (Lott et al., 1999).

Manning (1986) was the first to propose that liquid hydrocarbons might be an agent for metal transport. He reported metal concentrations in crude oil from a variety of locations and, noting elevated Cu and Zn concentrations, concluded that hydrocarbons should not be ignored when evaluating metal transport in ore-forming processes. To test this possibility for mercury, Miedaner et al. (2005) conducted experiments designed to measure the solubility of mercury in simple hydrocarbons (octane, dodecane and toluene) at temperatures between 100 and 200˚C (refer to section 1.1.4 for details). They measured Hg concentrations that reached 1190 ppm at 200˚C, which is considerably more than would be needed to form an ore deposit and is orders of magnitude higher than the solubility of Hg in hydrothermal liquids; Hg concentrations are very high in hydrothermal vapors because of the very high volatility of Hg^0. An example of a deposit in which the mercury may have been concentrated by hydrocarbons, is the Culver Baer deposit, California, in which hydrocarbon liquids are observed in contact with the ore mineral cinnabar (Peabody and Einaudi, 1992).

Other examples of deposit types in which the ores are closely associated with hydrocarbons include Carlin-type gold deposits, the Kupferschiefer deposit, the Witwatersrand deposits and the Zunyi Nickel-Molybdenum-PGE deposit (Figure 1.2). Despite the close association between metals and hydrocarbons observed in those deposits, their formation has invariably been attributed to hydrothermal fluids (e.g., Coveney, 1991; Engel and Macko, 1993; Giordano, 1994; Wilkinson et al., 2009). Where a role is attributed to the hydrocarbons it is most commonly to generate hydrogen sulfide through sulfate reduction to enable sulfide mineral formation (e.g. Coveney, 1992; Coveney, 1999; Townsend et al., 2003).

The first and most direct evidence that liquid hydrocarbons can transport ore metals was provided by Jedwab and Badaut (1999), who showed that bitumen in the Boss Mine, Nevada, U.S.A, carries significant concentrations of metals in the form of nanoparticles in bitumen-bearing veins and breccia hosted by dolomite. The bituminous aggregates contain potarite ((Pd, Au, Pt) Hg) nanoparticles and the overall metal content of the bitumen is 1.85 wt.% of Pd, 0.89 wt.% of Au+Pt, and 5.83 wt.% of Hg (Figure 1.3; Jedwab and Badaut, 1999). Jedwab and Badaut (1999) concluded that liquid hydrocarbons entered the wall rock, transporting and concentrating the potarite nanoparticles to form a potarite-rich ore deposit as the liquid hydrocarbons were transformed to bitumen.

Most recently, Fuchs et al. (2015) documented the presence of nanoparticles of uraninite (UO_2) in carbon seams (pyrobitumen) that host much of the uranium ore of the Witwatersrand deposits, South Africa (Figure 1.4). They showed that these nanoparticles are uniform in size (5 – 7 nm diameter) and form large aggregates (10s of microns in diameter) that had previously been interpreted to be fragments. Based on these observations, they concluded that the pyrobitumen represents the residues of hydrocarbon liquids that had transported uranium in solution and/or as uraninite nanoparticles. Independent evidence of the former existence of such liquids is provided by the occurrence of hydrocarbon fluid inclusions along fractures in detrital quartz grains and within overgrowths on these grains (England et al., 2002).

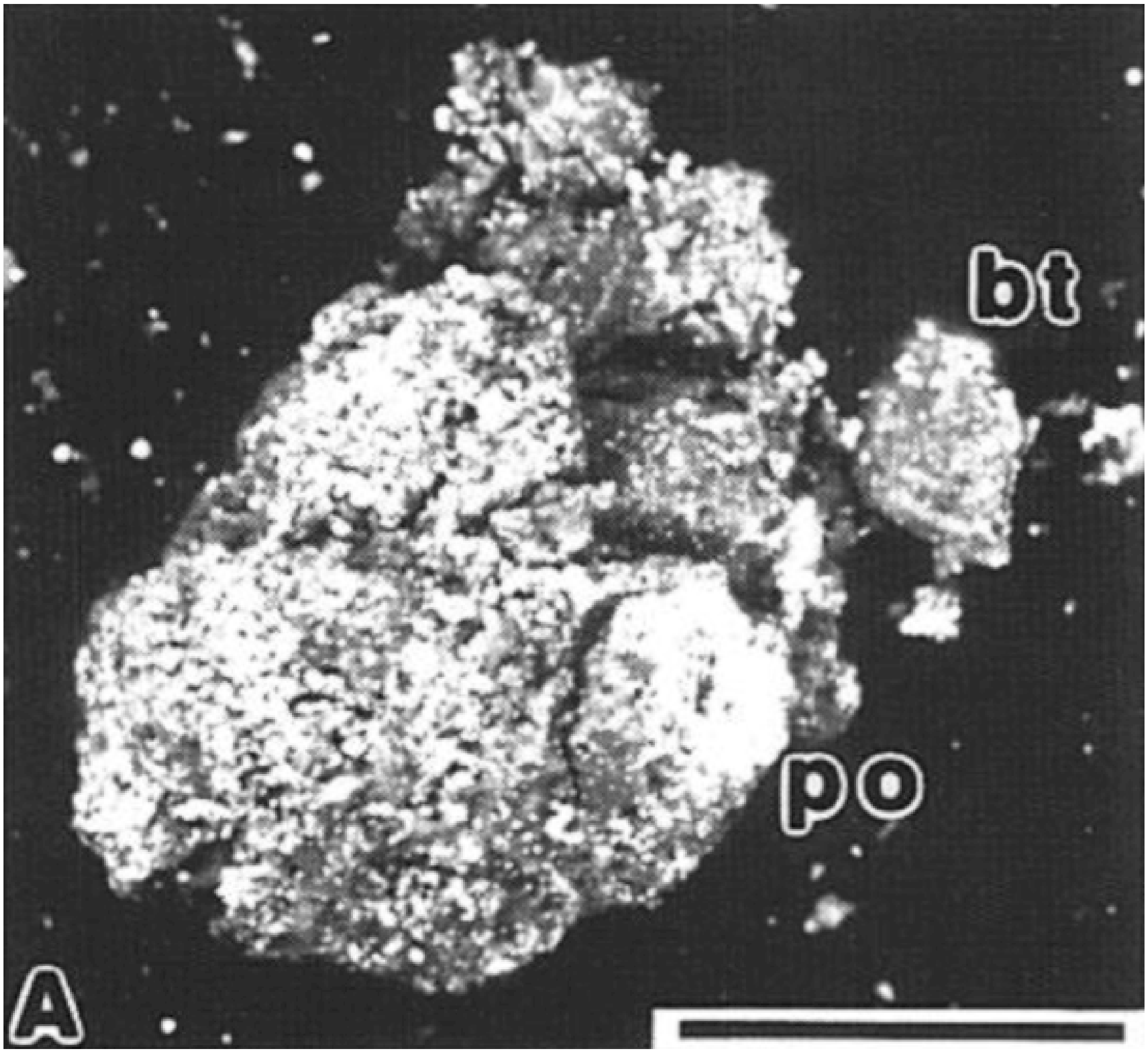


Figure 1.3. Backscattered electron image of a bitumen (bt) containing potarite (po; PdHg) and gold particles (Jedwab and Badaut 1999; scale bar = 100 µm).

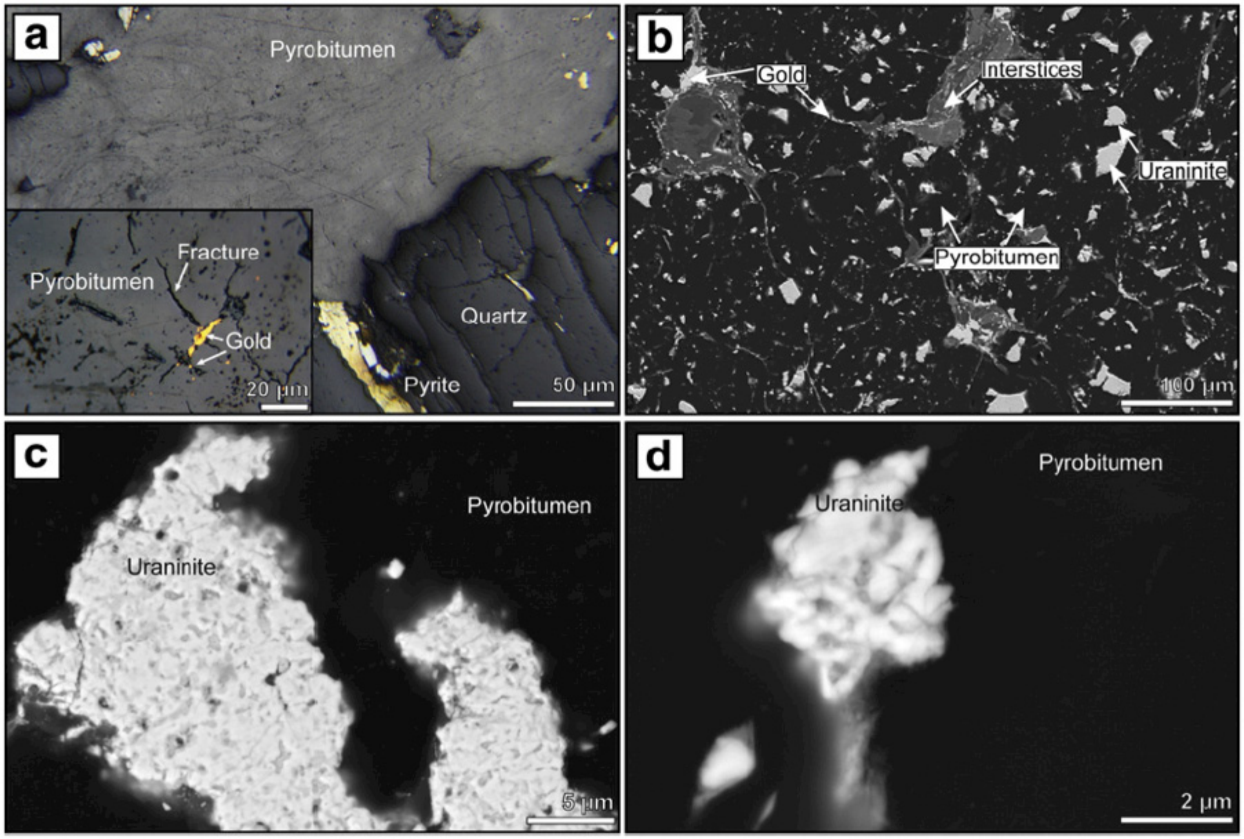


Figure 1.4. (a) eflected-light photomicrograph showing irregularly shaped pyrobitumen with native gold in fractures (inset). (b) scanning electron image showing part of a pyrobitumen seam with elliptical nodules (black) with uraninite (light grey). The interstices are commonly filled with phyllosilicates and are associated with florencite, crandallite and native gold. (c,d) scanning electron microscope images of uraninite grains with internal structures suggesting that they are aggregates of smaller crystals. All images are of samples from the Carbon Leader Reef, South Africa (Fuchs et al., 2015).

1.1.3. TRACE METALS IN CRUDE OIL

The fact that crude oils contain significant concentrations of metals has been known since the early 20th century (e.g., Treibs and Dieter, 1934; Karchmer and Gunn, 1952; Horeczy et al., 1955; Falk, 1964) and the concentrations of some of these metals have been determined routinely for many years. The reasons for this are that they can be used to identify potential pollutants, such as mercury, and fingerprint the source of crude the oil (e.g., Colombo and Sironi, 1964; Shah and Filby, 1970; Al-Shahristani, 1972; Ali et al., 1983; Al-Swaidan, 1996). Concentrations of individual metals vary considerably depending on the source of the crude oil (Table 1.4 and 1.5). In general, however, the metals present in greatest abundance in crude oil are vanadium, nickel, iron, zinc and molybdenum.

Table 1.4. Metal concentrations in crude oil from Manning and Gize (1993).

Metals in Petroleum

Concentration (ppm)

	Western Canada [a]		**Saudi Arabia** [b]		**Mollase Basin**		**Italy**		**Venezuela**		**Jones Review**
Metal	**Avg**	**Max**	**Avg**	**Max**	**Avg**	**Max**	**Avg**	**Max**	**Avg**	**Max**	**Max**
Ag			0.16	0.39		0.32					0.004
Al	1	1.4									7.8
As	0.11	1.99									2.4
Au	(0.44)[g]	(1.32)[g]									0.003
Ba											11.9
Ca			1.31	4.00					6.38	16	10
Cd			0.84	2.37							
Co	0.05	2.00			0.13	0.64		0.003[h]			12.75
Cr	0.09	1.68	0.65	1.18	0.11	0.45	3.15	10.7			3.6
Cu			0.32	0.88		2.5		5.5h	0.105	0.17	11.7
Fe	10.8	254	2.17	6.64	10	82		0.9h	4.98	26.00	120
Ga		0.04									0.8
Hg	0.05	0.4				0.5					29.6
Mn	0.01	3.85	0.05	0.15			1.2	9.7			0.15
Mo							2.27	183	0.572	2.00	10.1
Ni	9.38	74.1	7.96	18.3	13.5	55	46.6	155	40.2	105	105
Pb			0.89	1.57							2.1
Sb	0.01	0.03						0.035[h]			11
Sn				1.74							2.2
U											0.43
V	13.6	177	25.5	54.6	1.01	11.3	64.5	248	147	433	1580
Zn	0.46	5.92	0.81	2.55	1.54	21		0.9[h]			160
Zr											2.7

[a] Data for up to 88 samples, from Hitchon et a!. (1975)

[b] Data for 10 samples, for Ali et al. (1983)

[c] Data for 43 samples, for Ellrich et al. (1985)

[d] Data for 37 samples (except where otherwise noted), from Colombo and Sironi (1981) and Columbo et al. (1964)

[e] Data from Simoza et al. (1985)

[f] Data from Jones (1975)

[g] Concentrations in parentheses are ppb

[h] Data for 4 samples

Table 1.5. Metal concentrations in crude oils from Canada, showing compositional variability from different locations.

19 Metal Concentration in Crude Oil from various locations in Canada

Location	**Desan, B.C.**		**Suffield, B.C.**		**Canera Macoun, S.K.**		**Cape Allison, N.U.**		**Scotia Shelf, N.S.**		**Beaufort-Mackenzie, N.T.**					
Depth (ft)	1896		3106		4967		4957		7522		2267		4473		8164	
Coordinate	59.303˚N, -120.924˚W		50.684˚N, -110.985˚W		49.339˚N, -103.137˚W		77.769˚N, -100.292˚W		43.83˚N, -60.7089˚W		69.198˚N, -135.322˚W		69.26˚N, -135.019˚W		69.892˚N, -135.373˚W	
Metal	Conc.	±	Conc.	±	Conc.	±	Conc.	±	Conc.	±	Conc.	±	Conc.	±	Conc.	±
Ni (ppm)	27.41	0.24	26.09	0.16	10.90	0.15	1.12	0.09	0.07	0.02	1.07	0.35	0.56	0.05	0.03	0.02
V (ppm)	57.84	0.73	78.33	0.58	15.72	0.11	0.61	0.03	d.l.	d.l.	0.48	0.05	0.18	0.04	0.04	0.01
Zn (ppm)	175.65	5.29	6.28	4.79	29.50	35.78	13.18	6.60	5.41	1.46	14.19	7.83	8.86	3.19	5.51	3.30
Mo (ppb)	577.20	13.50	156.82	3.41	6.65	0.39	1.78	0.59	0.04	0.05	2.22	0.52	1.25	0.26	0.17	0.18
Ga (ppb)	40.28	0.60	36.87	3.58	5.41	0.19	240.19	2.20	d.l.	d.l.	5.22	0.09	3.65	0.22	0.32	0.17
Cu (ppm)	59.11	0.89	0.16	0.20	0.42	0.23	0.51	0.02	0.02	0.01	25.48	0.60	1.41	0.58	2.82	0.08
Au (ppb)	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Ag (ppb)	0.67	0.11	0.008	0.007	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Ir (ppb)	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Re (ppb)	0.23	0.02	0.01	0.02	0.21	0.05	0.003	-	0.02	-	0.005	0.007	0.005	0.004	0.002	0.001
Os (ppb)	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Pt (ppb)	1.78	0.02	1.15	0.82	1.79	1.74	1.12	0.80	2.09	0.70	1.26	0.80	1.12	0.83	1.72	0.69
Pd (ppb)	3.65	0.25	0.25	0.15	0.15	0.12	d.l.	d.l.	d.l.	d.l.	1.47	0.05	0.17	0.09	d.l.	d.l.
Rh (ppb)	1.80	0.06	0.07	0.02	0.14	0.03	0.12	0.10	d.l.	d.l.	0.90	0.06	0.13	0.04	0.21	0.03
Ru (ppb)	0.62	0.04	0.011	0.007	0.034	0.032	d.l.	d.l.	d.l.	d.l.	0.016	0.006	d.l.	d.l.	d.l.	d.l.
La (ppb)	0.38	0.02	1.11	0.02	0.14	0.04	1.42	0.06	0.021	0.024	0.24	0.02	0.48	0.02	0.02	0.0005
Hg (ppb)	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
U (ppb)	8.68	2.05	0.18	0.03	0.23	0.13	0.03	-	0.12	0.003	3.45	2.15	0.02	-	0.12	0.16
Pb (ppm)	13.18	4.03	0.11	0.01	1.10	0.17	1.27	0.24	0.08	0.001	10.21	0.09	1.16	0.01	8.68	0.08

*d.l. indicates that the element reached the lower detection limit

1.1.4. EXPERIMENTAL STUDIES OF METAL UPTAKE BY HYDROCARBONS

Experimental studies of the solubility of metals in hydrocarbon liquids have been limited to that of Miedaner et al. (2005) on mercury, and a preliminary investigation of the solubility of gold in crude oil (Williams-Jones and Migdisov, 2006). The study of Miedaner et al. (2005) was conducted on octane, dodecane and toluene at temperatures between 100 to 200˚C. The mercury concentrations in these liquids reached 821, 647 and 280 ppm, respectively, at 200 ˚C. Miedaner et al. (2005) proposed that mercury dissolves as Hg^0. They used scaled particle theory to show that the concentration of mercury in simple hydrocarbons increases linearly with increasing temperature due to the expansion of the cavities between hydrocarbon molecules. According to this model, the carbon number controls Hg solubility in simple hydrocarbons and thus at constant temperature the solubility of Hg in the different media increases in the order dodecane > octane > toluene. Williams-Jones and Migdisov (2006) measured concentrations of gold that reached a maximum of ~50 ppb at 250 ˚C and then decreased at higher temperature. The gold solubility did not vary with the composition of the oil. They did not attempt to determine the speciation of the gold but speculated that it may have “dissolved” through chelation in porphyrins, and/or adsorption on the surface of asphaltene macromolecules.

The only other experimental study that provides insight into the uptake of metals by hydrocarbon liquids is that of Plyusnina et al. (2000). These authors investigated the adsorption of platinum (Pt) by solid asphaltenes and asphaltic acids from Pt-bearing aqueous solutions at temperatures from 200 to 400˚C. At these temperatures, the amounts adsorbed were 10^{-4} molal (19.5 ppm Pt) and 10^{-2} molal (1.9 wt% Pt), respectively. In the world-class Pt deposits of the Bishveld Igneous Complex, South Africa (e.g., the Merensky reef), the average Pt concentration is 3.2 ppm Pt (Cawthorn, 1999). Thus, the concentration of Pt by adsorption on asphaltene is comparable to that of economic deposits formed from magmatic sulfides.

1.2. SPECIATION OF ORGANOMETALLIC COMPOUNDS IN CRUDE OIL

In order to understand the contribution of metal transport by liquid hydrocarbons to ore-forming processes, we need to understand the mechanisms of metal uptake and the nature of the organic compounds responsible for this uptake. Currently, only a few organic compounds have been identified in crude oil, which have been shown to contribute significantly to metal dissolution. In the following section, we consider the principal organic ligands and organometallic complexes that could potentially contribute to the transport of metals by liquid hydrocarbons.

1.2.1. METALLOPORPHYRIN

Metalloporphyrin is a macromolecule (part of the asphaltene fraction) composed of four pyrrole rings connected by methyne bridges (Table 1.6) containing metal at the center (Figure 1.5). The basic macrocyclic structure of the molecule is the same as that of chlorophyll (magnesium porphyrins in plants) and hemoglobin (iron porphyrins in blood). This molecule is widely considered to be the most important component controlling metal solubility in crude oil (Falk, 1964; Tissot and Welte, 1978; Manning and Gize, 1993). Nickel and Vanadyl porphyrins have been identified in crude oil in elevated concentrations, and many other elements, notably Mo, Zn and the PGE, are thought to be present in crude oils as metalloporphyrins, based on their apparent preference for the asphaltene fraction of crude oil (Manning and Gize, 1993; Selby et al., 2007; Fuchs et al., 2015). Although large numbers of porphyrins have been identified, five types (DPEP > Etio > Di-DPEP > Rhodo-Etio = Rhodo-DPEP) are thought to be dominant in crude oil (Barwise and Whitehead, 1980).

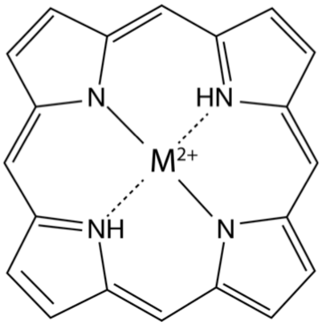
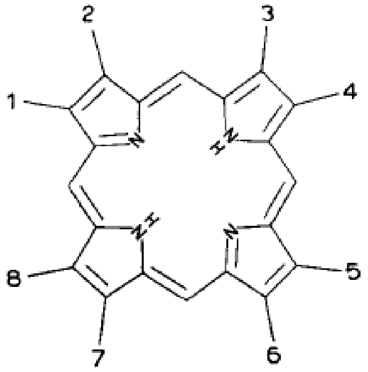


Figure 1.5. Example of a metalloporphyrin compound. The center of the molecule with the M^{2+} in the diagram is one example of where significant portions of precious metals could potentially concentrate in crude oil.

Table 1.6. Some examples of porphyrin compounds (Falk, 1964). Side-chain abbreviations: A = -CH_2COOH; B = -CH(OH)CH_3; H = -H; M = -CH_3; P = -CH_2CH_2COOH; V = -CH = CH_2.



	Side-chains							
Type of Porphyrins	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Aetioporphyrin I	M	E	M	E	M	E	M	E
Coproporphyrin I	M	P	M	P	M	P	M	P
Coproporphyrin II	M	P	P	M	M	P	P	M
Coproporphyrin III	M	P	M	P	M	P	P	M
Coproporphyrin IV	P	M	M	P	M	P	P	M
Uroporphyrin I	A	P	A	P	A	P	A	P
Uroporphyrin III	A	P	A	P	A	P	P	A
Protoporphyrin IX	M	V	M	V	M	P	P	M
Deuteroporphyrin IX	M	H	M	H	M	P	P	M
Haematoporphyrin IX	M	B	M	B	M	P	P	M
Mesoporphyrin IX	M	E	M	E	M	P	P	M

The process controlling the metalation of porphyrins is an ion exchange reaction, in which the two hydrogen atoms at the center of the porphyrin structure are liberated to permit incorporation of the metal (Eqn. 1.1). The reaction is controlled by the pH of the system as shown by the equation:

$$\underset{\text{Porphyrin}}{P[H_2]} + M^{2+} = \underset{\text{Metalloporphyrin}}{P[M]} + 2H^{+} \text{ (Eqn. 1.1)}$$

(Falk 1964). The stability of metalloporphyrins is also controlled by the geometry (size) and the coordination number (number of ligands) of the metal. Falk (1964) and Buchler (1987) devised a metalloporphyrin stability index, S based on the relationship:

$$S = ZE_n/r,$$

where Z is the ionic charge, E_n is the Pauling's electronegativity and r is the atomic radius of the metal. Table 1.7 reports stability indices for a number of metalloporphyrins. Based on this table, the order of stability of the different porphyrins referenced by the corresponding metals is Pt (2+) > Pd (2+) > Ni (2+) > Co (2+) > Ag (2+) > Cu (2+) > Fe (2+) > Mg (2+) > Cd (2+) > Sn (2+) > Li_2 > Na_2 > Ba (2+) > K_2. It should be noted that, as differences in the electronegativity of the transition metals are relatively small, uncertainties in electronegativity values may affect this order.

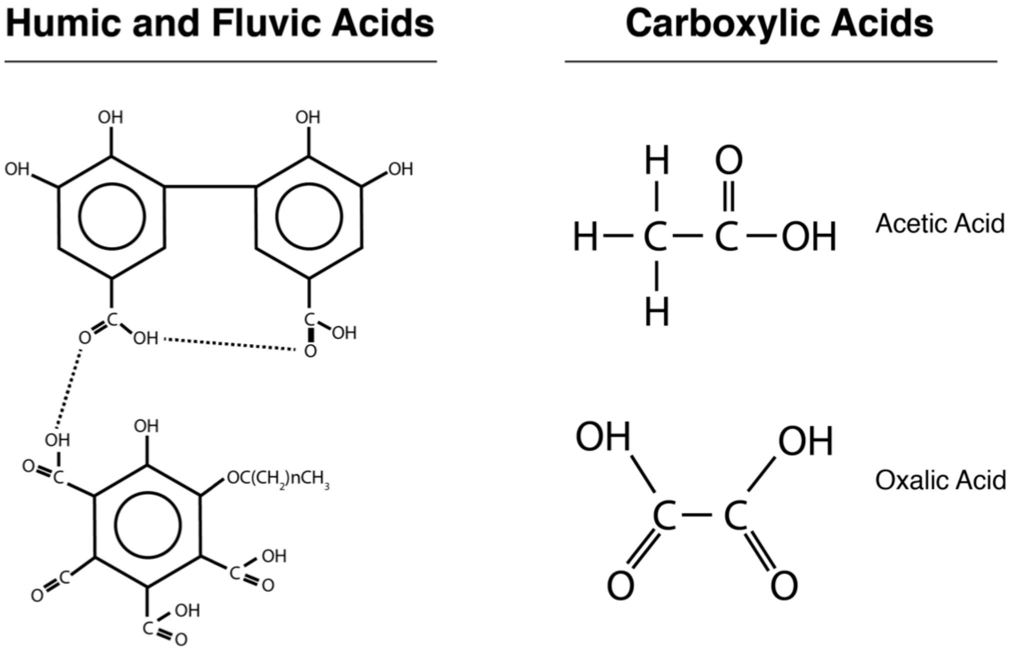
Table 1.7. The stability indices and classes that affect the stability of metals in porphyrin structures (Falk, 1964; Buchler, 1978; Manning and Gize, 1993).

Charge, Z	Cation	Stability Index	Stability Class
2	VO^{2+}	11.05	I
2	Pd^{2+}	6.9	I
2	Ni^{2+}	6.8	II
2	Cu^{2+}	6.1	II
2	Co^{2+}	5.8	II
2	Pt^{2+}	5.5b	I
2	Fe^{2+}	4.8	III
2	Zn^{2+}	4.5	III
2	Ag^{2+}	4.3b	II
2	Pb^{2+}	3.9	V
2	Hg^{2+}	3.9	V
2	Mn^{2+}	3.8	IV
2	Mg^{2+}	3.6	IV
2	Cd^{2+}	3.6	IV
2	Ca^{2+}	3	V
2	Sr^{2+}	1.6	V
2	Ba^{2+}	1.3	V
3	Co^{3+}	10.9	II
3	Au^{3+}	10.3	I
3	Al^{3+}	9.1	I
3	Ga^{3+}	8.8	II
3	Fe^{3+}	8.6	II
3	Cr^{3+}	8	I
3	Mn^{3+}	7.2	II
4	Si^{4+}	19	I
4	Pt^{4+}	14	I
5	Mo^{5+}	17.2	II
5	W^{5+}	18.8	I

Stability Class	Reagent	Degree of Demetallation
I	Pure H_2SO_4	Partial
II	Pure H_2SO_4	Complete
III	$HCl/H_2O-CH_2Cl_2$	Complete
IV	Pure CH_3COOH	Complete
V	$H_2O-CH_2Cl_2$	Complete

1.2.2. ORGANIC ACIDS

Organic acids, e.g., carboxylic, humic, fluvic and amino acids (Figure 1.6), are known to form organometallic complexes and have the potential to contribute to ore-metal transport. However, in the context of ore formation, they have only been considered as possible ligands in hydrothermal fluids. Moreover, humic and fulvic acids are potentially significant only at temperatures under 100˚C because they are unstable at higher temperature (Giordano, 1994). Ultimately, all the organic ligands investigated by Giordano (1985), notably nine carboxylate ligands for Pb and Zn, were deemed to be unimportant for metal transport because the corresponding solubility never exceed 1 ppb, which is well below the level needed in an ore-forming fluid (Giordano, 1985).



Humic and Fluvic Acids

Carboxylic Acids

Figure 1.6. Some examples of Humic, Fluvic and Carboxylic acids present in an ore-forming environment reported by Giodarno (1994).

According to Lewan and Fischer (1994), even at 25˚C, carboxylic acids with carbon numbers > 2 partition preferentially into organic liquids relative to aqueous solutions by a factor of up to 100:1, and the partitioning increases with increasing carbon number of the acid (Figure 1.7). Thus, if carboxylate ligands form strong metal complexes in the right ore fluid conditions (Giordano, 1994; Crisponi et al., 1999) they could contribute significantly to metal transport by liquid hydrocarbons.

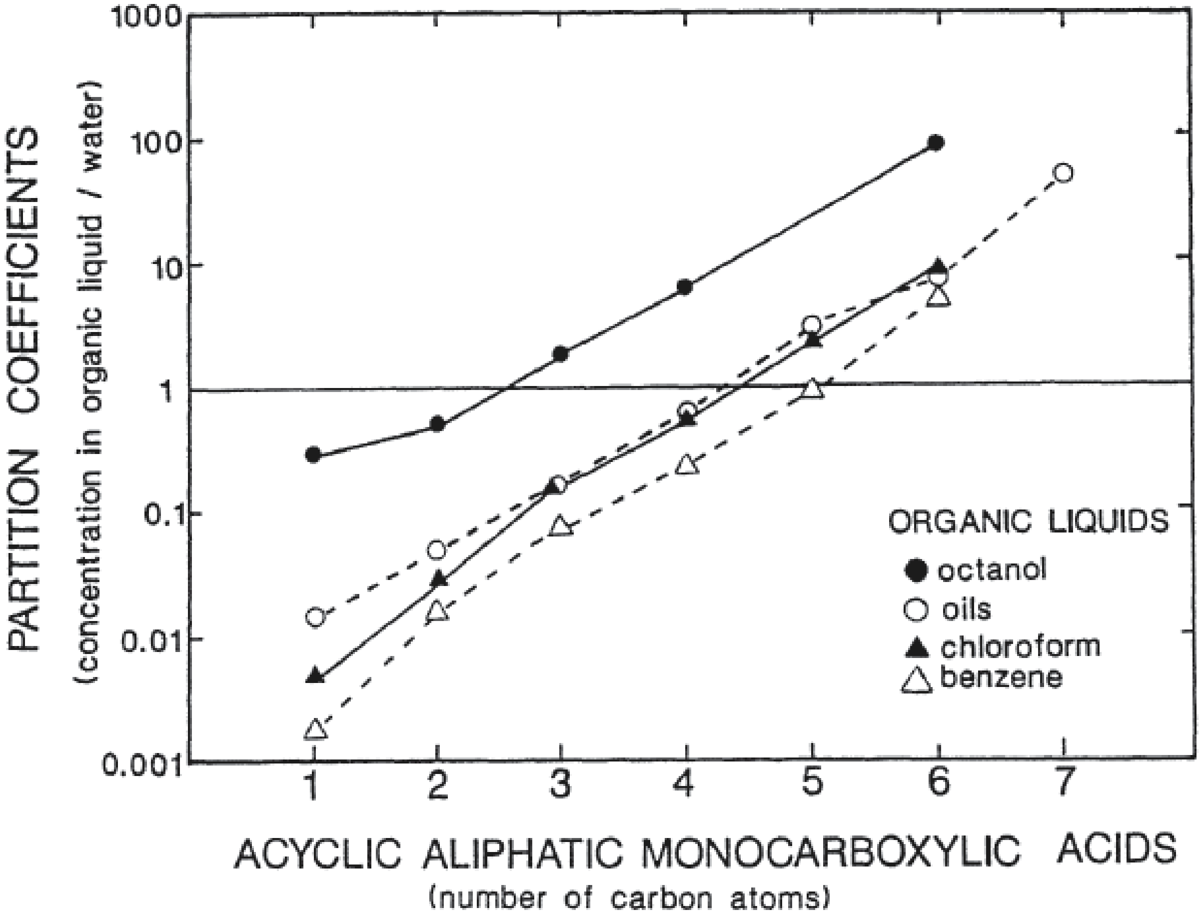


Figure 1.7. Partition coefficients of aliphatic monocarboxylic acids dissolved in organic liquid coexisting water at 25˚C (Lewan and Fischer, 1994).

1.2.3. ORGANOSULFUR COMPOUNDS

Organosulfur compounds (i.e., thiol functional groups also referred to as mercaptans) are known to exist in marine sediments, and are commonly identified in crude oil (Table 1.2; e.g., Ho et al., 1974; Tissot and Welte, 1978; Giordano, 1994). Sulfur is present in a variety of forms in crude oil, notably as native sulfur (S^0) and sulfides (-S-) (Ho et al., 1974; Tissot and Welte, 1978; Giordano, 1994). Some examples of organosulfur compounds are listed in Table 1.8. Ho et al. (1974) analyzed the organosulfur compounds present in crude oil from the extracted sulfur, and identified six different organosulfur compounds that are commonly present, all of which contain sulfur in the form of the thiol functional group (see Table 1.8) This is known to be a soft base and reacts preferentially with soft acids, e.g., Pd, Pt, Au, Cu (Pearson, 1963). Thus, it is likely that sulfur compounds of the type listed in Table 1.12 may play a role in the transport of soft metals, such as Pd (the subject of this thesis) in liquid hydrocarbons.

Table 1.8. Organosulfur compounds present in various crude oils (Ho et al. 1974).

Sulfur Species	Mean ± Standard Deviation (%)	Percent Variation	Number of Samples
Total Sulfur	1.64 ± 1.97	119.8	78
Aliphatic Sulfides	18.9 ± 9.2	48.7	25
Alkylaryl Sulfides	25.8 ± 9.7	37.7	24
Thiophenes	3.3 ± 1.8	55.4	43
Benzothiophenes	5.8 ± 3.4	59.3	78
Dibenzothiophenes	9.0 ± 4.6	50.7	78
Benzonaphthothiophenes	5.9 ± 2.3	39.4	26
Sulfur Not Recovered	42.8 ± 13.6	31.7	78

1.3. OBJECTIVES

From the previous sections, it is clear that a case can be made that metals of economic interest may have the potential to "dissolve" in liquid hydrocarbons in concentrations sufficient for them to constitute ore fluids, and that this may be important for understanding the genesis of a number of ore deposit types. In order to further test this hypothesis, it is necessary to measure the solubility of metals in crude oils at temperatures relevant for natural systems and understand the metal speciation. Thus, the objective of this thesis is to determine the solubility of a selected metal in crude oil for a range of temperatures relevant for ore forming systems and gain some insights into its speciation. The metal selected for these tasks is palladium, 1) because there is compelling evidence from nature that it dissolves in liquid hydrocarbons (Boss Mine; Jedwab and Badaut, 1999), 2) because it is known to forms strong porphyrin complexes and is a soft acid that could complex with soft bases like the alkylthiolate, 3) because it is relatively insoluble in hydrothermal fluids (its solubility in sulfur-bearing aqueous liquids is less than 10 ppb at 200˚C; Gammons and Bloom, 1993) and 4) because it is a valuable metal that is mineable at very low concentrations (~1 ppm).

The solubility of Pd in crude oil supplied by Statoil was determined experimentally at temperatures of 150, 200 and 250 °C. In addition, a technique was developed to accurately determine the concentration of Pd in the run products and in the unreacted crude oil.

1.4. THESIS ORGANIZATION

This thesis is divided into four chapters: a general introduction, two stand-alone manuscripts, and a general conclusion. The first of the two stand-alone chapters (Chapter 2) describes a method for analyzing metals in crude oils, and the second chapter (Chapter 3) reports the results of an experimental investigation of the solubility of Pd in crude oil. The research was conducted to investigate the possibility that liquid hydrocarbons could transport metals in concentrations sufficient to form ore deposits.

The analytical method described in Chapter 2 involved a combination of ashing (oxidation of the organic components using a combination of thermal combustion and exposure to a mixture of H_2O_2 and HNO_3), leaching of the residues by HCl and analysis of the leachates using inductively coupled plasma mass spectrometry (ICP-MS). To evaluate the accuracy and precision of the method, metal crude oil standards were also analysed using this method. Metal concentrations were measured in five different types of crude oils to demonstrate the applicability of the method.

Chapter 3 describes the experimental method employed to measure the solubility of Pd in crude oil and the results of experiments conducted on three compositionally different crude oils. The three crude oils ranged from light to medium in terms of their API gravity, and varied in their proportions of asphaltenes, the concentrations of sulfur and nitrogen and the total acid number (TAN). The selected crude oils were reacted with palladium oxide (PdO) in a quartz reactor for duration, which it had been determined was sufficient for equilibrium to be attained (>7 days). Analyses of the Pd in crude oils were conducted using the method developed in Chapter 2 of this thesis, summarized in the previous paragraph. The speciation of Pd was qualitatively assessed based on correlations of the Pd concentration with values of the parameters, asphaltene proportion, N and S concentration, and TAN.

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CHAPTER 2 INTRODUCTION

In the previous chapter, textural and some preliminary experimental evidence was presented showing that hydrocarbon liquids might be capable of transporting metals in concentrations sufficient to form ore deposits. The objective of the current study was thus to experimentally evaluate the hypothesis that one of these metals, namely palladium, might dissolve in crude oils in the concentrations necessary for liquid hydrocarbons to constitute ore fluids. An essential step in this study was to accurately analyze metal concentrations in crude oil. Although, crude oil has been analyzed for its metal content using a variety of analytical techniques, these techniques are either unreliable or are expensive and not readily accessible. Thus, in order to carry out this study, it was necessary to develop a simple, accurate and precise, cost effective, and accessible method for measuring metals in crude oils. One such method might be dry-ashing, but previous studies have found it unreliable.

In this chapter, a modified dry-ashing technique developed for reliably measuring the metal content of crude oils is described. Concentrations of two metals, nickel and vanadium, which were measured in oil standards and five crude oils using this technique are reported. The accuracy and precision of the results of these analyses for the oil standards are compared to those obtained in other studies for different standards using other methods. This comparison demonstrates the reliability of the newly modified dry-ashing technique.

CHAPTER 2

A Modified Dry-wet-ashing Sample Preparation and Analysis:
An Efficient Method for Analyzing Nickel (Ni) and Vanadium (V) in Crude Oil

Ichiko Sugiyama and A.E. Williams-Jones

2.1. ABSTRACT

Nickel and vanadium concentrations were measured in certified Ni and V oil standards (±2% error) and in light and heavy crude oils by using a dry-wet-ashing sample digestion technique in 10 ml Pyrex™ vessels. The crude oils were subjected to thermal combustion, chemical oxidation and leaching. The leachates were then diluted and analyzed using inductively coupled plasma mass spectrometry (Thermo Scientific iCapQ Quadrupole ICP-MS).

The measured concentrations of nickel in oil standards reported to contain 1, 100, and 1000 ppm Ni were 1.1 ±0.01, 99.8 ± 1.46, and 1025 ± 24 ppm respectively. The corresponding concentrations of V in oil standards reported to contain 2, 100, and 1000 ppm V were 1.93 ± 0.06, 104 ± 1.3, and 1027 ± 7.5 ppm respectively. Crude oil samples, A, B, C, D and E were determined to contain 5.59 ± 0.32, 4.05 ± 0.03, 6.22 ± 0.22, 33.8 ± 0.7 and 41.6 ± 3.5 ppm Ni, respectively. Their V contents were determined to be 11.98 ± 0.1, 12.2 ± 0.1, 16.5 ± 0.4, 34.7 ± 0.4, and 104 ± 8.9 ppm, respectively.

2.2. INTRODUCTION

Accurate determination of the concentrations of metals in crude oil is of importance for several reasons. Some metals cause catalytic poisoning during the refining processes, and corrosion in oil-fired power plants, and other metals, e.g., Hg will pollute the atmosphere if released during combustion of petroleum products; these metals need to be removed (Erdman and Harju, 1963; Al-Shahristani, 1972; Akinlua and Torto, 2006; Souza et al., 2006; Aucélio et al., 2007; Amorim et al., 2007; Quadros et al., 2010; Bettmer et al., 2012). Two metals, namely vanadium and nickel are consistently present in elevated concentrations (up to 1000 ppm and 200 ppm, respectively; Jones, 1975), and are measured routinely in crude oil to help fingerprint the source and determine migration pattern of the corresponding hydrocarbons, evaluate their maturation (mature oils contain lower concentrations of Ni and V porphyrins than immature oils), and assign responsibility in the case of oil spills from the crude oil fingerprint (Erdman and Harju,1963; Al-Shahristani, 1972; Shen et al., 1985; Barwise, 1990; Kesler et al., 1994; McKenna et al., 2009; Williams-Jones et al., 2009).

Analysis of the concentrations of metals in crude oil can be conducted either by direct instrumental analysis with little or no sample preparation (Table 2.1; non-destructive sample preparation), or with destructive sample preparation followed by instrumental analysis (Table 2.2). Direct analytical techniques usually involve dilution with either toluene or an aqueous solution containing an emulsifier (emulsion technique) followed by direct injection of the diluted samples into the instrument (See Table 2.1).

Table 2.1. List of methods used for direct analysis of crude oils.

Direct Sample Analysis

Crude oil samples are analysed for their metal concentrations directly using the methods listed below. Commonly, for methods 2, 3,4 and 5, the oil standards and samples are diluted using toluene or are emulsified (See table 2.1).

Analysis Instrument

1. Neutron Activation Analysis (NAA)
2. Graphite Furnace Atomic Absorption Spectrometry (GF-AAS)
3. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
4. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
5. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Table 2.2. Summary of sample preparation (non-destructive and destructive) and analytical methods used in determining metal concentrations in crude oils.

Sample Preparation Technique	Sample Preparation Method	Analysis Instrument
1. Wet Digestion (Destructive) Aliquots of acid and oil are mixed in a vessel and subjected to heat, microwaves or high pressure to digest the samples.	1a. High Pressure Asher (HPA) 1b. Microwave Digestion	ICP-MS, AAS or ICP-OES, etc.
2. Dry Ashing (Destructive) Oil initially undergoes combustion in a crucible in a muffle furnace. The refractory ash from the combustion is leached for metals using acids.	2a. Platinum Crucible and Muffle Furnace 2b. Quartz Crucible and Muffle Furnace	ICP-MS, AAS, or ICP-OES, etc.
3. Emulsion (Non-destructive) Oil-in-water or water-in-oil Mix various portions of oil, water and emulsifier prior to analysis.	3a. Emulsifier with oil in larger volume of water 3b. Emulsifier with water in larger volume of toluene and oil	ICP-MS or ICP-OES, etc.

These techniques are much more rapid than the destructive techniques (e.g. Murillo and Chirinos, 1994 and Duyck et al., 2002). However, they are generally less accurate because commonly it is necessary to use aqueous or oil standards that are not representative of the complex crude oil sample matrix (e.g., Filby and Olsen, 1994; Hardaway et al., 2004; Fischer and Krusberski, 2005; Mello et al., 2012). A discussion of the other issues associated with the direct analysis of crude oils is outside the scope of this study, but has been reviewed in detail by Filby and Olsen, (1994) and Mello et al., (2012).

The destructive sample preparation methods either involve wet digestion (oxidation with acids) or a dry-wet-ashing process (thermal combustion followed by acid digestion; Table 2.2). Sample preparation involving wet digestion is conducted using a high-pressure asher (HPA; high pressure and elevated temperature) or microwave-induced combustion (MIC; microwave energy with elevated temperature and pressure). In both cases, a small aliquot of oil is added to a large volume of acid in a closed vessel to fully remove the organic matrix and dissolve the metals from the oils (e.g., Souza et al., 2006 and Sanabria Ortega et al., 2013). This method of sample preparation results in highly accurate and reproducible results. However, the equipment is typically not readily accessible, can be costly and the number of sample that can be analysed per cycle is small (four quartz vessels for HPA and 12 teflon vessels for MIC per cycle). Furthermore, although the vessels for MIC and HPA contain safety mechanisms to prevent over-pressurization of the vessels, once the safety membrane (MIC) or cap (HPA) opens, the acids can spill out of the vessels, and can be dangerous.

Dry-wet-ashing avoids many of the problems that were mentioned above, and is conducted by placing an aliquot of hydrocarbon sample in a platinum (Pt) or quartz crucible and heating it to about 450 to 550˚C to remove most of the organic matrix with the assistance of a 1 bar oxygen atmosphere (Barin et al., 2007). The ash in the crucible is then oxidized and leached to fully remove the ash and place the metals in solution. The method is simple, avoids acid spills, affordable, and the equipment is readily available (e.g., Hardaway et al., 2004; Fischer and Krusberski, 2005; Barin et al., 2007). However, dry-wet-ashing has been criticized for poor recovery of metals, poor reproducibility due to the loss of material from the crucible during combustion and loss of metals through volatilization, and the long preparation time (e.g., Horeczy et al., 1955; Barin et al., 2007; Mello et al., 2012). Despite this criticism and the potential advantages of the technique, no quantitative assessments of the dry-wet-ashing technique or recommendations for its improvement have been published.

The purpose of our research was to develop a simple, affordable, and reliable method of analyzing metal concentrations in crude oil, by modifying the dry-wet-ashing technique. We modified the ashing technique to improve its accuracy and precision by using 10 ml volume Pyrex^{TM} vessel capped with quartz wool to prevent material loss (e.g., ash or oil) during combustion. This modification shortened the preparation time by avoiding the use of platinum or quartz crucible or a dish (Horeczy et al., 1955). Instead, slender Pyrex^{TM} vessels were used that allowed significantly more samples to be ashed in an oven simultaneously. Finally, the modification allowed ashing, leaching, oxidation and storing of the sample to be performed in a single vessel, minimizing the contamination of the sample.

2.3. SAMPLE DESCRIPTION

Nickel and vanadium crude oil standards were purchased from Conostan® division of SCP Science Ltd. The selected certified oil standards had been measured according to the protocol proposed by the American Society of Testing Material (ASTM) D5708 using the appropriate NIST standards (standard testing methods for nickel, vanadium and iron in crude oils and residual fuels by Inductively Coupled Plasma Atomic Emission Spectrometry). The nickel oil standards have concentrations of 1 (Conostan Cat. No. CB7-100-002), 100 (Conostan Cat. No. CB7-100-018) and 1000 ppm (Conostan Cat. No. CB7-100-019), and the vanadium oil standards concentrations of 2 (Conostan Cat. No. CB7-100-024), 100 (Conostan Cat. No. CB7-100-025) and 1000 ppm (Conostan Cat. No. CB7-100-026).

Five crude oils, A (lightest), B (light), C (medium), D (heavier) and E (heaviest) were provided by Statoil for this study. The crude oils were selected to provide a broad range of properties and compositions (Table 2.3). This range of crude oil compositions allowed us to evaluate the effect of crude oil chemistry on the precision.

Table 2.3. Properties of the five natural crude oil samples. Crude oils A to E are ordered from the lightest to the heaviest based on specific gravity.

Crude Oil Characterization

Parameters	A	B	C	D	E
API Gravity	26.6	25.0	19.0	13.4	8.5
Specific Gravity	0.895	0.904	0.940	0.976	1.011
Sulfur (wt%)	0.84	0.52	0.82	1.89	4.98
Nitrogen (wt%)	-	0.20	0.44	0.92	0.56
TAN (mgKOH/g)	0.2	2.9	2.3	0.92	2.7
Paraffins (vol%)	-	36.99	18.81	59.8	53.0
Naphthenes (vol%)	-	49.35	64.88	30.3	36.7
Aromatics (vol%)	-	13.36	14.95	10.0	10.2
Asphaltenes (wt%)	<0.3	0.3	1.4	18.6	17.2

2.4. ANALYTICAL METHOD (FIGURE 2.1)

The dry-wet-ashing treatment was applied to aliquots of the oil standards (5 ml) and the crude oils (5 ml), which were placed in clean 10 ml Pyrex^{TM} vessels that were stoppered with quartz wool and heated to 600˚C. Prior to the ashing process, the vessels and the wools were washed using trace metal grade nitric acid (75% HNO_3) for one day, neutralized for two hours with Milli-Q™ water, and dried in an oven at 100˚C for one hour to ensure dryness. Four samples of each oil standard (5 ml) and crude oil (5 ml) were prepared for ashing and analysis. Each vessel was stoppered with compressed quartz wool, placed in a Thermo Fischer Scientific, Inc. Thermolyne^{TM} muffle oven and heated at 600 °C for 12 hours. The thermally ashed samples were then cooled to room temperature. In order to ensure complete decomposition of the ash, four ml of trace metal grade nitric acid (75% HNO_3) and one ml of trace metal grade hydrogen peroxide (30% H_2O_2) were added the Pyrex^{TM} vessels. After decomposition of the residual ash, one ml of trace metal grade hydrochloric acid (35% HCl) was added to the vessels to dissolve any precipitates.

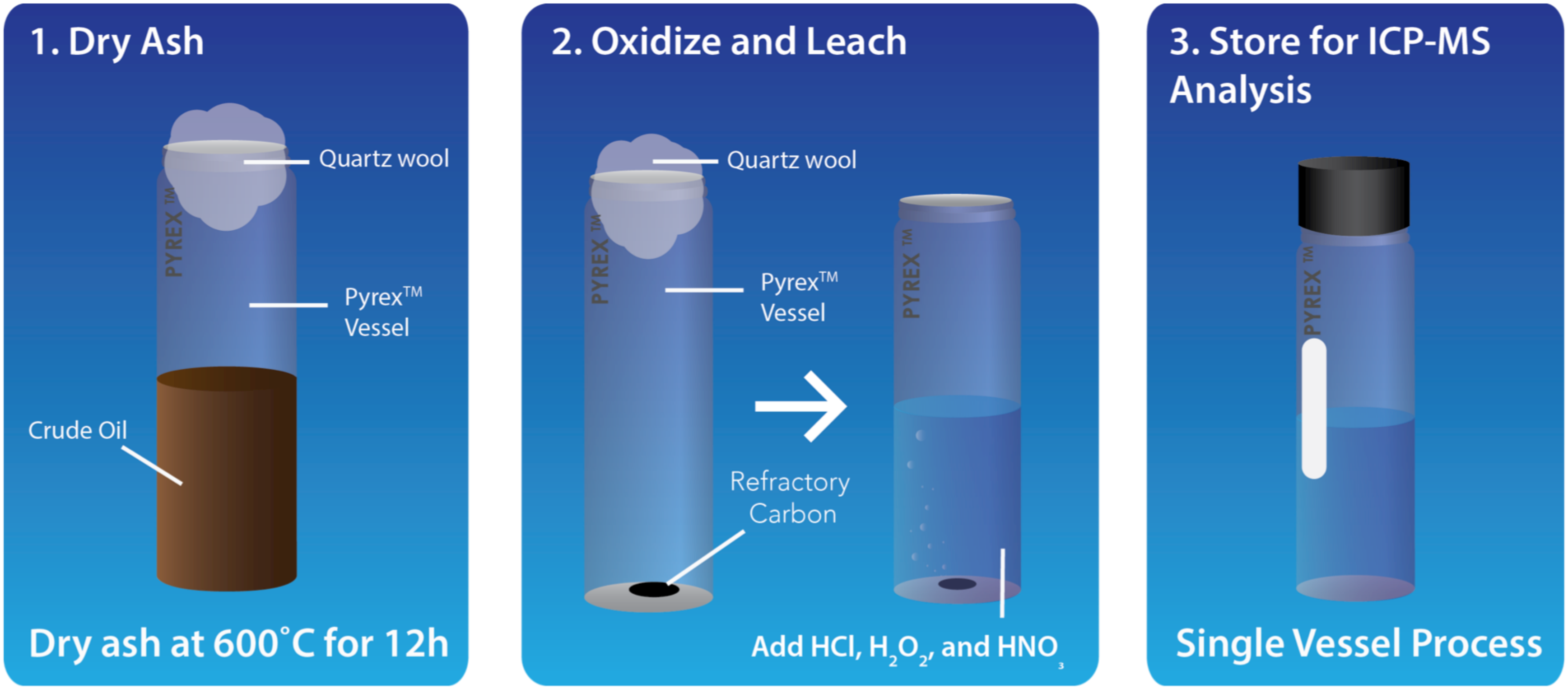

Figure 2.1. Sketches showing the steps employed in the dry and wet ashing and acid digestion of crude oils in preparation for the analysis of their metal content by ICP-MS.

The analytical protocol involved measuring the Nickel (^{60}Ni), Vanadium (^{51}V) and Yttrium (^{89}Y) counts of the digested acid samples (from the oil standards and crude oils), a series of Ni and V aqueous standards (0.5,1,5,10,15,20 and 50 ppb standards diluted from a 1000 ppm Ni and V aqueous standard supplied by SCP Science Ltd.), and the blank solution (1 ppb Y diluted down from an aqueous standard containing 1000 ppm Y supplied by SCP Science Ltd., 2% HNO_3 and Milli-Q™ water) using a Thermo Fischer Scientific, Inc. iCap-Q Quadrupole ICP-MS (conditions listed in Table 2.4). Yttrium was used as an internal standard to monitor the stability of the instrument and to ensure that instrumental errors did not affect the results. The blank solution was also used as a diluent for the digested acid samples and the aqueous standards. The solutions used to leach the ash from the Ni oil standards had concentrations of 1, 100 and 1000 ppm, and were diluted approximately 10^2, 10^4 and 10^5 times with the blank solution. The solutions used to leach the ash from the V oil standards with concentrations of 2, 100 and 1000 ppm, were diluted approximately 10^2, 10^4 and 10^5 times with the blank solution. The solutions used to leach the ash from the crude oils were diluted approximately 10^4 times, with the blank solution. All of the dilutions were conducted in centrifuge tubes, which were shaken thoroughly for a minute to homogenize the solution. The matrix of the experimental samples was diluted sufficiently to minimize the suppression effect of the ICP-MS analysis. This effect occurs when the ICP-MS analysis is conducted on a concentrated solution, leading to a competitive ionization of the analytes due to a lack of ionization by the limited plasma source (Thomas, 2013).

Table 2.4. Analytical conditions for the ICP-MS used in determining metal concentrations in diluted samples.

Inductively coupled plasma	
Plasma Power (W)	1548
Plasma Ar gas flow (l min^{-1})	15
Auxiliary Flow (l min^{-1})	0.8
Nebulizer	PFA-ST
Nebulizer Flow (l min^{-1})	1.11
Spray Chamber	PFA Cyclonic
Peltier cooling Temperature (°C)	2.7
Sample and Skimmer Cones	Ni
Plasma Cooling Water Flow (l min^{-1})	3.32
Interference reduction system	iCapQ

Data Acquisition	
Mass Analyzer system	Quadrupole
Isotopes measured	^{60}Ni, ^{51}V, ^{89}Y
Settling time, s	60
Sampling time, s	60
Total acquisition time, s	120
Peristatic Pump speed (rpm)	20
Detection mode	Digital mode

Once the counts for ^{60}Ni, ^{51}V and ^{89}Y had been measured with the ICP-MS, the data were processed to obtain the Ni and V concentrations in the oil standards and in the crude oils. The nickel and vanadium counts for the digested samples, the external Ni and V aqueous standards, and the blank solutions were corrected initially using the yttrium internal standard (^{89}Y). This was done by dividing the measured ^{60}Ni and ^{51}V counts by the ^{89}Y counts to account for the instrumental fluctuation of the ICP-MS. The ^{60}Ni/^{89}Y and ^{51}V/^{89}Y ratios for the digested samples and the aqueous standards were subtracted from the blank ^{60}Ni/^{89}Y and ^{51}V /^{89}Y ratios, respectively, to account for the background ratios of the diluent. In order to convert the ^{60}Ni counts to concentrations, we constructed a calibration curve by plotting the ^{60}Ni/^{89}Y ratios (Y-axis) of the aqueous standards against the known Ni standard concentration (X-axis; Eq. 2.1). The same process was used to construct the V calibration curve (Eq. 2.2). All the calibration curves regressed linearly through the origin with a goodness of fit of 99.9%. Preliminary nickel and vanadium concentrations for the diluted oil standards and crude oils were calculated algebraically using the counts from the samples and the slope of the calibration curve indicated in equation 2.3 for Ni and 2.4 for V. The resulting data were corrected to obtain the concentrations the true concentrations by applying the dilution and density factor as indicated in equations 2.5 and 2.6 (mass of a fixed volume of solution in grams divided by the mass of the same volume of sample oil in grams to account for the density differences between the solutions analyzed and the original oil standards and crude oil samples).

$$\left(\frac{60\text{Ni}}{89\text{Y}}\right)_{\text{Standard}} = \text{Slope of the Calibration Curve} \times \text{Known Ni Concentration} \quad \text{(Eq. 2.1)}$$

$$\left(\frac{51\text{V}}{89\text{Y}}\right)_{\text{Standard}} = \text{Slope of the Calibration Curve} \times \text{Known V Concentration} \quad \text{(Eq. 2.2)}$$

$$C_{1\text{-Ni}} = \text{Ni Sample Concentration} = \frac{\left(\frac{60\text{Ni}}{89\text{Y}}\right)_{\text{Sample}}}{\text{Slope of the Calibration Curve}} \quad \text{(Eq. 2.3)}$$

$$C_{1\text{-V}} = \text{V Sample Concentration} = \frac{\left(\frac{51\text{V}}{89\text{Y}}\right)_{\text{Sample}}}{\text{Slope of the Calibration Curve}} \quad \text{(Eq. 2.4)}$$

$$\text{Final Ni Sample Concentration} = C_{1\text{-}Ni} \times \text{Dilution Factor} \times \frac{\text{Sample acid in grams}}{\text{Sample oil in grams}} \quad \text{(Eq. 2.5)}$$

$$\text{Final V Sample Concentration} = C_{1\text{-}V} \times \text{Dilution Factor} \times \frac{\text{Sample acid in grams}}{\text{Sample oil in grams}} \quad \text{(Eq. 2.6)}$$

2.5. RESULTS

2.5.1. NICKEL AND VANADIUM OIL STANDARDS: VALIDATION OF THE METHOD

Certified nickel and vanadium oil standards from Conostan (Ni and V in the form of metal alkyl aryl sulfanate in crude oil) with concentrations of 1, 100, and 1000 ppm for Ni and 2, 100, and 1000 ppm for V were measured in quadruplicate analyses (n=4) to test the reliability of the ashing method (the error reported by Conostan for the oil standards is ± 2%). The analyses of the oil standards with 1, 100, and 1000 ppm Ni yielded concentrations of 1.1±0.01, 99.8±1.46, and 1025±24 ppm, respectively (Table 2.5). By comparison, oil standards with 2, 100, and 1000 ppm V, yielded concentrations of 1.93±0.06, 104±1.3, and 1027±7.5 ppm, respectively (Table 2.5). The combined dry-wet-ashing technique and ICP-MS analyses reproduced the reported concentrations of Ni and V in the certified 1000-ppm standards to an error of ± 2 % and ± 3%, respectively, the 100-ppm standards to an error of ± 0% and ± 4%, respectively, and the 1-ppm standards to an error of ± 10% and ± 3%, respectively (Table 2.5). For the higher concentrations, these errors are comparable to those reported by Conostan. This provides confidence that the dry-wet-ashing-ICP-MS technique described here can be used reliably to determine the Ni and V contents of crude oils. For further discussion on the results of the analyses of the Ni and V oil standards, refer to section 2.6.

Table 2.5. The table lists the original concentration of the Ni and V oil standards from Conostan (± 2 %), and the founded Ni and V concentrations of the oil standards after it was subjected to the dry-wet-ashing process followed by ICP-MS.

Ni Oil standards (ppm)	Founded Ni Values (ppm)	V Oil standards (ppm)	Founded V Values (ppm)
1	1.11	2	1.99
1	1.12	2	1.89
1	1.11	2	1.89
1	1.09	2	1.96
Average (ppm)	**1.11**	**Average (ppm)**	**1.93**
Standard deviation (ppm)	**0.010**	**Standard deviation (ppm)**	**0.06**
Percent error (%)	**1**	**Percent error (%)**	**3**
100	98.6	100	106
100	101	100	105
100	98.5	100	104
100	101	100	103
Average (ppm)	**100**	**Average (ppm)**	**104**
Standard deviation (ppm)	**1.5**	**Standard deviation (ppm)**	**1.3**
Percent error (%)	**1**	**Percent error (%)**	**1**
1000	1027	1000	1018
1000	1057	1000	1028
1000	1017	1000	1037
1000	1001	1000	1025
Average (ppm)	**1025**	**Average (ppm)**	**1027**
Standard deviation (ppm)	**24**	**Standard deviation (ppm)**	**8**
Percent error (%)	**2**	**Percent error (%)**	**1**

2.5.2. NICKEL AND VANADIUM IN CRUDE OILS

The nickel and vanadium concentrations of the five crude oils were determined though quadruplicate analyses. The concentrations of Ni in crude oils, A, B, C, D and E were determined to be 5.59 ± 0.32, 4.05 ± 0.03, 6.22 ± 0.22, 33.8 ±0.7 and 41.6 ±3.5 ppm, respectively, and those for vanadium to be 11.98 ± 0.1, 12.2 ± 0.1, 16.5 ± 0.4, 34.7 ± 0.4, and 104 ± 8.9 ppm, respectively (Tables 2.6 and 2.7). The modified dry-wet-ashing-ICP-MS technique resulted in Ni and V concentrations in crude oil that were reproducible within 5%, with the exception of crude oil E, for which the reproducibility was within 10%. Thus, the modified dry-wet-ashing technique followed by ICP-MS analysis can accurately and precisely measure a wide range of metal concentrations in crude oil. For further discussion of the results from the crude oils, refer to section 2.6.

Table 2.6. The nickel concentration of crude oils A, B, C, D, and E determined using the modified dry ashing-ICP-MS technique described in this study.

Heaviness	**Lightest A (ppm)**	**Light B (ppm)**	**Medium C (ppm)**	**Heavier D (ppm)**	**Heaviest E (ppm)**
Analysis 1	5.59	4.01	6.52	34.21	41.66
Analysis 2	5.32	4.09	6.13	33.20	37.81
Analysis 3	5.41	4.05	6.00	33.30	46.26
Analysis 4	6.03	4.04	6.24	34.50	40.78
Average (ppm)	5.59	4.05	6.22	33.80	41.63
Standard Deviation (ppm)	0.32	0.03	0.22	0.65	3.50
Percent error (%)	5	1	4	2	8

Table 2.7. The vanadium concentration of crude oils A, B, C, D, and E determined using the modified dry ashing-ICP-MS technique described in this study.

Heaviness Name	**Lightest A (ppm)**	**Light B (ppm)**	**Medium C (ppm)**	**Heavier D (ppm)**	**Heaviest E (ppm)**
Sample 1	12.1	12.2	16.4	34.7	104
Sample 2	12.0	12.4	16.2	34.3	93
Sample 3	12.0	12.3	16.2	34.5	115
Sample 4	11.8	12.0	17.0	35.2	103
Average (ppm)	12.0	12.2	16.5	34.7	104
Standard Deviation (ppm)	0.1	0.2	0.4	0.4	8.9
Percent error (%)	1	1	2	1	9

2.6. DISCUSSION

2.6.1. RELIABILITY OF THE MODIFIED DRY-WET-ASHING TECHNIQUE

Our modified dry-wet-ashing-ICP-MS technique generated much more accurate and precise results than the original dry-wet-ashing technique developed by Horeczy et al. (1955). Horeczy et al. (1955) measured Ni and V concentrations in a gasoline blend with known concentrations of these metals using a dry-wet-ashing preparation followed by emission spectrograph analysis. The analysis underestimated the true concentrations of the metals by 54 and 88%, respectively, which was probably due to the volatilization of the metals during combustion. Their method of ashing involved combusting the oil in a wide, shallow Pt crucible placed in a muffled furnace oven, which undoubtedly led to considerable loss of oil, ash and metals during the combustion. Our modification of the method, namely replacing the Pt crucibles with slender Pyrex^{TM} vessels stoppered with quartz wool prevents the loss of oil and ash during the release of the gases produced by combustion, and therefore maximizes the recovery of the metals.

To further evaluate the reliability of our modified dry-wet-ashing-ICP-MS technique, we compared the accuracy and precision of our analyses to those obtained using other techniques (Table 2.8). Our modified technique has a level of accuracy and precision comparable to the HPA-ICP-MS and the MIC-ICP-MS techniques. Furthermore, our technique is more efficient at recovering metals from the crude oil standards relative to INAA, the original dry-wet-ashing technique, Emulsion-ICP-MS, and toluene-dilution-ICP-MS. Finally, we note that our technique yielded the highest precision of all the techniques referred to in Table 2.8. In summary, the dry-wet-ashing-ICP-MS technique described in this paper is simple, accessible, reliable, affordable, and generates very accurate and precise results.

Table 2.8. Comparison of the accuracy and precision of the different analytical methods used to measure the concentrations of Ni and V in crude oil standards.

Analysis Type	Standard Matrix	Metal	Certified Value (ppm)	Founded Value (ppm)	Precision (%)	Accuracy (%)	References
Direct Analysis with ICP-MS (Toluene Dilution)	**Crude Oil**	**Ni**	17.5 ± 0.2	15.5 ± 0.5	97	89	Duyck et al. (2002)
		V	28.2 ± 0.4	25.8 ± 0.6	98	92	
Direct Analysis with ICP-MS (Emuslification: Oil-in-water)	**Crude Oil**	**Ni**	29 ± 1	27 ± 2	93	93	Murillo and Chirinos (1994)
		V	56 ± 2	54 ± 2	96	96	
Direct Analysis with INAA	**Crude Oil**	**Ni**	120 ± 6	99.2 ± 5.1	95	80	Filby and Olsen (1994)
		V	398 ± 19.9	381 ± 23	94	96	
Microwave Induced Combustion followed by ICP-OES	**Crude Oil**	**Ni**	17.54 ± 0.21	18.2 ± 1	95	96	Souza et al. (2006)
		V	28.19 ± 0.40	27.6 ± 0.8	97	98	
High Pressure Asher followed by ICP-MS	**Crude Oil**	**Ni**	17.54 ± 0.21	17.3 ± 0.2	99	99	Ortega et al. (2013)
		V	28.19 ± 0.4	29 ± 0.4	99	97	
Dry ashing followed by ICP-MS	**Gasoline blend**	**Ni**	15.62	8.47 ± 0.25	97	46	Horeczy et al. (1955)
		V	12.44	11 ± 0.1	99	12	
Dry Ashing followed by ICP-MS	**Crude Oil**	**Ni**	1 ± 0.02	1.1 ± 0.01	99	90	This Study
		Ni	100 ± 2	99.8 ± 1.46	99	100	
		Ni	1000 ± 20	1025 ± 24	98	98	
		V	2 ± 0.04	1.93 ± 0.06	97	97	
		V	100 ± 2	104 ± 1.3	99	96	
		V	1000 ± 20	1027 ± 7.5	99	97	

2.6.2. REPRODUCIBILITY OF MEASURED NICKEL AND VANADIUM CONCENTRATIONS IN CRUDE OILS

Although the Ni and V contents of crude oils A to E were analysed with excellent using the modified dry-wet-ashing-ICP-MS technique, the precision was nonetheless greater for the light crude oils than the heavy crude oils (listed as percent error in Tables 2.6 and 2.7). As noted earlier, the poorest results were obtained for crude oil E, the heaviest and also most viscous of the crude oils analysed. This suggests that crude oil E may be less homogeneous than the other crude oils due perhaps to the presence of colloidal asphaltene compounds (crude oil E contains 20 wt.% asphaltenes) and organic aggregates (Yin et al., 2008). A solution to this problem would be to analyse larger samples as mechanical mixing at room temperature is ineffective owing to the very high viscosity. However, this was not attempted as the 10% reproducibility was deemed acceptable. In summary, our dry-wet-ashing-ICP-MS technique can be used to measure metal concentrations in a variety of crude oils with great accuracy and precision.

2.7. CONCLUSION

The analytical technique described in this paper provides a simple, easily accessible, and affordable method for analyzing metal concentrations in crude oil. The results obtained using it to analyze the Ni and V contents of a selection of oil standards are in excellent agreement with the certified values and demonstrate that the modifications introduced in the method of sample preparation have successfully addressed criticisms that dry-wet-ashing cannot be used reliably in analyzing crude oil. Indeed, the accuracy and precision of the analyses compare very favorably with those obtained by other more expensive and less accessible methods and in many cases are superior to them. Thus the technique developed in this study, which involves a combination of dry and wet ashing followed by ICP-MS analysis provides a means for efficiently and reliably analyzing the metal content of crude oils in any laboratory equipped with an ICP-MS and an oven.

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CHAPTER 3 INTRODUCTION

In the previous chapter, we described a modified dry-wet-ashing technique that enables accurate and precise analyses of metal concentrations in crude oils. This was necessary to permit the second part of this study, namely the conduct of experiments designed to measure the solubility of palladium in crude oils at elevated temperature.

In this chapter, results are reported of experiments that measured the solubility of palladium oxide (PdO) in three crude oils, A, B and C, of varying composition, at temperatures between 150 to 250°C. The crude oils were selected to vary widely in their API gravity, asphaltene content and concentrations of nitrogen, and sulfur, parameters that may control palladium. Through this choice of crude oils, it was hoped that correlations of Pd solubility with one or more of these parameters might afford insight into the speciation of Pd, e.g., a correlation with asphaltene and nitrogen content migh point to the transport of Ni and V as porphyrin complexes.

CHAPTER 3

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

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3.1. ABSTRACT

Here we report the results of experiments designed to measure the solubility of palladium oxide (PdO) in crude oil and test the hypothesis that liquid hydrocarbons could act as ore fluids. The PdO was reacted with three crude oils containing 0.2, 0.3 and 1.4 wt.% asphaltene, at 150, 200 and 250 ˚C for 7 or more days. Experiments conducted at 150˚C, yielded Pd concentrations of 141 ± 34 ppb, 160 ± 87 ppb, and 313 ± 51 ppb. The corresponding asphaltene proportions were 0.2, 0.3, and 1.4 wt. %. At 200˚C, the Pd concentrations were 129 ± 83 ppb, 401 ± 23 ppb, and 1183 ± 417 ppb and at 250˚C they were 77 ± 17 ppb, 76 ppb, and 790 ± 445 ppb. The background Pd concentrations in the oils ranged from 0.46 ± 0.07 ppb to 1.36 ± 0.67 ppb. These results show that Pd concentration reached a maximum in two of the three oils at 200˚C and then decreased with further increase of temperature. They also show that Pd solubility increases with increasing asphaltene content. Palladium concentrations of this magnitude indicate that liquid hydrocarbons have the potential to transport this metal in amounts sufficient to form ore deposits, and emphasize the need for more studies of environments in which palladium and hydrocarbons have been shown to be spatially associated.

3.2. INTRODUCTION

It is a widely held belief that aqueous liquids are the only non-magmatic crustal fluids capable of transporting metals in solution in concentrations sufficient to form ore deposits. However, a number of metals, including the platinum group elements (PGE) are intimately associated with hydrocarbons in several ore-forming environments, and it is thus reasonable to consider the possibility that hydrocarbon liquids may also be involved in metal transport (Table 3.1). For example, in the black-shale-hosted Kupferschiefer of Poland, palladium (Pd) and platinum (Pt) concentrations in black shales reach 1,900 and 600 ppm, respectively (Kucha and Przybylowicz, 1999) and in thurcolite reach 5,000 and 1,770 ppm, respectively (Vaughan, D. J. 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, province of Guizhou, China, namely 0.4 and 0.3 ppm, respectively (e.g., Coveney, 1991; Coveney et al., 1992; Lott et al., 1999). In both examples, however, the Pd and Pt mineralization is attributed by the researchers who have studied these deposits to the transport of the metals by oxidizing hydrothermal fluids and the subsequent precipitation of the metals due to reduction of the hydrothermal fluids by organic matter in the black shales (Coveney, 1991; Kucha and Przybylowicz, 1999; Lott et al., 1999).

Table 3.1. Characteristics of ore deposits with elevated Pd and Pt concentrations in which there is a close spatial association of the metals with organic matter.

Location	Pd (ppm)	Pt (ppm)	Host	Reference
Kupferschiefer, Poland	1900	600	Black shale clay organic matrix	Kucha et al. (1999)
Kupferschiefer, Poland	5000	1770	Thucholite	Kucha et al. (1999)
Boss Mine, Clark County, Nevada	18500	27400	Bitumen	Jedwab et al. (1999)
Zunyi Mine, Guizhou Province, China	0.4	0.3	Black shale and sulfides	Coveney, Jr. et al. (1991)

Arguably, the best example of a deposit for which a convincing case can be made that the platinum group elements were transported by liquid hydrocarbons is provided by the Boss Mine, Nevada, U.S.A (Jedwab et al., 1999). There, the ore comprises sub-vertical bituminous veins containing an average of 660 ppm Pd, 150 ppm Pt and 1315 ppm Au. The PGE occur in the bitumen, mainly as potarite, an alloy of Hg {(Pd_{81}, Au_{13}, Pt_{01}) Hg} but undoubtedly also as other phases because the bitumen contains a higher proportion of Pt than the potarite (1.85 wt.% Pd and 0.38 wt.% Pt). Most significantly, the potarite is present as particles, ranging from 5 to 30 nm in diameter, and as larger micron-scale clusters of these nanoparticles. This suggests that the corresponding metals were transported in liquid hydrocarbons (either in solution or as nanoparticles) and precipitated/flocculated in the bituminous residues. It is also significant that the PGE are associated with Hg, a metal that is not easily transported in hydrothermal fluids but dissolves in high concentrations in liquid hydrocarbons (>800 ppm at 200 °C; Fein and Williams-Jones, 1997; Miedaner et al., 2005). Similar observations of nanoparticles in pyrobitumen have been made recently for uraninite in the Carbon Leader of the Witwatersrand Au-U deposits, South Africa, and are interpreted as evidence of the transport of uranium by liquid hydrocarbons (Fuchs et al., 2015).

Despite the apparent potential of liquid hydrocarbons to transport Pd and Pt, 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, the organic matter was able to adsorb 0.02 and 1.95 g Pt per kg of organic matter (20 and 1950 ppm).

In this study we report the results of experiments designed to determine the solubility of Pd in crude oils at temperatures of 150, 200 and 250 ˚C at saturated vapour pressure. The oils were selected to provide a range of compositions, particularly in the proportion of the asphaltene component, which is widely believed to govern metal solubility in liquid hydrocarbons. The results are encouraging and show that liquid hydrocarbons can dissolve Pd in concentrations sufficient for them to potentially constitute ore fluids.

3.3. 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, asphaltenes and the contents of sulfur (S) and nitrogen (N). These are listed in Table 3.2.

Table 3.2. Properties of crude oils A, B and C.

Properties	A	B	C
API Gravity	26.6	25.0	19.0
Specific Gravity	0.90	0.90	0.94
Sulfur (wt.%)	0.84	0.52	0.82
Nitrogen (wt.%)	-	0.20	0.44
TAN (mgKOH/g)	0.20	2.90	2.30
Paraffins (wt.%)	-	37	19
Naphthenes (wt.%)	-	49	65
Aromatics (wt.%)	-	13	15
Asphaltenes (wt.%)	<0.3	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 water (Speight, 2001). Crude oils are distinguishable most simply by their API gravity, with A being the lightest (highest API number) and C the heaviest (lowest API number) crude oil in this study. To a large degree the API gravity reflects the asphaltene content. Thus, crude oil A has the lowest and crude oil C the highest asphaltene content. This is an important parameter, as asphaltene is known to contain porphyrins, which are macromolecules containing tetrapyrroles with a nitrogen functional group that forms strong bonds with a variety of metals, including Pd (Falk, 1964; Buchler, 1978; Manning and Gize, 1993). It therefore also follows that the N content is another important parameter because, in part, it is a measure of the porphyrin content; other nitrogen compounds include amine, pyridine, quinolone, pyrrole and carbazole (Tissot and Welte, 1978). The crude oil with the lowest N content is crude oil B, and that with the highest N content crude oil C. Another parameter that may be important in controlling metal uptake by crude oil is the S content as the thiol group 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 and that with the highest S content is crude oil A. Finally, TAN (mgKOH/g), which is a measure of acidity, is 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).

3.4. METHODOLOGY

3.4.1. 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 = 13 mm, ID = 11 mm) supplied by National Scientific Inc. 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 Pd was introduced in the form PdO powder, and was placed in a fused quartz ampoule (OD = 6 mm, ID = 4 mm) that had been cleaned using the method employed for the quartz reactors. The ampoules were stoppered with quartz wool (cleaned in 75% HNO_3) to prevent mechanical transfer of the powder to the reactor during experiments. To ensure that no powder was mechanically introduced from the outer walls of the ampoule, the latter were washed with Optima grade toluene, and the ampoule dried in an oven at 150 ˚C for 30 minutes. The ampoule was then placed in the reactor. Aliquots (4 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 PdO-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 the Thermo Scientific™ Thermolyne™

tabletop muffle furnace oven that had been preheated to the desired temperature (Figure 3.1). Temperature was controlled to ± 1 °.

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

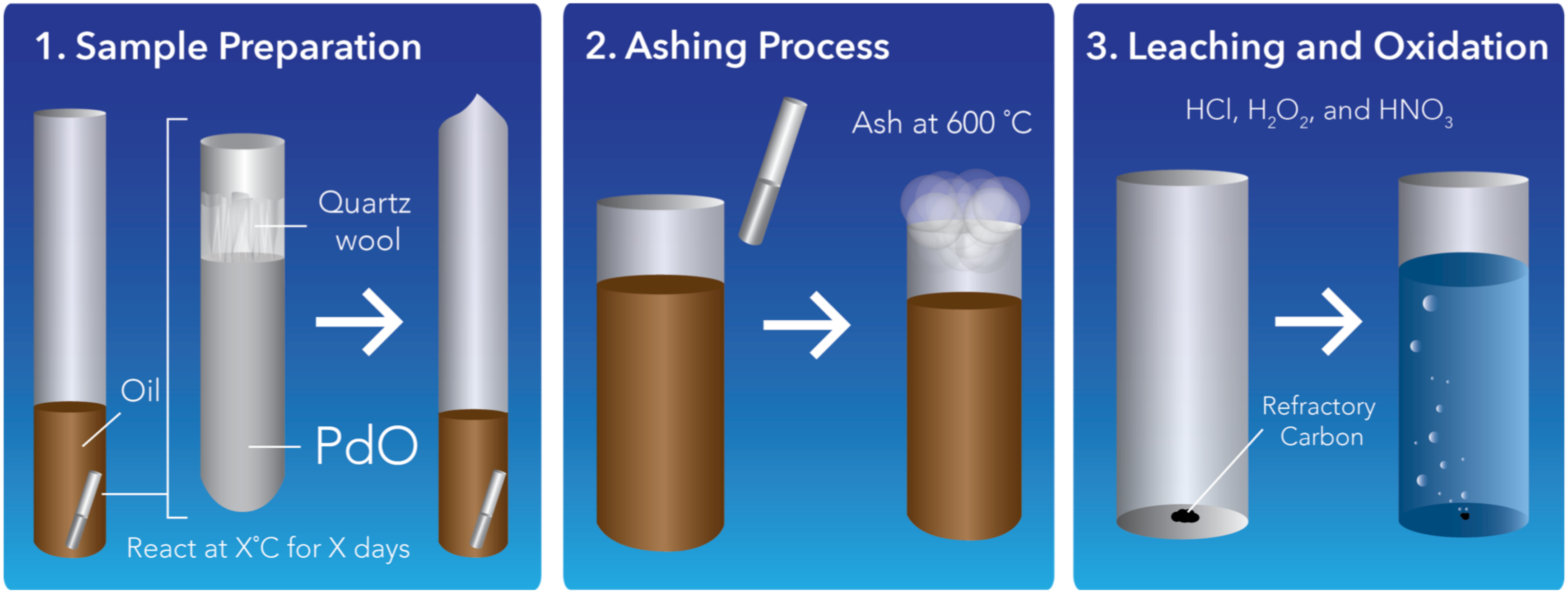


Figure 3.1. Illustration of the experimental method used to determine the solubility of Pd in crude oil.

3.4.2. ANALYTICAL METHOD

The unreacted and reacted crude oils were analysed by a method that involved dry-ashing using a combination of thermal combustion and chemical oxidation, leaching of the residues with HCl and analysis using ICP-MS (conditions listed in table 3.3). In the case of the reacted crude oils, the first step in the ashing was carried out by placing the reactors in the Thermo Fischer Scientific, Inc. Thermolyne^{TM} muffle oven at 600°C for 12 hours (Figure 3.2). For the unreacted crude oils, this step involved placing 4 ml of crude oil A. B and C, in 10 ml reusable *Pyrex®* vials stoppered with quartz wool. After thermal ashing and cooling to room temperature, the reactors typically contained a small proportion refractory material composed mainly of carbon (See Table 3.4). In order to ensure complete decomposition of this material 4 ml of hydrogen peroxide and 1 ml of nitric acid were added to the reactor together with 1 ml of hydrochloric acid to dissolve any precipitated Pd (Figure 3.1). Although this refractory material was not observed after thermal ashing of the unreacted crude oils, for consistency 4 ml of Optima grade hydrogen peroxide and 1 ml of Optima grade nitric acid were also added to the *Pyrex®* vials containing the thermally combusted unreacted crude oils. After ashing 1 ml of trace metal grade HCl were added to the reactors and *Pyrex®* vials to leach the metal that had been dissolved in the crude oil.

Table 3.3. Analytical conditions for ICP-MS used to determine Pd concentrations in the diluted leachates of unreacted and reacted crude oils.

Inductively coupled plasma	
Plasma Power (W)	1548
Plasma Ar gas flow (l min^{-1})	15
Auxilliary Flow (l min^{-1})	0.8
Nebulizer	PFA-ST
Nebulizer Flow (l min^{-1})	1.11
Spray Chamber	PFA Cyclonic
Peltier cooling Temperature (°C)	2.7
Sample and Skimmer Cones	Ni
Plasma Cooling Water Flow (l min^{-1})	3.32
Interference reduction system	iCapQ
Data Acquisition	
Mass Analyzer system	Quadrupole
Isotopes measured	^{105}Pd, ^{89}Y
Settling time, s	60
Sampling time, s	60
Total acquisition time, s	120
Peristatic Pump speed (rpm)	20
Detection mode	Digital mode

Table 3.4. Composition of ash residues determined by SEM-EDS analyses.

Element	**Atomic Percent (%)**	**Error (%)**
Carbon	89.54	9.1
Nitrogen	9.68	1.5
Sulfur	0.68	0.1
Chlorine	0.08	0
Aluminum	0.01	0

The analytical protocol involved measuring the Pd (^{105}Pd) and Yttrium (^{89}Y) counts in the acid solution obtained from the digested samples (derived from the unreacted and reacted crude oils), a series of standards (0.5,1,5,10,15,20 and 50 ppb standards diluted from a 1000 ppm Pd standard supplied by SCP Science Ltd.) and a blank solution (1 ppb Y diluted from an aqueous standard supplied by SCP Science Ltd. containing Y 1000 ppm, 2% HNO_3 and Milli-Q™ water) using a Thermo Fischer Scientific, Inc. iCapQ Quadrupole ICP-MS (the operating conditions are reported in Table 3.3). Yttrium was used as an internal standard to monitor the stability of the instrument and ensure that instrumental errors did not affect the results. The blank solution was also used as a diluent for the acid samples and the standards. The solutions used to leach the ash from the reacted crude oils and from the unreacted crude oils (section 3.3.1) were diluted approximately 80 times, with the blank solution. All of the dilutions were conducted in centrifuge tubes, which were shaken thoroughly for a minute to homogenize the solution. The matrix of the experimental samples was diluted sufficiently to minimize the space charge effect (i.e., suppression effect) in the ICP-MS analysis. Space charge effects occur when the ICP-MS analysis is conducted on a high concentration matrix element, leading to a lack of ionization due to the limited source of plasma (Thomas, 2013). In order to minimize this effect, all the samples and the standards were diluted to ppb concentrations.

After the ICP-MS analysis, the ^{105}Pd and ^{89}Y counts were processed to determine the Pd concentrations in the experimental solutions. The counts for all solutions, samples, external Pd standards and the blank solution, were corrected initially using the Yttrium (Y) internal standard by dividing the measured ^{105}Pd count by the ^{89}Y count (^{105}Pd/^{89}Y) to compensate for the slight instrumental fluctuations or errors of the ICP-MS. The ^{105}Pd/^{89}Y ratios of the samples and the standards were subtracted from the ^{105}Pd/^{89}Y ratio of the blank solution to account for the background ^{105}Pd/^{89}Y of the diluent. In order to convert ^{105}Pd counts to concentrations, we constructed a calibration curve by plotting the ^{105}Pd/^{89}Y ratio (Y-axis) against concentration (X-axis). The calibration curve was created by linearly regressing the data through the origin (Eq. 3.1). All the calibration curves had a goodness of fit of 99.99%. Preliminary values for the palladium concentrations for the reacted and unreacted crude oil were determined by evaluating the counts algebraically using the corresponding calibration equation (Eq. 3.2). These values were corrected by applying the dilution and density factor (sample solution in grams divided by sample oil in grams to account for the density differences between the solutions analyzed and the original crude oil samples).

$$\left(\frac{105\text{Pd}}{89\text{Y}}\right)_{\text{Standard}} = \text{Slope of the Calibration Curve} \times \text{Known Pd Concentration} \quad \text{(Eq. 3.1)}$$

$$C_1 = \text{Pd Sample Concentration} = \frac{\left(\frac{105\text{Pd}}{89\text{Y}}\right)_{\text{Sample}}}{\text{Slope of the Calibration Curve}} \quad \text{(Eq. 3.2)}$$

$$\text{Final Pd Sample Concentration} = C_1 \times \text{Dilution Factor} \times \frac{\text{Sample acid in grams}}{\text{Sample oil in grams}} \quad \text{(Eq. 3.3)}$$

3.5. EXPERIMENTAL CONDITIONS

3.5.1. 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 oil 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.

3.5.2. DURATION OF THE EXPERIMENT

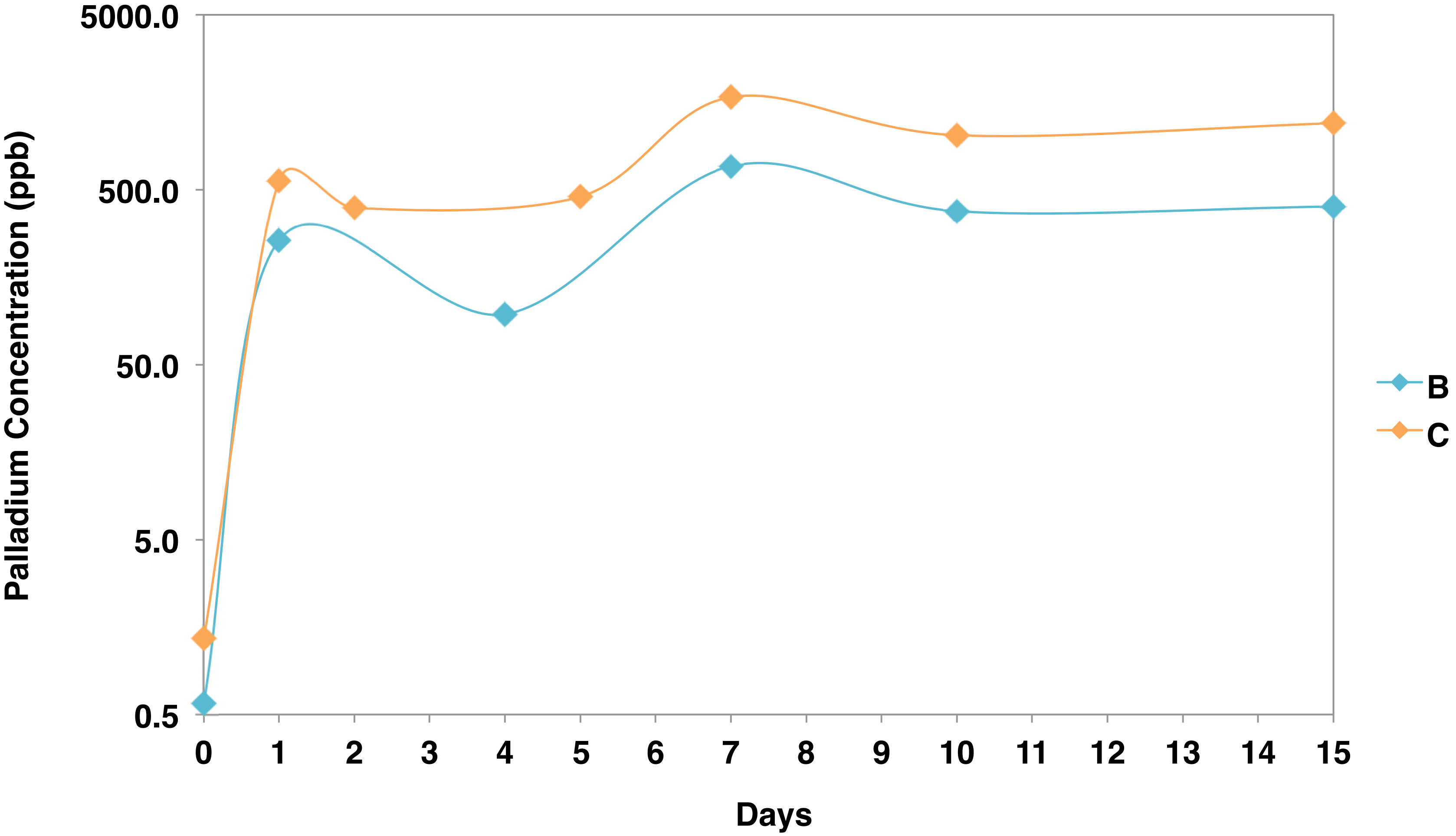
To establish the time required for the experiments to reach equilibrium, kinetic experiments were conducted at 200 °C using crude oils B and C. Aliquots of these crude oils were reacted with PdO for durations ranging from 1 to 15 days as described in section 3.3.1 and the Pd concentrations in the crude oils were determined as described in section 3.3.2. As is evident from Figure 3.2 and Table 3.5, palladium concentrations in the oils reached a steady state after approximately seven days. This steady state concentration is interpreted to indicate attainment of equilibrium.

Accordingly, experiments designed to determine the solubility of Pd in crude oils were conducted for durations of seven or more days at temperatures of 150, 200 and 250 ˚C.

Table 3.5. Concentrations of Pd as a function of time in Crude oils B and C at 200°C.

Days	**B**	**C**
0	0.58	1.36
1	256	560
2	-	394
4	97.2	-
5	-	457
7	681	1692
10	377	1025
15	401	1200

Figure 3.2. The solubility of PdO in crude oils B and C at 200 °C as a function of duration in days. The data indicate that the experiments reach equilibrium.



3.6. RESULTS

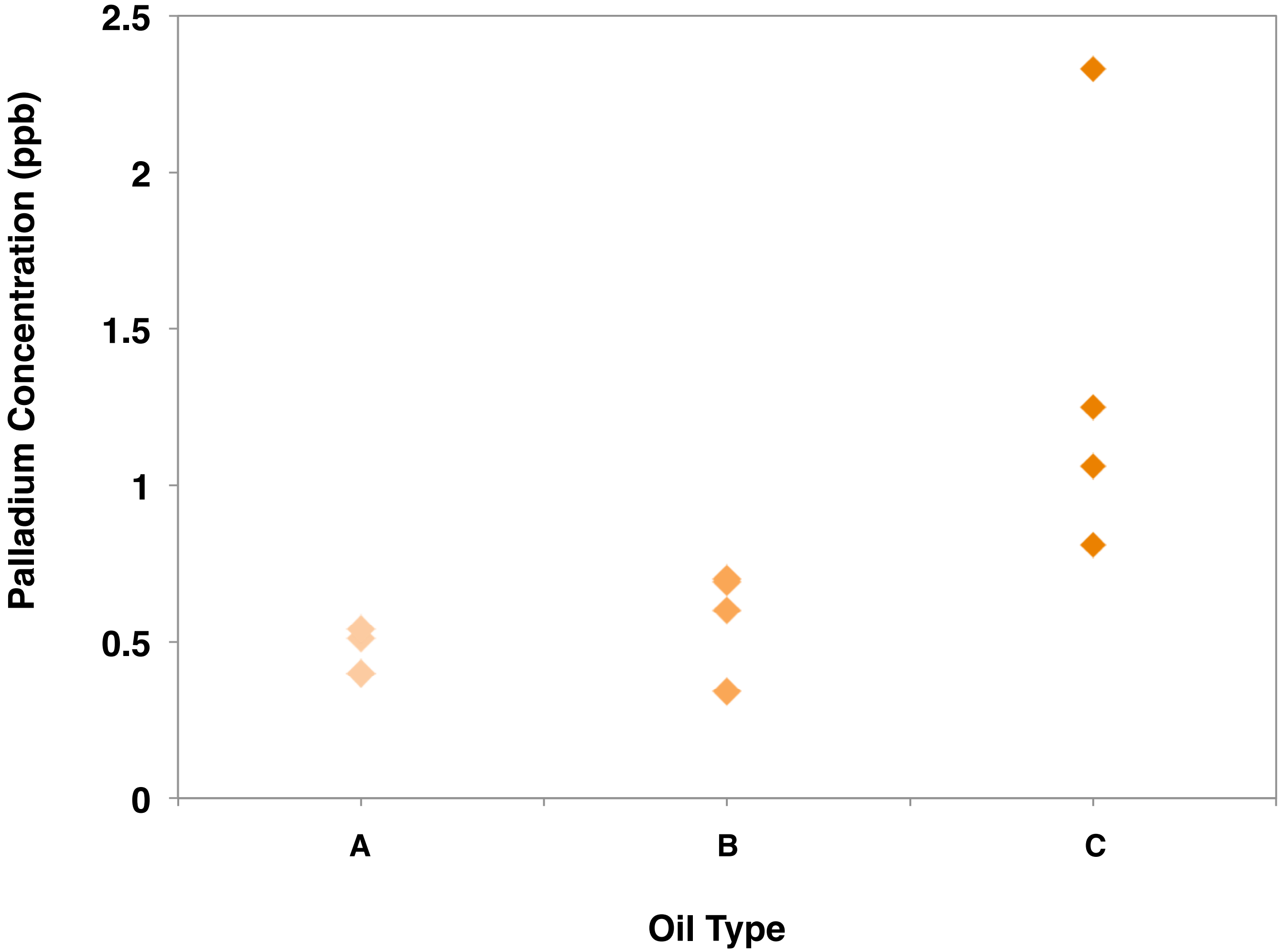
3.6.1. PALLADIUM IN THE UNREACTED CRUDE OIL

Four analyses were conducted on each of the unreacted crude oils A, B and C to evaluate their palladium concentrations prior to the solubility experiments (Table 3.6 and Figure 3.3; see section 3.3.2 for analytical details). These concentrations were determined to be 0.46 ± 0.07, 0.58 ± 0.17, and 1.36 ± 0.67 ppb, respectively. The errors were relatively high because the concentrations in the oils are near the lower detection limit of the ICP-MS. For further discussion of Pd concentrations in the unreacted crude oil, see section 3.6.

Table 3.6. Palladium concentrations in unreacted crude oils A, B, and C.

Name **API Gravity**	**A (ppb)** **26.6**	**B (ppb)** **25.0**	**C (ppb)** **19.0**
Sample 1	0.4	0.7	1.25
Sample 2	0.4	0.6	1.06
Sample 3	0.51	0.69	2.33
Sample 4	0.54	0.34	0.81
Average (ppb)	0.46	0.58	1.36
Standard Deviation (ppb)	0.07	0.17	0.67

Figure 3.3. The Pd concentration in unreacted crude oils A, B, and C.



3.6.2. PALLADIUM IN REACTED CRUDE OIL

As noted earlier, palladium oxide (PdO) was reacted with crude oil A, B and C at 150, 200 and 250 ˚C. The results of these experiments are reported in Table 3.7 and illustrated in Figure 3.4. At 150 ˚C, the concentrations of Pd in crude oils A, B and C, after subtracting the background concentrations (see section 3.5.1), were 140 ± 34, 159 ± 87, and 312 ± 51 ppb respectively (Table 3.8; n = 2, 3 and 3 respectively). The Pd concentration at 200 ˚C was substantially higher for crude oils B and C but, within error, the same for crude oil A as at 150 ˚C. After subtraction of the background concentrations, the Pd concentration was determined to be 129 ± 83 ppb, 400 ± 23 ppb, and 1182 ± 417 ppb for crude oils A, B and C, respectively (n = 4, 4 and 5 respectively). Experiments conducted at 250˚C yielded substantially lower Pd concentrations for crude oils A and B, i.e., 77 ± 17 (n = 2) and 75 ppb (n = 2), respectively, and a somewhat lower concentration for crude oil C of 789 ± 20 ppb (n = 2). For further discussion of the results, see section 3.6.

Table 3.7. Palladium concentrations in crude oils A, B, and C after reaction with PdO at 150, 200 and 250°C.

	Crude Oil A				**Crude Oil B**				**Crude Oil C**			
API[a]	**26.6**				**25.0**				**19.0**			
Temp. (˚C)[b]	**n[c]**	**Avg. (ppb)[d]**	**Stdev. (ppb)[e]**	**Error (%)[f]**	**n[c]**	**Avg. (ppb)[d]**	**Stdev. (ppb)[e]**	**Error (%)[f]**	**n[c]**	**Avg. (ppb)[d]**	**Stdev. (ppb)[e]**	**Error (%)[f]**
150˚C	2	141	34	24	3	160	87	54	3	313	51	16
200˚C	4	129	83	64	4	401	23	6	5	1183	413	35
250˚C	2	77	17	22	1	76	-	-	2	790	20	3

[a] API is an abbreviation for American Petroleum Institute Gravity.
[b] Temp. is an abbreviation for temperature in ˚C.
[c] n is an abbreviation for number of samples.
[d] Avg. is an abbreviation for average.
[e] Stdev. Is an abbreviation for standard deviation.
[f] Error indicates the percent error of the results.

Table 3.8. The average Pd concentrations after subtraction of the background Pd concentrations (concentrations in unreacted oils.

Temperature (°C)	A (ppb)	B (ppb)	C (ppb)
150	140	159	312
200	129	400	1182
250	77	75	789

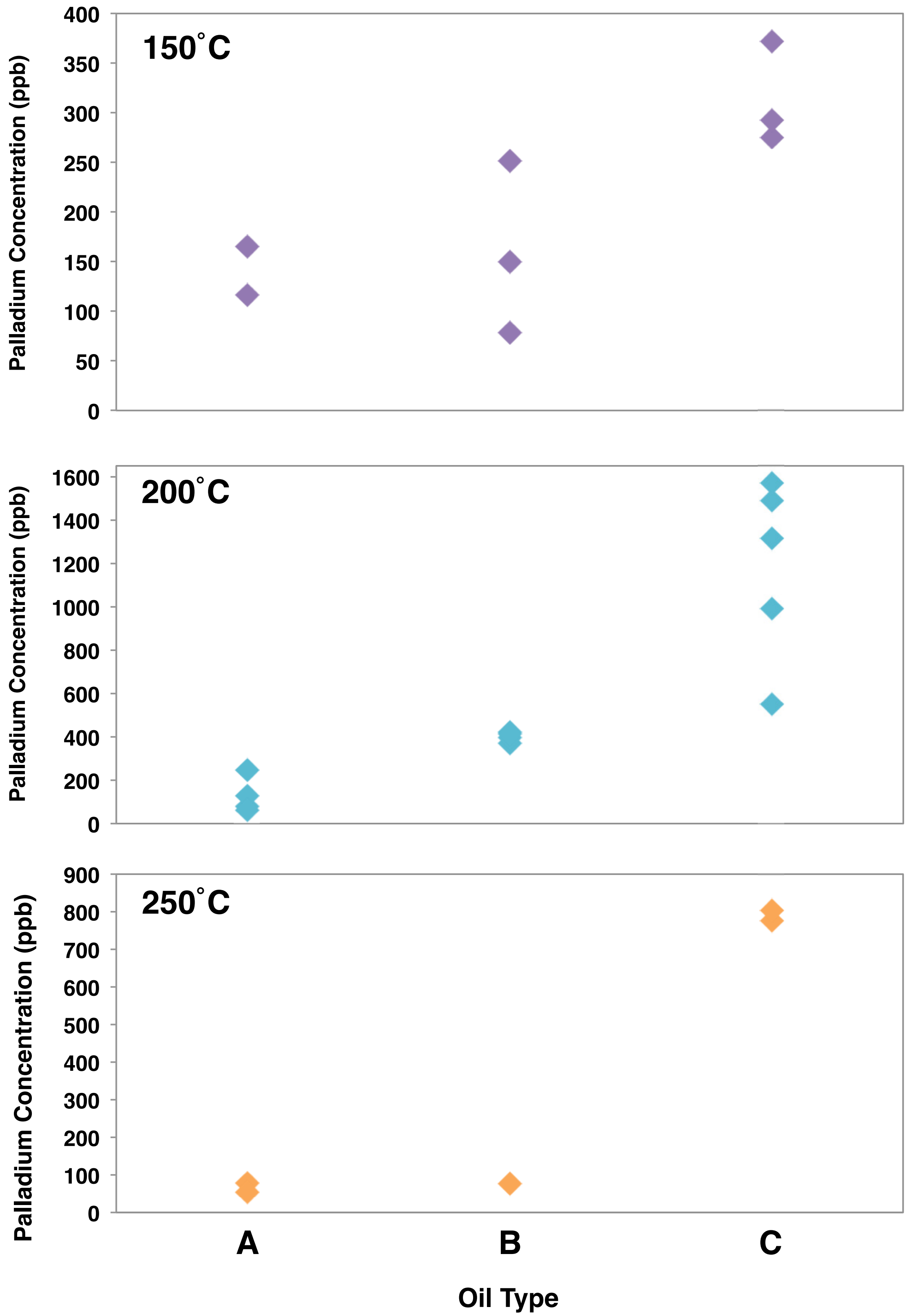


Figure 3.4. Palladium concentrations in crude oils A, B and C at 150, 200 and 250 ˚C.

3.7. DISCUSSION

3.7.1. CRUDE OIL CHEMISTRY AND PALLADIUM SOLUBILITY IN CRUDE OIL

The results of our experiments indicate that crude oil has the capacity to dissolve many tens of ppb to 1 ppm Pd, depending on the temperature and the composition of the oil. These concentrations are from several times to two orders of magnitude higher than that of gold in ore-forming hydrothermal fluids (Simmons and Brown, 2006). Our data therefore suggest strongly that liquid hydrocarbons have the capacity to be ore fluids for palladium. In the following paragraphs we consider the factors that might control the solubility of Pd in crude oil, and the reasons for the elevated Pd concentrations obtained in our experiments.

A key parameter that influences Pd solubility in crude oil is temperature. In Figure 3.5, we illustrate the average Pd solubility in the three crude oils (A, B and C) as a function of temperature. The Pd concentrations of crude oils B and C reached maximum values at 200 ˚C, whereas that of crude oil A was relatively unchanged between 150 and 200 ˚C but significantly lower at 250 ˚C. The reason for the thermal maximum of Pd concentration in crude oils A and B is not known. A possibility that must be considered is that the oils degraded somewhat on being heated and that a component of the oil that might have been involved in the formation of organo-palladium complexes became unstable. Significantly, a thermal maximum was also observed for the solubility of gold metal in a different set of crude oils, although the temperature was higher, namely 250 ˚C (A. Migdisov pers. comm., 2014).

In order to gain insight into other parameters that might control Pd solubility in crude oil, we plotted the solubility of Pd in the three crude oils against API gravity, asphaltene, nitrogen (N), total acid number (TAN) and sulfur (S) for the three temperatures investigated (Figures 3.6 to 3.10). From Figure 3.6, it is evident that Pd solubility increases with decreasing API number. As expected Pd, solubility correlates positively with the asphaltene proportion (Figure 3.7) because, as noted earlier, the reciprocal of the API number largely reflects the asphaltene content. Unfortunately, the nitrogen concentration is only known for crude oils B and C. However, crude oil C, which has over double the nitrogen content of crude oil B, is able to dissolve considerably more Pd than crude oil B. Indeed, the solubility is roughly four times higher at 200 ˚C than 150 ˚C and two and a half times higher at 250 ˚C (Figure 3.8). This is significant because it is well established that porphyrins, which comprise four pyrrole subunits (C_4H_4NH), are the main molecules dissolving Ni in crude oils (the Ni is chelated to the four N atoms), and these molecules concentrate in the asphaltene fraction (Falk, 1964; Buchler, 1978; Manning and Gize, 1993).

As metalloporphyrin formation is controlled in part by pH according to the reaction:

$$P[H_2] + M^{2+} = P[M] + 2H^+ \text{ (Eqn. 3.4)}$$

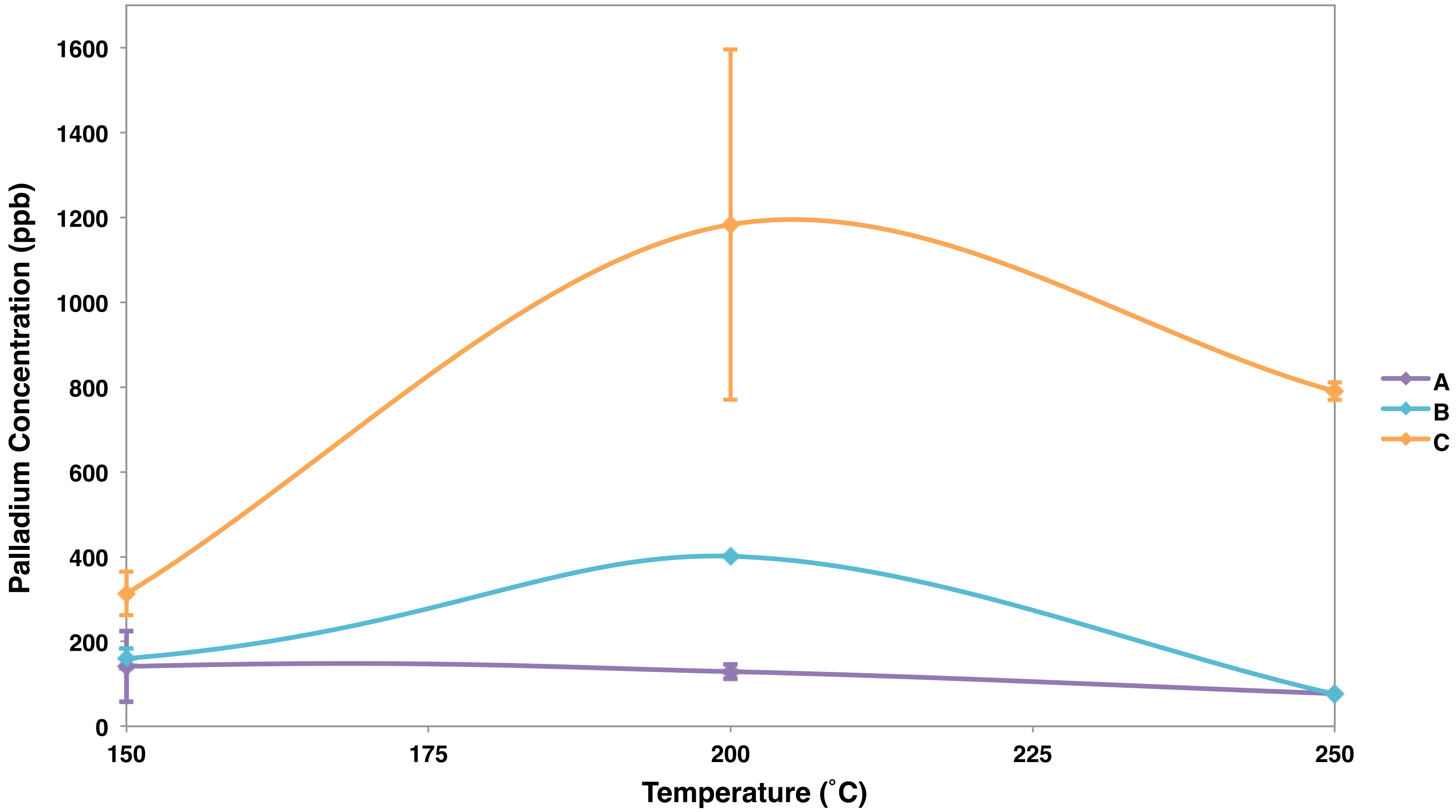


Figure 3.5. Average palladium concentrations in crude oil A, B and C versus temperature. The thermal maximum for Pd concentration in crude oils B and C is at 200 ˚C, whereas that for crude oil A is reached at or below 150˚C.

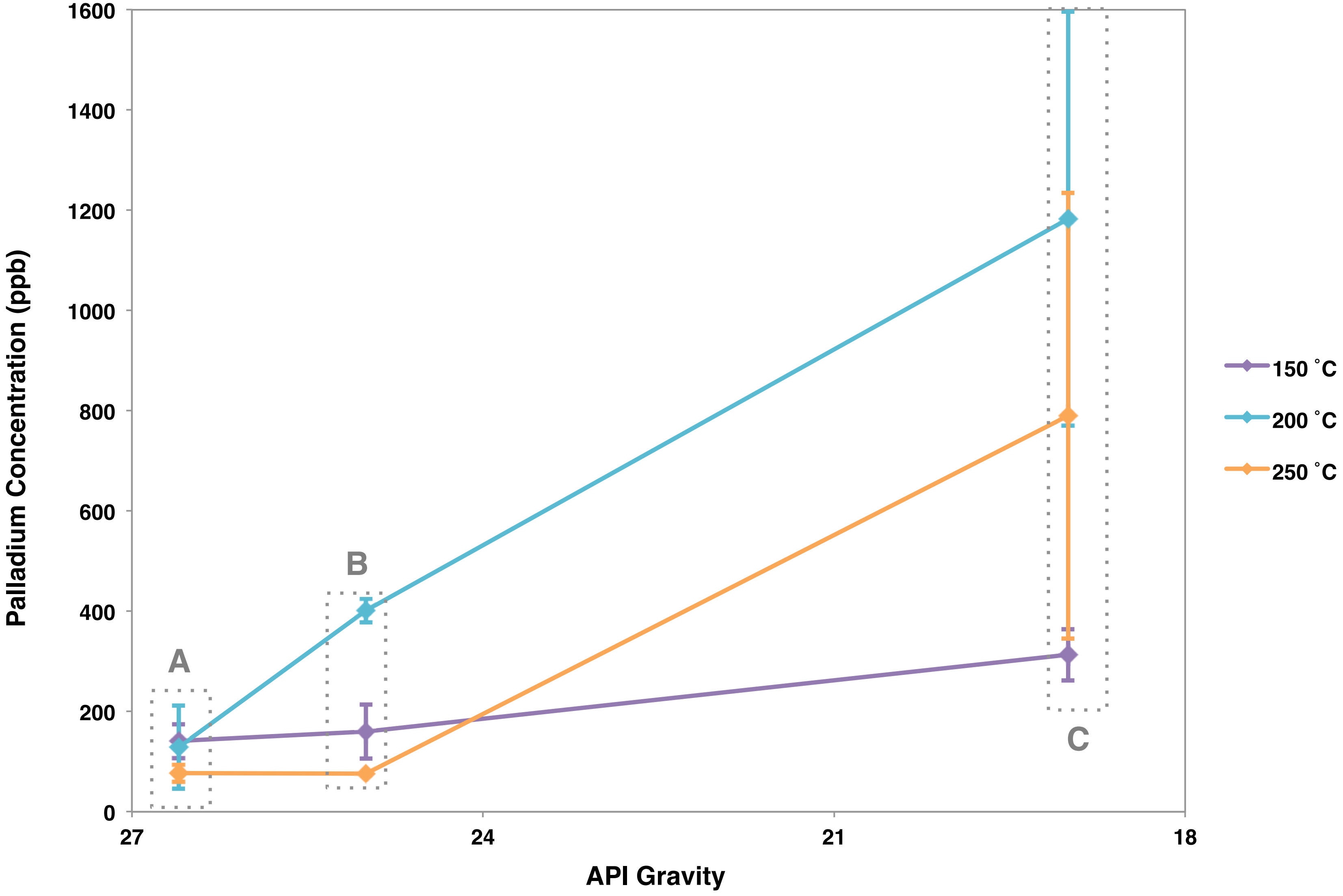


Figure 3.6. The average palladium concentration in crude oils A, B and C plotted versus API Gravity (i.e., specific gravity).

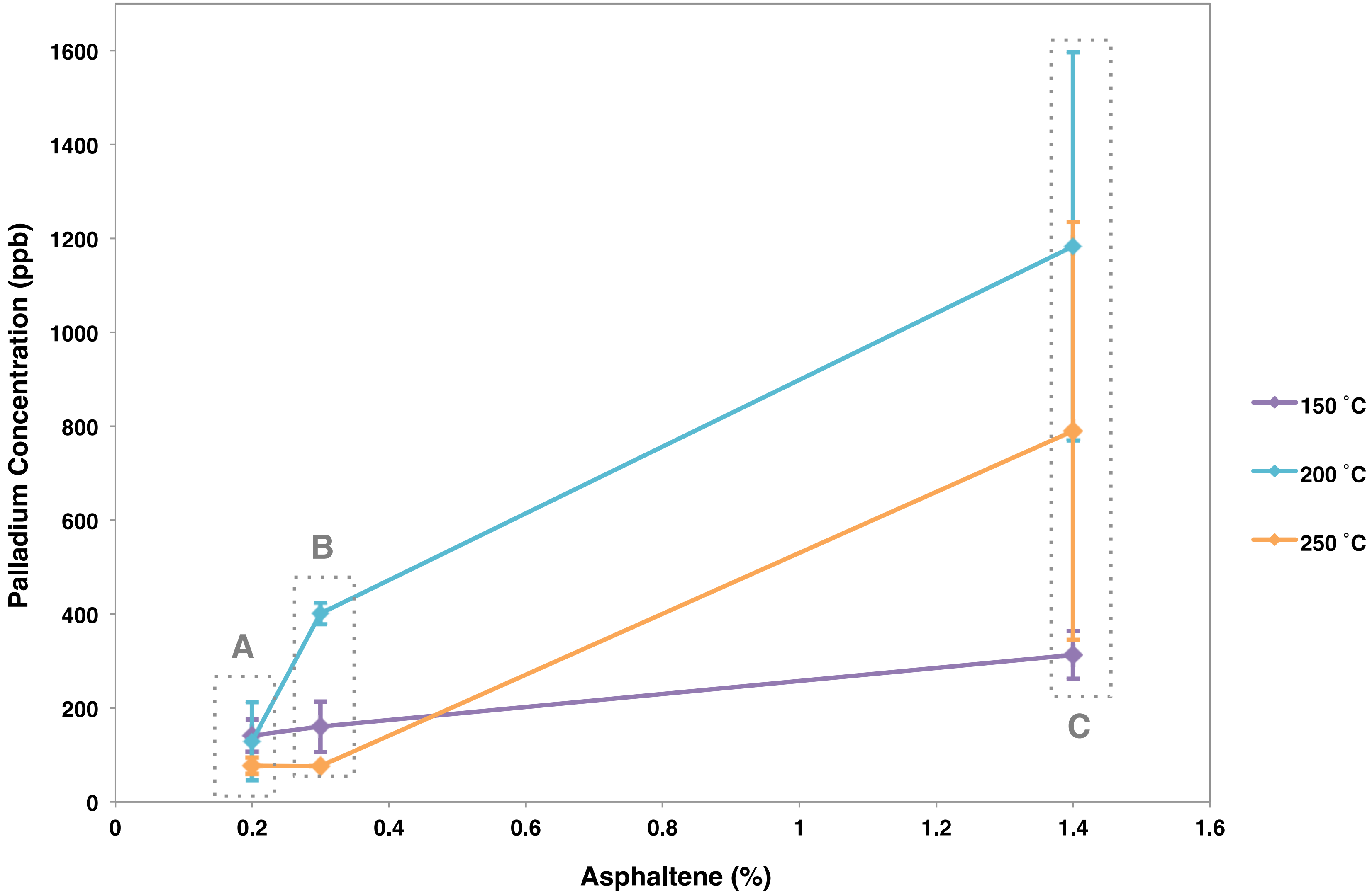


Figure 3.7. The average palladium concentrations plotted for crude oil A, B and C against asphaltene content (%).

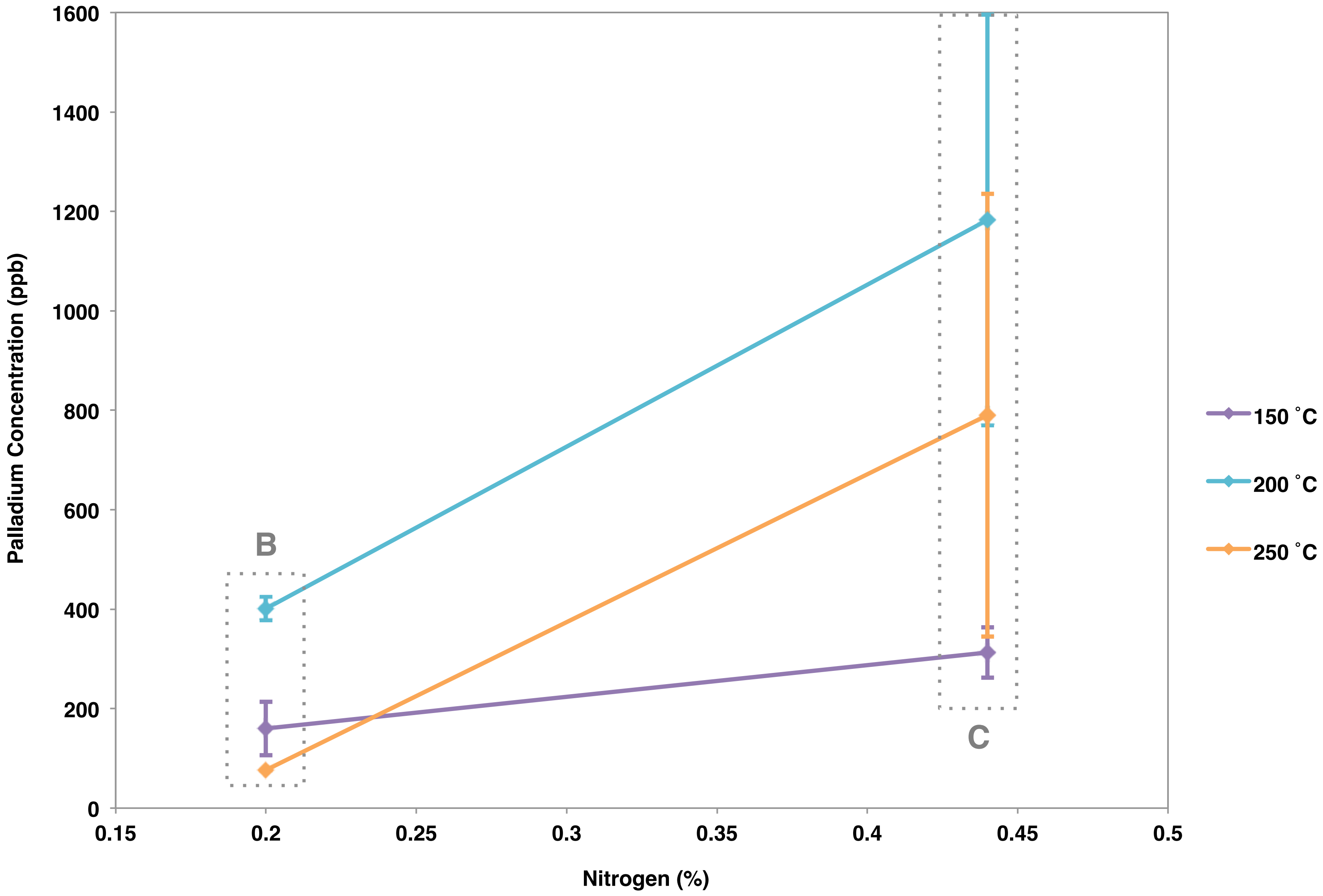


Figure 3.8. The average palladium concentrations for crude oil A, B and C plotted against nitrogen content (%).

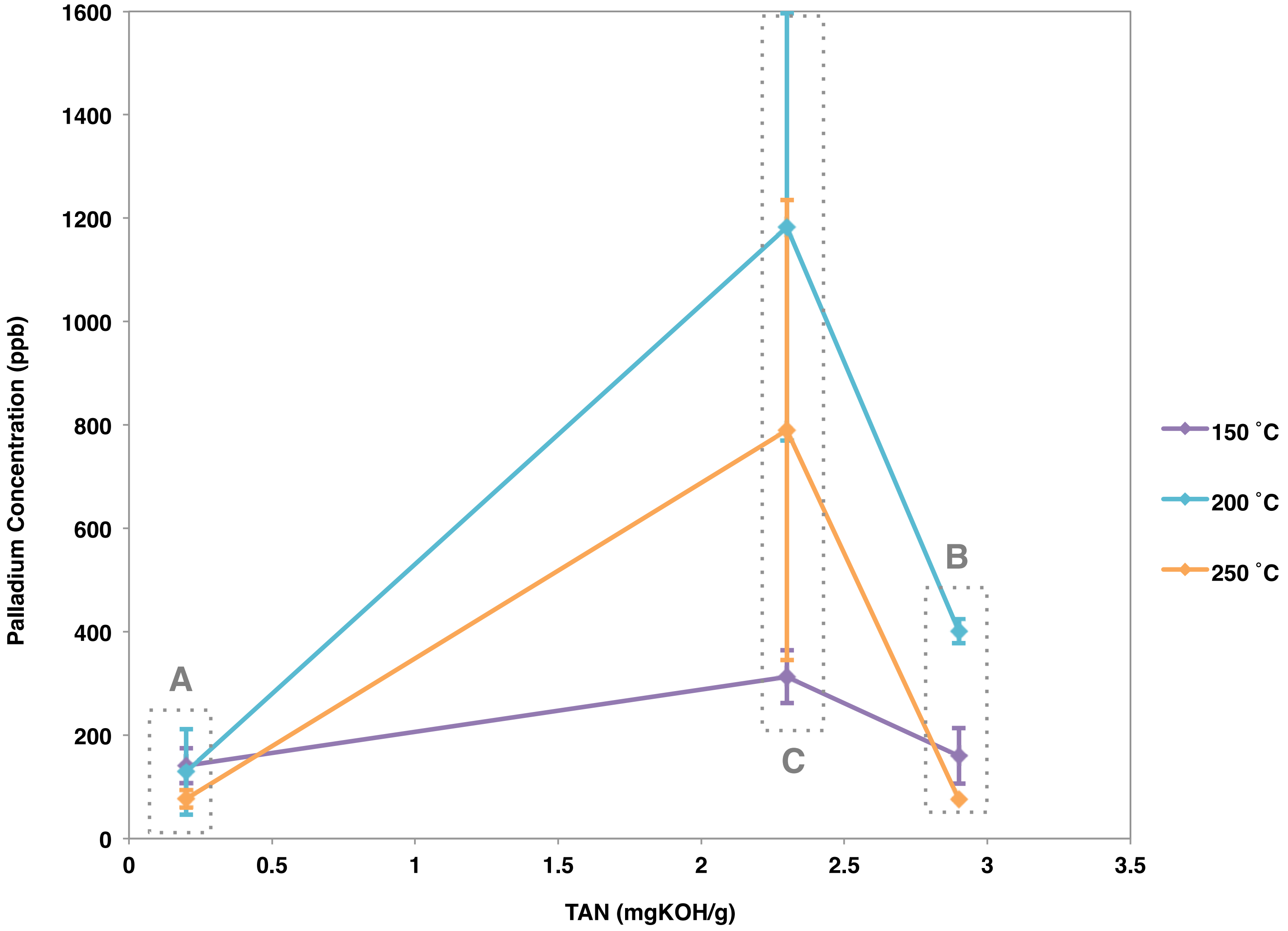


Figure 3.9. Average palladium concentrations in crude oil A, B and C plotted against Total acid number (TAN).

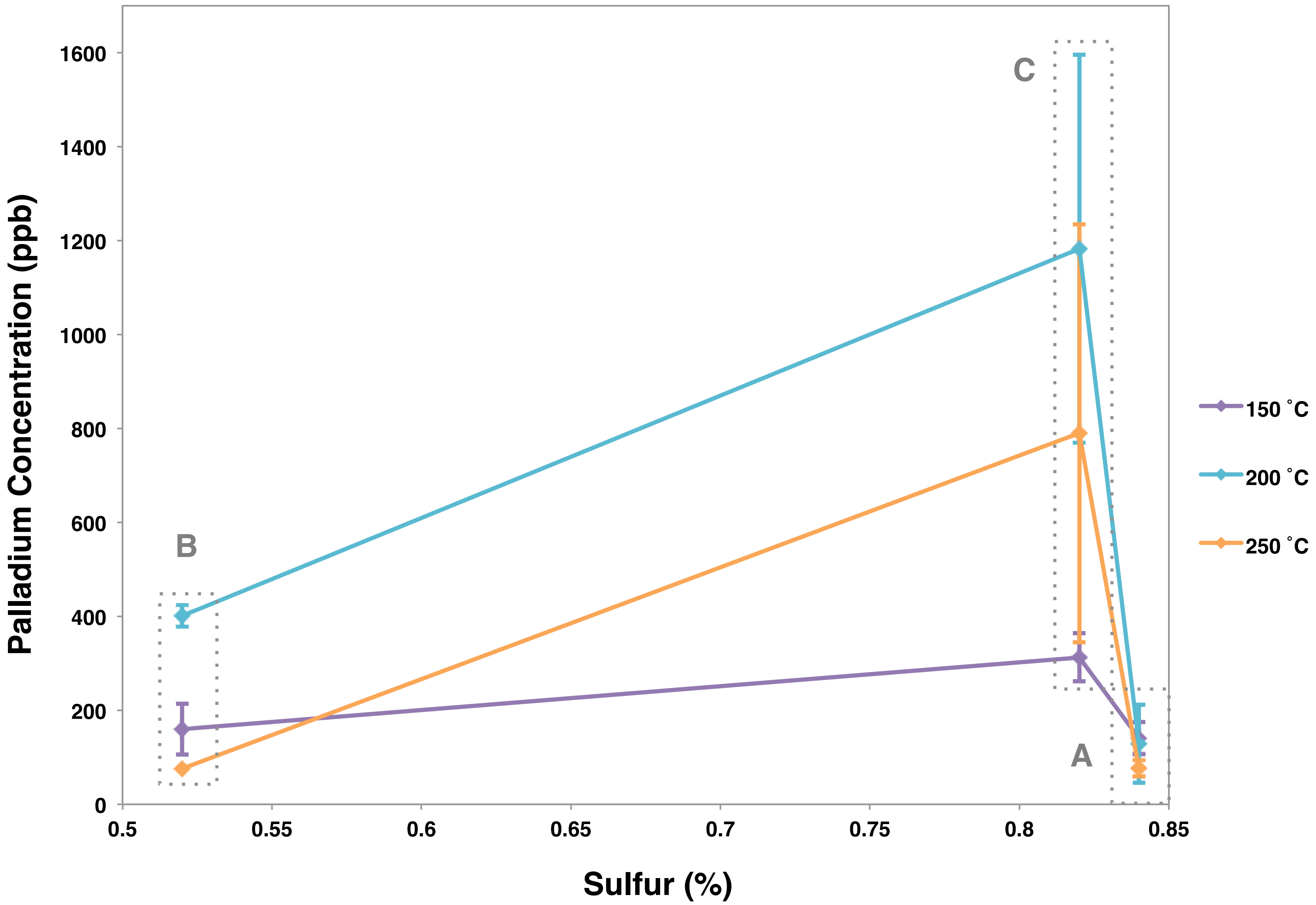


Figure 3.10. The average palladium concentrations for crude oil A, B and C plotted against sulfur content (%).

it would be expected that the metalloporphyrin content might correlate with the TAN value. Although the TAN value is lowest for crude oil A, which has the lowest carrying capacity of Pd (solubility), it may nevertheless be significant that crude oil C, which has the highest Pd carrying capacity has a lower TAN value than crude oil B (Figure 3.9). Further support for the notion that Pd may have dissolved as a metalloporphyrin during our experiments is that palladium porphyrins are second in stability only to platinum porphyrins {Pt (2+) > Pd (2+) > Ni (2+) > Co (2+) > Ag (2+) > Cu (2+) > Fe (2+) > Mg (2+) > Cd (2+) > Sn (2+) > Li_2 > Na_2 > Ba (2+) > K_2} (Falk, 1964; Buchler, 1978). Falk (1964) and Buchler (1978) determined the stability of metalloporphyrins by measuring their demetallation using a variety of acids. In the case of Pd, application even of concentrated sulfuric acid only resulted in its partial removal (demetallation), consistent with the observation that palladium porphyrins are remarkably stable.

In principle, thiol groups, which are soft bases, should form strong bonds with soft metals, such as Pd (Pearson, 1963). However, although crude oil C (high Pd solubility) has a high S content, the highest S content is that of crude oil A which has the lowest Pd solubility (Figure 3.10). We are therefore unable to attribute any role to sulphur functional groups in Pd solubility.

In summary, positive correlations of Pd solubility with API number, asphaltene proportion and N content, suggest that Pd dissolves in liquid hydrocarbons in proportions that depend on the availability of nitrogen functional groups and, in turn, the proportion of asphaltene macromolecules. The well-known stability of palladium porphyrins, the high proportion of asphaltenes, which concentrate in the porphyrin fraction, and the relatively low TAN number of Crude Oil C (which has the highest Pd solubility) further suggest that Pd dissolves in crude oils by forming porphyrin macromolecules.

3.7.2. PROCESSES CONTROLLING THE TRANSPORT OF METALS IN CRUDE OIL

Our data have established that crude oils are capable of dissolving significant concentrations palladium at temsperatures between 150 and 250 ˚C, and that these concentrations are sufficient for liquid hydrocarbons to constitute ore fluids for Pd. The data, however, do not show how the Pd is dissolved, although they demonstrate a strong association with asphaltenes and suggest a possible role for porphyrin molecules as palladium complexes. They also do not rule out the possibility that the Pd was adsorbed on the asphaltene macromolecules rather than being dissolved by them through chelation. It is thus possible that the apparent solubility of palladium in our experiments does not represent true dissolution. Finally, we remind readers of the observations of Jedwab and Badaut (1999) of potarite nanoparticles {(Pt,Pd,Au)Hg} in pyrobitumen in the Boss Mine, Nevada, and of Fuchs et al. (2015) of uraninite nanoparticles in the Witwatersrand Au-U deposit, and the suggestions of these researchers that the metals in question were transported in nano-particulate form by liquid hydrocarbons. Thus, although our experiments provide convincing evidence for the potential transport of Pd in nature by liquid hydrocarbons, they do not allow us to distinguish between complexation (chelation), adsorption and mechanical incorporation (nanoparticles) as possible mechanisms for this transport.

3.7.3. GEOLOGICAL APPLICATION

In the preceding paragraphs, we have provided convincing evidence that Pd can be “dissolved” in liquid hydrocarbons. Whether this occurs as a result of simple dissolution through complexation (chelation), adsorption onto asphaltene macromolecules or emulsification of nanoparticles is unknown. Irrespective of how it occurs, it seems likely that transport of Pd by liquid hydrocarbons does occur in nature. In order to form an ore deposit, however, a mechanism of precipitation for the Pd is required. As the Pd mineralization (and that of other metals) invariably occurs in bitumen, it is reasonable to assume that the precipitation mechanism is linked to that of bitumen formation.

One way of concentrating metals above their original concentration in liquid hydrocarbons is to thermally drive off the light, more volatile components and precipitate/flocculate the heavier, asphaltene-rich component as bituminous veins (Emsbo et al., 2003; Williams-Jones et al., 2009). This may have been the case at El Rodeo and Alligator Ridge in the Carlin District, where bitumen veins enriched in gold and vanadium appear to mark the paths of migration of liquid hydrocarbons from their source beds (Figure 3.11). Alternatively, liquid hydrocarbons may be destabilized by mixing with aqueous fluids, e.g., oil field brines, leading to the flocculation of bituminous material. The latter was demonstrated experimentally by Chaala et al. (1994), who showed experimentally that addition of water enhances asphaltene flocculation and that this effect increases with increasing temperature (> 60˚C). They also showed that addition of paraffins or aromatics has a similar effect. This does not directly explain the precipitation of metallic minerals in hydrocarbons. However, it is attractive to propose that flocculation of asphaltenes, whether induced thermally or by mixing with hydrothermal fluids, may lead to concomitant metallic mineral nanoparticulate precipitation and flocculation, as seems to have been the case for potarite in the Boss Mine (Jedwab and Badaut, 1999) and uraninite in the Witwatersrand Carbon Leader (Fuchs et al., 2015).

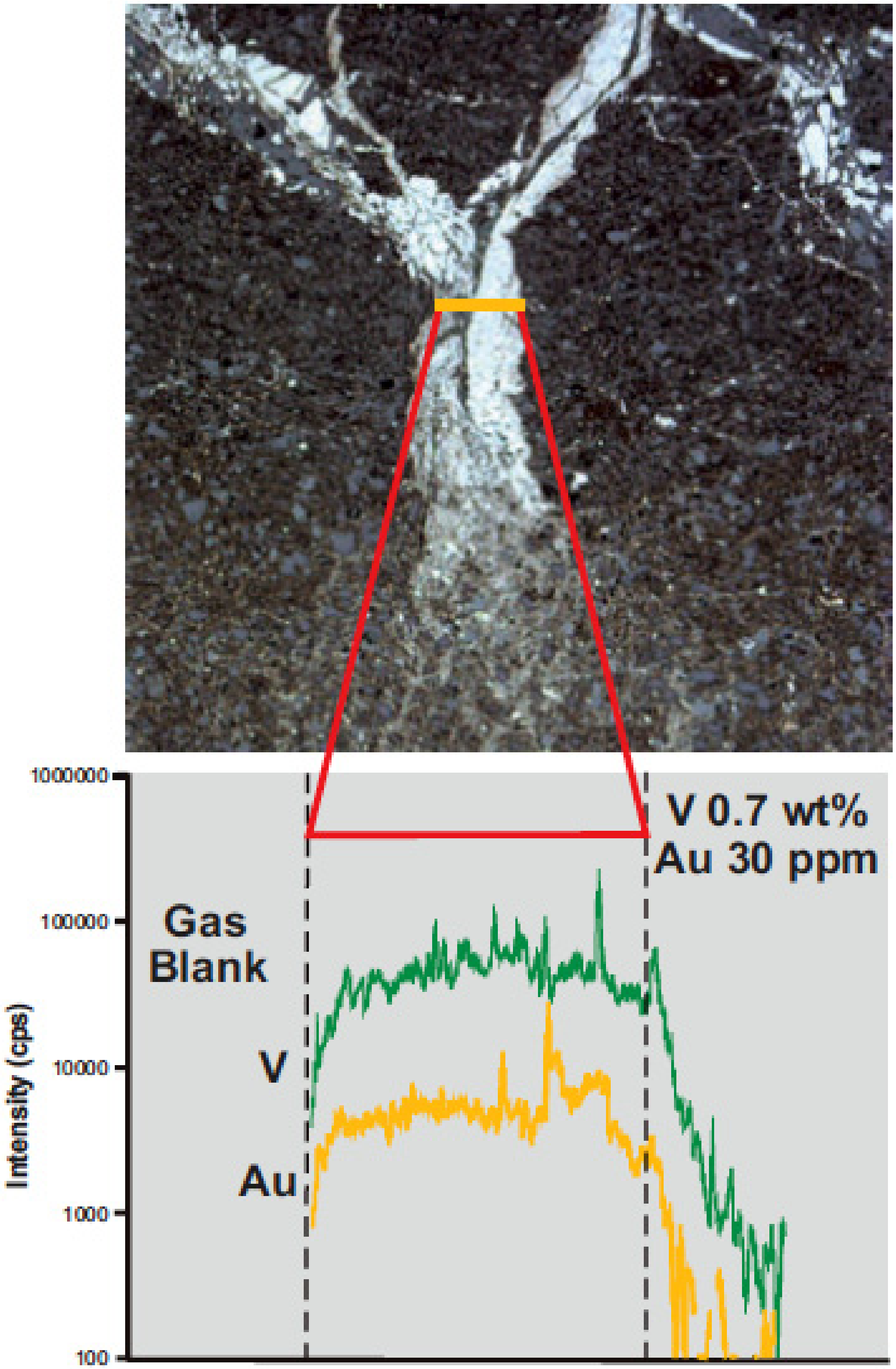


Figure 3.11. Pyrobitumen vein containing 30-ppm gold from the El Rodeo deposit, Carlin Trend, Nevada (Williams-Jones et al., 2009).

3.8. CONCLUSION

Palladium (in the form of PdO) was reacted with crude oil at variable temperature (150, 200 and 250˚C) to determine if it could be dissolved in concentrations significant for ore formation. We found that Pd solubility is high (tens of ppb to 1 ppm) and reaches a concentration maximum at 200˚C (Crude oil C). Based on the positive correlation between Pd concentration and the proportion of asphaltenes and N concentration, the elevated Pd concentration might reflect the formation of palladium porphyrins. However, we do not exclude the possibility that it was adsorbed onto asphaltenes. The results of this study demonstrate that Pd transport by liquid hydrocarbons may be an important process for forming some deposits in which there is a close spatial association between the Pd mineralization and bitumen.

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CHAPTER 4

GENERAL CONCLUSION

4.1. THESIS CONCLUSION

The modified dry-wet-ashing technique coupled to ICP-MS instrumental analyses allows accurate and precise measurements of the concentration of Ni and V in crude oil standards, providing confidence that it might be applied to these and other metals in crude oils generally. The precision and accuracy of the analyses for Ni and V in the oil standards were 97 to 99% and 90 to 100%, respectively, which is comparable to results obtainable using more costly and less accessible techniques. The results of analyses of crude oils A, B, C, and D showed a very high level of precision. That of crude oil E was a little less precise because of its heterogeneity. The method can measure contents of a wide range of metals in crude oil by removing the ash with negligible loss of metals during combustion and wet oxidation.

The palladium oxide solubility experiments in crude oils A, B and C yielded a wide range of concentrations that depended mainly on temperature and the asphaltene content of the crude oil. In crude oils B and C, Pd concentration reached a maximum at 200˚C; it decreased with increasing temperature in crude oil A that had the lowest asphaltene content. The reason for the decrease in Pd concentrations at 250˚C might be the slight degradation of the crude oil at high temperature. In crude oil C, the crude oil with the highest Pd solubility, concentrations reached over 1 ppm. These results indicate that crude oil has the capacity to carry concentrations of palladium more than sufficient for them to constitute ore fluids. In addition to Pd content correlating positively with the asphaltene content, it also correlates positively with the nitrogen content and negatively with the acidity. These correlations suggest that porphyrins may play an important and perhaps dominant role in controlling the solubility of Pd in liquid hydrocarbons. This study provides the first convincing experimental evidence showing that liquid hydrocarbons may be important as agents of metal transport in ore-forming systems and sets the stage for more comprehensive studies of metal solubility and speciation in crude oils and for studies of deposits in which hydrocarbon transport of the metals may play a role in ore formation.

4.1.1. FUTURE WORK

In order to strengthen the case that metal transport by liquid hydrocarbons is an important process in ore genesis, it will be necessary to expand the experiments reported in this study to other conditions and metals. It will also be necessary to conduct experiments designed to assess the speciation of these metals and thereby understand the potential controls on metal transport and deposition. As deposits that may have formed from hydrocarbon liquids are currently interpreted to form by hydrothermal processes, it will likewise be important to carry out experiments in which the partitioning of metals between aqueous liquids and hydrocarbons liquids is evaluated. Once these experiments have been conducted, it will be possible to develop models with which to understand metal behavior in natural systems and in turn the formation of ore deposits that are spatially associated with hydrocarbons.