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Zinc solubility, speciation and deposition: A role for liquid hydrocarbons as ore fluids for Mississippi Valley Type Pb-Zn deposits.

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1. Abstract

Although the ore fluid for Mississippi Valley Type (MVT) deposits is universally considered to be a basinal brine, the common occurrence of liquid hydrocarbons as inclusions in one of the ore minerals (sphalerite) raises the question of whether liquid hydrocarbons could play a role in metal transport. Here we explore the potential of liquid hydrocarbons to act as an ore fluid by determining the steady-state concentration of zinc in crude oil and evaluating the factors that promote its dissolution. To this end, zinc wires were reacted with a series of oils (labelled oils A, B and C) at 150, 200 and 250 ^{o}C, and the steady-state concentration of Zn was determined. Zinc concentrations were observed to increase with temperature and with the Total Acid Number (TAN) of the oils, the latter of which is strongly correlated to the carboxylic acid content of crude oil. Crude oil B, the highest TAN oil, dissolved 1,700 ± 0.8 ppm at 250 ^{o}C, which is comparable to the highest Zn concentration inferred to have been dissolved in brines interpreted to represent MVT ore fluids. X-ray Photoelectron Spectroscopic (XPS) analyses performed on the residual oil coating the zinc wires after the reaction supported the conclusion that Zn has a strong chemical affinity for carboxylic acids in crude oil. Finally, an experiment designed to precipitate sphalerite crystals from a Zn-rich synthetic oil at room temperature showed that

sphalerite precipitation from liquid hydrocarbons proceeds efficiently in a carbonate-buffered, H_2S -rich environment.

2. Introduction

Zinc ([Ar] 3d10 4s2) is the 24th most abundant element in the Earth's crust and the second most abundant metal in the human body after iron (Huang and Gitschier, 1997). Unlike the transition metals, the Zn (2+) ion has a full d-orbital and so does not participate in redox reactions but rather acts as a Lewis acid accepting electrons to form stable complexes with variety of ligands and in different geometries. This makes Zn a metal of noteworthy biological significance, serving as an essential enzymatic co-factor for the growth, development and differentiation of all types of life, including micro-organisms, plants and animals (McCall et al., 2000). It also explains its accumulation and retention to significant levels in organic matter (Jones, 1975; Shuman, 1999), including liquid hydrocarbons (see below).

Since Roman types, when it was alloyed with copper to form brass, zinc has been an important metal in human development (Craddock, 1978), and currently some 13 million tons of the metal are used annually in a large variety of industrial applications (Thomas, 2018). Much of the current production of zinc is from the mining of deposits hosted by carbonate-rich sedimentary rocks, in which it occurs as the mineral, sphalerite (ZnS), making zinc a chalcophile or "sulphur-loving" element (Lee and Saunders, 2003). Many of these deposits belong to the Mississippi Valley Type (MVT) deposit class (Anderson and Macqueen, 1982; Leach et al., 2010), and are epigenetic, typically occurring on the flanks of sedimentary basins, orogenic forelands, or foreland thrust belts inboard of clastic rock-dominated passive margin sequences (Leach et al., 2010). Nearly all of them are dolomite-hosted with the zinc and lead ore minerals (sphalerite and galena) occurring commonly within cavities or as breccia cements in the carbonate rocks (Anderson and Macqueen, 1982).

The generally accepted hypothesis for the formation of MVT deposits is that the metals are transported in basinal brines (oil field brines) that migrate into carbonate reservoirs (limestone reefs) formerly occupied by liquid hydrocarbons; the hydrocarbons, which have lower density than the brines, precede the latter. There, the brines deposit the metals as a result of mixing with fluids from the backreef, in which sulphate is thermally reduced to H_2S by interacting with the hydrocarbon residues (Leach et al., 2010). This hypothesis is supported by the close association of MVT deposits with hydrocarbons, such as bitumen (Anderson and Macqueen, 1982). However, hydrocarbons are also commonly present as fluid inclusions in the sphalerite ores (Roedder, 1979; Anderson and Macqueen, 1982; Etminan and Hoffmann, 1989), which raises the possibility that instead of acting solely as reductants, the hydrocarbons could also have served as agents of metal transport. This latter hypothesis would be consistent with the observation that the oil window (80 - 160 °C; Peters et al., 2004) overlaps with the temperatures at which MVT deposits commonly form (100-150 °C; Anderson and Macqueen, 1982; Parnell, 1988). It is also supported by the observation that crude oils commonly contain high concentrations of Zn (up to 160 ppm, Jones, 1975).

In this paper, we examine the hypothesis that, in some cases, liquid hydrocarbons can dissolve enough Zn to act as ore fluids for MVT deposits. To this end, we experimentally investigated the solubility of zinc in crude oils of variable composition at temperatures up to 250 °C. As sulphur in these deposits is generally considered to come from evaporites and to be supplied for mineral precipitation as H_2S through the process of bacterial sulfate reduction (BSR) or thermochemical sulphate reduction (TSR), we also report the results of experiments designed to precipitate sphalerite from a synthetic liquid hydrocarbon fluid.

3. Materials and methods

3.1 Crude oil characterization

The crude oils A, B and C used in this study, as well as data on their compositions and physical properties, were supplied by Statoil Canada. These oils differ markedly from one to another, both compositionally and in respect to their physical properties (Table 1). For example, the oils vary greatly in their sulphur content and the proportions of different sulphur compounds (thiols, polysulphides, thiophenes, benzothiophenes). Certain sulphur compounds, notably thiols, are well-known for their ability to form organometallic complexes with chalcophile elements (Lewan, 1984; Giordano, 1994; Speight, 2001) and so are of particular interest when studying metal solubility in oil. Our oils also differ considerably in their Total Acid Number (TAN), a measure of oil acidity, which is strongly correlated to carboxylic acid content (Meredith et al., 2000). Significantly, short-chain carboxylic acids have been proposed as potentially effective ligands for the transport of Zn in aqueous fluids, such as those thought to be responsible for the formation of MVT deposits (Giordano, 1985; Sverjensky, 1986; Giordano and Kharaka, 1994). Consequently, the carboxylic acid content of an oil, which is reflected in its TAN, may also play an important role in controlling zinc solubility in liquid hydrocarbons. Lastly, the nitrogen and asphaltene content of the oils are parameters that should be considered because of their association with nitrogen-bearing ligands such as porphyrins, which are well-known for their ability to form organometallic complexes. Indeed, nickel and vanadium porphyrins are very commonly present in crude oil, and chromium, titanium, cobalt and zinc porphyrins have all been identified in oil shales (Duyck et al., 2007).

Table 1. The composition and properties of the three crude oils, A, B and C, employed in our experiments.

Parameters	**Oil A**	**Oil B**	**Oil C**
API Gravity	26.6	25	19
Specific Gravity	0.895	0.904	0.94
Sulphur (wt.%)	0.84	0.52	0.82
Thiols/sulphides (ppm)	44	0	52
Thiophenes/Disulphides (ppm)	1400	37	1050
Benzothiophenes (ppm)	3890	1880	3160
Dibenzothiophenes (ppm)	2580	2740	2020
Benzonaphtothiophenes (ppm)	490	549	109
Nitrogen (wt.%)	---	0.2	0.44
TAN (mgKOH/g)	0.2	2.9	2.3
Paraffins (wt.%)	---	37	19
Naphthenes (wt.%)	---	49	65
Aromatics (wt.%)	---	13	15
Asphaltenes (wt.%)	<0.3	0.3	1.4

3.2 The solubility and speciation of zinc in liquid hydrocarbons

In order to determine the steady-state concentration of elemental zinc in crude oil, zinc wires were reacted in crude oils A, B and C at 150, 200 and 250 °C. This involved reacting a zinc wire in oil inside a sealed quartz tube for variable durations (5, 10, 15 and 30 days). After the experiments, the tubes were quenched in water at room-temperature and the metal wire was removed. The oil was then combusted in a furnace at 550°C for 24 hours and the resulting char was leached in a solution composed of 2:1:1 parts H_2O_2:HNO_3: HCl for a further 24 hours. The leaching solution was diluted in a 2% HNO_3 solution and analysed by ICPMS using Y as an internal standard. Further details of the experimental and analytical methods are given in Sanz-Robinson et al., (in review) and Sugiyama and Williams-Jones (2018).

After reaction with oil, the zinc wires were removed, rinsed in toluene and vacuum dried for 24h. The residual oil coating the wires was analysed by X-ray Photoelectron Spectroscopy (XPS) to gain insight into the types of ligands in oil, which preferentially bind to zinc. The surface composition of the wires was characterized by XPS on a Thermo Scientific Kα spectrometer, using Al Kα radiation (1486 eV) and an X-ray spot size of 100 μm. Scans were made with a pass energy of 50 eV and a resolution of 0.1 eV. We used the Thermo Scientific Kα spectrometer etching capability to progressively etch the zinc wire and analyse the freshly exposed zinc surface. Progressive etching removes ligands that are weakly bound to the surface of the wire, thereby exposing ligands, which have a greater chemical affinity for zinc and are more deeply embedded in the wire.

3.2.1 Temperature and duration of the experiments

The oil window extends from 80 to 160 °C (Peters et al., 2004). Pyrolysis experiments (Price and Wenger, 1992) and evidence from liquid hydrocarbons entrapped in black smokers (Peter and Scott, 1988), however, both suggest that oil remains stable to temperatures above 300 °C for protracted periods of time. Thus, the range of experimental temperatures selected for this study (150-250 °C) was based on oil window temperatures and oil stability considerations.

In order to determine the steady state-concentration of zinc in an oil at a given temperature, zinc wires were left to react in the oil for different durations (See Figure 1). Zinc concentrations were measured after reaction with the oils at 5, 10, 15 and 30 days. Every data point in Figure 1 is the average of three trials performed at the same temperature and duration and the associated error bars represent the standard deviation of the three trials. As is evident from Figure 1, a steady state concentration was reached in less than 30 days, and in some cases in as little as 5 days. However, the experimental errors for oils B and C decreased, if reaction times were prolonged to the full 30 days. Experimental errors for oil A remained the same for all durations. Zinc concentration in the crude oils was deemed to have reached a steady state when the concentration reached a plateau value and the experimental error was at a minimum. All subsequent experiments were conducted for durations predicted to produce a steady state concentration.

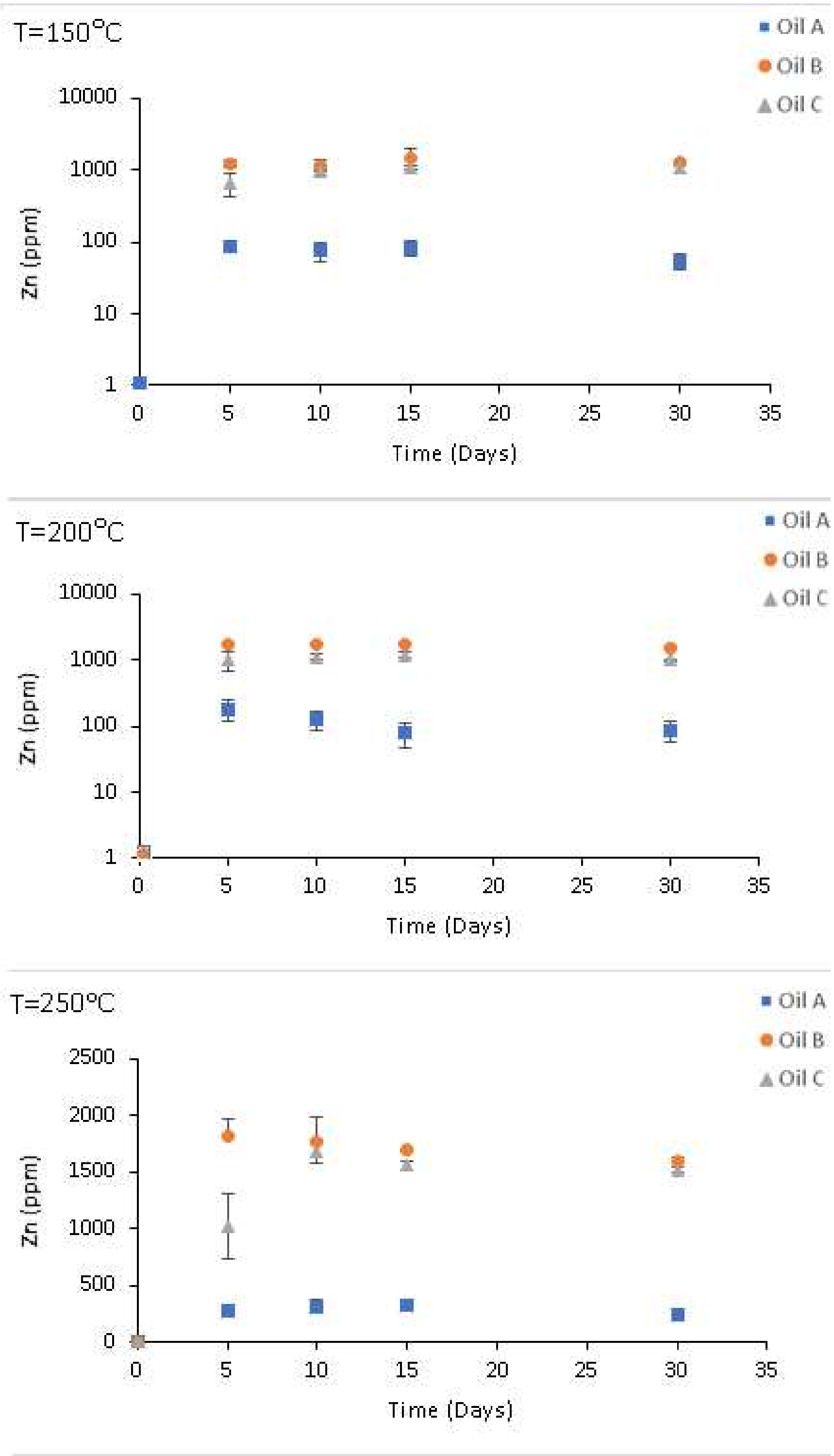

Figure 1. Concentration of Zn in crude oils A, B and C at 150, 200 and 250 ˚C as a function of the duration of the experiments. The vertical lines are error bars indicating the experimental uncertainty.

3.3 Precipitation of sphalerite from a synthetic zinc-rich oil

The Conostan® 1000 ppm Zn oil standard (Catalogue #CB7-100-032), which is composed of Zn-alkylaryl sulfonate (1000 ppm Zn) dissolved in crude oil (compositional information for this Zn oil standard is provided in Appendix A), was injected into a reaction vessel atop a layer of calcite-buffered, 15 wt% NaCl brine. Hydrogen sulfide gas was generated in an external flask by dripping 38% hydrochloric acid onto sodium sulfide. The hydrogen sulfide gas was pumped through the reaction vessel under positive pressure for five (5) minutes to ensure a hydrogen sulphide atmosphere (Appendix B, Fig. A1). The reaction vessel, which was at room temperature, was then sealed and left to rest for 24 hours. Sphalerite crystals were seen to precipitate from the oil after 10 minutes. The crystals were separated by centrifuging the brine, and their composition was confirmed using a Rigaku SmartLab X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda = 0.154$ nm).

4 Results

4.1 Solubility and speciation of Zinc in crude oil

The Zn solubility increases with temperature for the three oils tested (Table 2). In addition, zinc solubility increases with TAN concentration at the three temperatures considered (Fig. 2). Oil B, our highest TAN oil (Table 2), with a TAN value of 2.9 mgKOH/g, dissolved 1700 ppm Zn at 250 ^{o}C, which was the highest Zn concentration dissolved in any of our experiments. At the same temperature, Oil C, with a TAN value of 2.3 mgKOH/g, dissolved 1520 ppm Zn and Oil A, with a TAN value of 0.2 mgKOH/g, dissolved 244ppm. Steady state concentrations of Zn in the crude oil were observed to correlate strongly and exclusively with oil TAN values. By contrast, the sulphur and thiol contents of the oils showed no correlation with Zn concentration. Moreover, Oil B, which dissolved the highest concentration of Zn, contained no detectable thiols.

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

	Oil A			Oil B			Oil C		
Temp.	**n***	**Zn (ppm)**	**Error (ppm)**	**n***	**Zn (ppm)**	**Error (ppm)**	**n***	**Zn (ppm)**	**Error (ppm)**
25 ˚C	3	0.120	0.110	3	0.190	0.190	3	0.150	0.090
150 ˚C	3	54.30	13.70	3	1280	120	3	1080	54.5
200 ˚C	3	87.0	29.0	3	1570	50.5	3	1200	88.7
250 ˚C	3	244	20.9	3	1700	0.80	3	1520	28.4

n* is the number of experiments conducted

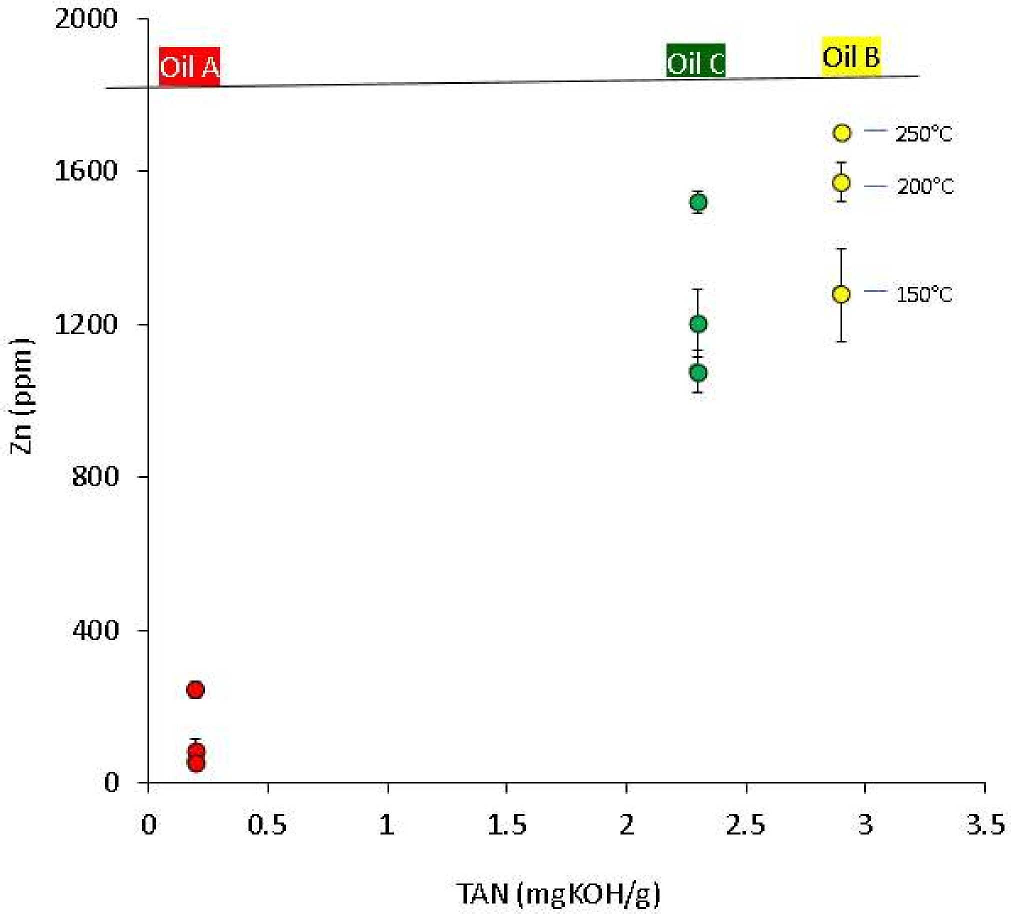

Figure 2. Zn solubility (ppm) in crude oils A, B and C versus the oil TAN (mg KOH/g).

As noted earlier, X-ray Photoelectron Spectroscopy analyses were performed on the residual oil coating the zinc wires after reaction with crude oil (See Fig. 3). The zinc wires were covered in a layer of carbon (C), oxygen (O) and sulphur (S). Progressive etching of the Zn wires led to an increase in the relative abundance of Zn and O and a decrease in the relative abundance of C as detected by XPS. The relative abundance of S did not change significantly during etching. This indicates that Zn has a strong chemical affinity for the oxygen-bearing fraction of crude oil, a weaker affinity for S and a weaker affinity still for C in crude oil.

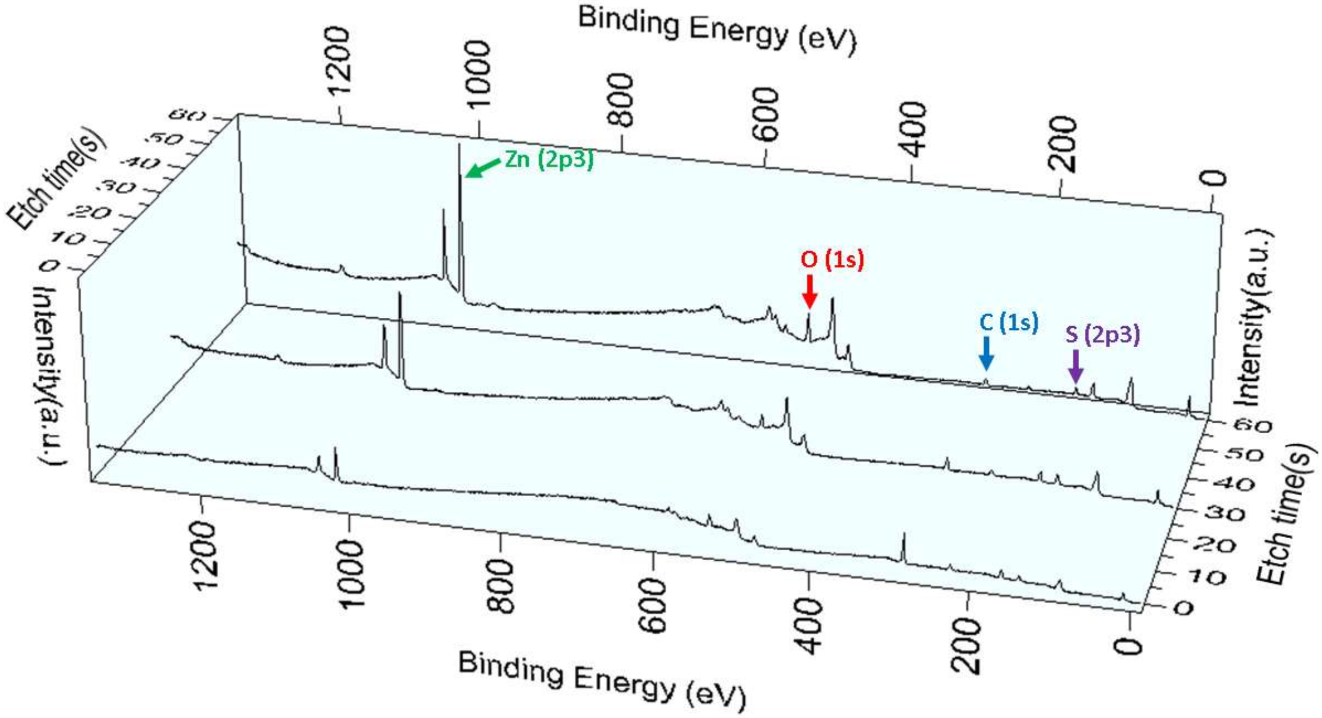

Figure 3. An XPS spectrum identifying the major elements bound to the Zn wire after reaction with Oil C at 200˚C. The relative abundances of these elements changed as the wire was progressively etched.

4.2 Precipitation of sphalerite from a Zn-rich oil

A reaction designed to precipitate Zn from oil in the presence of hydrogen sulfide gas was carried out successfully (details of the experimental setup are provided in Section 3.3). Although the reaction was allowed to proceed for 24 hours, sphalerite crystals were seen to precipitate at the oil-brine interface as a cloud of small, white crystals after just 10 minutes (Fig. 4). The composition of the crystals was confirmed using XRD (see Figure 5). The mass of sphalerite that precipitated was measured and shown to represent for 44% of the Zn initially present in the oil (See Appendix B for details of the calculation).

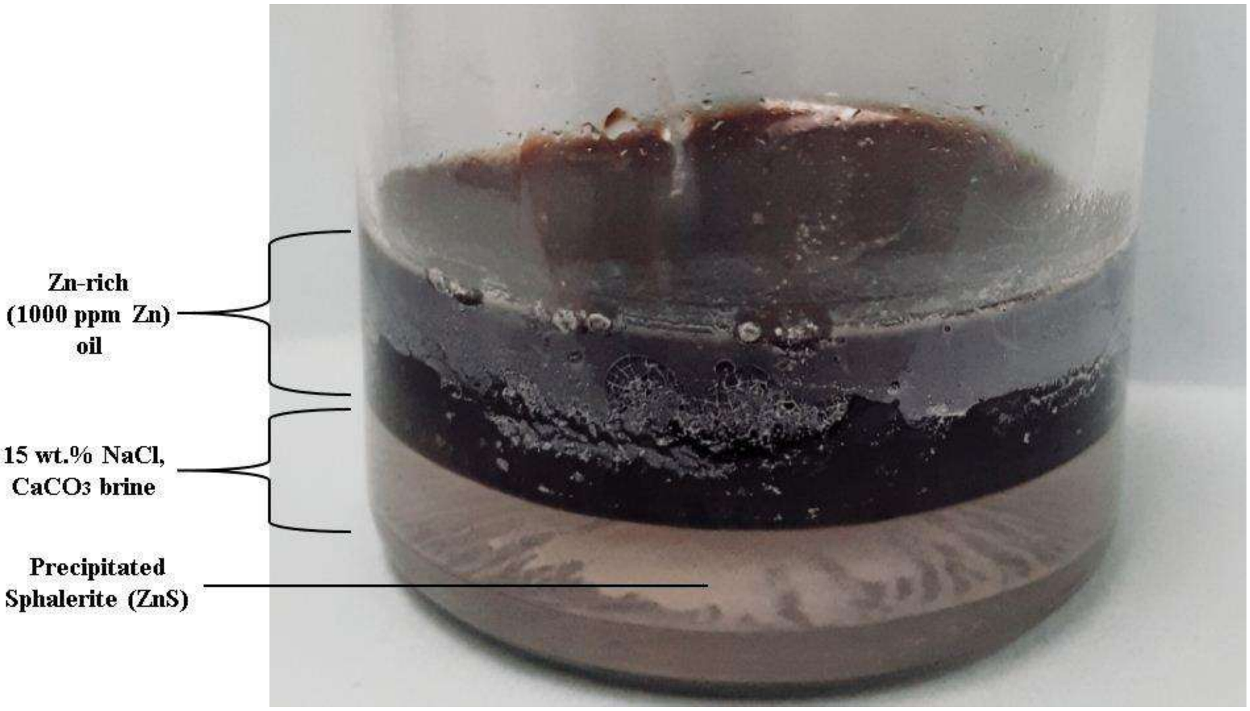

Figure 4. Reaction vessel containing sphalerite that was precipitated from a 1000 ppm zinc-sulfonate oil.

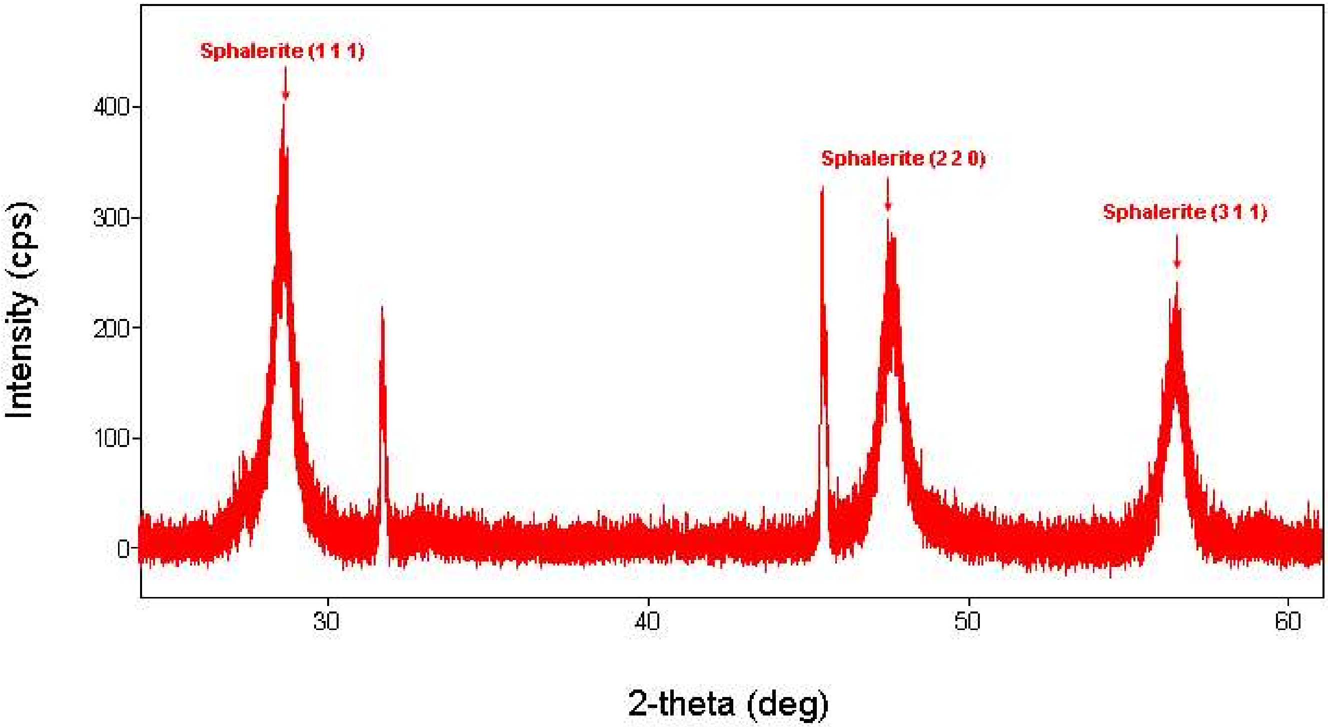

Figure 5. A XRD spectrum for sphalerite precipitated from a 1000 ppm zinc-sulfonate oil.

5 Discussion

5.1 Factors affecting the solubility and speciation of Zn in crude oil

The results of the experiments illustrated in Figure 2 show that zinc solubility in crude oil increases with the TAN value for all temperatures investigated. The total acid number (TAN) is a variable, which quantifies the acidity of an oil and is strongly correlated to its carboxylic acid content (Meredith et al., 2000). Thus, the carboxylic acid content appears to exert an important control on Zn solubility in crude oil. In addition, as is evident from Figure 3, the results of XPS analyses of the Zn wires reacted in crude oil show that Zn has a strong chemical affinity for oxygen compounds in the oil. This is reflected by the growth of the Zn peak and the O peak upon etching of the wire. As most of the oxygen in petroleum is contained in carboxylic acids (Seifert, 1975), this independently reinforces the hypothesis that Zn is complexed primarily by carboxylic acids in crude oil. In contrast, the carbon peak in Figure 3 shrinks upon etching, which indicates that carbon is only loosely bound to the zinc wire. The observation that the sulphur peak changes little upon etching indicates that the chemical affinity of Zn for S in oil may be very limited. This is confirmed by the fact that Oil B, our most Zn-rich oil, has the lowest sulphur content of the three oils. In addition, thiols were not detected in Oil B. This contrasts sharply with the conclusion that thiols form the dominant organic complexes with Zn in aqueous ore fluids (Giordano, 1994).

Heavy crude oils from geologically young formations tend to have the highest carboxylic acid contents. This high content is due primarily to bacterial biodegradation (Meredith et al. 2000; Li, et al. 2010). Redox processes during late diagenesis involving the reaction of kerogen or hydrocarbons with mineral oxidants, such as hematite (Fe_2O_3) in red beds, however, may also be a significant source of carboxylic acids (Surdam et al., 1993).

5.2 The potential of liquid hydrocarbons to act as zinc ore fluids.

It has long been thought that water-soluble carboxylic acids, such as acetic acid, may be effective ligands for the transport of Zn in oilfield brines (Giordano, 1985; Sverjensky, 1986; Giordano and Kharaka, 1994) but little consideration has been given to the possibility that liquid hydrocarbons may act as ore fluids for Zn. High TAN crude oils can contain as much as 3 wt% carboxylic acids, making these acids potentially important ligands for complexation with Zn (Seifert, 1975). Oil B, our highest TAN oil (2.9 mg KOH/g, corresponding to a carboxylic acid content of 8.6 mg/g; See Appendix C for calculation), dissolved 1700 ppm Zn at 250 °C, which is comparable to the maximum amount of Zn inferred to have been dissolved in brines trapped as fluid inclusions in sphalerite from MVT deposits based on thermodynamic modelling (Stoffel et al., 2008). It is important to note, however, that the TAN of Oil B is much lower than that of some oils reported in the literature. For example, the Muglad basin and Great Palogue Field in Sudan are known to produce oils with TAN values of up to 16.2 mg KOH/g (Li et al., 2010) and 10.4 mg KOH/g (Dou et al. 2008), respectively. Lower but still significant TAN values (up to 3.6 mg KOH/g) have been reported for crude oils from offshore oilfields along the Brazilian coast (Barbosa et al., 2016). Based on the results of our experiments, all these oils have the potential to transport significantly greater concentrations of Zn than Oil B.

It is noteworthy that not only can crude oils dissolve significant quantities of Zn but in some MVT deposits, e.g., San Vincente in Peru, Laisvall and Vassbo in Sweden, those of the Canning Basin in Western Australia and Gays River in Nova Scotia, there is evidence for the epigenetic injection of petroleum into the ore zone from an underlying shale sequence (Gize and Barnes, 1987; Etminan and Hoffman, 1989; Spangenberg, 1999; Saintilan et al., 2016). In the case of the Cadjebut deposit, one of the largest Pb-Zn deposits in the Canning basin, brine inclusions commonly coexist with hydrocarbon inclusions in sphalerite from the ore zone. Hydrocarbon inclusions appear as areas of purple zoning in the sphalerite, which can constitute up to 30% volume of the crystals (Etminan and Hoffmann, 1989). This is consistent with the observation from stratigraphic reconstruction, seismic depth mapping and basin modeling, that large portions of the Ordovician-Devonian source rock sequence below the Cadjebut deposit were within the oil window when the deposit formed at 350 Ma ± 15 Ma (Warren and Kempton, 1997; Wallace et al., 2002). Significantly, this also coincided with a time of extension and subsidence in the region (Wallace et al., 2002). It has, therefore, been proposed that the MVT-related hydrocarbons were driven up from the source rocks into the ore zone through compaction-induced flow and compactional dewatering (Wallace et al., 2002). If, as seems plausible from the scenario described above, the hydrocarbons were generated at the same time as the brines and traveled with them to the site of ore deposition, then it is reasonable to speculate that the hydrocarbons may have played a role in transporting the zinc.

Before concluding that liquid hydrocarbons could play a role in the transport of Zn in MVT ore-forming systems, it is necessary to establish whether it is possible to mobilise petroleum in the quantities required to form a MVT deposit. The Cadjebut deposit has reserves of 3.5 million metric tons of 17 percent combined Zn + Pb (Tompkins et. al., 1994). Assuming that the ore fluid was an oil with a density 850 kg/m^3 (similar to the oil used in our sphalerite precipitation experiments), it would require 0.7 km^3 of oil with a concentration of 1000 ppm Zn to form 3.5 million tonnes of ore grading at 17 wt% Zn. Given the oil productivity of the Canning Basin, this volume of oil could have been easily supplied (Refer to Appendix D for relevant calculations). For example, the Ordovician, organic-rich Goldwyer Shale in the Canning Basin has risked oil and condensate reserves in place of 38.8 km^3 (EIA, 2015), and this probably only constitutes a small fraction of the original hydrocarbon producing potential of the basin. These observations, when considered in light of the results of our experiments showing that carboxylic acid-rich crude oils can transport very large concentrations of Zn, strengthens the case that a hypothesis involving the transport of Zn by liquid hydrocarbons during MVT ore formation, merits consideration.

5.3 Precipitation of sphalerite from zinc-rich oils

The calculations described above have shown that it should be possible, in principle, to form a MVT deposit from a liquid hydrocarbon ore fluid. These calculations, however, assume that a mechanism is available for efficiently precipitating sphalerite from the hydrocarbon liquid. In MVT deposits, the sphalerite (and galena) is commonly precipitated from the ore fluid as a result of the reduction of sulphate by organic matter (Thom and Anderson, 2008). This generates large amounts of H_2S gas, which is postulated to react with the dissolved Zn species in the ore fluid, thereby inducing deposition of sphalerite and other base metals (Machel, 2001). Sulphate reduction can occur at low temperature (from 0 to 80°C) through a microbially mediated process known as Bacterial Sulphate Reduction (BSR) but can also start to occur abiotically at temperatures between 100 and 140 °C through a process which is referred to as Thermochemical Sulphate Reduction (TSR) (Machel, 2001).

We have evaluated sphalerite deposition experimentally for the case in which the ore fluid is a hydrocarbon liquid rather than a brine by placing a 1000 ppm Zn synthetic oil, in contact with a calcite-equilibrated, 15 wt% NaCl brine. The resulting fluid was purged with hydrogen sulphide gas so as to simulate the geochemical conditions imposed by BSR or TSR inside a carbonate reservoir. The experiment was conducted at room temperature and led to precipitation of 44 wt% of the Zn initially contained in the oil as sphalerite, indicating that Zn dissolved in crude oil will precipitate readily in the presence of H_2S. Although this is an extremely efficient process at ambient temperature, it does not follow that the process would be similarly efficient at the temperature of MVT ore-formation. However, the results of calculations reported by Williams-

Jones and Migdisov (2014) show that any Zn present in brines at temperatures corresponding to those of MVT deposits will precipitate entirely in the presence of an equivalent amount of H_2S. Thus, if any of the Zn dissolved in the oil were to partition into the coexisting brine, a process that would be favoured by elevated temperature, it would precipitate spontaneously in the presence of H_2S. This supports the hypothesis that liquid hydrocarbons could play a significant role in the formation of MVT deposits as an agent for metal transport.

Bacterial sulphate reduction and TSR take place spatially at the confluence of organic matter (kerogen, bitumen or oil) with sulphate-rich brines. The aqueous sulphate for this reaction is thought to be derived locally from gypsum in the carbonate host rocks (Machel, 2001). In MVT systems, such as those that formed the Cadjebut deposit, there is evidence for multiple ore fluid pulses due to regional extension and subsidence (Tompkins et al., 1997). During the initial pulses, Zn-rich fluids (petroleum and water) migrate into the carbonate-sulphate reservoir, where, in the presence of minerals such as gypsum and magnesite, sulphate reduction leads to the precipitation of an early generation of sphalerite ore. Subsequent fluid pulses may not only be enriched in Zn but may also re-dissolve some of the pre-existing ore and reprecipitate it higher up in the stratigraphy. Thus, it is likely that the locus of sulphate reduction, which coincides with the organic phase-water interface, mobilises Zn with each fluid pulse and so the ore in these systems becomes progressively enriched in a pulse-wise manner, thereby providing further support for the hypothesis that liquid hydrocarbons may play a role in Zn transport in MVT ore-forming systems.

Conclusions

The solubility of Zn in crude oil correlates positively with the Total Acid Number (TAN), and XPS analyses performed on zinc wires after reaction in crude oil indicate that Zn has a strong chemical affinity for the oxygen ligands in crude oil. Both the oxygen content and TAN correlate with the carboxylic acid content of crude oil, indicating that carboxylic acids are the main enabling ligands for Zn dissolution in crude oils. Most importantly, from the perspective of MVT ore-genesis, the concentrations of Zn dissolved in our high TAN crude oils are comparable to the inferred concentration of zinc in sphalerite-saturated brines representative of MVT deposits; even higher concentrations are predicted for oils reported to have TAN considerably higher than the highest in our study. This, and the preservation of liquid hydrocarbons in MVT ores, support the hypothesis that these hydrocarbons play an important role in transporting the zinc required for the formation of some MVT deposits. Finally, the results of our experiments simulating the geochemical conditions imposed by Thermochemical Sulphate Reduction (TSR) show that sphalerite is precipitated efficiently from liquid hydrocarbons through interaction with H_2S in exactly the same way as it is proposed to precipitate from hydrothermal fluids.

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Appendix

A. Composition of the zinc oil standard used in experiments designed to precipitate sphalerite from a zinc-rich oil

Sphalerite was successfully precipitated from a Conostan® 1000 ppm Zn oil standard (Catalogue #CB7-100-032) using the technique detailed in Section 4.2. of our methodology. Zinc is dissolved in the oil standard as a Zn-alkylaryl sulfonate (1000 ppm Zn). The sulfonate functional group binds stably to zinc, whereas the alkylaryl component facilitates the dissolution of the compound in oil. The oil is composed of a blend of light mineral oil (short-chain alkanes) and Hibernia crude oil. Compositional information pertaining to the Hibernia crude oil used in the oil standard is detailed below (Table A1).

Table A1. The composition and properties of the Hibernia Crude oil used in the Conostan® Zn oil standard.

Parameters	
Specific gravity	0.84-0.86
Carbon (wt%)	86
Hydrogen (wt%)	13
Nitrogen (wt%)	0
Saturates (wt%)	79
Aromatics (wt%)	15
Resins (wt%)	4
Asphaltenes (wt%)	3
Waxes (wt%)	8

B. Experimental setup for the precipitation of sphalerite from a Zn-rich oil

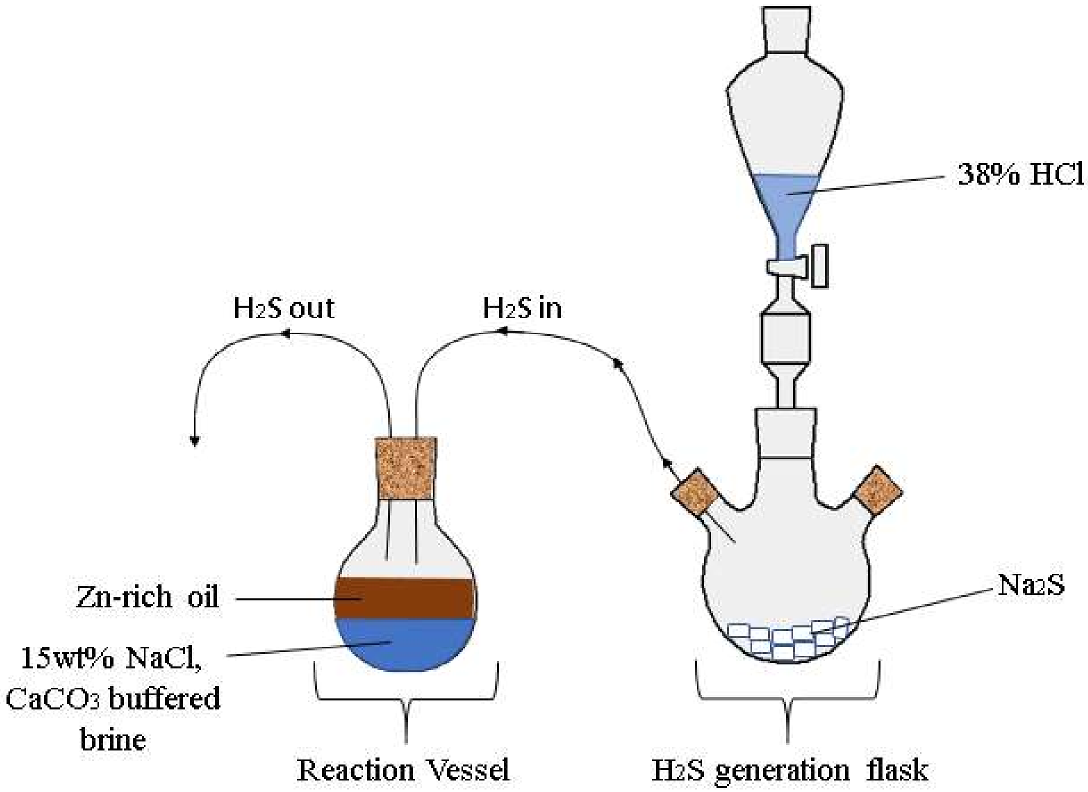

Figure A1. The experimental setup for the precipitation of sphalerite from a zinc-rich oil

Calculating the experimental yield

The experiment was performed with 20g of 1000ppm Zn oil.

Total Zinc = $\left(\left(\frac{1000g\ Zn}{10^6 g\ oil}\right) x20g\ oil\right) x\frac{1000\ mg}{g} = 20mg\ Zn$

Our experiment precipitated 13.11 mg of Sphalerite (ZnS)

Zinc in sphalerite = $\left(\left(\frac{13.11x10^{-3} g\ ZnS}{M_{ZnS}}\right) xM_{Zn}\right) x\frac{1000mg}{g}$ where M_{ZnS} is the molecular weight of ZnS and M_{Zn} is the atomic mass of Zn.

$$\text{Zinc in Sphalerite} = \left(\left(\frac{13.11x10^{-3}g\ ZnS}{97.47\frac{g}{mol}}\right)x65.38\frac{g}{mol}\right)x\frac{1000mg}{g} = 8.794\text{ mg Zn}$$

$$\text{Experimental yield} = \left(\frac{\text{Zinc in Sphalerite}}{Total\ Zin}\right)x100\% = \left(\frac{8.794\text{ mg Zn}}{13.11\ mg\ Zn}\right)x100\%\ = 44\%$$

44% of Zn contained in the oil was precipitated as sphalerite

C. Estimating the carboxylic acid content of crude oil from TAN values

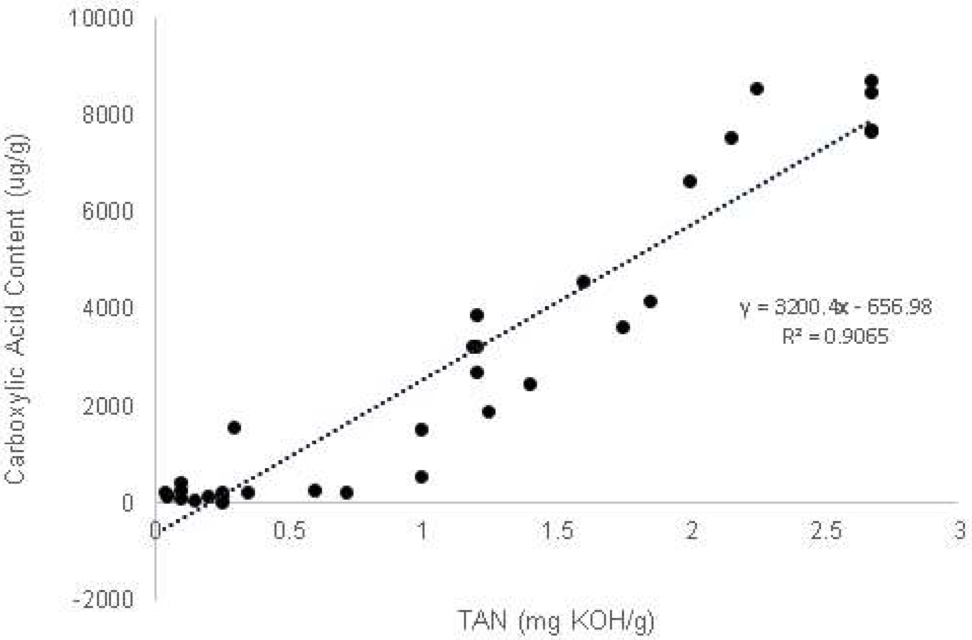

Figure A2. Oil TAN versus carboxylic acid content (modified from Meredith et al., 2000)

$$Carboxylic\ acids\ \left(\frac{\mu g}{g}\right) = 3200.4\ x\ TAN(\frac{mg\ KOH}{g}) - 656.98$$

Empirical equation derived from the data of Meredith et al., 2000.

Our most metalliferous oil has a TAN of 2.9 mg KOH/g.

This corresponds to a carboxylic acid content of **8620 µg/g**

D. Mass balance calculation to determine the amount of Zn-rich oil required to form a Zn deposit as large as the Cadjebut deposit in the Canning Basin, Australia.

The Cadjebut deposit has reserves of 3.5 million tonnes of ore grading at 17wt% Pb + Zn.

Mass of metal = 3.5 x10^{12} g x 0.17 = **5.95 x 10^{11} g Pb + Zn.**

<u>Calculation of the amount of oil required to form a Cadjebut-size deposit </u>assuming all the metal is Zn and assuming that the oil has a density (ρ) of 850 kg/m^3 and dissolves 1000 ppm Zn (equivalent to the density and Zn concentration of the oil used in our sphalerite precipitation experiments).

Concentration of Zn in oil = 1000ppm Zn $= \frac{1000\ kg\ Zn}{10^6 kg\ oik} = \frac{1000 kg\ Zn}{10^6 kg \big/ 850 kg\ m^{-3}} = \frac{0.85\ kg\ Zn}{m^3 oil}$

Amount of oil $= \frac{Mass\ of\ Zn\ deposit}{Concentration\ of\ Zn\ in\ oil} = \left(\frac{5.95x10^8 kg\ Zn}{0.85\ kg \big/ m^3}\right) \text{x} \frac{1\ km^3}{10^9 m^3} = 0.7\ km^3$

<u>Calculation of the oil reserves (in cubic kilometers) of the Goldwyer Shale in the Canning Basin</u>

Oil reserves = $244\ x\ 10^9 barrels\ x \frac{0.159\ m^3}{barrel}$ x $\frac{1\ km^3}{10^9 m^3}$ = 38.8 km^3 (EIA, 2015)