

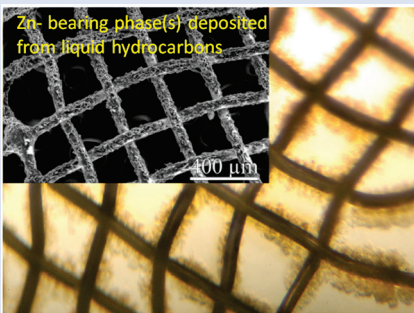
Hydrocarbons as ore fluids

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Abstract



Conventionally, wisdom holds that aqueous solutions are the only non-magmatic fluids capable of concentrating metals in the Earth's crust. The role of hydrocarbons in metal concentration is relegated to providing geochemical barriers at which the metals are reduced and immobilised. Liquid hydrocarbons, however, are also known to be able to carry appreciable concentrations of metals, and travel considerable distances. Here we report the results of an experimental determination of bulk solubilities of Au, Zn, and U in a variety of crude oils at temperatures up to 300 °C and of the benchtop-scale transport experiments that simulate hydrocarbon-mediated re-deposition of Zn at 25–200 °C. It has been demonstrated that the metal concentrations obtained in solubility experiments are within the range of concentrations that are typically considered sufficient for aqueous fluids to form ore bodies. It has also been shown that Zn can be efficiently transported and re-deposited by hydrocarbons. These results provide direct evidence of the ability of natural crude oils to mobilise metals available in hydrocarbon-associated host rocks, and transport them in concentrations sufficient to contribute to ore-forming processes.

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Introduction

A spatial association between hydrocarbons and metallic ores has been reported for a wide variety of deposits, notably the unconformity-type, sandstone-hosted, and quartz-pebble conglomerate U deposits, including the Witwatersrand Au-U deposits (e.g., Mossman *et al.*, 1993; Robb and Meyer, 1995), sedimentary copper deposits (Durieux and Brown, 2007), the Carlin gold deposits (Arehart, 1996), and Mississippi Valley-type lead-zinc deposits (Anderson and MacQueen, 1982). Genetic models dealing with ore formation in these systems, however, either attribute the role of the hydrocarbons to that of an immobile trap, in which redox sensitive elements, such as gold and uranium, deposit from aqueous fluids due to reduction and the insolubility of the reduced species (e.g., Parnell, 1988; Anderson, 1991; Cuney, 2009), or do not suggest any involvement of organic matter in ore formation. In any case, the role of the main scavenging and transporting agent in these models is attributed to hydrothermal solutions. However, considering the appreciable mobility of hydrocarbons (e.g., Hunt, 1984), their close, and, commonly overlapping, spatial occurrence with ore bodies, and their ability to carry dissolved metals (Lewan, 1984; Watkinson, 2007; Khuhawar *et al.*, 2012), it is tempting to propose that hydrocarbons can play an important

role as ore fluids. This hypothesis is now being discussed in the literature (Williams-Jones and Migdisov, 2007) as some indirect evidence has been found in natural systems. For example, it has been suggested that hydrocarbons may have contributed to the transport of gold in the Carlin-type deposits in Nevada (Emsbo and Koenig, 2007) and to the mobilisation of metals in MVT deposits (Banks, 2014). These findings are in agreement with an earlier report that shows gold can substitute Ni in porphyrin-like structures, which are abundant in natural oils (Manning and Gize, 1993). It has also been proposed that uranium and titanium in the Witwatersrand deposits were mobilised and concentrated by liquid hydrocarbons (Fuchs *et al.*, 2015). These studies, however, have assumed that at elevated temperatures, liquid hydrocarbons are able to scavenge metals of interest from their host rocks, transport them in appreciable concentrations, and deposit them in amounts that are economically exploitable. These assumptions remain to be tested. Further development of this hypothesis and its incorporation in models describing ore-forming systems therefore requires an indisputable demonstration of the ability of hydrocarbons to scavenge and transport metals. The purpose of this paper is to report results of experiments that provide this demonstration.

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Testing the Hypothesis

In order to evaluate the ability of liquid hydrocarbons to mobilise and transport metals available in host rocks, we performed a set of batch experiments aimed at determining the isothermal bulk solubility (100–300 °C) of selected metals in a variety of natural crude oils. Oil types and their properties determined before the experiments are reported in the Supplementary Information (Table S-1). Zinc, U and Au were selected for study based on observations of natural systems suggesting that hydrocarbons in some cases may be involved in the transport and concentration of these metals (Emsbo and Koenig, 2007; Banks, 2014; Fuchs *et al.*, 2015). The experiments were performed in titanium autoclaves to which 30 ml of oil were added; metals (wire) or U oxide were placed in the autoclaves in quartz holders. The autoclaves were sealed, and heated to the experimental temperature. After saturation, the autoclaves were quenched, opened, and the holders containing the solids were removed. Samples of the quenched oils were collected and analysed for the metals of interest using NAA methods. The remaining oil was then ashed and the metals from the ash and potential precipitates were dissolved in aqua regia (U, Au)

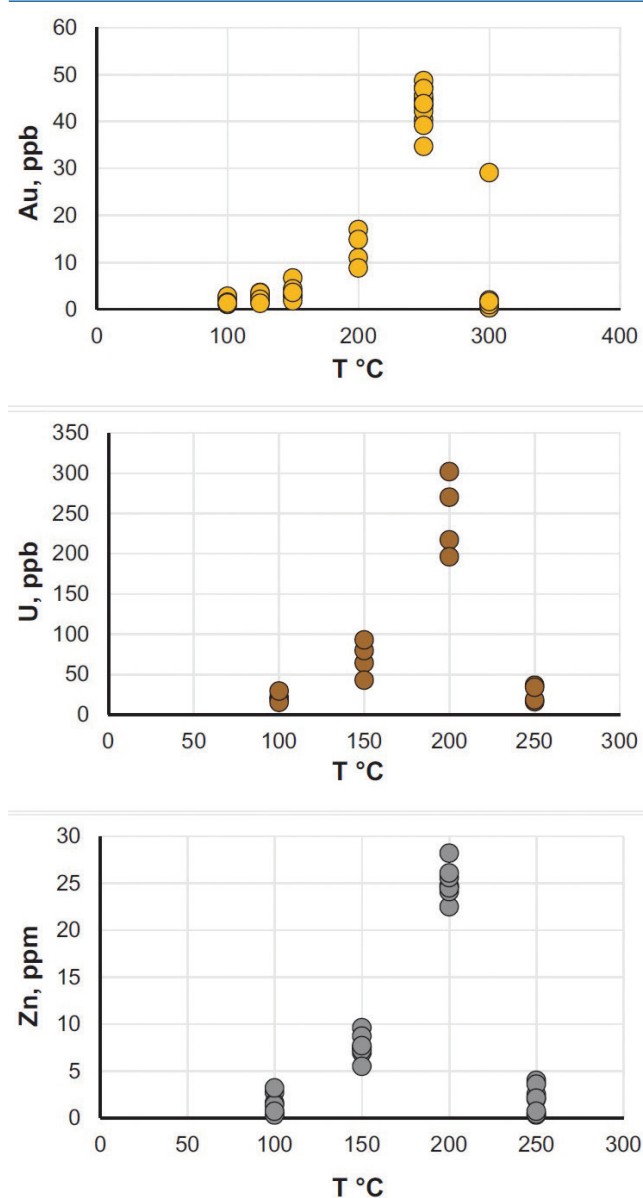


Figure 1 Solubility of metallic gold, zinc, and uranium oxide determined in a variety of crude oils during isothermal solubility experiments.

or concentrated hydrochloric acid (Zn). These solutions were analysed using ICP-MS and NAA methods. The solubility of metallic gold, zinc and uranium oxide thus determined for temperatures from 100 to 250 °C, or in the case of gold, 300 °C, is illustrated in Figure 1 (raw solubility data are reported in the Supplementary Information, Tables S-2 to S-4).

The oils used in our experiments are characterised by significantly different properties and compositions (Supplementary Information, Table S-1). For example, the concentrations of sulphur range from 0.01 to 3.24 wt. % and the API (60 °F) is in the range of 25.4 to 50.6. Surprisingly, the solubility of the metals showed very little dependence on the oil density and sulphur content, and was very similar for the different oils at each temperature investigated. In view of this, we consider that metal solubility in crude oils is controlled by sulphur-unrelated organo-metallic species, such as carboxylates, amides, or porphyrins (Lewan, 1984; Giordano, 1985; McKenna *et al.*, 2009). Thus, in Figure 1, we do not distinguish between different types of oils to emphasise the similarity of the solubility determined for each of them. As shown in this figure, the bulk solubility of the metals increases systematically with increasing temperature, reaching a peak at 200 °C (250 °C in the case of gold), and at higher temperature drops to levels similar to that determined at 100 °C. We suspect that this effect is caused by thermal degradation of hydrocarbons and destruction of the species responsible for metal transport in this medium.

It is important to note that the range of concentrations obtained in these experiments at $T < 250$ °C is within or approaches the range of concentrations which are typically considered sufficient for aqueous fluids to form ore bodies. For example, the concentration of Zn in aqueous solutions responsible for the formation of Mississippi Valley-type deposits is thought to be a few tens of ppm (saturation with sphalerite) (Leach *et al.*, 2006), *i.e.* similar to that in our experiments with crude oil at 200 °C. The same is true for the giant unconformity-type uranium deposits in Australia and Canada, which are interpreted to have formed from solutions containing between 200 ppb and 60 ppm of U (Richard *et al.*, 2011); our measured concentrations reached up to 300 ppb. Finally, hydrothermal solutions responsible for the formation of epithermal gold deposits have been shown, by analogy with geothermal fluids, to contain only a few tens of ppb of gold (Williams-Jones *et al.*, 2009), which is within the range of the solubility of gold in crude oils determined in this study. It should be noted, however, that the solubility peak determined in our experiments is located at temperatures above the “oil window”, the upper limit of which is typically between 120–170 °C (Philippi, 1965). These observations suggest that transport of metals by hydrocarbons is most efficient in the range of temperatures at which oils begin to undergo thermal degradation, producing gaseous hydrocarbons and bitumen (Schenk *et al.*, 1997). This may explain the occurrence of metalliferous pyrobitumen in natural systems, which has been used to make the case that metals can be transported by hydrocarbons (Emsbo and Koenig, 2007; Banks, 2014; Fuchs *et al.*, 2015). It also may explain the absence of ore deposits around large oil fields, which are generally at temperatures too low for efficient metal scavenging by the oils. Our data demonstrate that liquid hydrocarbons can potentially play an important role in ore formation by scavenging disseminated metals and delivering them to geochemical barriers, where they can be deposited in economic concentrations.

A plausible depositional mechanism that can be inferred from the data reported in Figure 1 is a temperature-driven process in which liquid hydrocarbons scavenge metals at elevated temperature, become saturated with these metals and deposit them when temperature decreases. In order to verify this hypothesis, we performed a benchtop-scale transport

experiment, in which we modelled the above temperature gradient driven mechanism for the transport and concentration of Zn (the metal demonstrating the highest solubility in the isothermal series) by the Statoil #3 type of oils (see Supplementary Information, Table S-1). The latter oil was selected because it possesses average/representative properties (API, sulphur) among those oils available in the required volumes in our collection. The experiments were performed in a set of 25–30 cm long sealed quartz tubes (1 cm diameter) filled by oil. One end of the tubes contained samples of metallic Zn and was heated to 200 °C; the other end contained precipitation targets (gold grids), which were cooled with a stream of air and maintained at room temperature (Fig. 2). This experimental design ensured convection of oil within the tube, causing dissolution of the metals in the heated part and their precipitation at the cooler end. Oils were exposed to this temperature

gradient for 5 to 10 days. Thereafter the precipitation targets were removed and the precipitates were collected and characterised using optical microscopy, SEM, ICP-MS, and synchrotron-based X-ray absorption spectroscopy (XAS). In parallel to the above experiments, blank experiments, which did not contain samples of Zn metal, were performed.

As expected, we did not detect any significant precipitation in the blank experiments. In contrast, as shown in Figure 2, all the experiments with metallic Zn produced precipitates. The composition of the phase analysed by EDS varied from 0.5 to 1.5 wt. % Zn, 5 to 8.5 wt. % N, and 6 to 10 wt. % O with the rest being carbon (Fig. 3). In order to obtain more accurate determinations of the concentrations of Zn in the precipitates, the sample shown in Figures 2 and 3 was digested in nitric acid and the resulting solution was analysed for Zn by ICP-MS methods. The concentration of Zn re-calculated

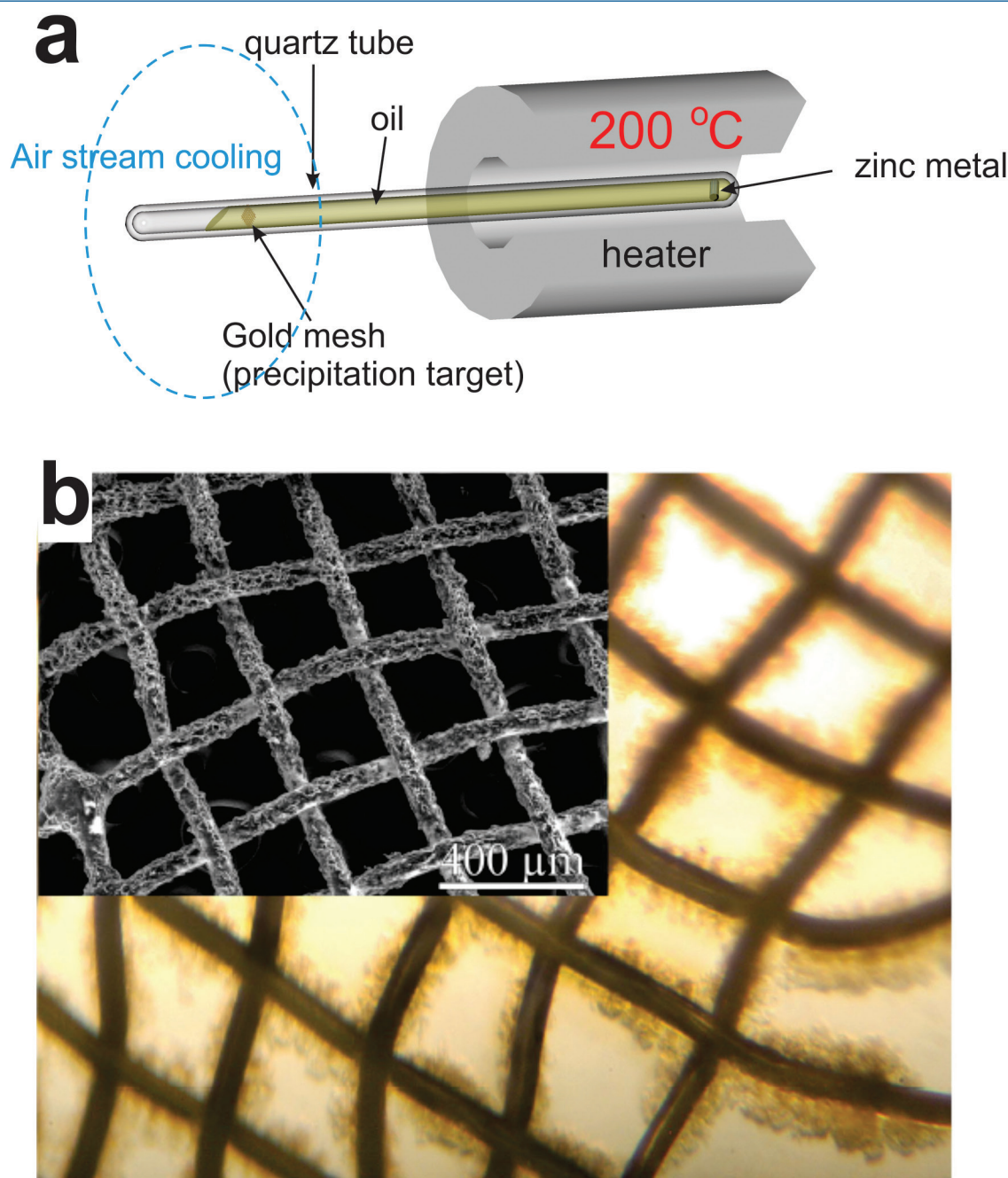


Figure 2 (a) A sketch of the experimental setup for qualitative determination of the ability of natural oils to transport metals at elevated temperatures. (b) A photo and a back scattered electron image of the precipitate discovered at the precipitation target in the experiments with Zn.

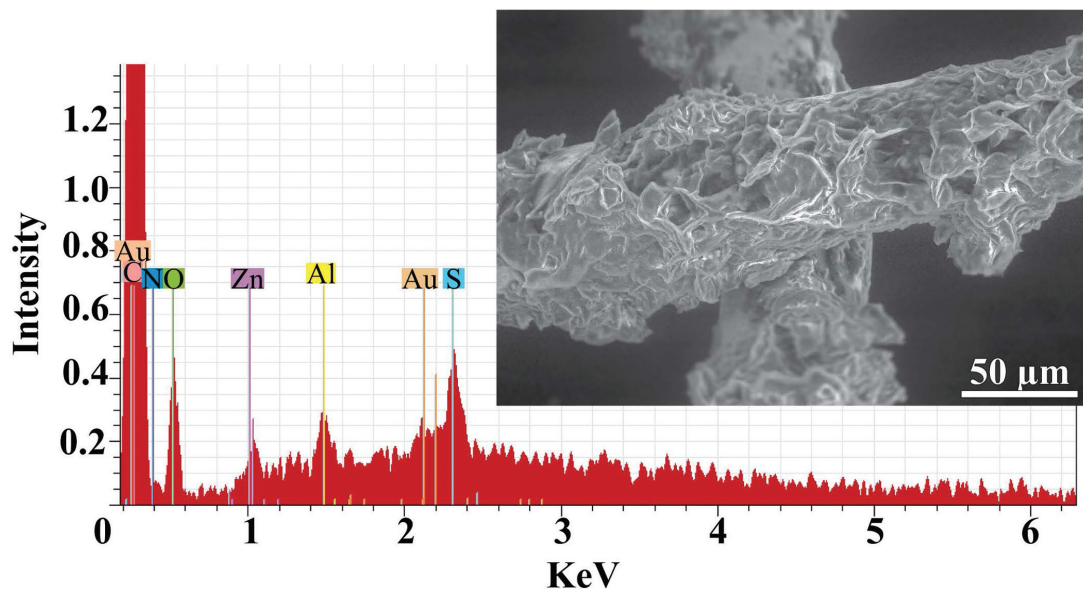


Figure 3 Results of an energy dispersive spectroscopic (EDS) analysis of precipitates obtained from the transport experiments with Zn.

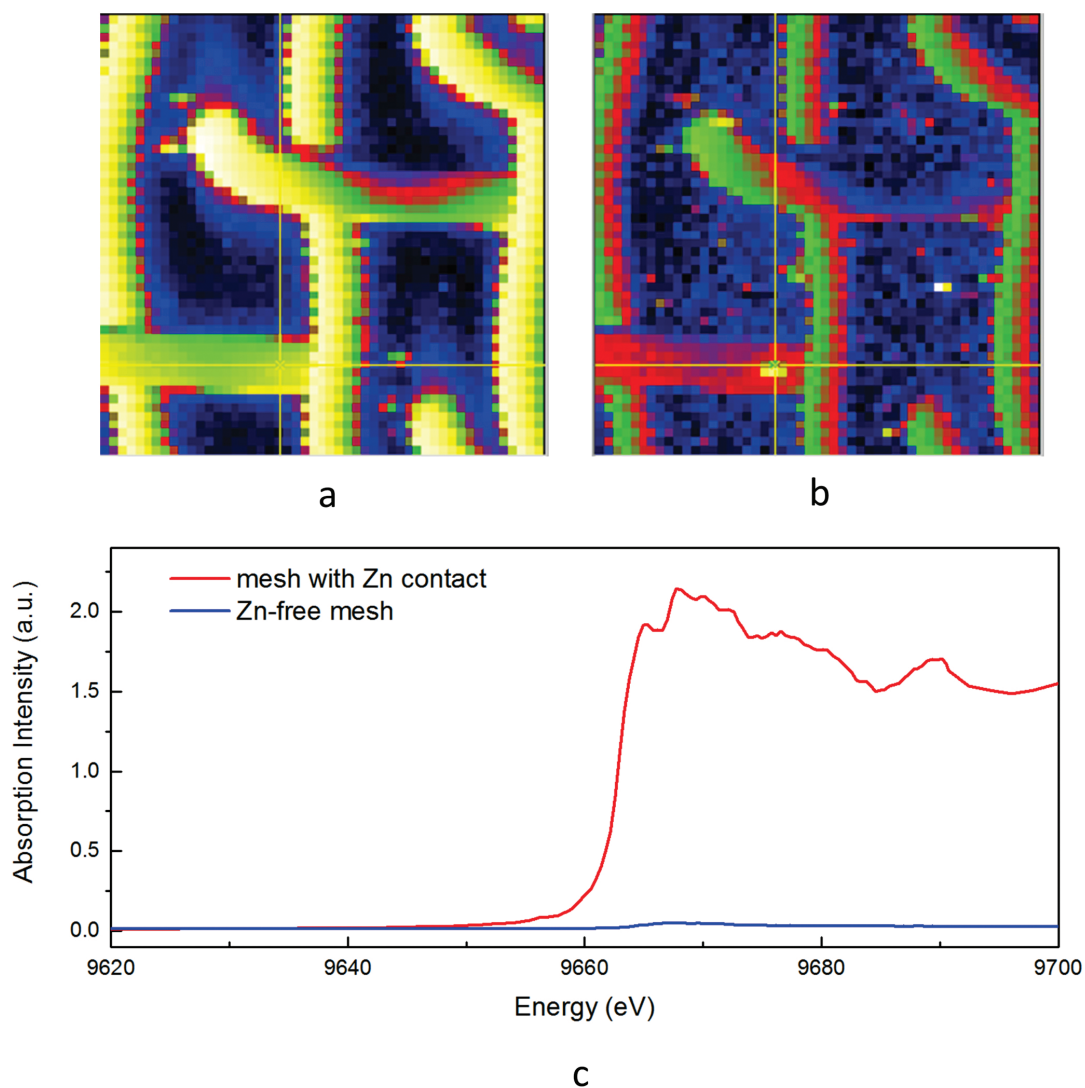


Figure 4 Synchrotron-based micro X-ray fluorescence (XRF) elemental maps showing the spatial distributions of (a) Au and (b) Zn, on a logarithmic scale of intensity (hot colours indicate higher intensity); Zn K edge X-ray absorption near edge structure (XANES) spectra (c) of Zn-bearing and Zn-free samples (the spectrum of the former was taken from the marker in (b)).

for the digested solid was 0.20 wt. %, in reasonable agreement with the semi-quantitative results by EDS. Considering that the total mass of the above sample was 3472 µg, over a time of 5 days, 7 µg of Zn were transported by 15 ml of oil. A second precipitate sample was investigated using synchrotron-based micro X-ray fluorescence (XRF) at beamline 20-ID-B of the Advanced Photon Source (APS), Argonne National Laboratory (Argonne, IL, USA). The sample displayed a strong correlation in the spatial distribution of Zn and Au on the gold grid and its vicinity (Fig. 4a,b; Supplementary Information, Figs. S-4 to S-6). The presence of Zn precipitates was determined by the characteristic Zn K-edge absorption peak (Fig. 4c red curve). For comparison, absorption curves from a gold mesh without Zn precipitates yield an intensity that is two orders of magnitude lower. Considering that Zn was detected in only trace concentrations in the oil prior to the experiment, that blank experiments performed without a Zn source did not produce any precipitates, and the clear evidence of precipitation of a Zn-bearing phase(s) in the experiments with Zn, we conclude that the latter resulted from dissolution of metallic Zn in the hot oil and its deposition upon cooling. Although these results are largely qualitative, they provide a first order insight into the behaviour of metals in liquid hydrocarbons, *i.e.* liquid hydrocarbons have the potential to mobilise and concentrate metals.

Conclusions

It should be stressed that the main purpose of this exploratory research was not to deliver a quantitative description of the solubility of metals in crude oils, but to test the hypothesis that liquid hydrocarbons can be powerful agents of metal re-distribution in the Earth's crust and may provide a means for concentrating metals to the levels needed to form ore deposits. We believe that our experiments, albeit preliminary, have shown that liquid hydrocarbons have all the characteristics required to mobilise metals and act as ore fluids. It can be argued that overall liquid hydrocarbons are likely to be less important in this respect than aqueous fluids, if only because they are much less abundant than aqueous fluids. However, inasmuch as hydrocarbons are commonly found in close association with some types of ore deposits, it is reasonable to consider the possibility that for these deposits at least, liquid hydrocarbons may have contributed significantly to ore formation as an agent of metal transport. The findings of our study may therefore raise serious questions about the validity of currently accepted models for the formation of some ore deposit types.

Acknowledgements

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Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1745

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