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Magnetic Susceptibility
of Petroleum Reservoir Crude Oils
in Petroleum Engineering

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1. Introduction

Magnetic methods are prominent in the area of petroleum engineering and geoscience. They have clear advantages for use in the petroleum industry, including high resolution and rapidity of measurements, non-destructive analysis and cost-effectiveness (Ivakhnenko, 1999). However, there is very limited available data about the magnetic susceptibility of the crude oils. The most resent and complete studies were by Ivakhnenko (2006), Ivakhnenko & Potter (2004) and Ergin & Yarulin (1979). These studies showed that the mass magnetic susceptibility of the crude oils varied from -0.942 to -1.042 (10^{-8} m^3/kg). Analysis of the crude oil components, which are plotted in Figure 1, showed that the most diamagnetic compounds are the alkanes, and the least diamagnetic hydrocarbon compounds are aromatic hydrocarbons such as benzol with its homologues, naphtheno-aromatic and polycyclic aromatic hydrocarbons. Cyclopentane and cyclohexane hydrocarbons populate intermediate positions between the most and the least diamagnetic hydrocarbon compounds. Alkanes with cyclopentanes and cyclohexanes ranged in value from about -1.00 to -1.13 (10^{-8} m^3 kg^{-1}). Aromatic hydrocarbons have a magnetic susceptibility range of -0.85 to -0.97 (10^{-8} m^3 kg^{-1}). In contrast, the oxygen and nitrogen compounds were significantly less diamagnetic. In general, the sulphur crude oil components exhibit a mass susceptibility range similar to that of the benzol homologues.

Also, the ferrimagnetic nature of naturally altered hydrocarbons has been observed by a few authors. The results of a study by McCabe et al (1987) show an association of secondary magnetite with biodegraded liquid crude oil at two localities from the Thornton Quarry (Illinois) and the Cynthia Quarry (Mississippi). The final product of microbial biodegradation, solid bitumen, has been found to be strongly magnetic. Other research also confirms the magnetic nature of gilsonite and hydrocarbon fluid inclusions within crystals of calcite in speleothems (Elmore et al., 1987), and biodegraded hydrocarbons in Venezuela (Aldana et al., 1996). The spatial connection of the hydrocarbon fluids in reservoirs with ferrimagnetic magnetite concentration has been occasionally reported by Gold (1990, 1991).

In this Chapter we detail a systematic study of the mass magnetic susceptibilities of natural crude reservoir oil. These included crude oils from various oil provinces worldwide.
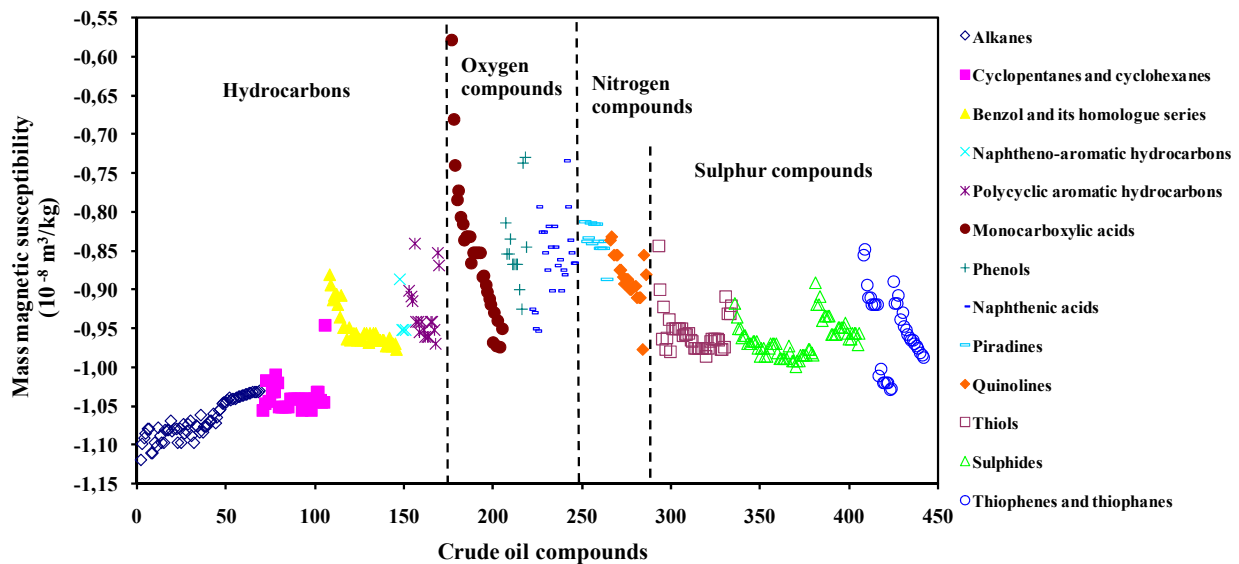
Fig. 1. Mass magnetic susceptibility of crude oil compounds, based on the data of Ergin and Yarulin (1979).

2. Magnetic susceptibility

All substances, solids and fluids, are affected by the application of a magnetic field. The direction of magnetic force lines changes in the presence of different types of magnetic substances. Diamagnetic substances cause a reduction in the density of magnetic force lines making the applied field weaker. In contrast paramagnetic and ferrimagnetic substances cause an increase in the density of magnetic force lines making the applied field stronger. The analogue of such a change of magnetic field inside a substance, named magnetic induction B, is described as follows in the SI system:

$$B = \mu_0(H+M) \tag{1},$$

where H is the magnetic field strength, μ_0 is the permeability of free space, and M is the intensity of magnetisation of a substance, related to the unit of volume. The μ_0 is equal to 4π 10^{-7} Henry/m. It is convenient to have the parameters in equation (1) independent of magnetic field strength. Thus dividing equation (1) by H we have:

$$\mu = B/H = \mu_0 + \mu_0 M/H = \mu_0 + \mu_0\chi_v \tag{2}$$

In this equation μ is the relative permeability, which is proportional to the dimensionless coefficient the volume magnetic susceptibility (χ_v). The volume magnetic susceptibility is a measure of how magnetisable a substance can become in the presence of a magnetic field (Equation 3).

$$\chi_v = M/H \text{ [dimensionless]} \tag{3}$$

Magnetic susceptibility is one of the most informative fundamental magnetic parameters (Ivakhnenko, 1999). Besides the volume susceptibility, there exists specific or mass magnetic susceptibility, χ_m,

$$\chi_m = M_m/H = \chi_v/\rho \quad [10^{-8} \text{ m}^3 \text{ kg}^{-1}] \qquad (4)$$

measured in m^3 kg^{-1}. Mass magnetic susceptibility is defined as the ratio of the mass magnetisation (M_m) to the magnetic field (H) or as the volume magnetic susceptibility (χ_v) divided by the density (ρ) of the substance (Equation 4).

3. Experimental measurements and procedures

Hydrocarbon reservoirs contain a variety of naturally occurring fluids (heavy and light oils, gas condensates, formation waters). Drilling and injecting operations will mean that the formation will also contain drilling mud and other injected fluids. The results in this Chapter consider only the main types of natural reservoir fluids in liquid form: crude oils and formation waters. A suite of representative samples of fresh crude oil were collected mainly from different oil fields from world oil provinces such as the Middle East, North America, Europe, the Far East and Russia. The samples of crude were chosen with a range of distinctive physical and chemical differences. The fluids were kept in their sealed containers until a few days before the measurements when they were poured into glass sealed tubes.

We also studied formation waters and a sample of sea water, which was pumped through the injected wells into the reservoirs, and a sample of distilled water for comparison. All the fluid samples were supplied free of solid (sand, clay, parts of metals, and carbonate sediment) or other fluid contamination.

For magnetic susceptibility measurements were used very sensitive measuring equipment comprising a Sherwood magnetic susceptibility balance (MSB). The MSB or Evans magnetic balance is designed as a reverse traditional Gouy magnetic balance. The Evans method uses the same configuration as the Gouy method except that instead of measuring the force with which a magnet exerts on the sample, the equal and opposite force which the sample exerts on a moving permanent magnet is measured. The magnets are at the end of a beam, and when the sample is placed in one of the magnets, the beam is not in equilibrium. A current is applied to the other magnet until the beam is back in equilibrium, and by measuring the current it is possible to measure the magnetic susceptibility.

The calibration of the MSB was made using distilled water, produced in the presence of air. A value of -0.9043 (10^{-8} m^3 kg^{-1}) for the mass magnetic susceptibility of water at 20 ºC (Selwood, 1956) was used for the calibration. Repeat calibration measurements were regularly made throughout the measurement period. The values of χ_m for the studied fluids were determined at room temperature (normally about 18-20 ºC), and corrected for the displaced air in the measuring tube. The volume magnetic susceptibility of the air displaced in the measuring tube has been taken as 0.364 (10^{-6} SI) due to 20.9% paramagnetic oxygen contribution at 20 ºC temperature and atmospheric pressure.

4. Mass magnetic susceptibility of crude oils

The analysis of the mass magnetic susceptibilities of the natural reservoir fluids shows that the mass magnetic susceptibilities of all the studied fluids are diamagnetic. In Figure 2 shown the measurements of the reservoir fluids from world-wide locations made on the Sherwood Scientific MSB balance. It shows that the mass magnetic susceptibility of crude

oils is changing from a value of -0.9634 (Russia) to -1.0401 (the Far East) (10^{-8} m^3 kg^{-1}). The mass magnetic susceptibility of this range of crude oils differs by no more than 7.37% in their magnetic susceptibility values. The formation waters from the North Sea oil province exhibit a distinctly different range from -0.8729 to -0.8862 (10^{-8} m^3 kg^{-1}), differing by only 1.5%.
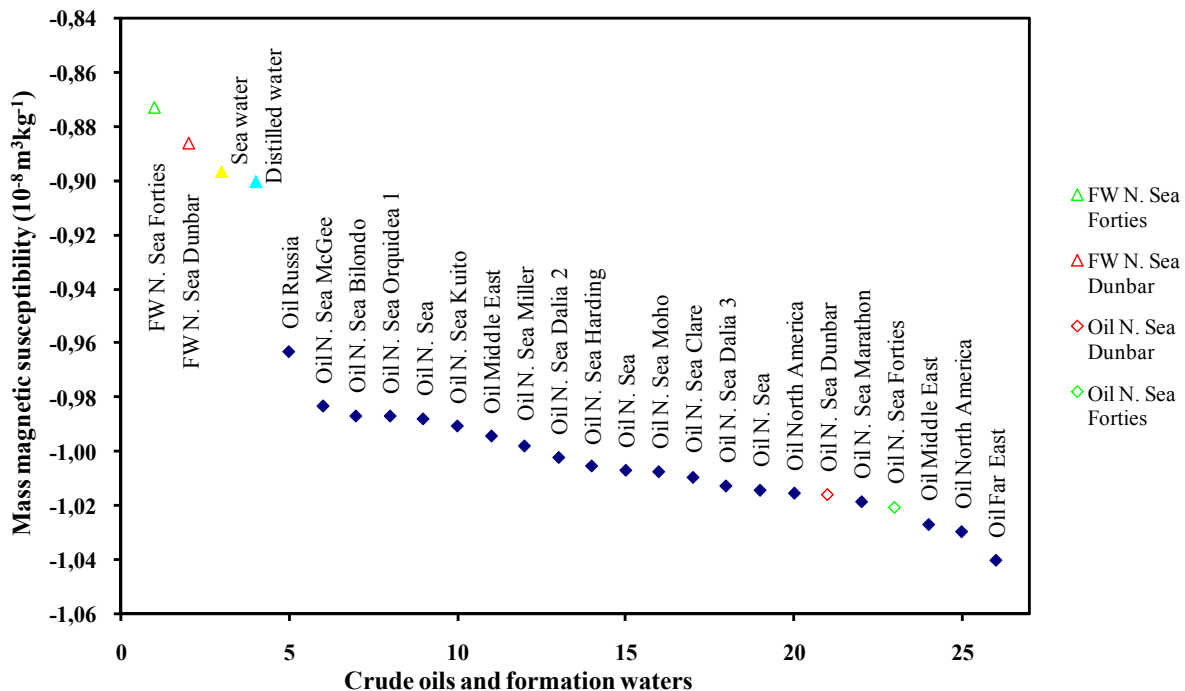

Fig. 2. Mass magnetic susceptibility of crude oils determined using a Sherwood MSB balance. The measurement errors are of the order of ±0.0035 (10^{-8} m^3 kg^{-1}), close to the size of the symbols.

As we can see from Figure 2 the formation waters are distinctly different from the crude oils (around 12%) in terms of their average mass magnetic susceptibilities. This difference is exemplified by the Dunbar and Forties results, where there are clear differences between the mass magnetic susceptibility values for crude oil and formation water from the same oilfield. The Forties formation water differs (less diamagnetic) from the Forties crude oil by around 14%, while the Dunbar formation water differs (again less diamagnetic) from the Dunbar crude oil by around 13%. This demonstrates that there is a real difference between the mass magnetic susceptibility of the crude oils and the formation waters, which may have been less clear-cut had we only measured crude oil from one site and compared it with formation water from another site.

Differences in the mass susceptibility values for the different water samples may be related to the solutes they contain. The studied formation waters contain significant amounts of sodium chloride (NaCl), calcium chloride hexahydrate (CaCl$_2$ 6H$_2$O), magnesium chloride monohydrate (MgCl$_2$ H$_2$O), potassium chloride (KCl), barium chloride (BaCl$_2$) and strontium chloride (SrCl$_2$). The injected sea water sample also contains sodium sulphate

(Na_2SO_4) and is characterised by the absence of the barium and strontium chlorides. The higher concentration of solutes in Forties formation water causes it to have a less negative susceptibility (-0.8729, 10^{-8} m^3 kg^{-1}) than Dunbar formation water (-0.8862, 10^{-8} m^3 kg^{-1}). This observation is also consistent with the lower value of the mass magnetic susceptibility of sea water, which contains the lowest quantity of sodium chlorite and calcium chloride hexahydrate among the studied waters. This is also consistent with the fact that the mass susceptibility of all formation and sea water solutes (Figure 3) was found to be less negative than susceptibility of distilled water at 20 ℃. The mass susceptibility of the distilled water at 20 ℃ is taken as a reference point of water based types of reservoir fluid. The presence of NaCl in the formation waters tends to decrease the water diamagnetism. Pure sodium chloride has a susceptibility value of -0.6451 (10^{-8} m^3 kg^{-1}).
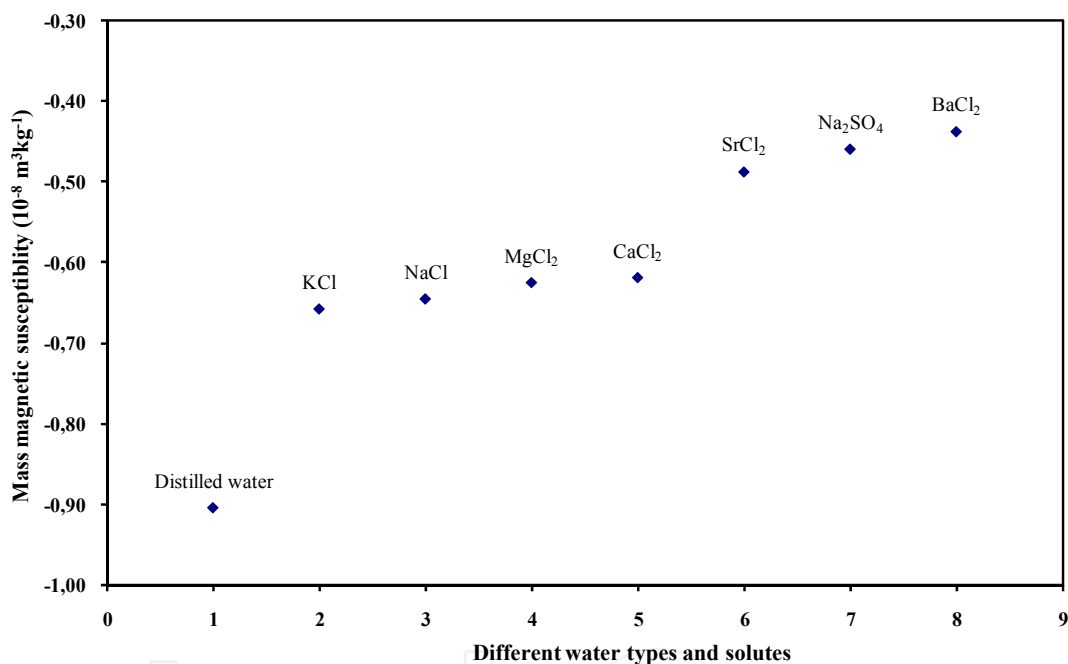

Fig. 3. Mass magnetic susceptibility of distilled water and formation water solutes.

It seems clear from Figures 2 that there are variations between the different crude oil samples, and these are related to their physical and chemical properties as described below.

4.1 Mass magnetic susceptibility and physical properties of reservoir crude oils

Mass magnetic susceptibility exhibits a good correlation with the density of the natural reservoir fluids. Figure 4 shows a plot of mass magnetic susceptibility versus density for the crude oils, formation waters, and other water samples. There is a trend of higher density corresponding to less negative mass magnetic susceptibilities, with a clear difference between the oils and the formation waters. The r^2 correlation coefficient of the density and mass susceptibility of the crude oils from my study (North Sea, North America, Russia, the Middle and Far East) shown in Figure 4 is 0.78.
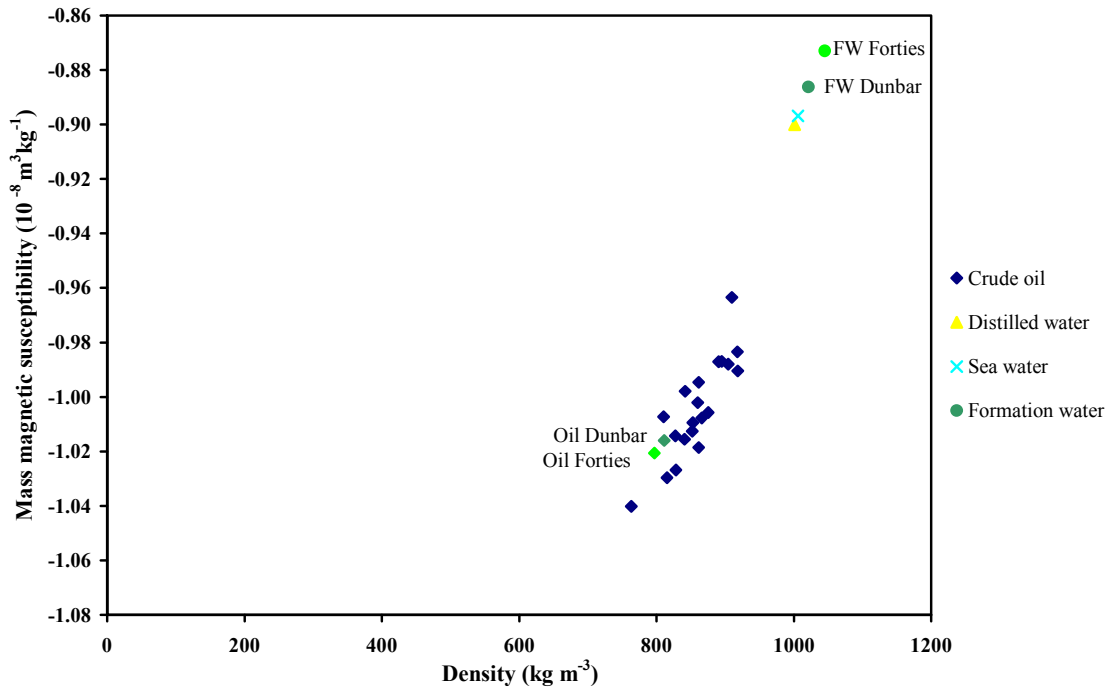
Fig. 4. Mass magnetic susceptibility versus density of crude oils and formation waters from this study. The mass susceptibility was determined using Sherwood MSB balance.
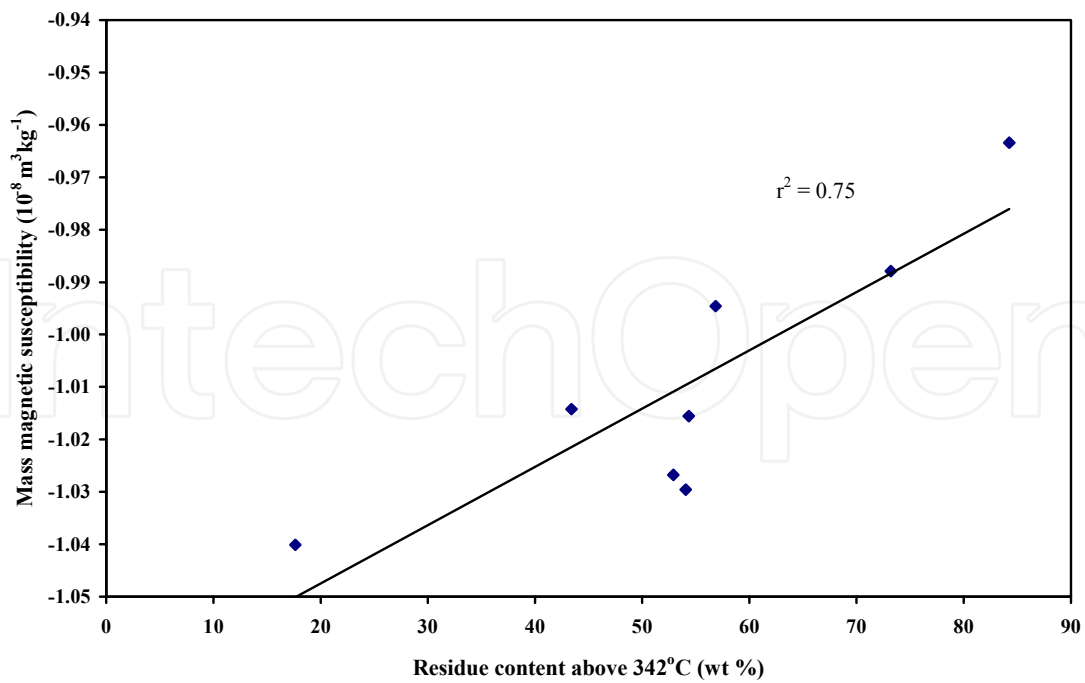

Fig. 5. Mass magnetic susceptibility versus residue content above 342 °C of crude oil samples. The measurement errors are of the order of ±0.0035 (10^{-8} m^3 kg^{-1}), close to the size of the symbols.

The mass magnetic susceptibility is strongly correlated with the content of the crude residue fraction. Figure 5 shows the residue content above 342 °C versus mass magnetic susceptibility for the crude oils for which we had compositional data. The residue is what remains after fractional distillation of the lighter hydrocarbon components. It is evident that the higher the residue content the higher is the mass magnetic susceptibility. The correlation coefficient r^2=0.75. The density of crude oils is primarily dependent on the residue content in the crude oils (Figure 6). The r^2 correlation coefficient between residue content above 342 °C and the density of crude oils is very high at 0.91. Therefore, the samples with higher residue content are also the samples with higher density, so the trend given in Figure 5 is consistent with the mass susceptibility versus density results in Figure 4.
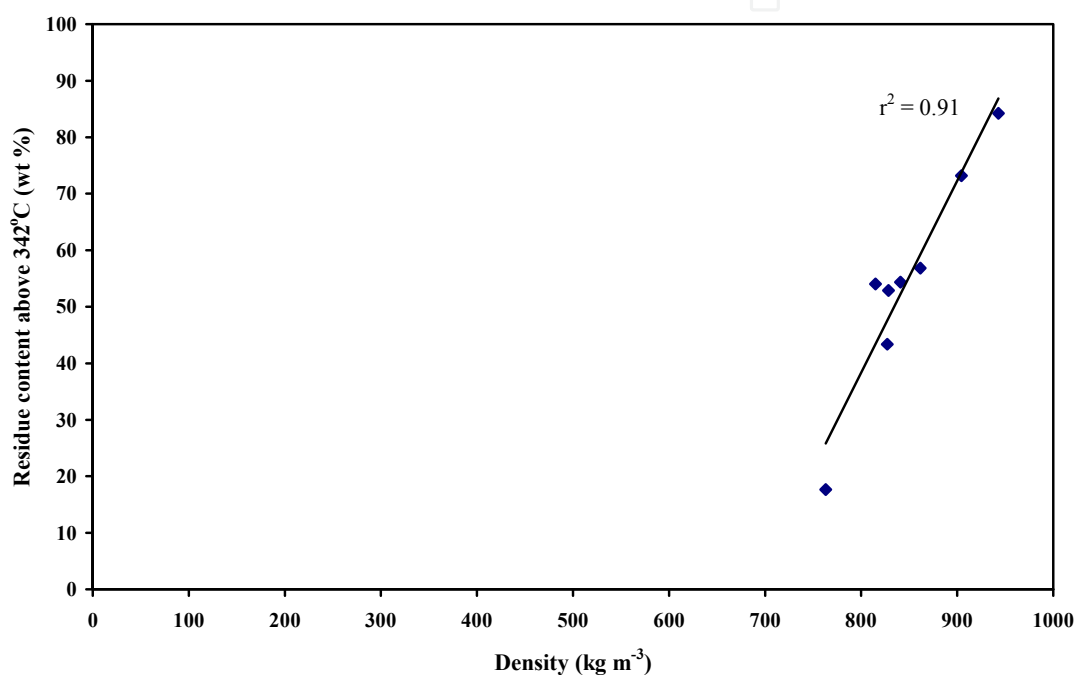

Fig. 6. Density versus relative residue content above 342 °C of crude oil.

The mass magnetic susceptibility versus stock tank oil gravity is given in Figure 7 for the crude oil samples. Stock tank oil is oil as it exists at atmospheric conditions in a stock tank (it tends to lack much of the dissolved gas present at reservoir temperatures and pressures). The gravity is expressed as API degrees as follows:

$$°API = [141.5 / S_o] - 131.5 \tag{5},$$

where S_o is the stock tank oil specific gravity, or relative density, to water at 298 K, and API is an acronym for American Petroleum Institute. For a value of 10° API, S_o is 1.0, the specific gravity of water. Figure 7 shows that there is a distinct trend of decreasing mass magnetic susceptibility with increasing gravity. The linear regression coefficient r^2 is 0.72. This trend is consistent with the expected trend on the basis of the susceptibility versus density results.

The values of the API gravity form the common basis of the oil classification system (Table 1). In general I found that the mass susceptibility and API gravity are related via the
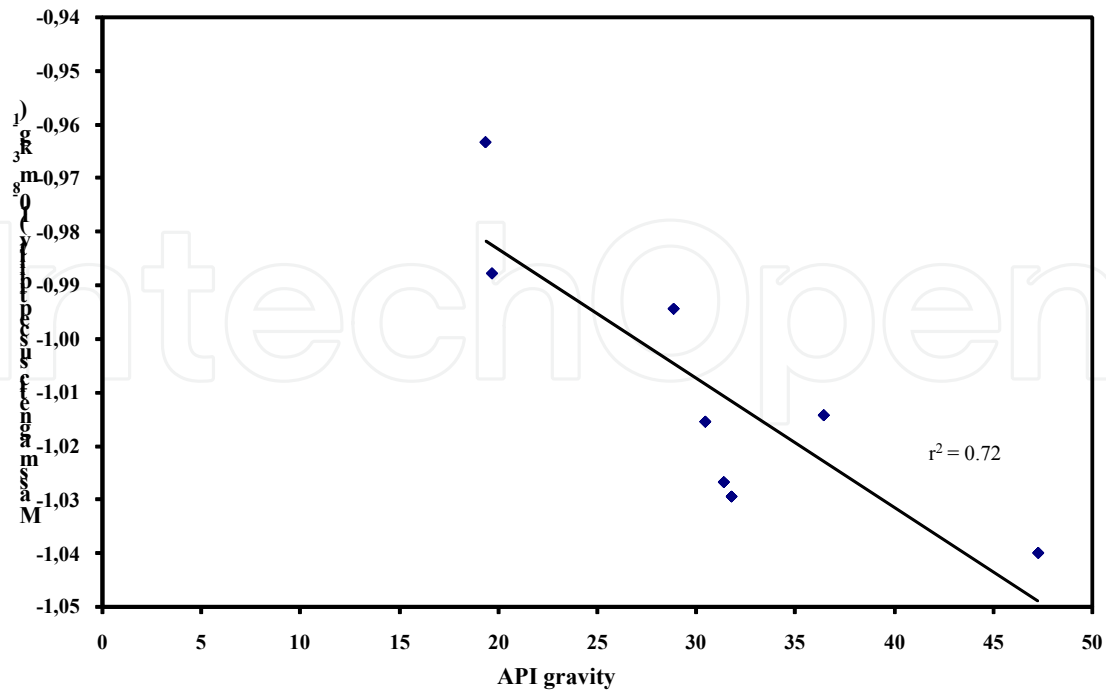
Fig. 7. Mass magnetic susceptibility versus stock tank oil gravity of crude oil samples.

empirical equation (1) below. Therefore, it appears possible use mass magnetic susceptibility for oil type classification.

$$\chi_m \cdot 10^{-8} = -0.0024 \, API - 0.94 \tag{6}$$

Table 2 shows in general that tar with API gravity less than 10° is characterized by mass susceptibility values higher than -0.9592 (10^{-8} m^3 kg^{-1}). Heavy oils correspond to susceptibility in the range -0.9592 to -0.9952 (10^{-8} m^3 kg^{-1}). "Black" low shrinkage and "volatile" high shrinkage oils are characterized by mass susceptibility ranges of -1.0072 to -1.0312 and -1.0312 to -1.0552 (10^{-8} m^3 kg^{-1}) respectively.

Reservoir fluid	Surface appearance	API gravity	Typical composition (mole %)					
			C_1	C_2	C_3	C_4	C_5	C_6
Tar	Black substance	$<10^o$	-	-	-	-	-	90+
Heavy oil	Black viscous liquid	10°-25°	20	3	2	2	12	71
"Black" low shrinkage oil	Dark brown to black viscous liquid	30°-40°	49	2.8	1.9	1.6	1.2	43.5
"Volatile" high shrinkage oil	Brown liquid - various yellow, red or green hues	40°-50°	64	7.5	4.7	4.1	3	16.7

Table 1. API gravity ranges of various oil types and their typical mole composition.

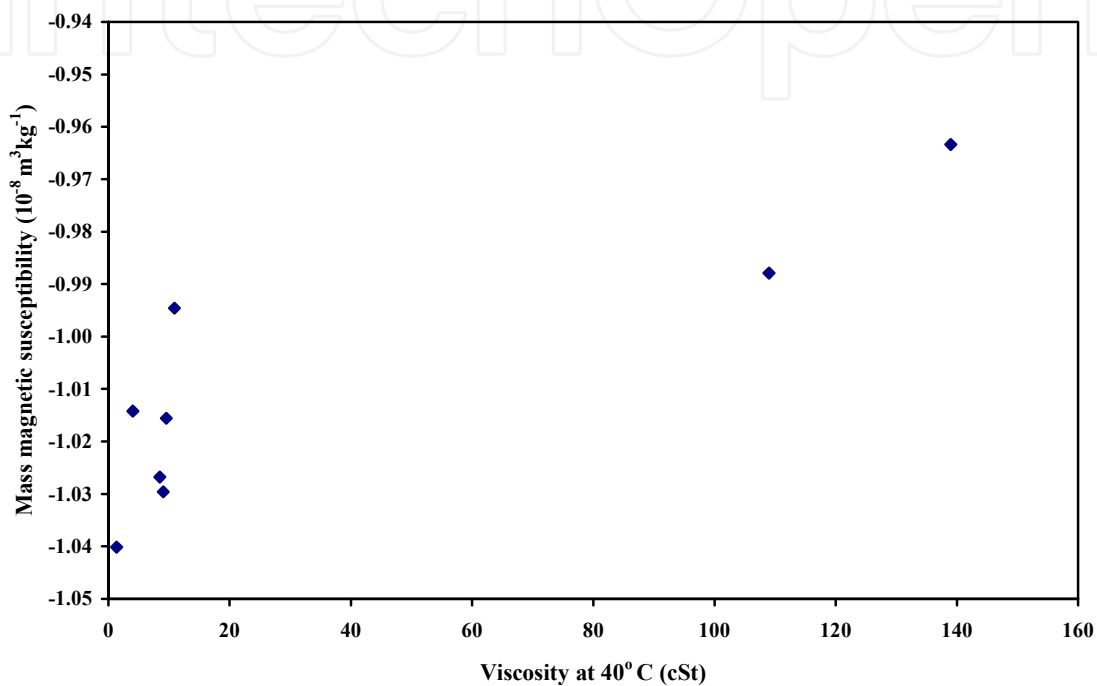| Reservoir fluid	API gravity	Mass magnetic susceptibility (10^{-8} m^3 kg^{-1})
Tar	<10°	>-0.9592
Heavy oil	10°-25°	-0.9592 - -0.9952
"Black" low shrinkage oil	30°-40°	-1.0072 - -1.0312
"Volatile" high shrinkage oil	40°-50°	-1.0312 - -1.0552

Table 2. Mass magnetic susceptibility ranges of oil types.

Fig. 8. Mass magnetic susceptibility versus viscosity at 40 ^{o}C of crude oil samples.

Figure 8 shows results for the mass magnetic susceptibility versus the viscosity at a temperature of 40 ^{o}C for crude oils. This also showed a trend of increasing mass susceptibility with increasing viscosity. I have omitted the linear regression line, where r^2=0.73, since it is fairly meaningless given that there appear to be two clusters, and the correlation may be non-linear. The broad trend we observed might be expected since the samples with higher viscosity are also the ones with higher density, which gave higher (less negative) values of magnetic susceptibility.

4.2 Mass magnetic susceptibility and concentration of sulphur and other chemical compounds

Mineral compounds in crude oils consist of complex organometallic compounds, salt solutions of organic acids and also colloidal mineral substances. At present more than sixty different chemical elements have been found in crude oils, such as Ni, V, Ca, Fe, Si, Ln, Cu, Al, Mg, Na, Sn, Ti, Sr, Pb, Co, Ag, Mn, Cd, As, Hg, etc. Vanadium and nickel exhibit relatively high concentrations of 10^{-3} to 10^{-6}% in oil samples around the world. These two elements usually are concentrated in the asphalt-resin fraction of crude oil.
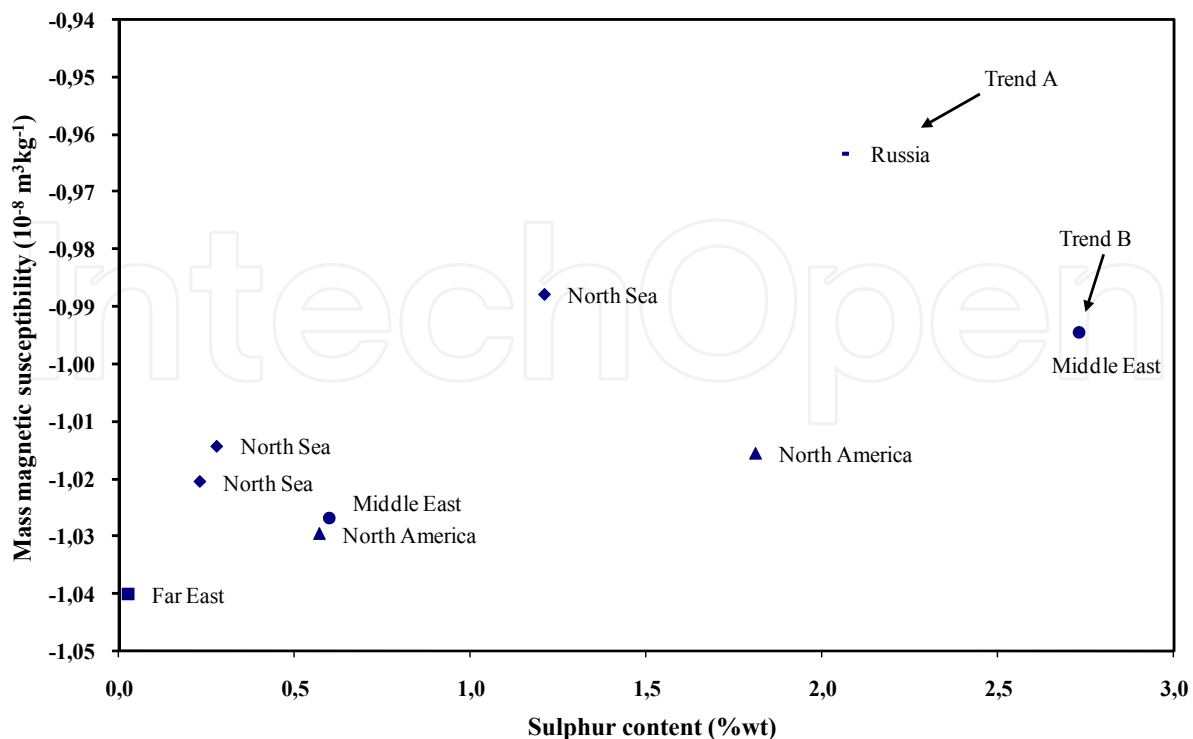
Fig. 9. Mass magnetic susceptibility versus sulphur content of crude oil samples.

It might therefore be expected that the mass magnetic susceptibility of crude oils will reflect their chemical composition. Figure 9 shows the mass magnetic susceptibility versus sulphur content for the crude oils for which I had compositional data. In general, a higher sulphur content corresponds to a higher (less negative) mass susceptibility. There is a suggestion of possibly two trends: one (trend A) including the Russian and North Sea samples, and the other (trend B) containing the North American and Middle East samples. The Russian and uppermost North Sea sample have higher residue concentrations and higher densities than the North American and Middle East samples. Trend A gave a correlation coefficient $r^2=0.95$, and for trend B $r^2=0.97$. Higher sulphur content also generally corresponds to higher residue content and density within each of the two trending groups.

The carbon residue content and mass magnetic susceptibility show a good correlation (Figure 10) with a linear regression coefficient $r^2=0.72$.

The relationship between metal content (usually in the form of organometallic compounds) in crude oils and mass magnetic susceptibility appears to yield certain correlations. The higher the metal content the higher (less negative) the susceptibility. For instance, mass magnetic susceptibility and vanadium content exhibit a linear coefficient of correlation $r^2=0.78$ (Figure 11). Lead content and mass magnetic susceptibility are correlated with $r^2=0.75$ (Figure 12). The relationships of mass magnetic susceptibility with nickel and cadmium is characterised by similar linear regressions. Nickel displays a slightly higher $r^2=0.69$ (Figure 13) than cadmium, where $r^2=0.63$ (Figure 14). The correspondence of mass susceptibility and iron content are consistent with the trend of other metals. However, Figure 15 shows that the linear correlation coefficient is very low with $r^2=0.37$.
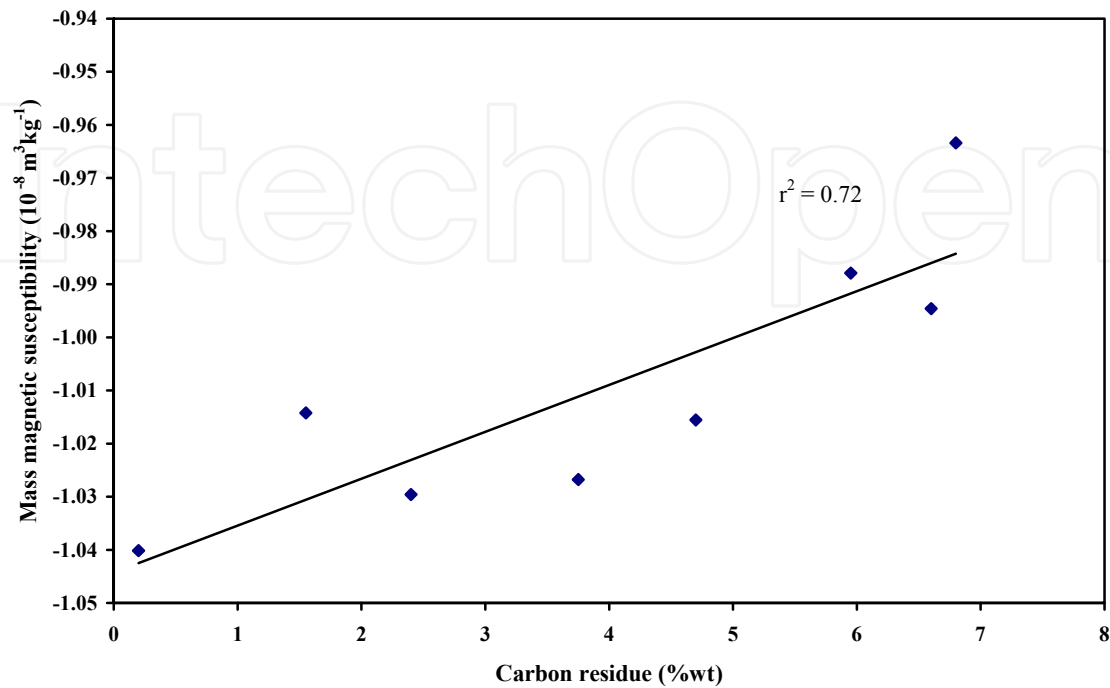
Fig. 10. Mass magnetic susceptibility versus carbon residue content of crude oil samples.
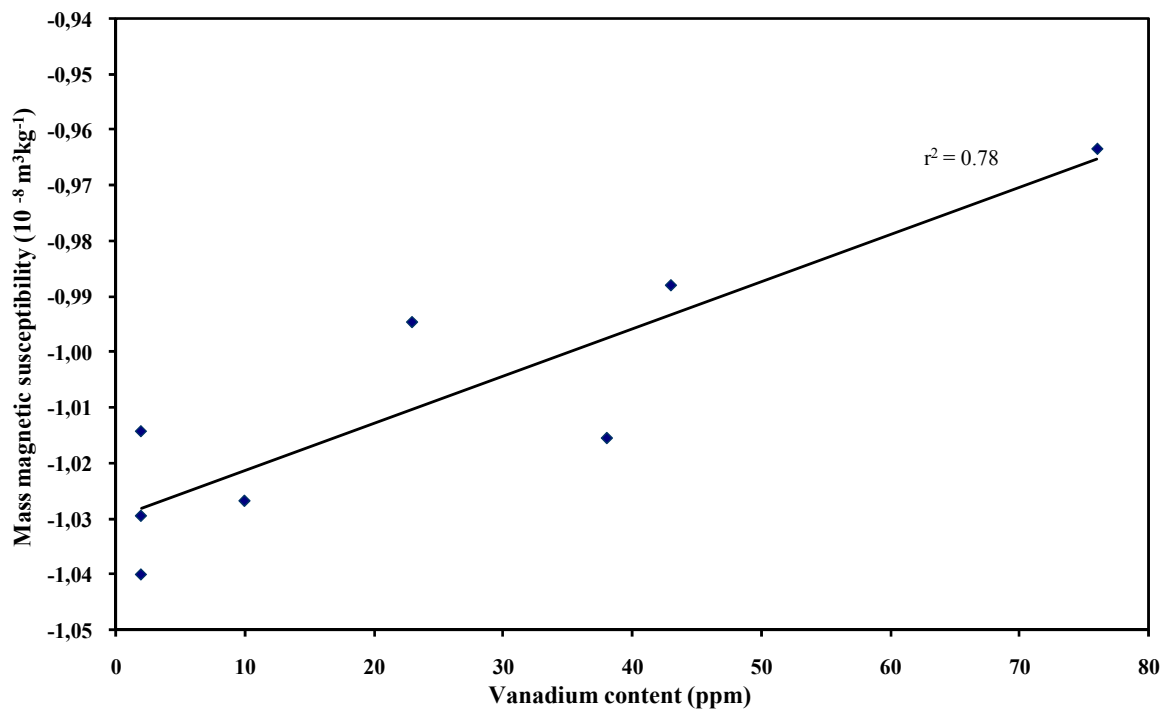

Fig. 11. Mass magnetic susceptibility versus vanadium content of crude oils.
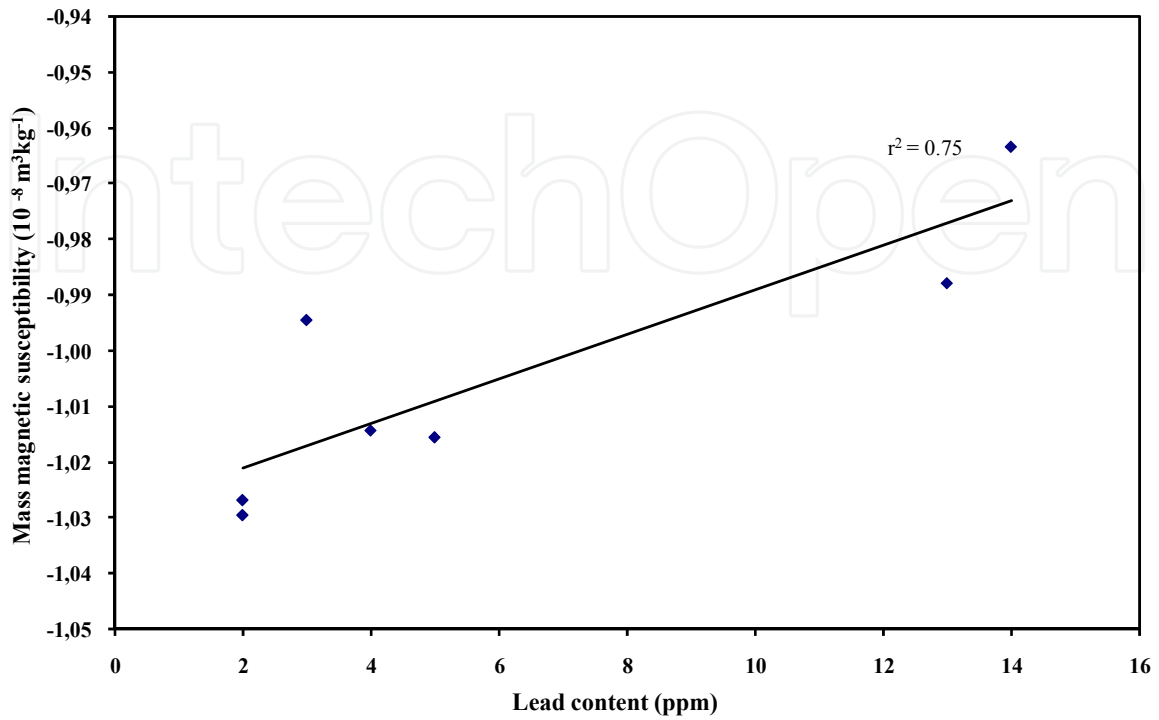
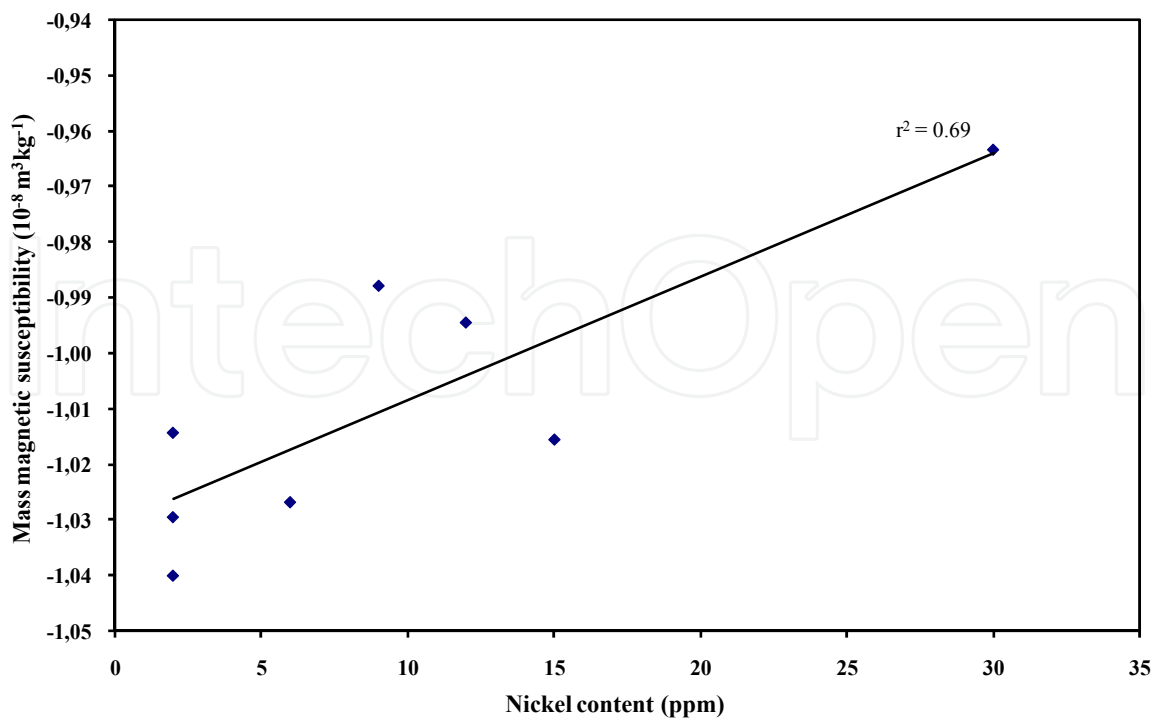Fig. 12. Mass magnetic susceptibility versus lead content s of crude oils.

Fig. 13. Mass magnetic susceptibility versus nickel content of crude oils.
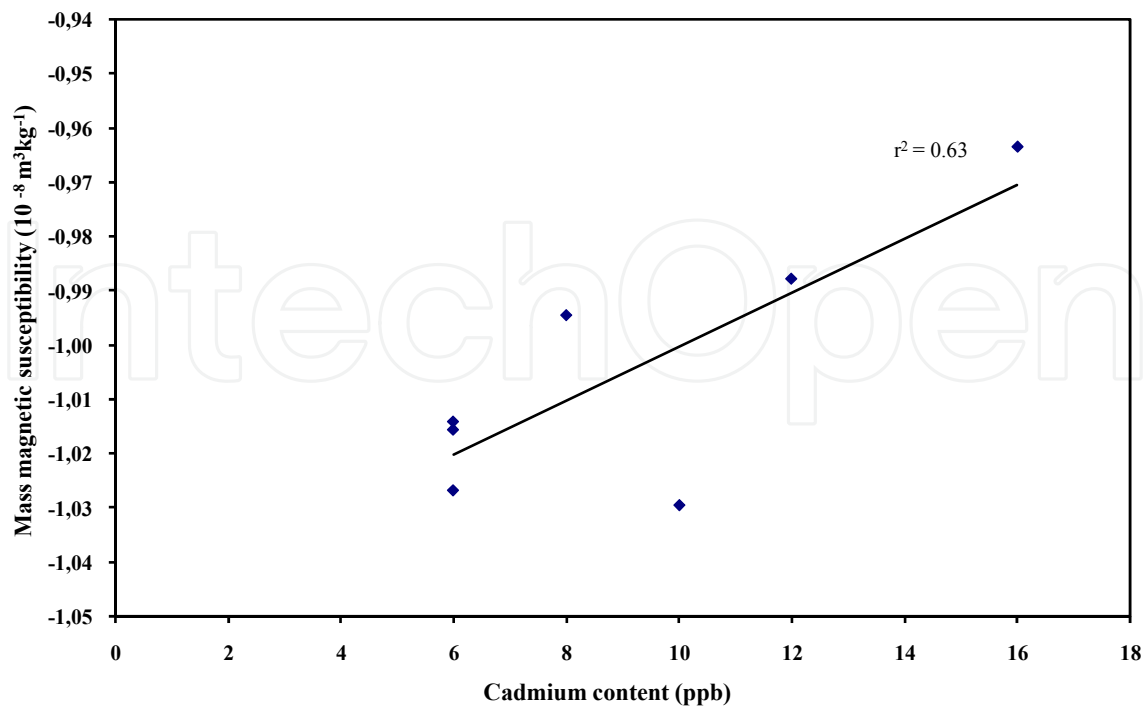
Fig. 14. Mass magnetic susceptibility versus cadmium content of crude oils.
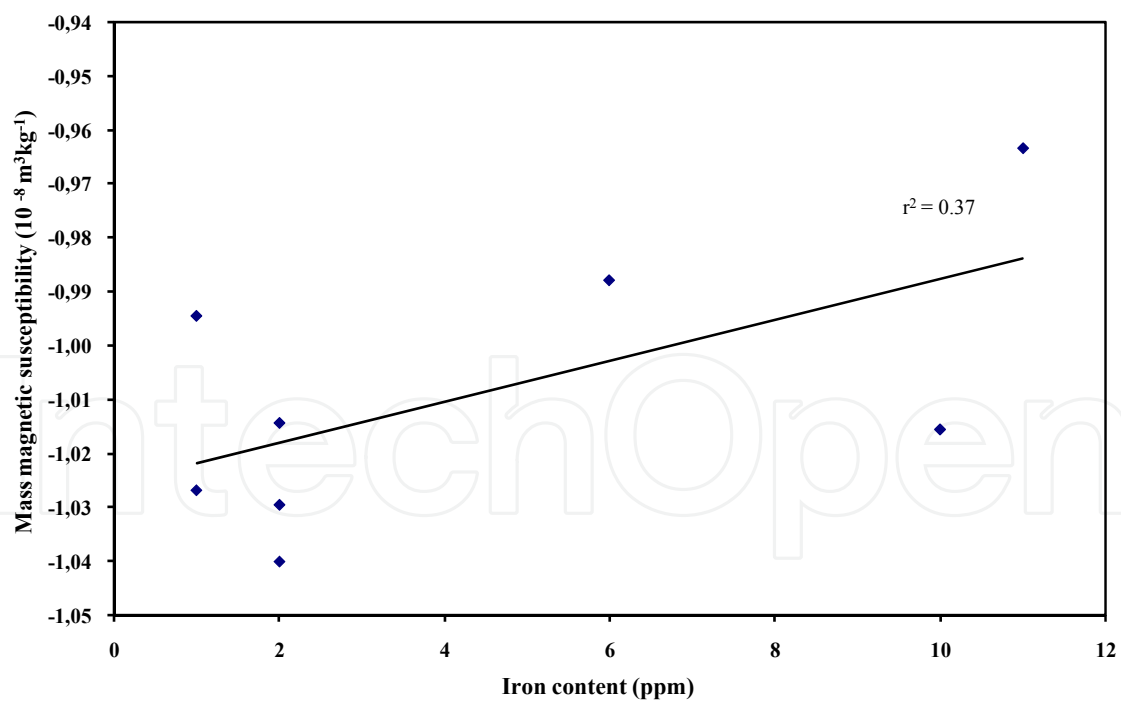

Fig. 15. Mass magnetic susceptibility versus iron content of crude oils.

The results show that in each case there appears to be a trend of higher mass magnetic susceptibility with increasing metal content. This trend might ordinarily be expected. However, the results should be treated with some caution as it was noticed that samples

with higher metal content also had higher density, which also corresponds to higher mass susceptibility. The relative roles of the metal content versus the intrinsic fluid density are presently unclear. It seems that crude oil samples with higher density have higher residue content and that these contain greater amounts of organometallic compounds (Ivakhnenko & Potter, 2004). If the metal content was due to elemental metal, then trace amounts would have a significant effect on the susceptibility. For instance, just 10 ppm by weight of ferromagnetic elemental iron would increase the mass susceptibility of the sample by about 0.7 (10^{-8} m^3 kg^{-1}). In reality the metals are likely to be components in organometallic compounds, which would have substantially lower intrinsic values of magnetic susceptibility, and without knowing the exact composition of these compounds their precise influence on the magnetic susceptibility of the crude oils remains uncertain.

4.3 Regional characteristics of the mass magnetic susceptibility of crude oils

Any magnetic differences between crude oils of different regions may reflect specific features of the geological and geochemical history of the oil provinces, and might provide some support to the suggestion by Ergin and Yarulin (1979) that crude oils from different provinces might be distinguished on the basis of their magnetic susceptibility.
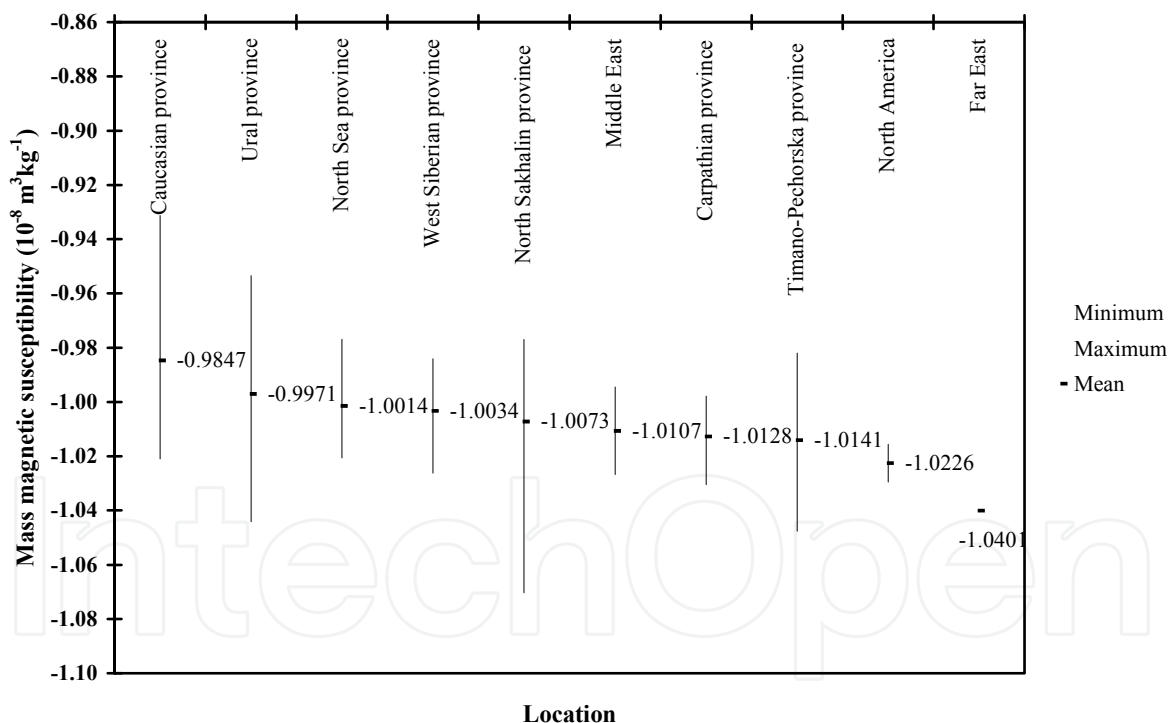

Fig. 16. Average, minimum and maximum values of mass magnetic susceptibility in relation to specific oil provinces.

Our analysis of the mass magnetic susceptibility data for crude oils from different oil provinces (the North Sea, Caucasian, Ural, Timano-Pechorska, West Siberian, Middle East, North America, Far East, and Carpathian provinces) seems to show some differences between the various oil provinces (Figure 16). The crude oils of the Caucasian province

demonstrate the highest average value of mass susceptibility (-0.9847, 10^{-8} m^3 kg^{-1}), whereas the mass susceptibility of oils from North America and the Far East appear to be the most diamagnetic with -1.0226 and -1.0401 (10^{-8} m^3 kg^{-1}) respectively. However, some of the oil provinces are represented by few samples. Clearly more samples need to be studid in order to confirm any broad consistent differences between the various oil provinces.

4.4 Comparison between the mass magnetic susceptibility of reservoir fluids and petroleum reservoir minerals

It may be useful in terms of rock-fluid interactions to compare the mass magnetic susceptibilities of crude oils and formation waters in relation to some typical petroleum reservoir minerals, such as the diamagnetic matrix minerals and the paramagnetic clays. The comparisons are shown in Figures 17 and 18. The reservoir mineral data comes from previously published experimental results. The average values of the mass magnetic susceptibilities of the reservoir fluids are comparable to the diamagnetic susceptibilities of the main matrix minerals (quartz, calcite; Figure 17). However, they are distinctly different from the higher positive values of the paramagnetic permeability controlling clays such as illite (Figure 18). The magnetic properties of reservoir rocks and minerals are described in more details by Ivakhnenko (2006). The experimental values for the minerals were taken from (Borradaile et al., 1990; Hunt et al., 1995; Thompson & Oldfield, 1986).
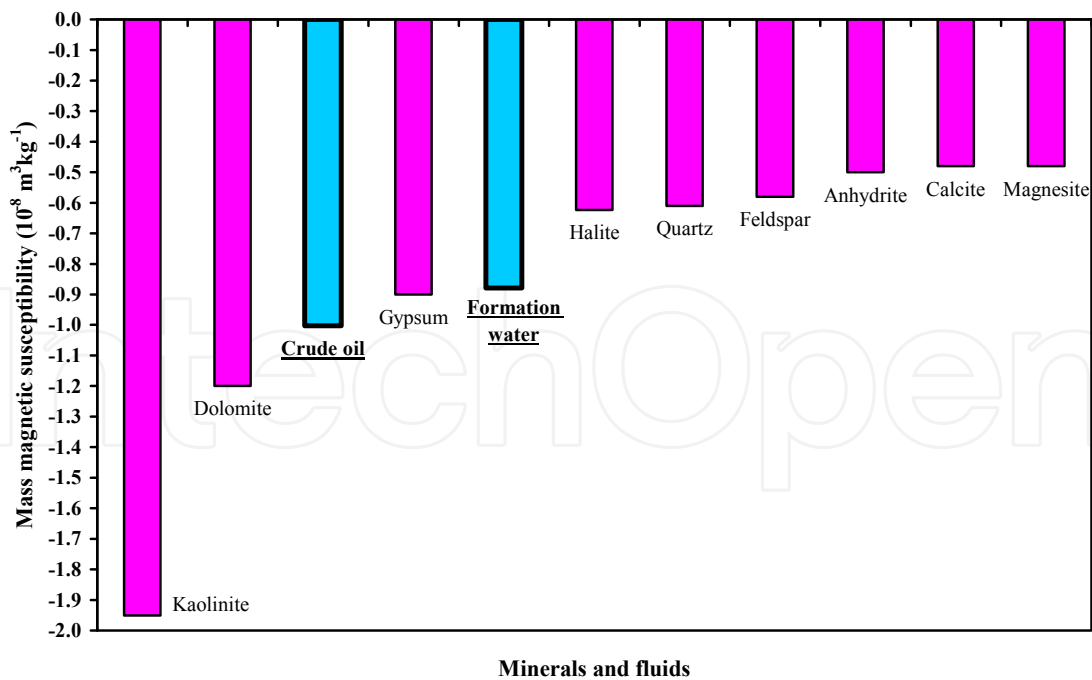

Fig. 17. Mass magnetic susceptibility of typical reservoir diamagnetic minerals in relation to average crude oil and formation water values.
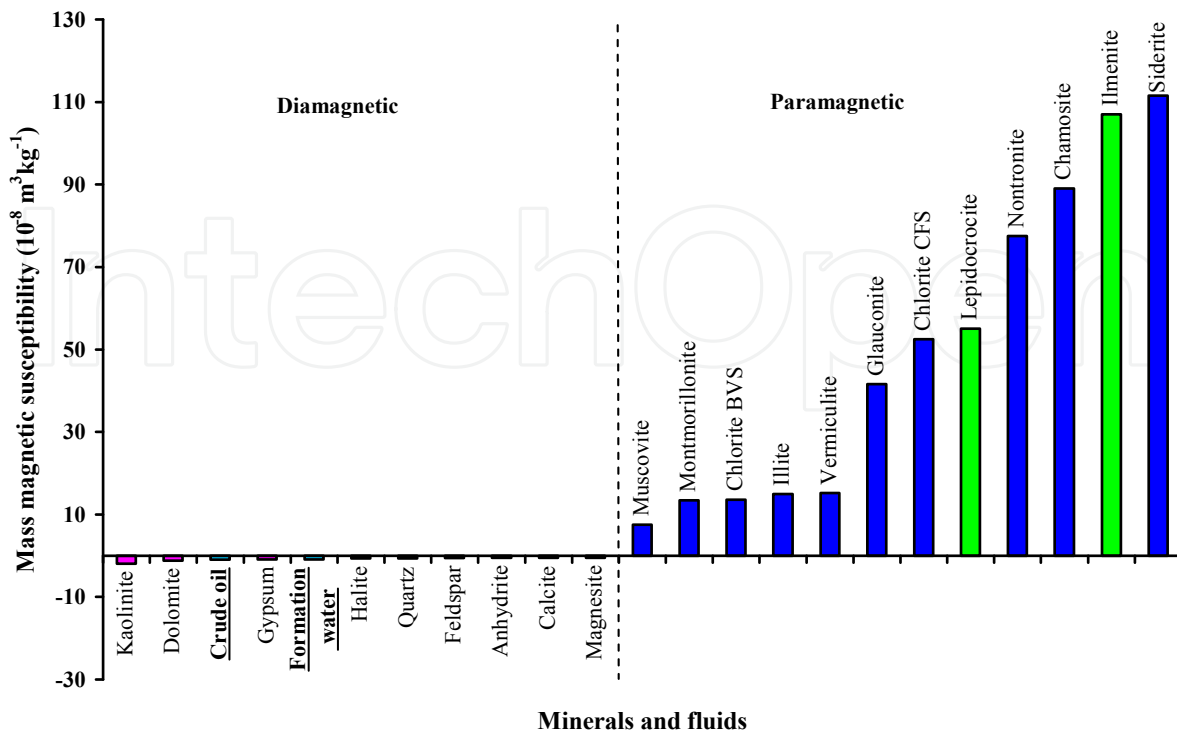
Fig. 18. A comparison of the mass magnetic susceptibility of typical reservoir diamagnetic and paramagnetic minerals in relation to average crude oil and formation water values.

5. Potential applications for petroleum reservoirs

Magnetic susceptibility measurements might find a use in passive sensors in reservoirs for distinguishing between formation waters and crude oils (for example, in helping to determine the onset of water breakthrough). Such sensors would provide an environmentally friendly alternative to radioactive tracers. Although viscosity meters might also distinguish between formation waters and crude oils, the magnetic sensors have a further advantage in that they could also rapidly detect small concentrations of ferrimagnetic minerals or migrating fines, such as paramagnetic clays.

Since mass magnetic susceptibilities of the natural reservoir fluids are more negative than the majority of the diamagnetic matrix reservoir minerals such as quartz, feldspar and calcite, and at the same time the values are significantly less diamagnetic than the clay kaolinite, it appears that magnetic properties may possibly play some role in rock-fluid interactions. The relative magnetic forces between quartz and formation water and between quartz and crude oil, in the Earth's field, might be a factor in determining the wettability (water wet or oil wet) of the reservoir rock. For reservoir rocks containing significant amounts of paramagnetic clays, such as illite, the relative magnetic roles of formation water and crude oil could be reversed (compared to the quartz case) according to Figures 17 and 18, possibly influencing the changes in wettability that one often observes between clean sandstone (quartz rich with little clay) and muddy sandstones containing paramagnetic clays. Recent work has shown links between nuclear magnetic resonance (NMR) and

wettability (Guan et al, 2002) and so a link between magnetic susceptibility and wettability may also be a possibility.

The magnetic susceptibility of reservoir fluids appears to be important parameter for rapidly characterising the following:

- Types of reservoir fluids: formation water and crude oil.
- Quantitatively distinguishing different crude oils. Further work may show that this is better than other methods, such as refractive index or fluorescence.
- Major physical properties.
- Fractional and compositional constitution of crude oils, and content of chemical elements, such as metal content.
- The solute (or anion and cation) composition in the water based types of fluids (formation waters, injected waters).
- Detecting the presence of fines and contaminants.
- Detecting changes in fluids in-situ in the presence of the background reservoir rock matrix signal.

6. Conclusions

The following conclusions can be drawn from this Chapter:

- There were distinct differences between the mass magnetic susceptibilities (χ_m) of crude oils and formation waters. All the samples studied were diamagnetic, but the values for the crude oils were more negative.
- The values of χ_m for the crude oils and formation waters correlated with their densities. The values for crude oil also correlated with other physical properties, namely residue content (and group hydrocarbon content), stock tank oil gravity, and viscosity. The results suggest that the magnetic measurements could potentially be used to rapidly characterise the physical differences between various petroleum reservoir fluids.
- The values of χ_m for the crude oils also showed correlations with trace amounts of chemical components, namely the contents of sulphur, vanadium, lead, cadmium, nickel and iron. The results, however, should be treated with some caution, since the samples with higher contents of these elements also generally have higher density, which also correlates with the mass susceptibility. It appears that crude oils with higher density have higher residue content, and also contain higher concentrations of the above components. The relative contributions of intrinsic fluid density and these trace components to the total magnetic susceptibility signal is presently unclear. The values of χ_m for the formation waters were related to their solute composition.
- There is suggestion from the results that crude oils from different world oil provinces might be distinguished on the basis of their magnetic susceptibility. However, there are significant ranges and overlaps between the results for some provinces, and more samples need to be measured before consistent differences can be confirmed.
- The mass magnetic susceptibilities of the reservoir fluids are much closer in value to the main diamagnetic matrix minerals (for example quartz and calcite) than the paramagnetic permeability controlling clay minerals.

7. Acknowledgment

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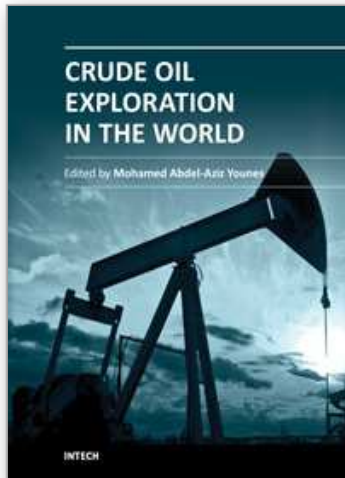
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