EPR and EOM studies in well samples from some Venezuelan oil fields: correlation with magnetic authigenesis

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Electron paramagnetic resonance (EPR), magnetic susceptibility (MS) and extractable organic matter (EOM) measurements were carried out in drilling fines, from near-surface levels, from producer and non-producer wells, with the purpose of examining a possible causal relationship between magnetic contrasts and underlying hydrocarbons. Organic matter free radical concentration (OMFRC) and EOM anomalies were found only at the producer wells, in the same zone where MS anomalies were observed. The EOM anomalies coincide in depth with the MS ones, while the OMFRC anomalies lie close to them. The results could be explained if a net transfer of electrons from reduced organic matter, possible induced by the underlying reservoir, to Fe(III) (*e.g.* hematite) occurs. This process alters the original organic matter and produces the formation of EOM and Fe(II) magnetic minerals (*e.g.* magnetite), with both anomalies coexisting.

Keywords: Electron paramagnetic resonance; extractable organic matter; free radicals

Medidas de resonancia paramagnética electrónica (EPR), susceptibilidad magnética (MS) y materia orgánica extraible (EOM) fueron realizadas en muestras de niveles cercanos a la superficie de pozos productores y no-productores, con el propósito de examinar una posible relación causal entre contrastes magnéticos y el reservorio subyacente. Sólo se encontraron anomalías de concentración de radicales libres de la materia orgánica (OMFRC) y de EOM en los pozos productores, en la misma zona donde se observan anomalías de MS. Las anomalías de EOM coinciden en profundidad con las de MS, mientras que las de OMFRC están en niveles cercanos a ellas. Los resultados pueden ser explicados si ocurre una transferencia neta de electrones de la materia orgánica reducida, posiblemente inducida por el reservorio subyacente, al Fe(III) (ej. hematita). Este proceso altera la materia orgánica original y tiene como resultado la formación de la EOM y minerales magnéticos con Fe(II), (ej. magnetita), y por tanto la coexistencia de ambas anomalías.

Descriptores: Resonancia paramagnética electrónica; materia orgánica extraible; radicales libres.

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1. Introduction

Since the pioneering works by Donovan [1], some authors have argued that the measurement of bulk magnetic susceptibility (MS) in near-surface samples can be used as an alternative means of exploring and assessing hydrocarbon reservoirs [2]. The idea is based on the hypothesis that these anomalies could be the result of the existence, at shallow levels, of abundant diagenetic magnetite, by-product of the alteration of primary Fe oxides in a reducing environment induced by the underlying reservoir [3]. Recently we have performed MS and electron paramagnetic resonance (EPR) in near-surface samples (300-5000 foot depth) from wells located in two Venezuela oil fields [4-6] and soil samples [7]. These studies have shown a relationship between MS contrasts and anomalies of organic matter free radical concentration (OMFRC), the possible result of the presence of an underlying reservoir. In this work we have extended these studies by performing extractable organic matter (EOM) measurements, in an attempt to identify the possible origin (associated or not with hydrocarbon seepage) of the observed anomalies.

2. Experimental

In this study we have worked with producer (GF-3x, LVT-1x and LVT-4x) and non-producer (GF-8x) wells. LVT wells are located in La Victoria oil field while GF wells are in the Guafita oil field, located at the Apure-Barinas sedimentary basin (southwestern Venezuela). A regional map showing the location of these fields is presented in Ref. 5. Drill cuttings (unconsolidated rock samples) were taken at intervals of about 50 feet from the first 5000 feet of these wells. HCl_3 treatments were applied to the samples in order to extract the EOM [6]. EPR has been used to determine the OMFRC [6] in the original samples, which contain the total organic matter. The EPR spectra were recorded at room temperature using a Bruker EMX spectrometer working in the X-band ($\nu \approx 9.4$ GHz), with a rectangular cavity and 100 kHz modulation. Experimental conditions (microwave power and modulation amplitude) were adjusted to avoid saturation effects. MS measurements were performed in a Bartington susceptometer at room temperature. High temperature MS measurements were performed on some representative samples using a Bartington MS2 with a MS2W probe that permits continuous susceptibility and temperature readings.

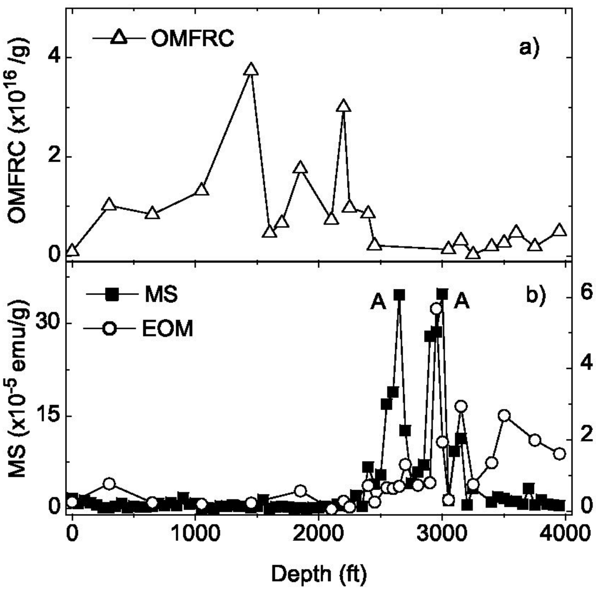

FIGURE 1. GF-3x (producer well): a) OMFRC and b) MS and EOM profiles.

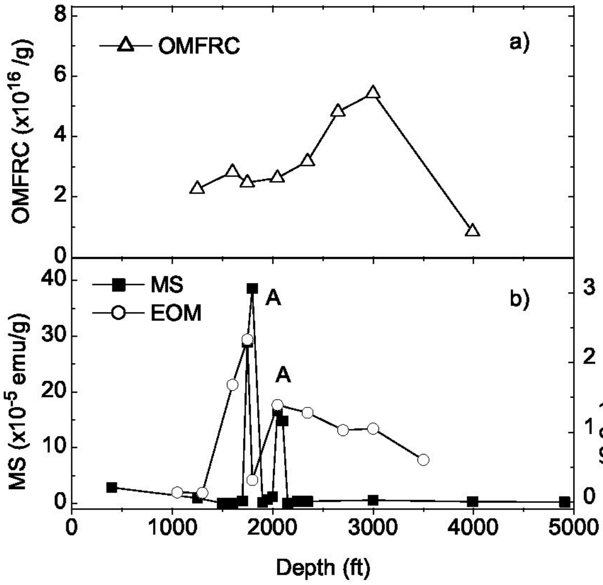

FIGURE 3. LVT-4x (producer well): a) OMFRC and b) MS and EOM profiles.

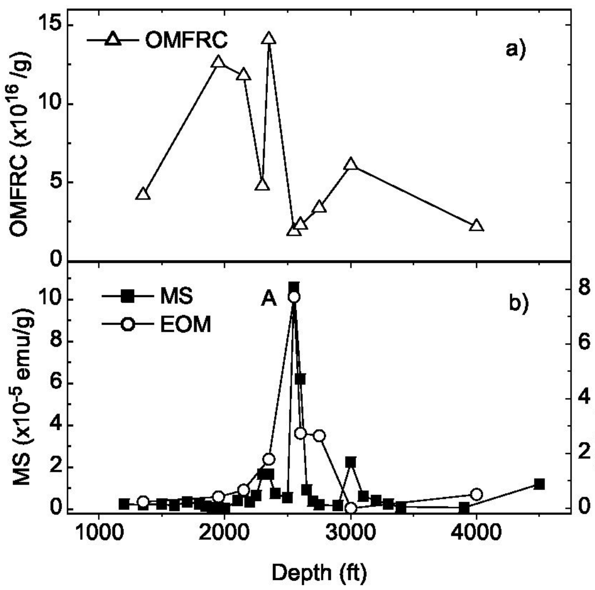

FIGURE 2. LVT-1x (producer well): a) OMFRC and b) MS and EOM profiles.

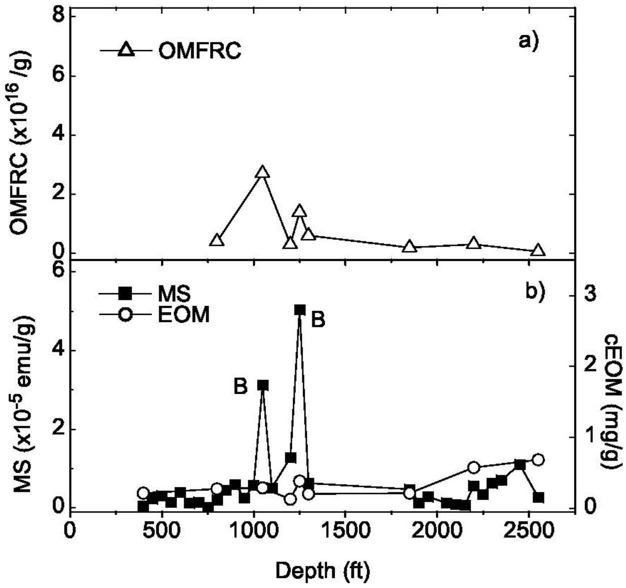

FIGURE 4. Gf-8x (non-producer well): a) OMFRC and b) MS and EOM profiles.

3. Results and Discussion

MS, EOM and OMFRC values for the wells studied are presented in Figs. 1 to 4. At these wells, two kinds of MS anomalies have been recognized (*i.e.* A and B)[5]. Anomaly A was observed only in the producer wells (Figs. 1 to 3) and is related to the presence of Fe-rich spherical aggregates, identified by scanning electron microscopy (SEM), and low coercivity magnetic phases, probably of authigenic origin [4-6]. At the non-producer wells, the observed anomalies are always B-type (Fig. 4). In this case, no spherical aggregates were identified by SEM. Although a low coercivity magnetic mineral has been identified at these levels (*e.g.* magnetite), mineral composition analyses indicate that such MS peaks probably reflect a lithological contrast rather than autigenesis of primary magnetic minerals [5]. EOM and OMFRC anomalies were found only at the producers wells, in the zone where anomalies A have been identified. As shown in Figs. 1 to 3, the EOM anomalies coincide in depth with the MS ones, while the OMFRC anomalies lie close to them. Low and high temperature susceptibility results for anomaly A level of LVT-4x are presented in Figs. 5 and 6. The occurrence of the Verwey transition around 120K (Fig. 5) and the sharp reversible drop at about 580°C (Fig. 6) suggest the presence of magnetite as the chief magnetic mineral. It has

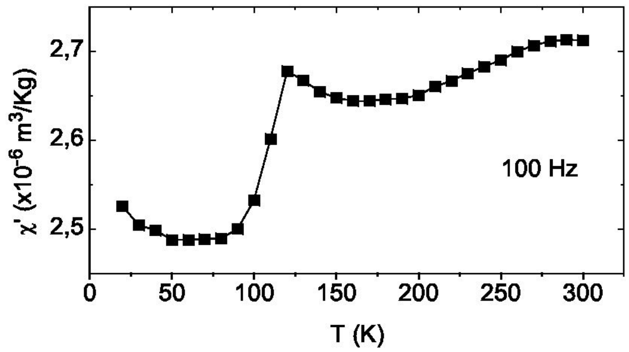

FIGURE 5. LVT-4x: AC low temperature MS for A anomalous level (see Fig. 4).

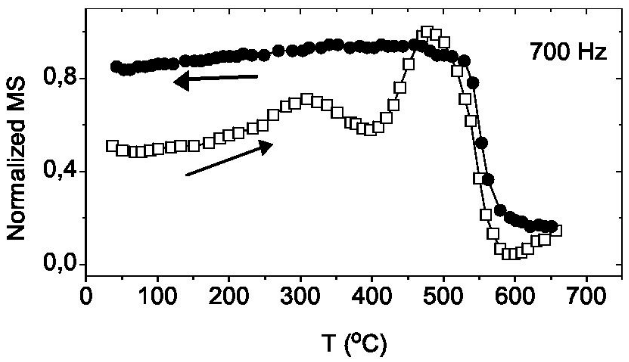

FIGURE 6. LVT-4x: AC high temperature MS for A anomalous level (see fig. 4); heating and cooling curves.

been hypothesized that magnetite in a variety of sedimentary environments may have resulted from organic matter oxidation coupled with Fe(III) reduction [8]. On the other hand, previous results obtained in soil samples from the Andean Range suggest that hydrocarbon gas leakage could be associated with degradation or alteration of the organic matter [7]. In this sense, iron in the Fe(III) form should have existed initially at these anomalous levels together with reduced organic matter, in our case probably resulting from the underlying reservoir. So a net transfer of electrons from this altered organic matter to Fe(III) should occur [9]. This process alters the original organic matter and produces the formation of EOM and Fe(II) magnetic minerals (*e.g.* magnetite). Due to the net transfer of electrons from the organic matter, low OMFRC values are detected at these same levels. MS, EOM and OMFRC anomalies define a reducing zone where the appropriate conditions for authigenesis precipitation could take place [6]. On the other hand, for the non-producer GF-8x, the OMFRC do not show a clear anomaly and no anomaly is observed inthe EOM profile either. Notice that LVT-4x and GF-8x EOM and OMFRC profiles are at the same scale. This suggests, as previously indicated, that another process (*e.g.* lithological contrasts due to a change of sedimentary conditions), and not hydrocarbon induced magnetic authigenesis, could have taken place.

Hence the combined results of EPR, EOM and MS seems to support a correlation between magnetic authigenesis, MS A anomalies and hydrocarbons. These results could be regarded as a step forward in establishing a link between contrasts of magnetic properties and the presence of hydrocarbons.

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