EPR studies in soil samples from a prospective area at the Andean Range, Venezuela

M. Aldana[a], M. Díaz[b], V. Costanzo-Alvarez[a], F. González[a], and I. Romero[c]
[a]*Departamento de Ciencias de la Tierra, Universidad Simón Bolívar, Apartado 89000, Caracas 1081-A, Venezuela*
[b]*Centro de Física, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020A, Venezuela*
[c]*PDVSA-INTEVEP, Los Teques, Edo. Miranda, Venezuela*

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Analyses of electron paramagnetic resonance (EPR), in order to determine the organic matter free radical concentration (OMFRC), and magnetic susceptibility (MS) measurements were carried out in soil (surface and depth ($\approx$ 1-2 meters)) samples from a prospective area located at the southern flank of the Andean Range in Venezuela. The results indicate the presence of anomalous zones in this area. These anomalous values could be the result of the reducing environment induced by the hydrocarbon gas leakage. Results for demineralized samples allowed discussing differences between surface and depth ones in terms of weathering effects and change in organic matter type.

Keywords: Electron paramagnetic resonance; soils; free radicals.

Se realizaron análisis de resonancia paramagnética electrónica (EPR), para determinar la concentración de radicales libres en la materia orgánica (OMFRC), y medidas de susceptibilidad magnética (MS) en muestras de suelo (superficiales y en profundidad ($\approx$ 1-2 metros)) pertenecientes a un área prospectiva localizada en el Flanco Surandino en Venezuela. Los resultados indican la presencia de zonas anómalas en esta área. Estos valores anómalos podrían ser el resultado del ambiente reductor inducido por la migración vertical de hidrocarburos. Resultados obtenidos en muestras desmineralizadas permitieron discutir las diferencias observadas entre muestras de fondo y superficie en términos de efectos de meteorización y cambio en el tipo de materia orgánica.

Descriptores: Resonancia paramagnética electrónica; suelos; radicales libres.

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1. Introduction

Aeromagnetic surveys over oil fields [1] as well as magnetic susceptibility (MS) measurements in soils, sediments, and drill cuttings, have been suggested as possible means to locate anomalous magnetizations associated with hydrocarbon microseepage [1,2]. These magnetic contrasts have been hypothesized as the result of the existence, at shallow levels, of abundant diagenetic magnetite, the alteration by-product of primary Fe oxides in a reducing environment induced by the H_2S released by the underlying reservoir [3]. Surface microseeps could be the result of vertical hydrocarbon migration, due to mechanisms such as diffusion and effusion, from the reservoir to the surface [4,5]. Hence geochemical techniques, that include soil gas hydrocarbon analyses, and measurements of bulk magnetic properties in soil and shallow samples, could provide direct surface evidence for the presence of oil deposits. More recently MS and electron paramagnetic resonance (EPR) studies have been carried out in near-surface samples (100-1500 meters depth) from wells located in two Venezuela oil fields [6-8]. These studies have shown a relationship between MS contrasts and anomalies of organic matter free radical concentration (OMFRC), detected by EPR, the possible result of the presence of an underlying reservoir. In this work we report EPR and MS measurements of soil samples (0 and $\approx$ 1-2 meters) from a prospective area, trying to identify features associated with hydrocarbon microseepage. Ethane gas analysis performed in the area [9] and S-ratio measurements complement these results.

2. Experimental

The samples analyzed belong to the Rubio Valley, an oil prospective zone, of approximately 262 km^2, located in the southwestern flank of the Venezuelan Andean Range. The samples, collected by hand tools in order to avoid drilling contamination by steel particles from bit wear, were taken at surface and $\approx$1-2 meters depth. The Rubio Valley is a fairly isolated region, therefore soil contamination by anthropogenic materials could be precluded. Their areal distribution is shown in the contour map of Fig. 1. EPR has been used to precisely determine the OMFRC in these unconsolidated samples by reference to a standard [8]. The EPR spectra were recorded at room temperature using a Bruker EMX spectrometer working in the X-band ($\nu \approx$ 9.4 GHz), with a rectangular cavity and 100 kHz modulation. HF-HCl demineralization treatments [8] were applied to some selected samples. MS measurements were performed in a Bartington susceptometer at room temperature. We have also carried out S-ratio measurements [7] that give an estimate of the relative concentrations of low (*e.g.*, magnetite) and high coercivity (*e.g.*, hematite) magnetic minerals.

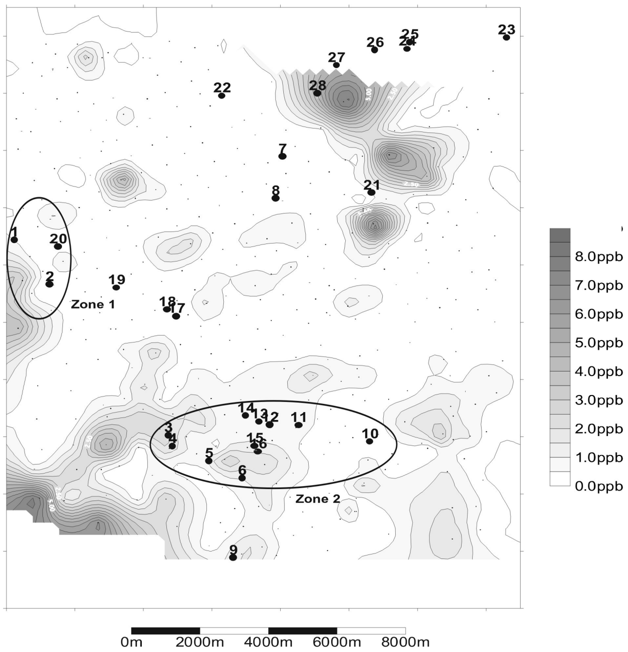

FIGURE 1. Contour map of ethane concentrations (ppb), after [9] including areal distribution of the studied samples.

3. Results and discussion

Ethane concentrations, MS and OMFRC normalized values for both depths, along with S-ratios for the depth ones, are plotted against the relative position of 22 sampling sites sequentially arranged from north to south (Fig. 2). For the depth samples these results indicate a similar behavior for MS and OMFRC (see also Fig. 3a) data. Notice the two zones where these values are significantly high compared with their background (anomalous zones). In these two zones high S-ratios are observed indicating the presence of low coercivity magnetic minerals (*e.g.*, magnetite). These two anomalies lie close to or coincide with two main regions of high ethane concentrations (Fig. 1). The southern ethane anomaly (zone 2) has been interpreted [9] as the result of the vertical seepage of hydrocarbon gases produced by a "Cretaceous kitchen" located at an underlying stratigraphic trap. This Ethane-MS-OMFRC anomalous zone also resembles the "swathe or reducing zones, identified at shallow depth levels of some producing oil wells [8], where the thermochemical conditions were the right ones for precipitation of authigenic magnetite and the presence of OMFRC anomalies. In fact, high concentrations of free radicals can be found in water-logged or poorly-drained soils, where reducing conditions prevail [10]. In this work, the EPR results, compared with the ethane measurements, suggest that the high values of OMFRC could also be associated to the degradation or alteration of the organic matter. This degradation is the possible result of hydrocarbon gas leakage. On the other hand, MS anomalies, associated to high S-ratios and mostly due to the presence of magnetite, could be linked to a reducing environment induced by the vertical migration of hydrocarbon gases. At shallow depths

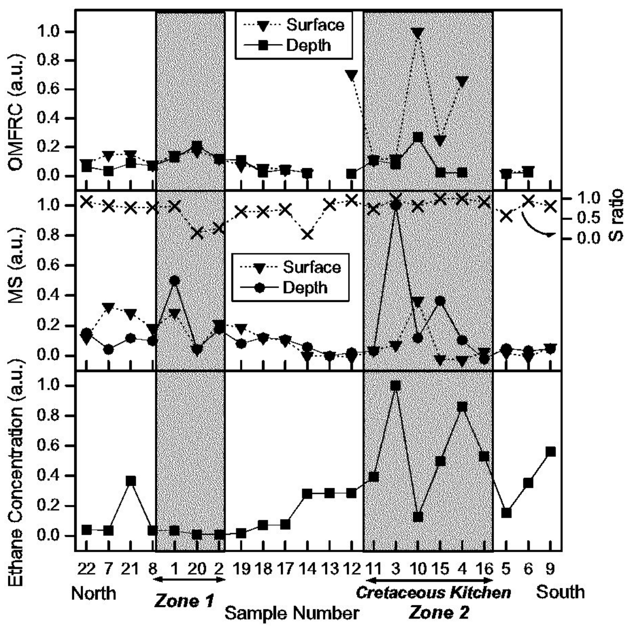

FIGURE 2. Ethane concentration, S-ratio, MS and OMFRC normalized values for the studied samples.

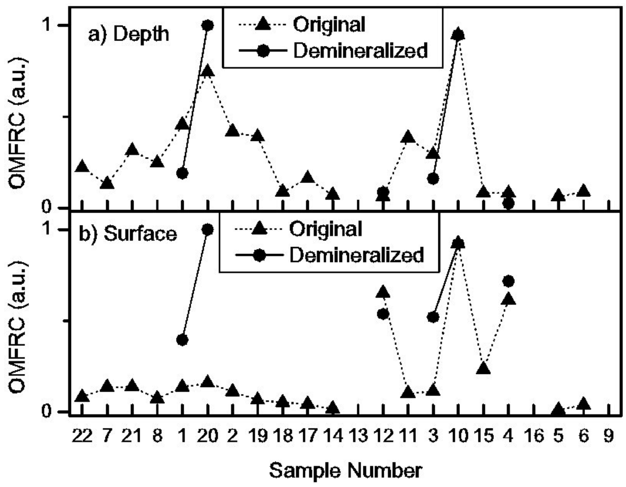

FIGURE 3. OMFRC values for original and demineralized samples.

bacterial activity is enhanced. These bacteria consume light hydrocarbons (*e.g.*, ethane) and produce carbon dioxide and hydrogen sulphides that are the responsible for the formation of secondary by-products (*e.g.*, magnetite) above hydrocarbon reservoirs [5]. Hence, this vertical migration could be responsible for the reducing environment that produces changes in the magnetic mineralogies detected as anomalies by the MS measurements and OMFRC highs detected by EPR. Differences exist between surface and depth MS values, *e.g.*, for the surface samples in zone 2 a lower MS anomaly has been detected. These differences could be attributed to weathering effects on the surface samples, that alters the magnetic mineral concentrations, and hence the MS anomalies observed. The same tendency is observed for surface and depth OMFRC values, but in the reducing zone 2 higher values are measured at surface samples. Two possible causes may be responsible for the OMFRC anomalies and the increased values at surface samples: 1) an increase in the organic matter content of the samples; or 2) an increase in the free radical concentration due to the a change in the organic matter type. In order to determine which process takes place, demineralization treatments were performed in selected samples. As expected, in all cases an increase in the OMFRC was found due to the mineral reduction and, hence, an increase in the free radical quantity per sample gram. To visualize the results, these values were normalized to the OMFRC of sample #10 (see Fig. 3). As can be observed, the relative variation of these values is the same, namely a maximum is observed in the OMFRC at the same samples with or without demineralization treatments. For the depth samples, the ratio between the two OMFRC anomalies detected (zones 1 and 2) is the same independently of the treatment. These results support that, in this case, the observed OMFRC anomalies are associated to an increase in the free radical concentration of the organic matter present in the samples, possible associated to the existence of a reducing environment. For the surface samples, this ratio is different, and the values at zone 1 increase highly after demineralization. In this case a combination of both effects could exist. On the other hand, the linewidth of the EPR signal varies from 4.7 Gauss for surface samples, to 4.9 Gauss for depth samples. As changes in EPR parameters indicate a change in the nature of the organic matter [11], this confirms the demineralization results that suggest a change in the free radical concentration due to a change in the organic matter type between surface and depth samples. Finally, it is important to notice the good correlation of independent data (*i.e.*, magnetic, EPR and geochemical) observed for the Rubio through and environs. These results illustrate the promise of this kind of integrated near surface studies as a fast and reliable means of detecting atypical diagenesis in soils, possible related to hydrocarbon seepage.

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