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Framboidal magnetic minerals and their possible association to hydrocarbons: La Victoria oil field, southwestern Venezuela

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RESUMEN

En los últimos años, las anomalías detectadas en las propiedades magnéticas totales (e.g. Susceptibilidad (MS) y Magnetismo Remanente Natural (NRM)) medidas en estudios aeromagnéticos o en muestras de superficie sobre campos petrolíferos, han sido atribuidas a la presencia, en niveles someros, de agregados esferoidales de magnetita autigénica, producto del ambiente reductor inducido por el reservorio subyacente. De verificarse la relación causal entre las anomalías medidas en las propiedades magnéticas y la presencia de hidrocarburos, este tipo de estudio podría ser utilizado como una herramienta rápida, efectiva y económica para estimar la distribución de crudos en zonas en explotación. En este trabajo se realiza una validación de la técnica, utilizando muestras en profundidad de tres pozos (dos productores, uno no productor), pertenecientes al campo La Victoria, Edo. Apure, Venezuela. Los registros de MS y NRM correspondientes a niveles someros (hasta 1500 metros de profundidad), se complementan con estudios de difracción de Rayos X, Microscopía Electrónica (Transmisión y Barrido), curvas de Termoremanencia, Remanencia Magnética Isotermal y Experimentos de Lowrie. Los resultados obtenidos confirman una concentración mayor de magnetita en los niveles anómalos, presente en forma de agregados esferoidales, respecto a otros minerales magnéticos. Se estaría confirmando así una relación causal entre anomalías en las propiedades magnéticas, medidas en niveles someros, y la presencia de hidrocarburos causantes de un ambiente reductor que favorece la nucleación y recristalización de agregados esferoidales de magnetita autigénica, planteándose la potencialidad de este tipo de estudios como una herramienta para la exploración y posible evaluación de zonas prospectivas.

PALABRAS CLAVE: Anomalías en propiedades magnéticas totales, mineralogías magnéticas secundarias, framboides de minerales magnéticos.

ABSTRACT

Magnetic contrasts observed in aeromagnetic studies and in surface samples above oil fields have been attributed to the presence of secondary magnetic minerals produced by a reducing environment that has been induced by the underlying reservoir. However, an unequivocal relationship between these anomalies and the presence of hydrocarbons has not yet been established. We report rock magnetic and magnetic mineralogy results of a preliminary study carried out in drilling fines at different depth levels from three oil wells at La Victoria oil field. Profiles of magnetic susceptibility (MS) and bulk magnetization (|M|), corresponding to the first 1500 meters are complemented by studies of X-rays diffraction, Electronic Microscopy (Scanning and Transmission), thermoremanence and Isothermal Remanent Magnetization acquisition curves, and thermal demagnetization of composite IRMs. There is a higher concentration of spherical aggregates (framboids) of submicronic magnetic minerals in levels with conspicuous peaks of MS and |M| values. If such aggregates represent the authigenic outcome of near-surface reduction caused by hydrocarbon seepage, these results could establish a link between the contrast of magnetic properties and the presence of hydrocarbons.

KEY WORDS: Bulk magnetic susceptibility, magnitude of the natural remanent magnetization, framboids of magnetic minerals.

INTRODUCTION

In 1979 Donovan identified pronounced aeromagnetic anomalies in the Cement oil field (Oklahoma). He suggested that these anomalies were due to near-surface authigenic magnetite produced by the chemical alteration of Fe-oxides in a reducing environment induced by the reservoir. Donovan *et al*. (1984), Saunders and Terry (1985), Saunders *et al*. (1991), Foote (1984 and 1992) and others argued that aeromagnetic anomalies over oil fields, and bulk magnetic properties (e.g. magnetic susceptibility) in surface samples, could be used for exploration, exploitation and even assessment of hydrocarbon reservoirs. However, these anomalies could also be due to other factors related to natural or anthropogenic processes (e.g. Reynolds, 1982; Machel and Burton, 1991; Gay, 1992; Liu *et al*., 1994).

Benthiem and Elmore (1987), McCabe *et al*. (1987) and Elmore *et al*. (1987 and 1993) have identified, by scanning electronic microscopy (SEM), spherical aggregates of submicron crystals of authigenic magnetite in samples of solid bitumen and speleothems with hydrocarbon inclusions. These characteristic framboidal structures seem to be directly associated to biodegradation of the oil. At present, the appearance, origin and importance of magnetic mineralizations associated to oil accumulations is still debated (e.g. Gay, 1992; Schumacher, 1996).

We report results from a preliminary rock-magnetic and magnetic mineralogy study of three oil wells (two producers: LVT-1X and 4X and one non producer: LVT-2X) at La Victoria oil field, in southwestern Venezuela.

Our primary objective was to identify characteristic authigenic magnetic mineralogies that could account for the conspicuous peaks observed in profiles of magnetic susceptibility (MS) and magnitude of the bulk magnetization (|M|). All measurements were carried out in drilling fines taken at different shallow depth levels within the first 1500 meters. The study includes Electronic Microscopy (Scanning SEM and Transmission TEM), strong field thermomagnetic curves, Isothermal Remanent Magnetization (IRM) acquisition curves, thermal demagnetization of composite IRMs (Lowrie, 1990) and X-rays diffraction and fluorescence analyses.

LOCATION AND GEOLOGICAL BACKGROUND

La Victoria oil field, in the Apure-Barinas sedimentary basin (Figure 1), is an anticline with a NE-SW regional strike. This oil field is edged, at its easternmost end, by an inverse fault with more than 120 meters of displacement (Figure 2).

The producer wells LVT-1X and 4X, drilled at the summit of the anticline, proved more than 3000 PBBD of 36° API in the Upper Cretaceous levels (Escandalosa formation), whereas the non-producer LVT-2X was drilled in order to study the stratigraphic folds at the flank of the structure (Figure 2). Production tests show average rates of 470 to 800 m^3/d (2952 to 5024 b/d).

The hydrocarbons of La Victoria have gravity values ranging from 30° to 36° API. They also have kerogen type III according to the hydrogen index (mg Hc/gr C org) and to the content of organic carbon (medium to medium-good) with respect to the weight percentage of the whole rock (La Morita-Quevedo formations).

The geothermal gradient in the Barinas Basin, extrapolating towards Los Llanos Basin, indicates a decrease from El Baúl arch area (ca. 4°F/30 m) to the southwest (sub-Andean trench). This trend is not gradual; in fact, some anomalies coincide with the Mérida and Arauca arches, where thermal gradients are higher. At La Victoria oil field the thermal gradient ranges between 1.5 and 2.0 °F / 30 m.

Source rocks are rather immature; the maturation of hydrocarbons seems to diminish progressively eastwards. By projections of the maturation gradients, obtained by vitrinite reflectance analyses, it can be inferred that the oil window is located southwest of this field at approximately 4800 m depth. Mathematical simulations for the origin of hydrocarbons at La Victoria, calibrated with log information from oil wells (Chigné,1985), suggest that they were produced at the deepest southwesternmost part of the Basin ca. 12 Ma ago (mid-Miocene, Ro = 0.62). It has been inferred that the peak of oil generation was reached at this same area ca. 3.8 Ma ago (Pliocene, Ro = 1) when the sedimentary section was approximately 6600 m thick. The oil probably migrated about 70 km northeast up to the Arauca arch through the porous media of the recipient rocks at the deepest formations (mostly Tertiary) and along unconformities keeping most of its original volatile components (Kiser, 1989).

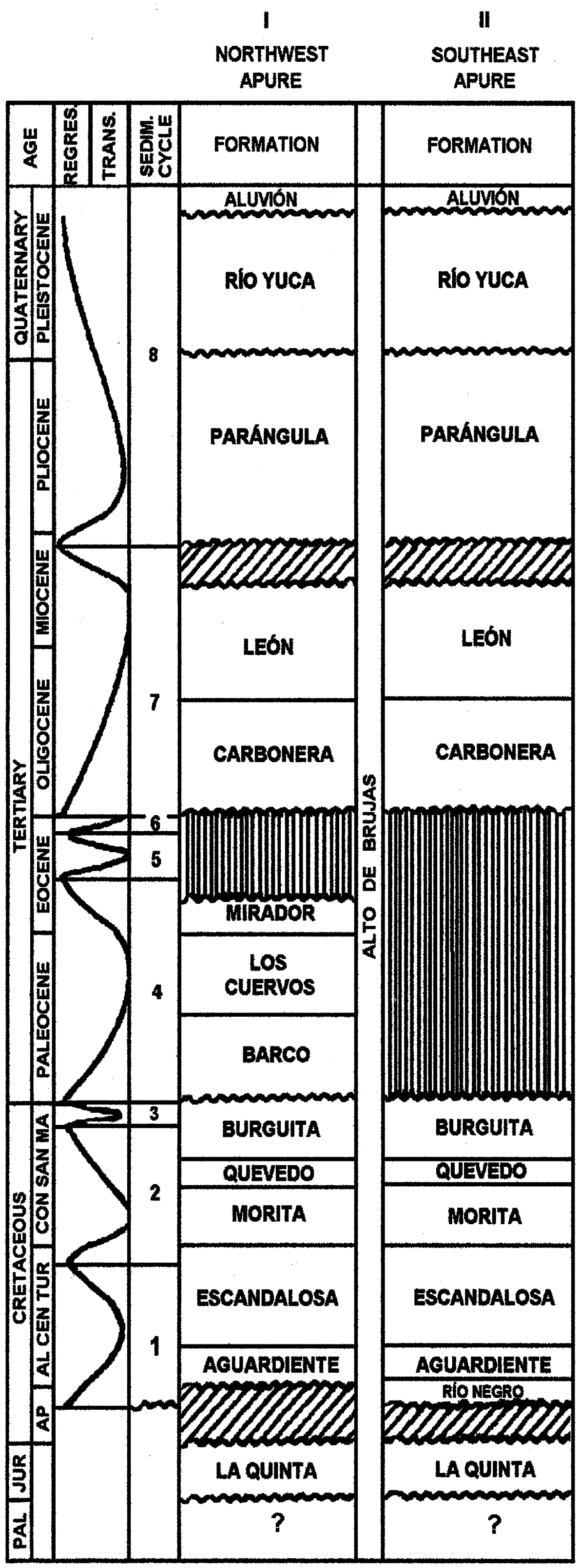
The drilling fines were taken at intervals of about 15 meters from the first 1500 meters of oil wells LVT-1X, LVT-2X and LVT-4X (Figure 2). These fines are unconsolidated rock samples belonging to a single group of molasses of fluvial-deltaic provenance, which comprises the filling of the Apure-Barinas Basin and had their origin during the uplift of the Andean Range during Miocene to Mid-Pliocene times (Guayabo group, Río Yuca/Parangula formation). The sediments of the Guayabo group contain two major sequences (González de Juana *et al*., 1980): a basal layer of conglomerates with needle-shaped grains of quartz, cherts and poorly sorted coarse-grained sandstones, capped with a top layer of fine-grained bleached sandstones and gray and mottled clays. The lithologies for the near-surface strata of LVT-1X, 2X and 4X correspond solely to the upper section of the Guayabo group. They are homogeneous yellow to brownish typical sandstones without visible compositional differences between the various samples analyzed. Textual analyses rendered impossible since we were studying unconsolidated samples.

MS AND |M| PROFILES

The MS measurements were performed in a Sapphire SI-2 susceptometer, which determines the magnetic susceptibility of a rock by the contrast of inductance in a coil with and without the sample in. Each coil inductance is measured to better than 7 significant figures. The dynamic range is from 10^{-6} to > 1 cgs units. MS readings for every single sample were repeated 5 times and a standard deviation of less than 10% was found for each MS sample-average.

The |M| measurements were obtained with a Schonstedt SSN-1A spinning magnetometer. Eleven grams of unconsolidated drilling fines for each level analyzed were placed in cubic plastic containers of 8 cc and amalgamated in a magnetically innocuous polymer matrix made by a controlled reaction of aldehyde, amine and urea hardened at room temperature. Profiles of MS and |M| versus depth are shown in Figure 3.

LVT-4X shows two peaks of bulk magnetic properties (MS and |M|) at depth level intervals of 534-564 and 625-655 meters (Figure 3a). LVT-1X has also a pronounced MS



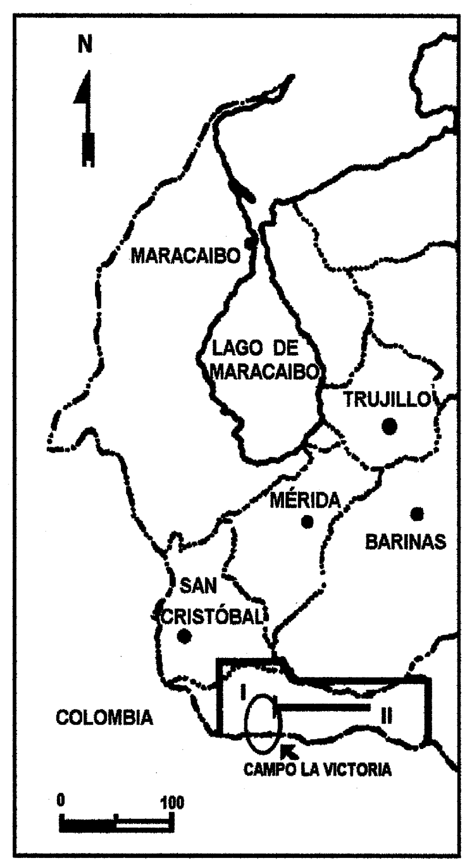


Fig. 1. Regional map of southwestern Venezuela showing the location of La Victoria oil field and a stratigraphic column (after González de Juana *et al*,, 1980) with the main sedimentary formations in the Barinas-Apure sedimentary Basin. The first 1500 meters of drilling fines analyzed in this study belong to a single sedimentary sequence within the Pleistocene Río Yuca formation (top of the stratigraphic column).

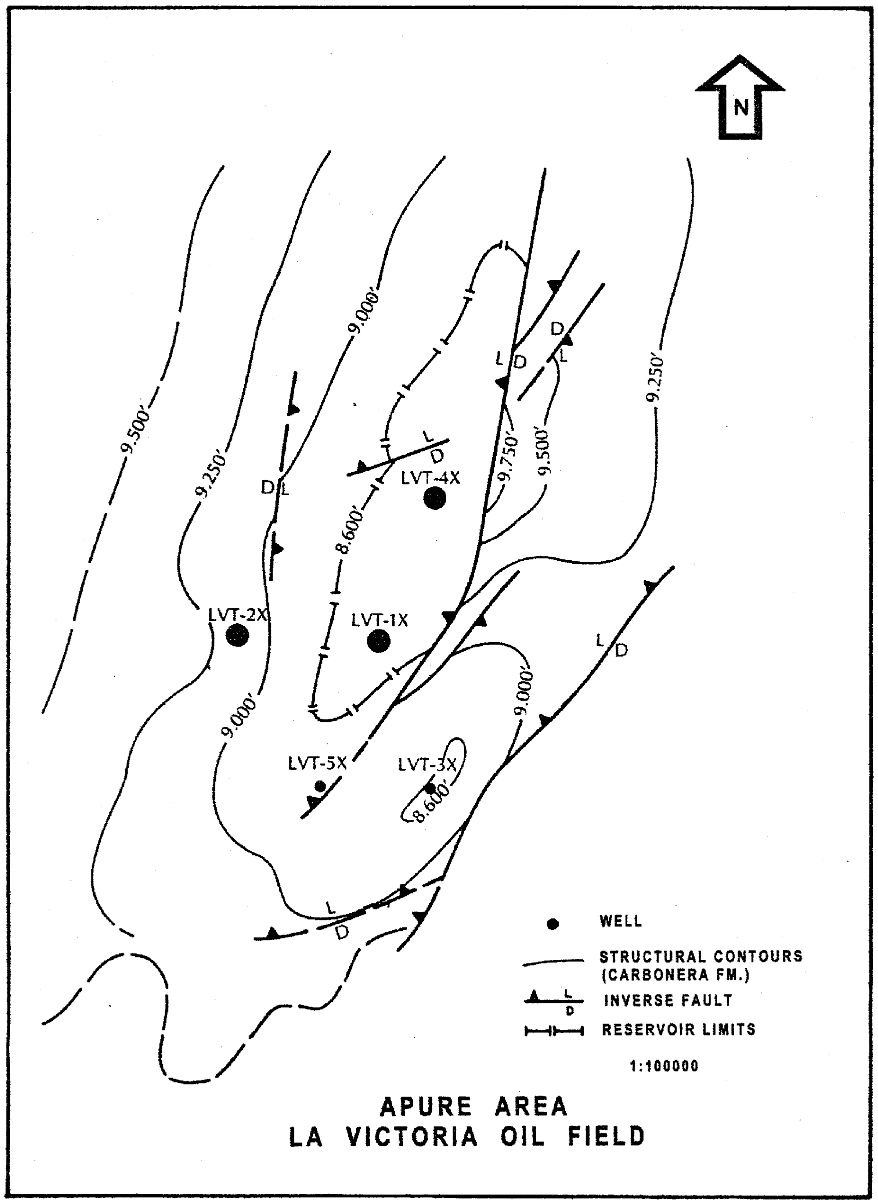


Fig. 2. Structural map of La Victoria oil field (after Chigné, 1985), showing the location of the three oil wells in this study (LVT-1X, 2X and 4X).

peak at 750-810 meters (Figure 3b) whereas in well LVT-2X the MS and |M| peaks appear at 610-655 meters (Figure 3c).

SCANNING AND TRANSMISSION ELECTRONIC MICROSCOPY

Magnetic separates obtained by applying a hand magnet to a suspension of finely-ground drilling cuts in acetone were used for SEM and TEM analyses. In order to disperse these small amounts of sample they were mixed with ethanol and exposed to an ultrasonic bath for approximately 5 minutes. For SEM analyses a drop of this preparation was placed on a thin layer of polyethylene set on a carbon holder, and covered by a carbon film (~ 10 nm). In the TEM analyses a drop of the dispersed separates was placed on a copper grid covered by a carbon film. The samples come from some of the depth levels of LVT-1X, 2X and 4X that showed either peak or low profile (average) MS and |M| values.

For SEM analyses we used a Phillips SEM 505 scanner with an EDAX PV 9100/60 X-ray dispersion analyzer. The SEM photomicrographs are topographic images of sec-

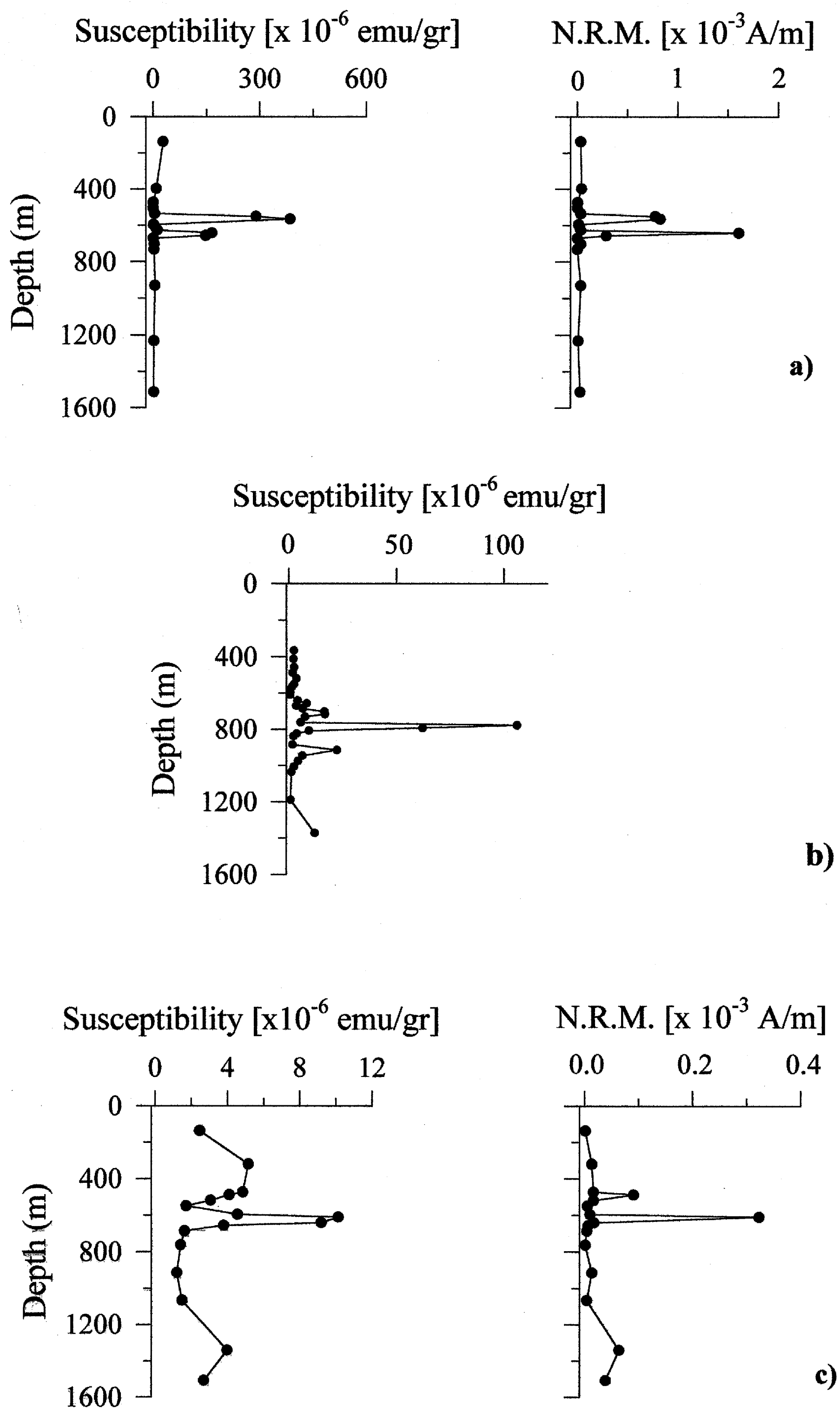


Fig. 3. Magnetic susceptibility (MS) and magnitude of bulk magnetization (|M|) plotted versus depth levels for oil wells (a) LVT-4X (MS and |M|), (b) LVT-1X (MS) and (c) LVT-2X (MS and |M|). LVT-4X (producer well) shows two peaks of the bulk magnetic properties (MS and |M|) at depth levels of 534-564 and 625-655 meters. LVT-1X (producer well) also has a pronounced MS peak at 750-810 meters. In LVT-2X (non producer well), MS and |M| peaks appear to be located at 610-655 meters.

ondary electrons. For the TEM we used a Phillips EM 420 with an EDAX PV9900 X-ray analyzer by energy dispersion.

SEM analyses show spherical aggregates of submicronic crystals (diameters ranging between 5 and 30 μm) only at levels with high values of bulk magnetic properties. Figures 4 (a, b and c) and 5 (a and b) are photomicrographs of some of these framboidal mineral structures for levels of peak MS and |M| values at LVT-4X, LVT-1X and LVT-2X. X-ray energy dispersion spectra for the spherical aggregates indicate a mostly Fe composition and absence of S and Ti.

In levels of low-profile MS and |M| values, spherical aggregates were not observed. In fact, Fe-rich minerals do not have a characteristic shape as shown in Figure 6 for well LVT-4X.

Some representative diffraction patterns (TEM analyses), obtained for the same magnetic separates used for SEM purposes, and corresponding to levels of conspicuous MS and |M| values, are shown in Figure 7. These patterns reveal the presence of magnetite (face centered cubic crystal) with d_o = 8.32Å for LVT-4X (Figure 7a), d_o = 8.37Å for LVT-1X (Figure 7b) and d_o = 8.25Å for LVT-2X (Figure 7c).

ROCK MAGNETIC EXPERIMENTS

We have also performed rock magnetic experiments for wells LVT-1X, 2X and 4X in some of the levels with high and average MS and |M| values. Some results of thermoremanence (magnetic separates), isothermal remanent magnetization (IRM) curves (whole sample) and thermal demagnetization of composite IRMs (whole sample) are shown in Figures 8, 9 and 10.

None of the representative normalized IRM acquisition curves shown in Figures 8a, 9a, 9b and 9c reach complete saturation due perhaps to the presence of minute amounts of high coercivity magnetic minerals such as hematite and/or Fe-sulfides. However, the rapid initial increase (between 0 and ~100 mT) of the IRM in most of these samples (e.g. levels of conspicuous MS and |M| values for LVT-4X (Figure 8a), LVT-1X (Figure 9a) and LVT-2X (Figure 9b)) indicates that it is dominated by the presence of a low coercivity cubic magnetic phase (e.g. magnetite).

Figure 9c illustrates the normalized IRM acquisition curve for a level of average MS and |M| values at LVT-4X (i.e. 915-930 meters) that contrasts with the examples shown in Figures 8a, 9a and 9b. This IRM does not saturate even at fields as high as 600 mT, which seems to indicate a significant content of high coercivity magnetic phases (hematite or Fe-sulfides). The same behavior was observed for other levels of low-profile MS and |M| values in all wells.

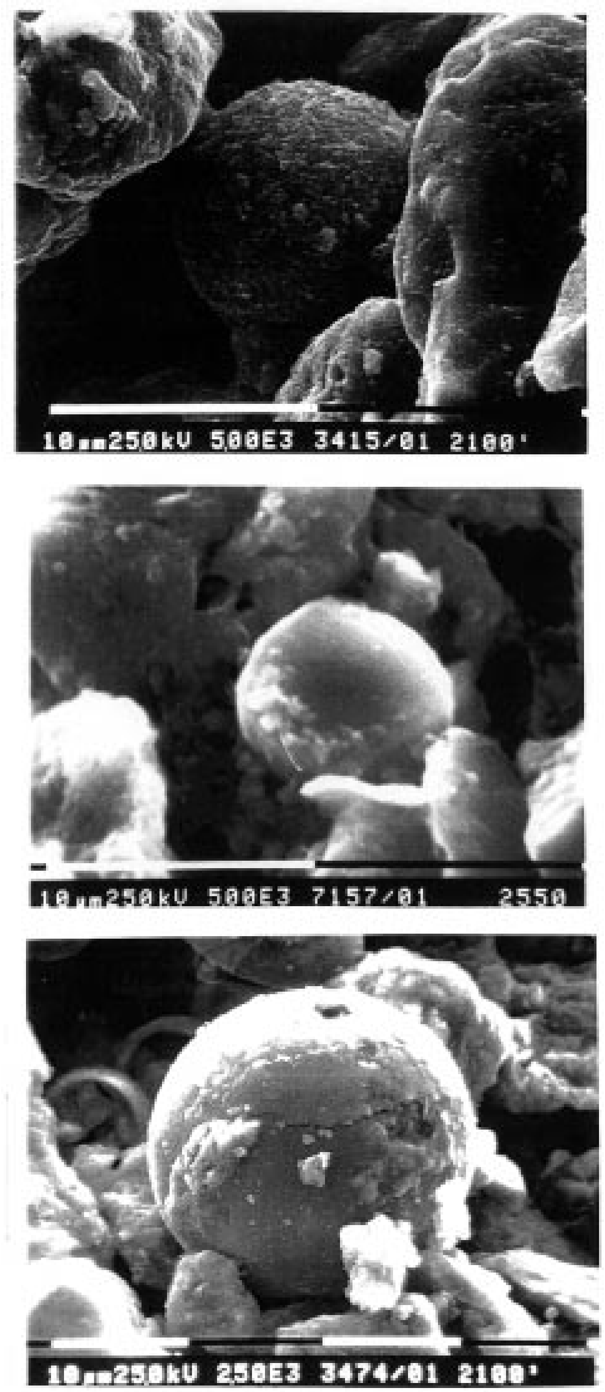
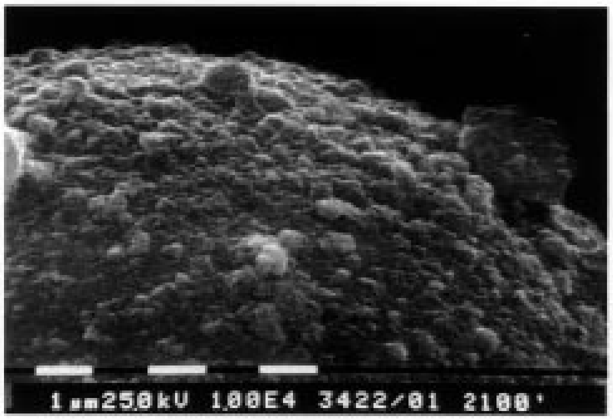
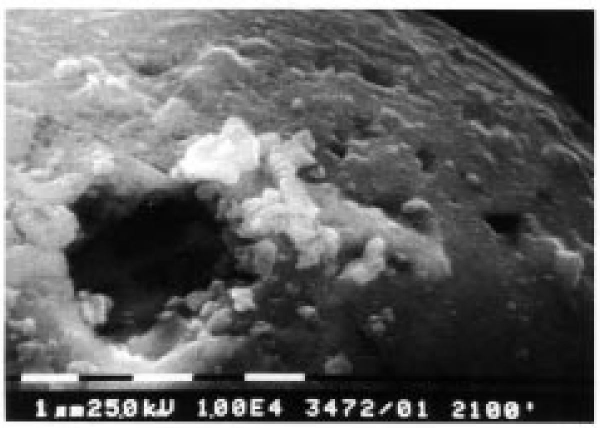


Fig. 4. Scanning electron photomicrographs (topographic images of secondary electrons) showing spherical aggregates of submicronic crystals of authigenic magnetic minerals (diameters between 5 and 30 μm). The samples are magnetic separates for levels with anomalous MS and |M| values from (a) LVT-4X (625-640 meters depth interval), (b) LVT-1X (775-790 meters depth interval) and (c) LVT-2X (640-655 meters depth interval). X-ray energy dispersion spectra for the framboidal structures reveal a Fe composition with total absence of S and Ti.



(a)



(b)

Fig. 5. Scanning electron photomicrographs (topographic images of secondary electrons) showing magnification of framboids of authigenic magnetic minerals for (a) LVT-4X (625-640 meters depth interval) and (b) LVT-2X (640-655 meters depth interval). Spherical aggregates observed in producer wells such as LVT-4X have a characteristic granular texture (a) that contrasts with non-producer well LVT-2X (b).

The thermoremanence curve of Figure 8b is typical of those obtained for levels of high MS and |M| values (e.g. 625-640 m in LVT-4X). Thermoremanence analyses were performed in air using a saturating field of 200 mT. In Figure 8b this curve shows the characteristic shape obtained for a mixture of magnetite and hematite (Piper, 1987). Although magnetite content in this sample could be concealed by the high Curie point (over 650°C) distinctive of hematite, its presence seems to be indicated by the considerable drop of the initial magnetization, observed in the cooling curve, and most likely resulting from magnetite oxidation during heating.

We also conducted stepwise thermal demagnetizations of composite IRMs induced along the X (0.12 T), Y (0.4T)

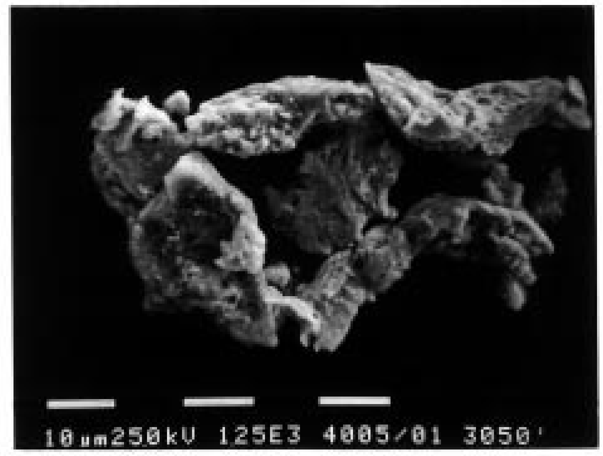


Fig. 6. Scanning electron photomicrograph (topographic image of secondary electrons) of a non-spherical aggregate of Fe-rich submicronic magnetic minerals (as found from X-ray energy dispersion spectra). This sample comes from a magnetic separate of a level with low MS and |M| values (LVT-4X; 915-930 depth interval).

and Z axis (3T) (Lowrie, 1990). These experiments were performed in cylindrical samples (1.5 x 1.5 cm) of whole rock drilling fines selected from representative depth levels of well LVT-4X. The unconsolidated samples were set together in a magnetically innocuous matrix made of Rescor 750 (Cotronics), a porcelain-like material that solidifies at 20°C and stands temperatures as high as 1200°C.

In order to compare results between different depth levels, IRMs were normalized to their highest initial value. Absolute values for higher coercivity IRMs, induced along Y (0.4T) and Z axis (3T), fell below the sensitivity of the magnetometer and such results were discarded.

Thermal demagnetization of IRMs, induced by a magnetic field of 0.12T along the X-axis, is shown in Figure 10 for different depth intervals of well LVT-4X. Each curve represents a specific depth interval. The levels of higher MS and |M| values (Figure 3) are the same that show the more discernible IRMs (i.e. depth levels 549-564 m and 640-655 meters). Because of the maximum blocking temperatures, observed in the thermal demagnetization curves of Figure 10, the main magnetic phases, at levels of conspicuous MS and |M| values, seem to be either multidomain magnetite or titanomagnetite ($T_B \approx 250°C$) and fine-grained magnetite ($T_B \approx 580°C$).

X-RAY FLUORESCENCE

We carried out some X-ray fluorescence experiments (LVT-4X) in order to determine relative concentrations of

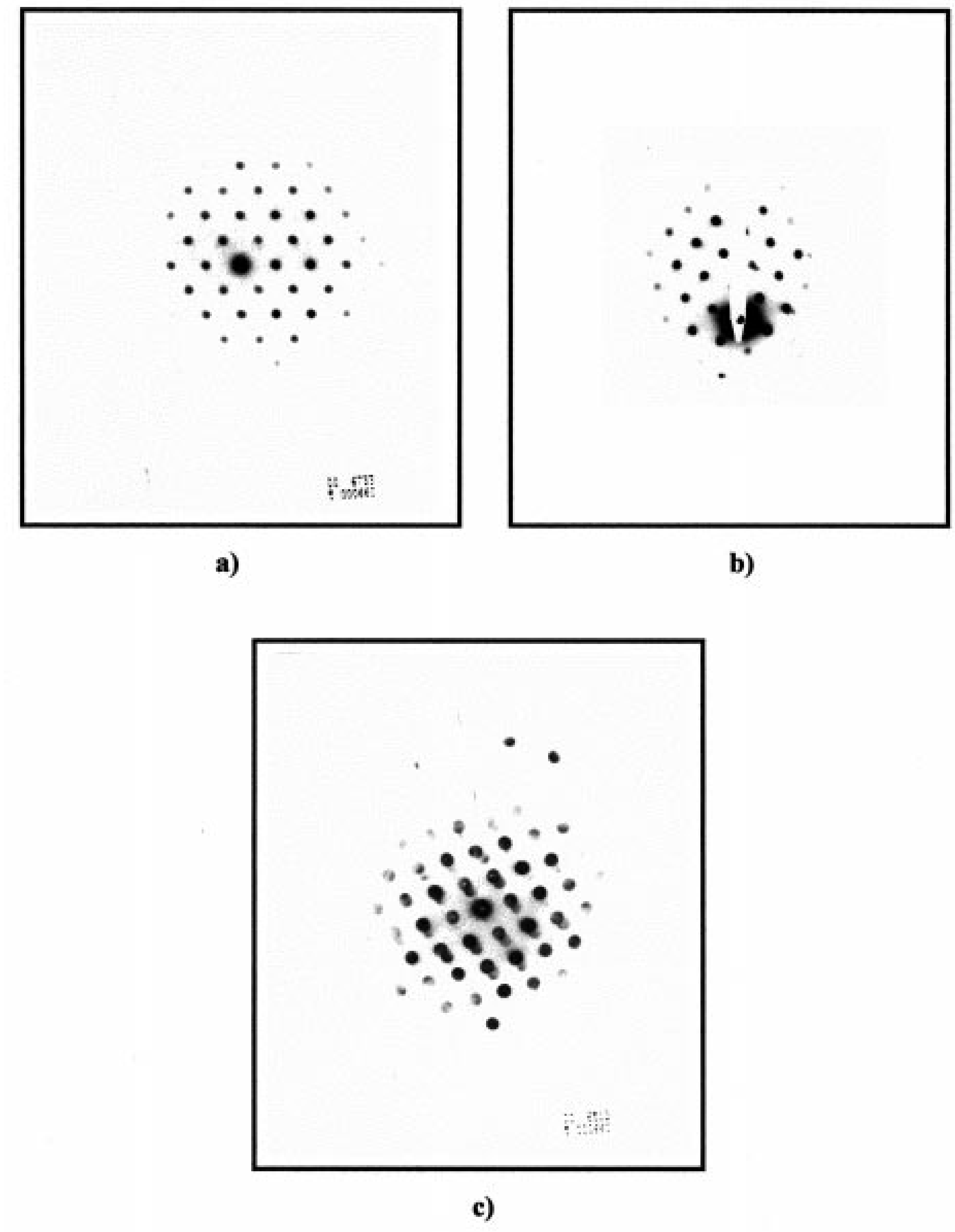


Fig. 7. Characteristic diffraction patterns (Transmission Electronic Microscopy by X-ray energy dispersion) obtained for magnetic separates corresponding to levels of high MS/|M| values. These patterns reveal the presence of magnetite (face centered cubic crystal) with d_O = 8.32Å for LVT-4X (a), d_O = 8.37Å for LVT-1X (b), and d_O = 8.25Å for LVT-2X (c).

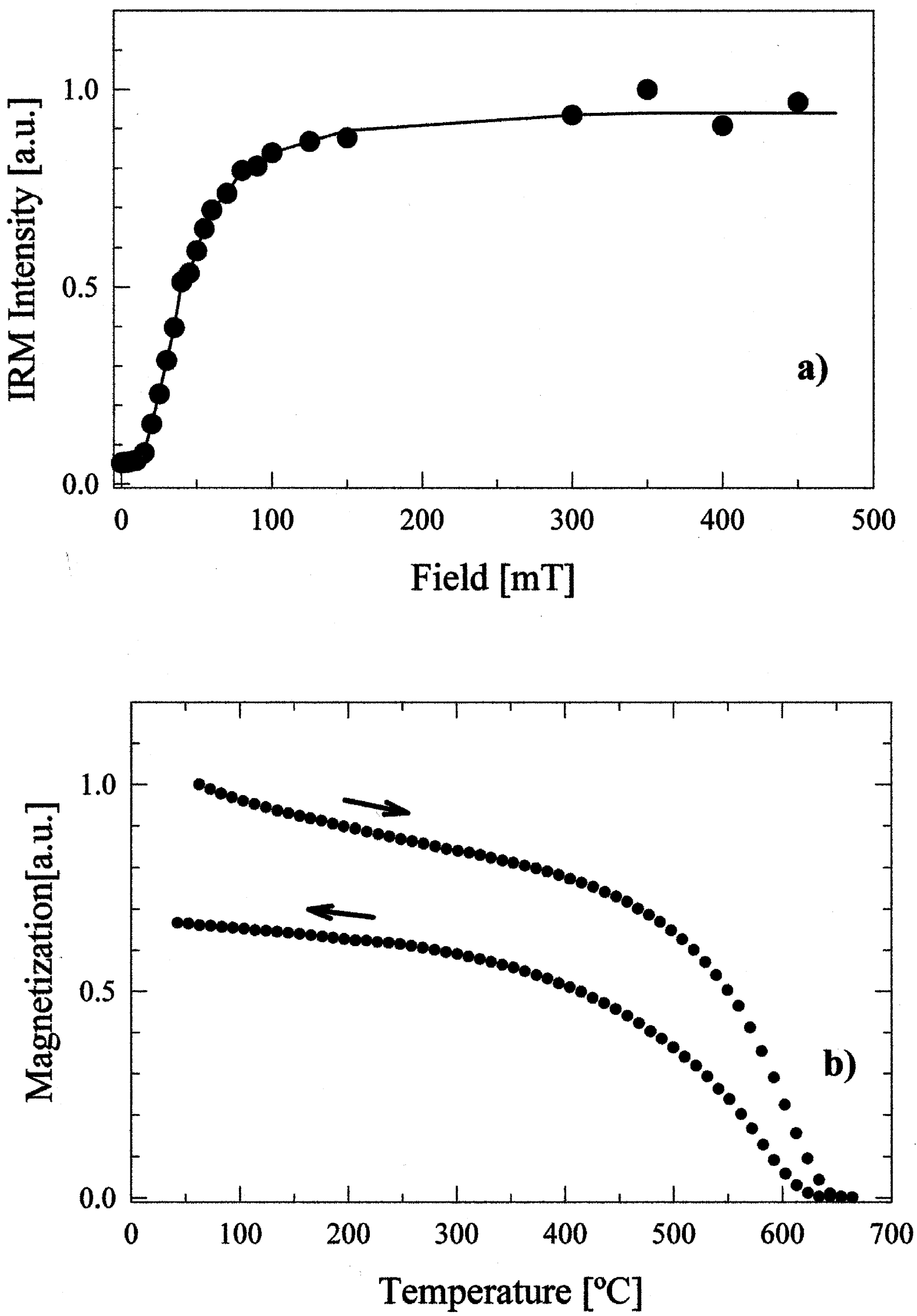


Fig. 8. (a) Isothermal Remanent Magnetization (IRM) acquisition curve (whole rock) and (b) strong field thermomagnetic curve (magnetic separates) for a representative sample of a level with high MS and |M| values in well LVT-4X (depth interval 625-640m). The IRM acquisition curve does not reach complete saturation due perhaps to the presence of minute amounts of high-coercivity magnetic minerals. Both curves show the characteristic shape obtained from a mixture of magnetite and hematite (Piper, 1987). Although the high Curie point (over 650°C) of hematite could mask magnetite content in this sample, its presence is suggested by the drop of the initial magnetization, observed in the cooling curve resulting from oxidation of original magnetite during heating.

Fe, Sr, Pb, Zn, Zr and Ca. We used a Phillips Noreilco diffractometer with X-ray source made of copper (λ=1.5405 nm) and a radioisotope source of cadmium 109 for identification of elements with Z > 20. Concentrations of O, Si, Na

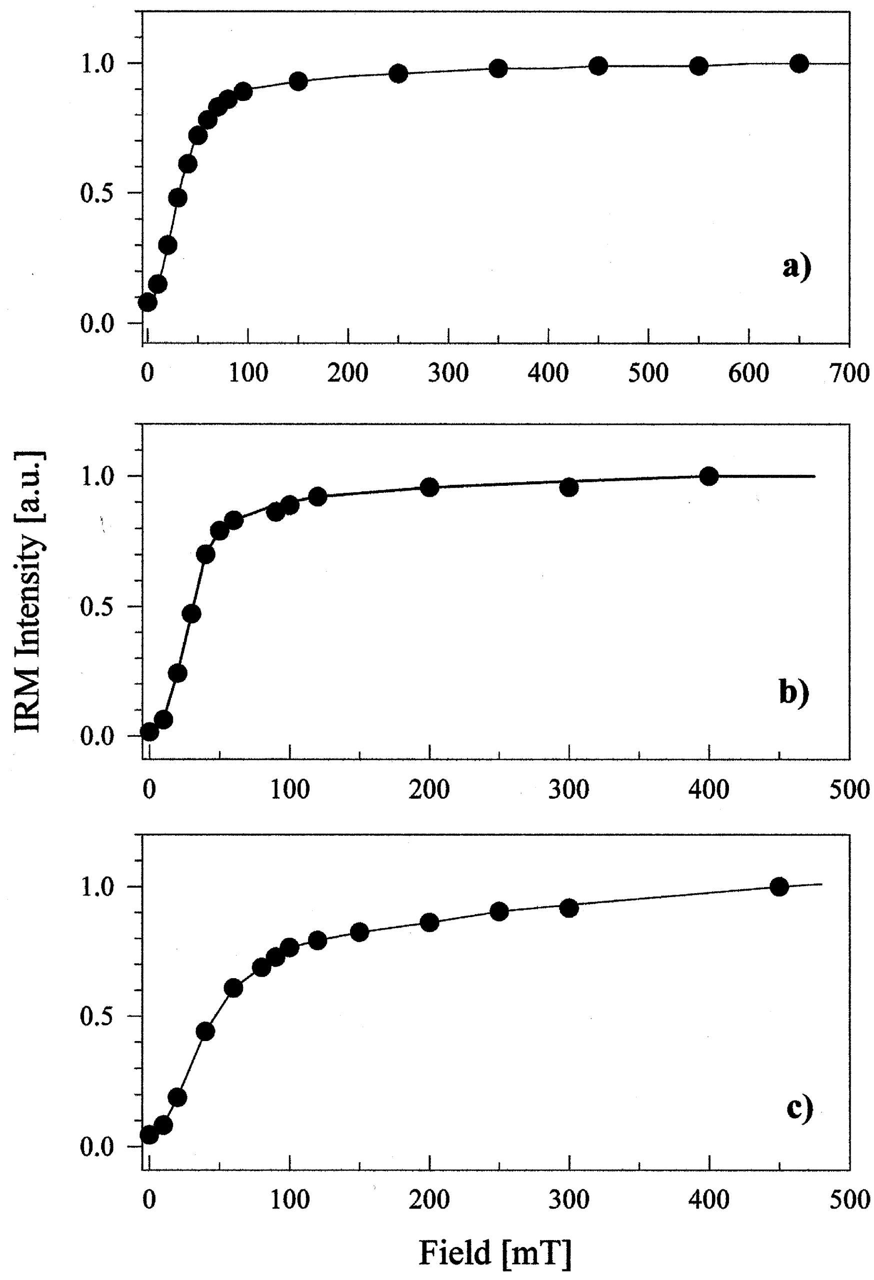


Fig. 9. Typical normalized IRM acquisition curves (whole rock) for representative samples of (a) depth interval 775-790 meters of high MS and |M| values in LVT-1X, (b) depth interval 610-625 meters of high MS and |M| values for LVT-2X, and (c) depth interval 915-930 meters of low MS and |M| values at LVT-4X. The rapid initial increase between 0 and ~100 mT of the IRM in samples from levels of high MS and |M| values (a and b) seem, to be dominated by the presence of a low coercivity magnetic phase. The IRM from a level of low MS and |M| values (c) does not saturate even at 600 mT which seems to indicate a dominant concentration of high coercivity magnetic phases.

and Al could not be determined.

The results are far from being conclusive, but it is interesting that atypical values of relative concentrations of Fe, Sr, Pb, Zn, Zr and Ca (Figure 11) appear at the same levels of the high MS and |M| values (Figure 3).

DISCUSSION

For magnetite-bearing sediments, MS is a reasonable measure of the concentration of magnetite. Conversely |M| is a less sensitive parameter because of its strong magnetite grain-size dependence. However, the |M| profiles of wells

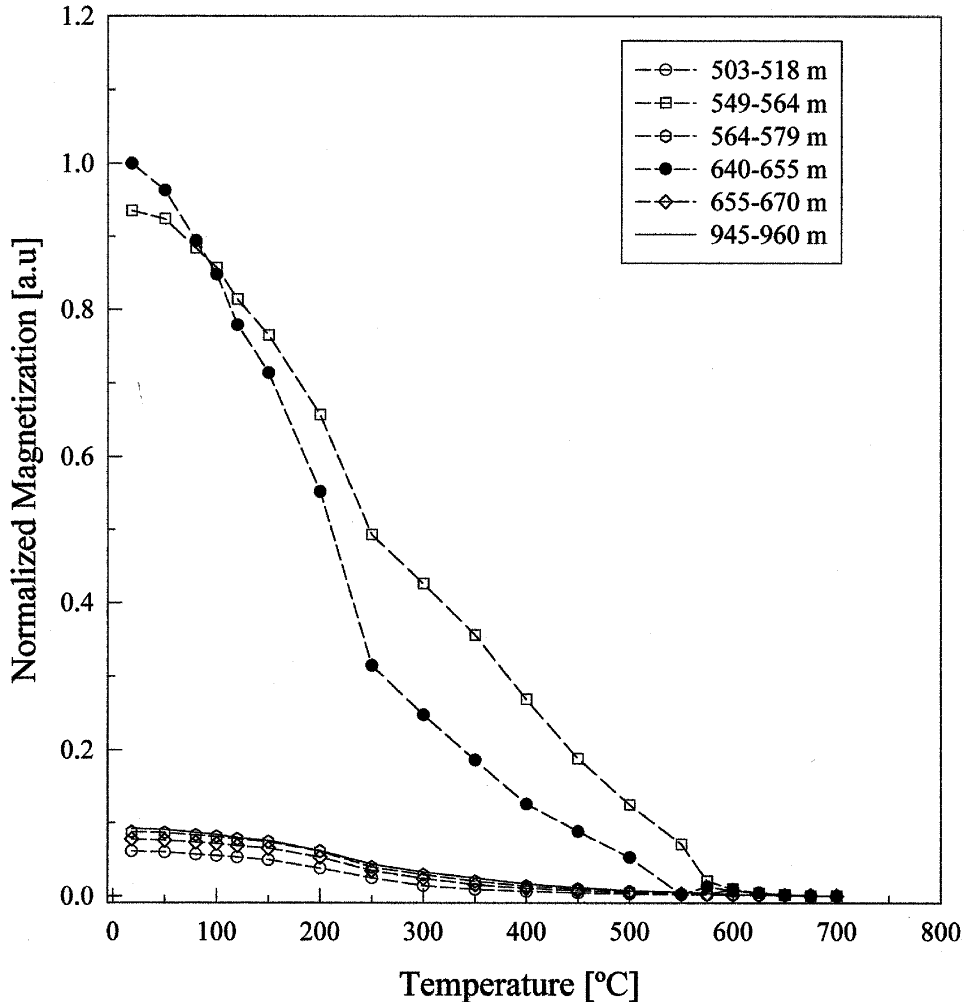


Fig. 10. Stepwise thermal demagnetizations of 0.12T IRMs induced along the X axes of cylindrical samples (Lowrie, 1990). These experiments were performed in whole-rock drilling fines selected from representative levels of well LVT-4X. Each curve corresponds to a different depth level. IRM values were normalized to the highest initial magnetization. Levels of higher MS and |M| values are the same with the more discernible IRMs (depth intervals 549-564 and 640-655 meters). Absolute values for higher coercivity IRMs, induced along Y (0.4T) and Z axis (3T) fell below the sensitivity of the magnetometer and were discarded. According to the maximum blocking temperatures the magnetic phases could be multidomain magnetite or titanomagnetite ($T_B \approx 250°C$) or fine-grained magnetite ($T_B \approx 580°C$).

LVT-4X and 2X show a good correspondence with the MS profiles.

The peaks in the profiles of Figure 3 may reflect the presence of localized and atypical concentrations of high susceptibility magnetic minerals such as magnetite and/or Fe-sulfides. Although not entirely conclusive, rock magnetic analyses (IRM acquisition curves and thermal demagnetization of IRMs) suggest that magnetite is the main magnetic phase in levels of high MS and |M| values. No traces of Fe-sulfides were found.

Peaks of MS and |M| appear at discrete depth levels, which excludes the possibility that they are caused by drilling contamination. Small remnants of the drilling barrel were identified by SEM analyses as fine metallic shavings, but they represent a small fraction of the sample and are not restricted to levels with large MS and |M| values. The mud employed in the drilling was a mixture of bentonite and water without magnetic contaminants.

Yet MS and |M| peaks can not been unambiguously associated to the underlying reservoir. Hydrocarbon microseepage may generate magnetic anomalies in near-surface soils and sediments (Henry, 1988; Saunders *et al.*, 1991; Ellwood and Burkart, 1996). However, shallow magnetic anomalies can be also related to syngenetic magnetic sources such as detrital magnetite and magnetic sedimentary forma-

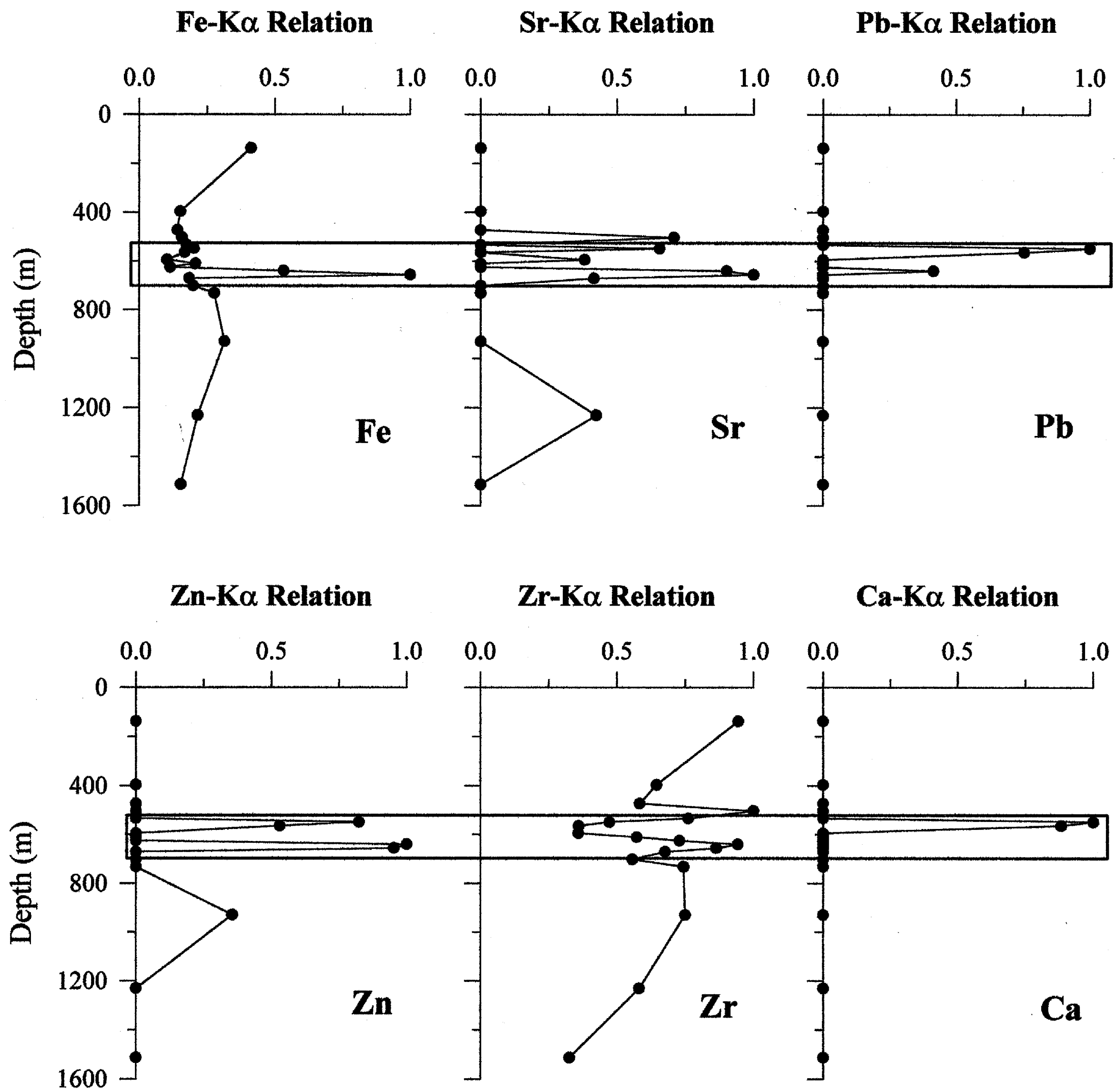


Fig. 11. Profiles of relative Fe, Sr, Pb, Zn, Zr and Ca concentrations determined by X-ray fluorescence in LVT-4X whole rock samples. Atypical values of these elements appear at the same levels of high MS and |M| values. The lithological uniformity observed across the upper 1500 meters of these wells seems to suggest that anomalies of Fe, Sr, Pb, Zn, Zr and Ca in reflect local postdepositional chemical changes rather than a major shift in sedimentary conditions.

tions (Gay, 1992). Moreover, increases in soil magnetic susceptibility can be the result of pedogenic formation of magnetite and maghemite associated to rainfall and climate (e.g. Liu *et al.*, 1994).

The La Victoria MS and |M| peaks could reflect lithological contrasts, but all the samples are typical sandstones from a single geological group. Although there are not visible differences of rock types between the various depth levels, textural differences among these lithologies cannot be reliably determined from unconsolidated drilling fines.

SEM and TEM studies were performed to identify, in those levels of MS and |M| peak values characteristic magnetic mineralogies that could be related to the presence of hydrocarbons. The framboids or spherical aggregates of Fe-rich submicronic magnetic crystals, found only at high levels may be the cause of observed contrasts in bulk magnetic properties. However, the genetic relationship to hydrocarbons in the underlying reservoir is not entirely clear-cut.

Framboidal textures are usually associated with pyrite of either organic or inorganic origin. According to Sawlowicz

(1992) the main condition required for the formation of framboids is the availability of iron and sulfur. This condition can be achieved in the geochemical chimney at petroleum traps (Davidson, 1982). However, rock magnetic and magnetic mineralogy analyses in wells LVT-1X, 2X and 4X do not indicate the presence of Fe-sulfides. SEM observations were made exclusively on magnetic separates; and the sole presence of magnetite crystals revealed by TEM analyses suggests that the spherical aggregates are not pyrite framboids. Other minerals, such as magnetite, can occur in the same shape as the result of replacement (oxidation) of pyrite framboids (Suk *et al*., 1990), or by direct reduction of precursor oxides such as hematite (e.g. Elmore *et al*., 1987; McCabe *et al*., 1987; Machel, 1995).

Framboidal magnetite may form in rocks in the absence of hydrocarbons (Suk *et al*., 1990), but studies of solid bitumen and speleothems with hydrocarbon inclusions have also detected spherical aggregates of submicronic magnetite (e.g. Benthien and Elmore, 1987, McCabe *et al*., 1987, Elmore *et al*., 1987 and 1993).

We cannot exclude a hydrocarbon-independent process for the formation of spherical aggregates. However, this possibility seems remote in the geological setting of La Victoria field, dominated by an underlying oil reservoir and cut by a network of major faults which might have served as natural conduits for fluid circulation (e.g. Oliver, 1986; Peirce *et al*., 1998). Although textural analyses render impossible in drilling fines there are no visible compositional differences between framboid-rich and framboid-depleted samples. This compositional uniformity suggests that anomalies of Fe, Sr, Pb, Zn, Zr and Ca determined by X-ray fluorescence analyses, reflect local postdepositional chemical changes rather than sedimentary changes.

Preliminary studies of electron Paramagnetic Resonance (EPR) in samples from wells LVT-2X and 4X (Aldana *et al*, 1996) indicate a positive correlation between concentration of free radical spins, probably associated with the presence of asphaltenes, (a major component in highly biodegraded hydrocarbons) and high MS and |M| values. McCabe *et al*. (1987) and Elmore *et al*. (1987) have reported magnetic contrasts due to the inorganic/chemical formation of magnetite framboids. Spherical aggregates of magnetite (diameters ranging between < 20 and 40µm) formed as the likely result of the biodegradation of hydrocarbons of crude oil in carbonate rocks. Elmore *et al*. (1993) reported spherical aggregates of authigenic magnetite in hydrocarbon-impregnated speleothems. They found a positive correlation between the percentage of extractable organic matter and the intensity of chemical remanent magnetization (ChRM). Such a correlation suggests that the chemical conditions created by the hydrocarbons may have caused the precipitation of magnetite and the acquisition of ChRM.

According to Machel (1995), the thermodynamic conditions leading to the formation of magnetites, for a complete range of pH and Eh, include near-surface depths (within the upper 1500 meters), 25°C, 1 bar total pressure and an aqueous environment with $a_{HCO3-}=10^{-2}$, $a_{Fe2+}=10^{-2}$ and $a_{HS-}=10^{-12}$. Such a setting involves shallow depths, similar to those in which La Victoria framboids have been detected, and extremely low total dissolved sulfur contents to prevent the precipitation of Fe-sulfides. Carbonate rocks may have a different diagenetic behavior than their clastic counterparts, but authigenic magnetite, without Fe-sulfide precursors, was recognized in red sandstones by Perroud *et al*. (1995). These workers argue that migration of hydrocarbons in porous sandstones with a high hematite content may lead to hematite dissolution by geochemical or microbial processes. The primary magnetization disappears and the iron can re-precipitate as magnetite.

The average diameter of the spherical aggregates recognized in wells LVT-1X, 2X and 4X (5 to 30 µm) lies near the lower limit (< 20µm) estimated by McCabe *et al*.(1987) and Elmore *et al*. (1987) for framboids not related to magnetosomes. However, such a consideration is not sufficient, to prove or to rule out the inorganic/chemical origin of framboids.

Spherical aggregates, observed in producer wells LVT-1X and 4X (Figure 5a), have a characteristic surface granular texture in contrast with those of non-producer well LVT-2X. The latter are smoother and more consolidated (Figure 5b). Machel (1995) suggests that differences of surface textures in magnetite framboids could be indicative of their origins (i.e. replacement of pyrite). However, we suggest that contrasts of surface textures could also be related to an ongoing process of growing and nucleation still taking place in the producer wells. Conversely, spherical aggregates of Fe-rich minerals in non-producer LVT-2X could be a fossil indication of the presence of hydrocarbons in the past, and of their migration towards their present position in the reservoir.

CONCLUSIONS

1 Profiles of bulk magnetic properties (MS and |M|) for near-surface strata in La Victoria oil field show higher values at discrete depth levels (LVT-4X: 534-564 and 625-655 meters; LVT-1X: 750-810 meters and LVT-2X: 610-655 meters). The samples were drilling fines of yellow to brownish sandstones from molasses of the Guayabo group. Textural differences cannot be determined in these unconsolidated fines, but magnetic contrasts do not seem to be caused by lithological changes since there are no visible differences of rock types between the various samples analyzed.

2 Rock magnetic analyses (IRM acquisition curves and thermal demagnetization of composite IRMs) suggest that magnetite is the chief magnetic mineral in levels of high MS and |M| values. Fe-sulfides were not detected. Drilling contamination can be excluded as the main source of magnetite in these samples.

3 SEM analyses show that characteristic spherical aggregates of Fe-rich submicron crystals appear only at levels with high MS and |M| values. They are missing for low MS and |M|. The presence of atypical concentrations of Fe-rich framboids seems to be a reasonable explanation for the contrasts observed in the bulk magnetic properties.

4 Framboidal textures are usually associated with pyrite of organic or inorganic origin. However, characteristic diffraction patterns (TEM analyses), obtained for magnetic separates used for SEM purposes (corresponding to peaks of MS and |M| values) reveal only magnetite. The fact that SEM observations were made exclusively on magnetic separates seems to rule out the possibility that these spherical aggregates are pyrite framboids.

5 We cannot exclude a hydrocarbon-independent process for the formation of the spherical aggregates. Yet such possibility seems remote considering the geological setting of La Victoria field. There is no evidence of lithological changes that could explain, independently of the geochemical conditions induced by hydrocarbon seepage, the formation of these framboids. Anomalies of Fe, Sr, Pb, Zn, Zr and Ca which coincide with levels of high MS and |M| values, are interpreted as local post-depositional chemical changes.

6 Preliminary studies of Electron Paramagnetic Resonance (EPR) in samples from LVT-2X and 4X indicate a positive correlation between concentration of free radical spins, probably associated with the presence of asphaltenes, and high MS and |M| values. Magnetic contrasts due to the inorganic/chemical formation of magnetite framboids have been reported due to biodegradation of hydrocarbons in carbonate rocks. The thermodynamic conditions that may have lead to the formation of magnetites include (i.e. La Victoria oil field) near-surface depths (within the upper 1500 meters) and an extremely low total dissolved sulfur content that prevents precipitation of Fe sulfides. Carbonate rocks can have a different diagenetic behavior than their clastic counterparts, but authigenic magnetite, without Fe-sulfide precursors, has been found in porous red sandstones where hydrocarbon seepage leads to hematite dissolution and the iron re-precipitates directly as magnetite.

7 Spherical aggregates of La Victoria have average diameters (5 to 30μm) close to the lower sizes estimated for framboids whose origins are not related to magnetosomes (i.e. $<20\mu m$). However, this purely qualitative consideration can not be used as sole evidence for proving or ruling out their inorganic/chemical origin. On the other hand, the granular surfaces of the spherican aggregates, observed in producer wells, are probably associated to an ongoing process of growing and nucleation that is still taking place. Conversely, their counterparts in non-producer LVT-2X show a smoother surface that could be the fossil documentation of the presence of hydrocarbons in the past as that specific location.

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