Latinmag Letters, Volume 7, Special Issue (2017), MR04, 1-6. Proceedings Juriquilla, Qro, Mexico

EFFECTS OF HYDROCARBON-INDUCED DIAGENESIS ON THE MAGNETIC SIGNATURE OF AN OIL WELL IN THE NORTHERN NEUQUÉN BASIN (VACA MUERTA FORMATION, SW ARGENTINA)

V. Costanzo-Álvarez[1]*, A. Rapalini[2], M. Díaz[3], T. Luppo[2], M. Aldana[1], Ma. P. Iglesias-Llanos[2],
A. Ma. Walther[2]

[1] Departamento de Ciencias de la Tierra. Universidad Simón Bolívar, Caracas, Venezuela
[2] Laboratorio de Paleomagnetismo Daniel A. Valencio, IGEBA, Departamento de Ciencias Geológicas, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina.
[3] Centro de Física, Instituto Venezolano de Investigaciones Científicas, Altos de Pipe, Edo. Miranda, Venezuela
*e-mail: vcosta@usb.ve

ABSTRACT

A rock magnetism and electronic paramagnetic resonance (EPR) combined study was performed in samples from an oil well drilled in the Vaca Muerta Formation (northern Neuquén Basin, SW Argentina). The aim of this work was to characterize the diagenetic processes involved in the origin of the magnetic mineralogy present in hydrocarbon-impregnated rocks. The primary magnetic minerals were affected by diagenesis due to a little-biodegraded crude oil, with low to medium sulfur content. A first reducing stage probably dissolved such minerals, forming pyrite and siderite. Consequently, some depth intervals along the core show a decrease of the magnetic signature in inverse relation to the concentrations of extractable organic matter (EOM) and organic matter free radicals (OMFR). On the other hand, for a specific section of the core, that appears to be a lithological microtrap, a second diagenetic stage reduced pyrite to framboidal authigenic pyrrhotite, increasing the magnetic signature in direct proportion to the EOM and to the OMFR content. This "microtrap" seems to be framed by two small peaks of Mn^{2+}, a proxy of the calcareous cementation, the porosity and the permeability of these rocks. Indeed, in the rest of the samples, the M^{2+} content shows negative correlations with the EOM and the OMFR, and positive correlations with the magnetic parameters. Hence, the negative correlations between magnetic properties and both, the EOM and the OMFR, suggest that, with lower porosity and/or permeability, there is less hydrocarbons infiltration and, consequently, lower diagenetic destruction of the primary magnetic signature.

Key words: Diagenesis, rock magnetism, hydrocarbons, EPR, SEM, framboids

RESUMEN

Se realizó un estudio combinado de magnetismo de rocas y resonancia paramagnética electrónica (EPR) en muestras de un pozo petrolero perforado en la Formación Vaca Muerta (norte de la Cuenca Neuquina, suroeste de Argentina). El objetivo del trabajo fue caracterizar los procesos diagenéticos involucrados en el origen de las mineralogías magnéticas presentes en rocas impregnadas de petróleo. Los minerales magnéticos primarios sufrieron diagénesis por efecto de un hidrocarburo poco biodegradado, con contenido bajo a medio de azufre. Una primera etapa reductora habría disuelto estos minerales formando pirita y siderita. Consecuentemente, para algunas profundidades a lo largo del núcleo, se observa una disminución de la firma magnética en proporción inversa al contenido de materia orgánica extraíble (MOE) y de radicales libres de la materia orgánica (RLMO). Por otro lado, para una sección específica, en lo que sería una "microtrampa" litológica, una segunda etapa diagenética redujo pirita a pirrotita framboidal, aumentando la firma magnética en proporción directa al contenido de MOE y de RLMO. Esta microtrampa estaría enmarcada entre dos pequeños altos de Mn^{2+} ,un indicador de la cementación calcárea, de la porosidad y de la permeabilidad de la roca. De hecho, en el resto de las muestras, el contenido de M^{2+} correlaciona negativamente con la MOE y los RLMO, y positivamente con los parámetros magnéticos. De aquí que, las correlaciones negativas que se observan entre las propiedades magnéticas y la concentración de MOE o de RLMO, sugieren que a menor porosidad y/o permeabilidad, menor infiltración de hidrocarburos y, por lo tanto, menor destrucción diagenética de la firma magnética primaria.

Palabras Clave: Diagénesis, magnetismo de rocas, hidrocarburos, EPR, SEM, framboides

1. Introduction

The oil shales of the Vaca Muerta Formation are the main source rocks in the Neuquen basin (southwestern Argentina). The lithologies of this ca 400 meters-thick formation, vary from mature black shales, to marls and limestones. These sediments were accumulated in an anoxic marine environment, during the upper Jurassic and the early Cretaceous.

In this work we carried out a combined study of rock magnetism and electronic paramagnetic resonance (EPR), on 31 rock samples taken along 8 sections of a well core drilled in the northern Neuquen Basin. Our main objective is to unravel the primary or secondary character of the NRMs measured in these oil-bearing samples of the Vaca Muerta Formation. According to previous studies, in drill cuttings from oil wells in Venezuelan and Colombia, the OMFR and the MOE are related to hydrocarbons microseepage, resulting in a highly reducing environment that induces chemical alterations of the primary Fe oxides (*e.g.* Aldana *et al.*, 2003, Costanzo-Alvarez *et al.* 2006; Guzmán *et al.* 2011).

The depth range analyzed is approximately 315 meters thick (2425 to 2740 meters). Each sample comprises about 4 specimens taken in 31 intervals of 6 meters-long, all over the core (130 specimens). Most samples are pelites and calcipelites, except P7 and P8: a 5 meters-thick Miocene andesite intrusion. Rock magnetic analyses (thermosusceptibility curves, room temperature volume magnetic susceptibility κ, NRM and SIRM/χ) were carried out in the Daniel Valencio Paleomagnetic Laboratory of the IGEBA (Instituto de Geociencias Básicas, Aplicadas y Ambientales de Buenos Aires). The EPR experiments were performed at the Physics Center of the Venezuelan Institute for Scientific Research. In addition, we carried out scanning electron microscopy (SEM) and electron X-ray energy dispersion (EDX) experiments at the Surfaces Laboratory of the Universidad Simón Bolívar (Caracas, Venezuela).

2. Experimental Results

Figure 1a displays the values of κ and total organic matter free radicals (OMFR), sequentially arranged downcore, showing the sample numbers on the vertical axis. Figure 1b are the profiles of Mn^{2+}, κ, NRM, SIRM/χ, extractable organic matter (EOM) and OMFR (chloroform-treated and untreated samples) plotted against depth. The two rectangles encompass: P7/P9 (2471/2476.64 m), an andesitic intrusion and its contact zone; and P18/P23 (2666/2693 m), the only interval where κ, NRM, EOM and OMFR values vary likewise.

The SIRM/χ values lie within the ranges reported by Peters and Deckers (2003) for magnetite, hematite and pyrrhotite. From the the thermosusceptibility curves we identified hexagonal pyrrhotite. The heating and cooling curves also reveal the neoformation, throughout heating, of magnetic Fe sulfides. The progressive decay between 500°C and 600° C, of a small tail in all the heating curves, indicates the presence of magnetite. IRM acquisition curves show saturation at fields between 360 and 600 mT.

The EPR technique was used to detect minute amounts of OMFR and Mn^{2+}. There is no difference between the OMFR signal before and after treatment with chloroform, which is employed to extract the soluble components of the crude oil. This result precludes the presence of asphaltenes, a soluble OMFR typical of highly biodegraded hydrocarbons (Fig. 1b).

SEM and EDX analyses were performed in: the andesitic intrusion (P8), the P18/P23 interval (P18, P22 and

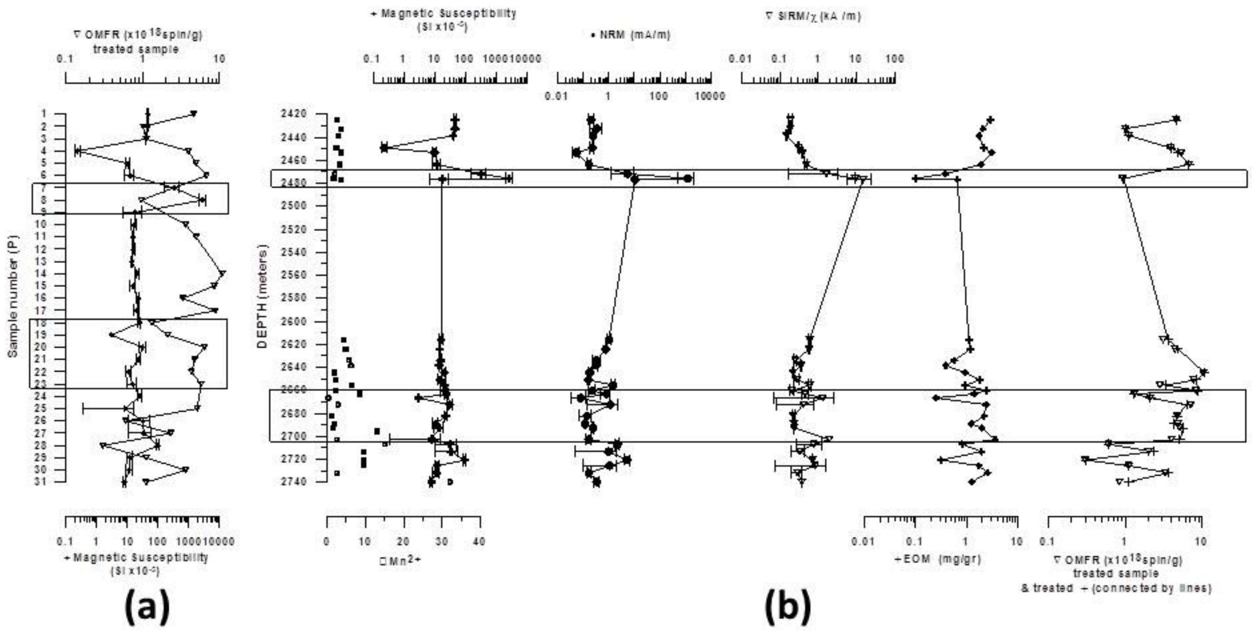

Figure 1. Profiles of Mn^{2+}, κ, NRM, SIRM/χ, EOM and OMFR. (a) Values of κ and OMFR plotted downcore, with the sample number on the vertical axis. In (b) the vertical axis shows the actual depths. The rectangles comprise the stratigraphic levels: (P1/P9) andesitic intrusion and its contact zone, and (P18/P23) interval where the magnetic parameters vary in direct relation to the concentrations of EOM and OMFR.

P23) and those levels, greater than P10, that exclude P18/P23 (*i.e.* P10 and P26). Framboids of authigenic Fe sulfides (probably pyrrhotite), associated to hydrocarbons, were identified only in samples from P18/P23 (Figs 2a., b and c). In P10 and P26, outside this interval, we solely recognized aggregates of Fe sulfide

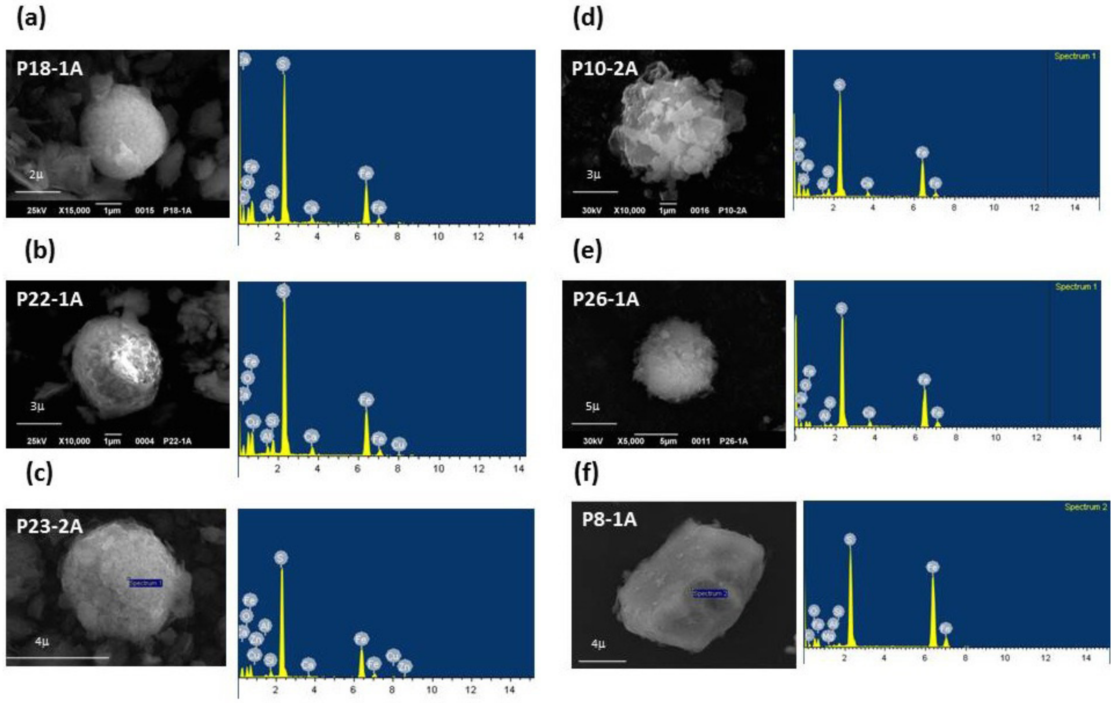

Figure 2. SEM images and EDX (electron scattering) spectra for framboids indentified in (a) P18 (b) P22 and (c) P23 (P18/P23 interval); Fe and S microcrystal aggregates identified in (d) P10 and (e) P26 (below the andesitic intrusion and excluding the P18/P23 interval) and Fe and S magnetic mineral in (f) P8 (andesite).

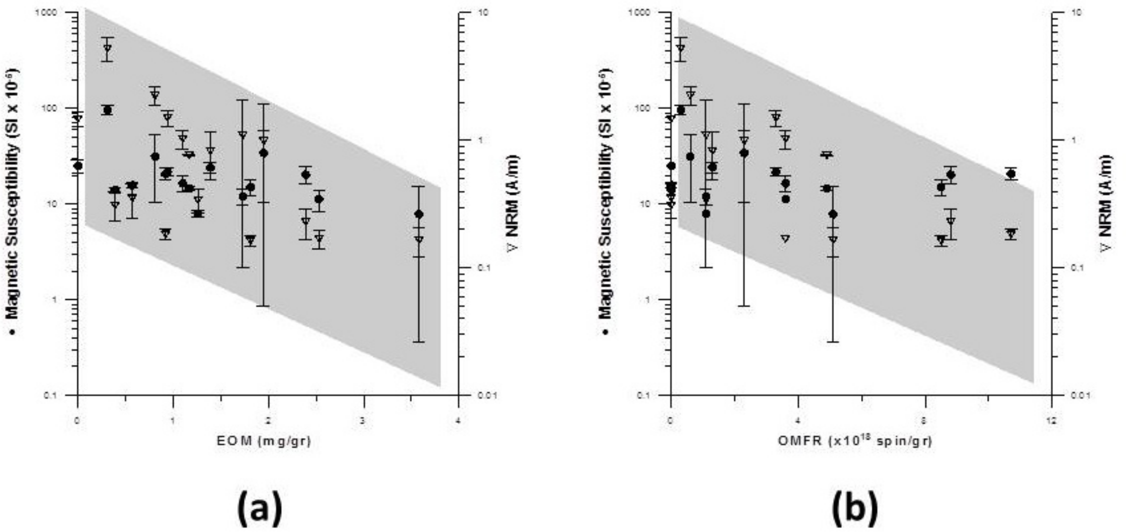

Figure 3. Average susceptibility and NRM values, for each depth level, plotted against (a) EOM and (b) OMFR. Samples from the P1/P9 (andesitic intrusion and its contact zone) and P19/P23 intervals, are excluded.

microcrystals that appear to be fragments of framboids, like those observed by Kilgore and Elmore (1989) in oil-saturated sands (Figs. 3d and e). A magnetic separate was obtained from P8 (andesite), however we did not identify aggregates of Fe-rich microcrystals in this sample (Fig. 3f).

3. Discussion

Machel (1995) propose a modeling of the possible magnetic minerals that are formed, destroyed or survive when the primary magnetic minerals, in a sedimentary rock, go through oil-induced diagenesis. According to these models, between about 1600 and 3300 meters depth (100°C/300 bars), in hydrocarbon-impregnated rocks with low to medium sulfur content, the primary magnetic minerals tend to be unstable or to precipitate as paramagnetic siderite and/or pyrite. The consequence of this process would be a low or negative magnetic signature. On the other hand, Kilgore and Elmore (1989) analyze some hydrocarbon-impregnated sands concluding that, in such a highly reducing environment, the primary hematite is removed to form authigenic magnetite and/or pyrrhotite, with a positive magnetic signature.

P18/P23 is the only interval where both EOM and OMFR vary in direct relation to the magnetic properties (Fig. 1). These are also the only samples where framboids of authigenic Fe sulfides were observed, suggesting that hydrocarbon infiltrations are responsible for the formation of new magnetic minerals (Figs. 3a, b and c).

For the rest of the samples, excluding the andesitic intrusion and its contact zone, there is an inverse relationship between the magnetic parameters and both the EOM and the OMFR values (Fig. 3). A similar trend was previously observed by Emmerton *et al*. (2013) in hydrocarbon-impregnated samples from different oil fields around the world. We argue that, in those cases where there is such an inverse relationship, the diagenetic processes involved lead to the partial destruction of the primary magnetic minerals, and/or neoformation of paramagnetic pyrite and siderite. Therefore, the κ, NRM and SIRM/χ measured in these samples would correspond to the primary magnetic minerals that have survived oil-induced diagenesis.

On the other hand, samples at the P18/P23 interval, might have gone through a second diagenetic event, in which authigenic pyrrhotite and/or magnetite framboids, formed at the expense of the total reduction of primary hematite and/or pyrite, and the electrons available from the OMFR. The fact that such a process has selectively affected these samples, might be related to a special feature of their corresponding lithologies. Indeed, most of these samples show very low Mn^{2+} concentrations (Fig. 1). Hence, the /P23 interval would be an anomalous sequence of oxygenated sediments, within a rather anoxic context, where dissolved Mn^{2+} concentrations diminished after oxidizing to insoluble MnO_2 (Burdige and Gieskes, 1983). Such a paleoenvironment probably favored the stability of hematite too. Moreover, the two small Mn^{2+} peaks that frame P18/P19 (Fig. 1) could be the seals of a sort of microtrap that would give rise to the prolonged effect of hydrocarbons on these rocks, impeding their mobility. Indeed, previous EPR studies in marine sediments (e.g. Otamendi *et al.*, 2006) show that the Mn^{2+} is mainly bound to the carbonate phases. Therefore, it would be expected that the Mn^{2+} values increase with the calcareous cementation in the rock, that directly impinge on a decrease of its porosity and/or permeability.

For those samples at depths greater than 2600 meters (excluding the P18/P23 interval) we plotted the Mn^{2+} versus EOM, OMFR and the magnetic parameters (Fig. 4a). The inverse relationship between the EOM and the Mn^{2+}, as well as between the Mn^{2+} and the OMFR, could result from the decrease of the porosity and/or permeability too. That is to say, a higher content of Mn^{2+} implies a lower amount of hydrocarbon infiltration and, therefore, a lower concentration of EOM and OMFR. As a consequence, a decrease of the oil destructive effects on the primary magnetic minerals would result in the positive correlations observed in the scatter plots of Mn^{2+}versus κ, NRM and SIRM/χ (Figs. 4b, c and d).

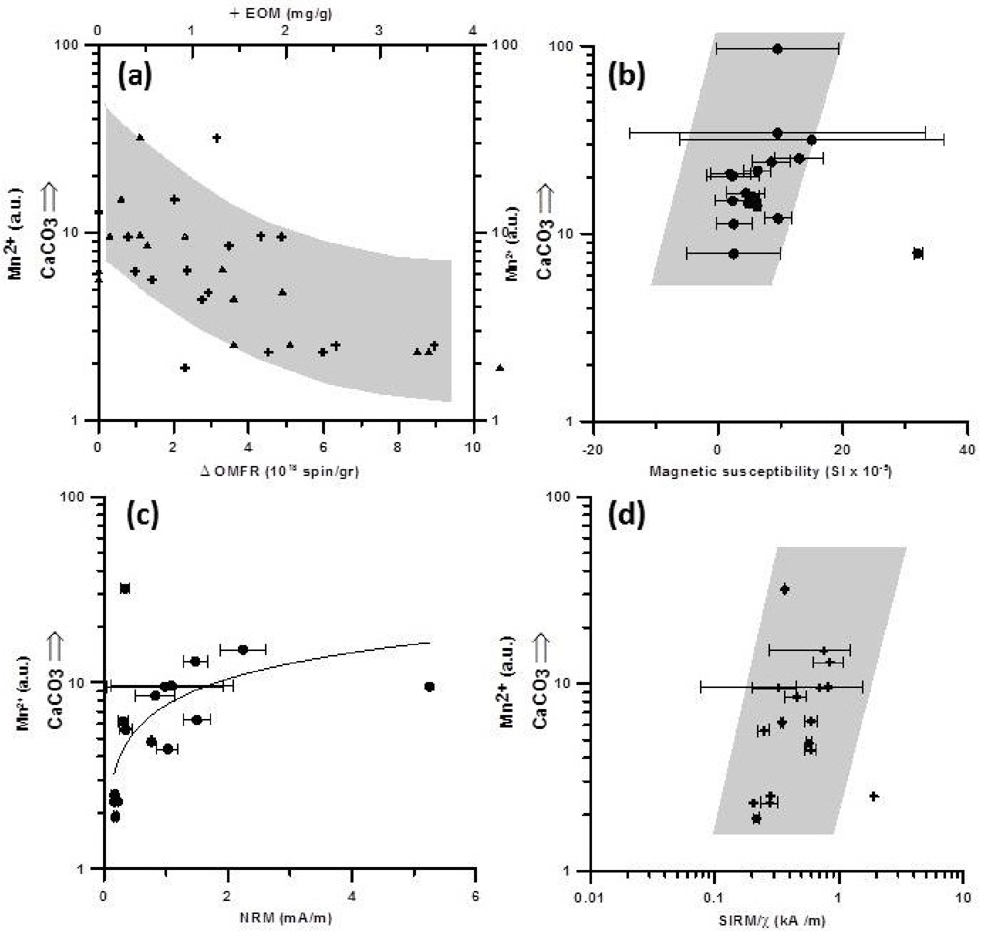

Figure 4. Scatter plots of Mn^{2+} content versus (a) EOM and OMFR; (b) average values of κ; (c) NRM and (d) SIRM/χ. Samples from the P1/P9 (andesitic intrusion and its contact zone) and P19/P23 intervals, are excluded.

References

Aldana M., Costanzo-Álvarez V. and Díaz M., 2003.Magnetic and mineralogical studies to characterize oil reservoirs in Venezuela. *Lead. Edge 22*, 526–529.

Boughriet A., Ouddane B., Wartel M., 1992. Electron spin resonance investigations of Mn compounds and free radicals in particles from the Seine river and its estuary. *Mar. Chem.37*, 149–169.

Burdige, D. J., And J. M. Gieskes, 1983. A pore water/solid phase diagenetic model for manganese in marine sediments. *Am. J. Sci. 283*, 29-47.

Costanzo-Álvarez V., Aldana M., Diaz M., Bayona G., Ayala C., 2006.Hydrocarbon-induced magnetic contrasts in some Venezuelan and Colombian oil wells. *Earth Planets Space58*, 1401–1410.

Emmerton S., Muxworthy A.R., Sephton M.A., Aldana M., Costanzo-Álvarez V., Bayona G., Williams W. , 2013. Correlating biodegradation to magnetization in oil bearing sedimentary rocks. *Geochim. Cosmochim. Ac. 112*, 146-165.

Guzmán O., Costanzo-Álvarez V., Aldana M., Diaz M., 2011.Study of magnetic contrasts applied to hydrocarbon exploration in the Maturin sub-basin (eastern Venezuela). *Stud. Geophys. Geod. 55*, 359–376.

Kilgore B., Elmore R.D., 1989. A study of the relationship between hydrocarbon migration and the precipitation of authigenic magnetic minerals in the Triassic Chugwater Formation, southern Montana. *Geol. Soc. Am. Bull. 101*,1280-1288

Machel H. (1995) Magnetic mineral assemblages and magnetic contrasts in diagenetic environments – with implications for studies of palaeomagnetism, hydrocarbon migration and exploration. In Palaeomagnetic Applications in Hydrocarbon Exploration (eds. P. Turner and A. Turner). *Geol. Soc. London Spec. Publ.98*, 9–29.

Otamendi A.M., Díaz M., Costanzo-Álvarez V., Aldana M., Pilloud A., 2006.EPR stratigraphy applied to the study of two marine sedimentary sections in southwestern Venezuela. *Phys. Earth Planet. In.154*, 243–254.

Peters C., Dekkers M.J., 2003. Selected room temperature magnetic parameters as a function of mineralogy, concentration and grain size. *Phys. Chem. Earth 28*, 659–667.