A PRELIMINARY STUDY OF MAGNETIC PROPERTIES IN SEDIMENTS FROM THE ANLLÓNS RIVERBED, AND THEIR POSSIBLE ASSOCIATION TO ANTHROPOGENIC POLLUTION

Vincenzo Costanzo-Álvarez[1], Diego López-Rodríguez[2], Rosa Devesa-Rey[3], María Teresa Barral-Silva[4]

[1] Departamento de Ciencias de la Tierra, Universidad Simón Bolívar, Caracas, Venezuela.

[2] Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Ciudad Universitaria, 28040 Madrid, España

[3] Centro Universitario de la Defensa, Escuela Naval Militar, Universidad de Vigo, Marín (Pontevedra), España

[4] Departamento de Edafología y Química Agrícola, Universidad de Santiago de Compostela, España

ABSTRACT

We analyzed thermomagnetic and hysteresis curves of 13 samples from the Anllóns riverbed (Spain) in order to relate their rock magnetic properties to metallic elements contamination. Thermomagnetic curves appear to indicate the inversion of maghemite to hematite in most samples. The tightly grouped Mrs/Ms and Hcr/Hc ratios lie in the middle range of the theoretical MD+SD mixing curves of a Day plot, overlaping the clay fractions of the Luochuan paleosols that have a dominant maghemite fraction. We do not find straightforward linear relationships between metal concentrations and the Mrs/Ms ratios. We argue that the possible association between concentration of some metallic elements, and magnetic parameters in these samples may be due to a later incorporation, via adsorption, of these elements on the surface of the magnetic carriers already present in the soils. Anomalous rock magnetic results for a single sample taken at the river mouth, are attributable to recent anthropogenic industrial and agricultural activity in the region.

Key words: metals contamination, maghemite, thermomagnetic curves, hysteresis parameters

Introduction

The basin of the Anllóns River, in Galicia (northwestern Spain), drains through an approximately 516 km^2 rural catchment that has a long record of agricultural, forestry and cattle activities (fig. 1). In this preliminary study we try to characterize the magnetic mineralogies of 13 samples taken in pits of 24 to 144 cm deep, at 7 depositional areas evenly distributed between the locality of Carballo and the river mouth in Ponteceso (about 30 km long transect). We worked with a mesh < 63 µm for every single sample analyzed.

Devesa *et al.* (2006) suggested that due to a rather good linear correlation between concentration of metallic elements such as Cr, Ni, Co, Cu and Zn, and bulk magnetic susceptibility in these samples, the latter could be used as an indicator of pollution in the fluvial basin. Thus we also analyzed this hypothesis in the light of new rock magnetic data (*i.e.* thermomagnetic curves and hysteresis loops).

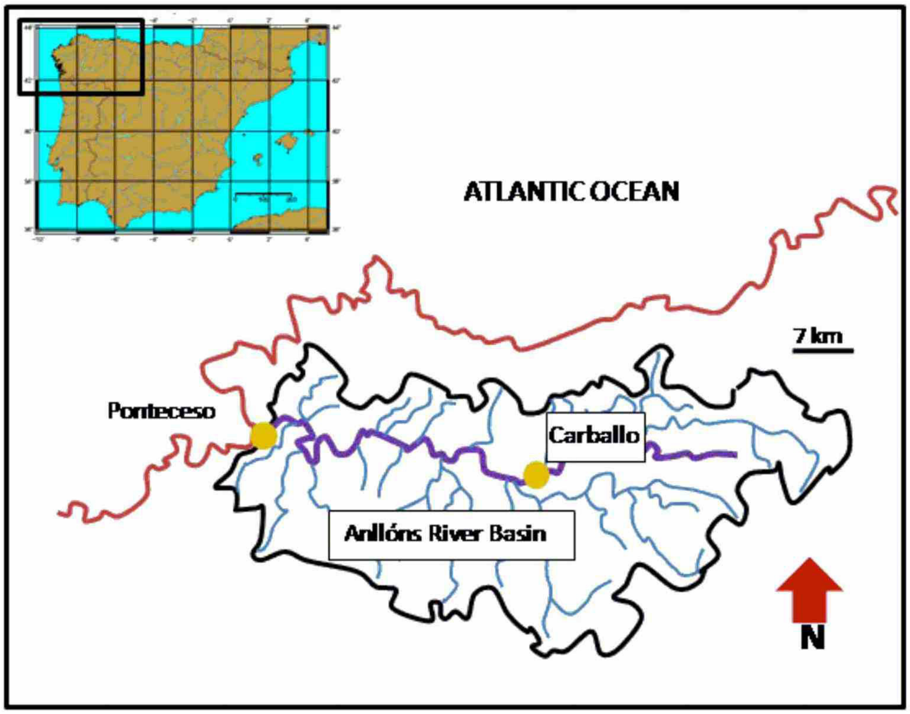

Figure 1: Anllóns River basin in northeastern Spain

Experimental Results

Thermomagnetic curves for heating and cooling cycles were obtained in air atmosphere using a susceptibility bridge AC Geofyzika KLY-4S (Agico). The saturation remanence–saturation magnetization (Mrs/Ms) and coercivity of remanence–coercive force (Hcr/Hc) ratios were also obtained from hysteresis loops (-6,000 to 6,000 Oe) measured at room temperature, with a coercivity-spectrometer manufactured in the University of Kazan (Rusia).

Most thermomagnetic curves have two phase transitions at 250–350 and 450–550° C, such as the curve of a sample from the Agra site, close to Carballo, shown in the example of Figure 2a. The first transition may indicate the inversion of maghemite to hematite. The second one corresponds to the transformation of hematite to a strong magnetic phase in presence of organic matter (Hanesch *et al.* 2006) and revealed by the highly irreversible cooling curve. The only sample that does not follow this behavior is the one from Ponteceso (fig. 2b) from a sampling pit at the mouth of the Anllóns River (fig. 1). The cooling curve for this sample, whose vertical axis is augmented by a logarithmic scale, reveals the presence of small amounts of both magnetite and hematite. Opposite to the rest of the samples, this one does not have the characteristic 250–300° C inversion of maghemite to hematite (inset fig. 2b).

Mrs/Ms and Hcr/Hc ratios are shown in the Day plot of Figure 3. The tightly grouped data from the Anllóns River lie in the middle range of the synthetic MD+SD mixing curves (Dunlop, 2002). The Anllóns group also overlaps the clay fractions (< 2μm) of the Luochuan paleosols from China, with a dominant maghemite fraction (Hao *et al.* 2012). Once again, the anomalous Ponteceso sample has a behavior that departs from the rest of its counterparts, with a high Mrs/Ms ratio characteristic of fine–grained magnetite.

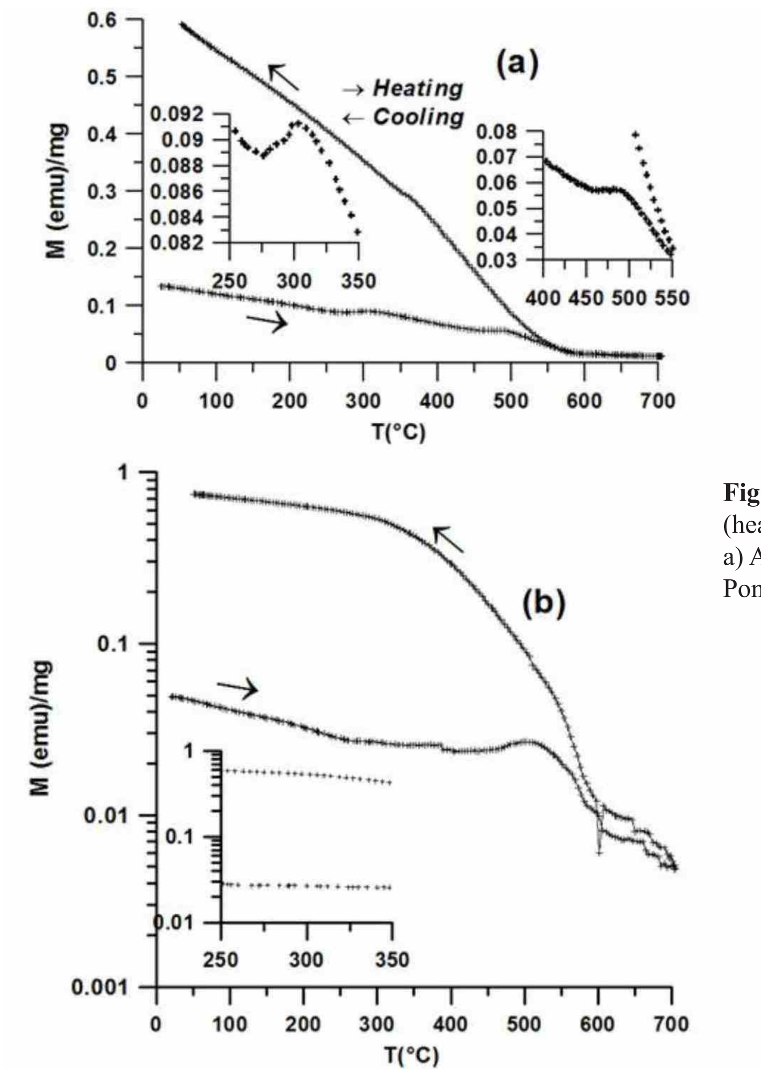

Figure 2. Thermomagnetic curves (heating and cooling) for samples: a) Agra (close to Carballo) and b) Ponteceso (at the river mouth).

Discussion

Devesa *et al.* (2006) showed a rather good correlation between bulk magnetic susceptibility and the concentration of some metallic elements produced by mining and industrial activities in the region. They also argued that there are no major differences in the bulk magnetic susceptibility measurements for either the 2 mm or the 63µm meshes used in their work. However, we do not find such a good agreement between metallic elements concentrations and the Mrs/Ms granulometric ratios, which increase as the grain sizes of magnetite decrease.

The widely observed association between concentration of heavy metals and magnetic parameters is usually due to the incorporation of contaminants into the crystalline structure of magnetite and/or hematite-rich fly ashes (≤ 1µm) produced by point and/or diffuse anthropogenic sources. Thus, the pollutant load released into the atmosphere and accumulated in soils, may sometimes be related to a fraction of fine-grained magnetic minerals. In these cases a link between heavy metals and grain size would be expected. Conversely, this association may be also due to a later incorporation, via adsorption, of heavy metals on the surface of the magnetic carriers already present in the soils. This mechanism could be the one that applies to most of our samples (except for Ponteceso) since maghemite is usually a byproduct of weathering or low-temperature oxidation of detrital, pedogenic and/or anthropogenic magnetite. In this case the pollutant load would be rather linked to the bulk magnetic susceptibility, a first order measure of the amount of ferrimagnetic minerals in soils and sediments.

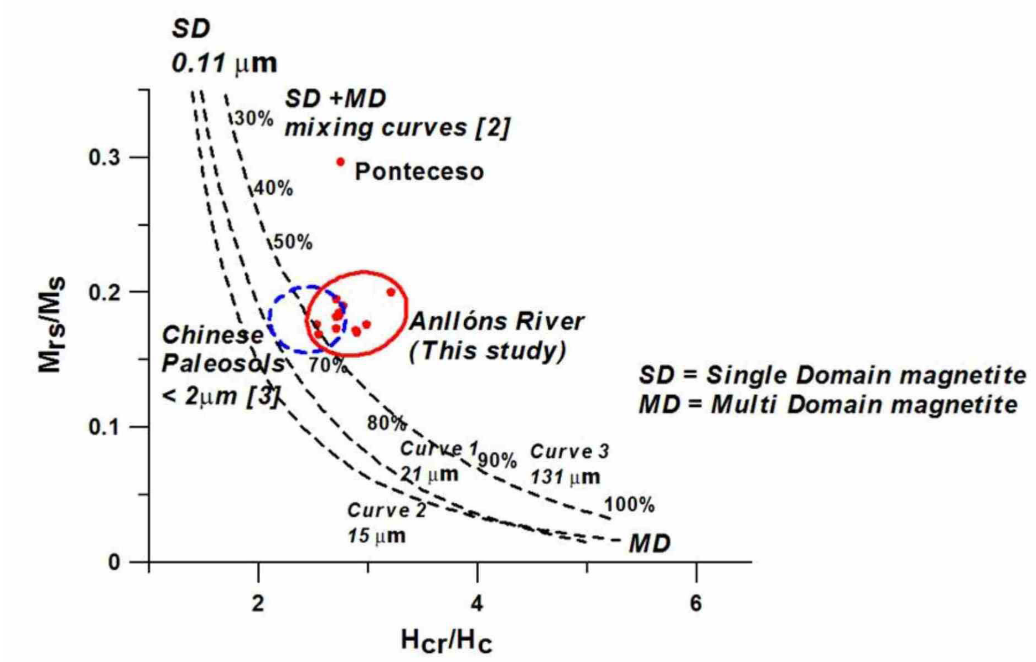

Figure 3: Day plot showing the Anllóns River hysteresis data (red dots) and grouping (red elipse), the Luochuan paleosols data grouping as a green ellipse (after Hao *et al.* 2012) and some of the theoretical SD–MD mixing curves (after Dunlop, 2002).

On the other hand, the anomalous behavior of the Ponteceso sample could be explained from its location at the river´s mouth. Indeed, Devesa *et al.* (2006) reported one of the highest average bulk magnetic susceptibility values for this sampling pit. They argued that this result might be the consequence of the intense agricultural activity in the area, favoring the erosion of the upper soils and the accumulation of high susceptibility minerals in the riverbed. They also found a significant correlation between bulk magnetic susceptibility and content of Cu and Co, likely related to industrial activity in the area (*i.e.* a water treatment plant and a seafood canning factory). A similar case was previously studied by Chaparro *et al.* (2004) for some stream sediments sampled in the northeastern Buenos Aires Province. As in Anllóns River, they found a magnetic susceptibility enhancement, probably related to recent anthropogenic input of pollutants in the region, for the uppermost sediments that come exclusively from those sites at the coastal plain, where the stream flows into the La Plata River.

Further rock magnetic experiments, for an extended number of samples, are still pending. Our next goal would be to better identify the magnetic mineral assemblages contained in these samples, as well as their relative concentrations, via a direct signal analysis of the isothermal remanent magnetization (IRM) curves (Aldana *et al.* 2010). As an outcome of these experiments we would have that a likely agreement between metallic element concentrations and relative amounts of different magnetic minerals could be tested on these samples. We also expect to obtain a well defined $\log B_{1/2}$ value for maghemite.

Acknowledgments:

Marisa Osete López, Fátima Martín Hernández and Sara Guerrero Suárez, Facultad de Ciencias Físicas y Matemáticas, Universidad Complutense de Madrid, Spain.

References

Aldana M., Costanzo-Álvarez V., Gómez L., González C., Díaz M., Silva P., Rada M., 2010. Identification of magnetic minerals related to hydrocarbon authigenesis in Venezuelan oil fields using an alternative decomposition of isothermal remanence curves. *Stud Geophys Geod*, *55,* 343−358.

Chaparro M. A. E., Bidegain J. C., Sinito A.M., Jurado S. S., Gogorza C.S.G., 2004. Relevant magnetic parameters and heavy metals from relatively polluted stream sediments – vertical and longitudinal distribution along a cross-city stream in Buenos Aires province, Argentina, *Stud Geophys Geod, 48,* 615−636

Devesa R., Barral M. T., Díaz-Fierros F., 2006. Magnetismo ambiental y contaminación antropogénica en el río Anllóns (Galicia): estudio preliminar, in MAGIBER IV Congreso de Paleomagnetismo Ibérico, Vigo, España, 28–29 Septiembre.

Dunlop D. J., 2002. Theory and application of the Day plot (Mrs/Ms versus Hcr/Hc) 2. Application to data for rocks, sediments, and soils, *J Geophys Res, 107 (B3),* EPM5-1–15

Hanesch M., Stanjek H., Petersen N., 2006. Thermomagnetic measurements of soil iron minerals: the role of organic carbon, *Geophys J Int*, *165,* 53–61

Hao Q., Oldfield F., Bloemendal J., Guo Z., 2012. Hysteresis and thermomagnetic properties of particle-sized fractions from loess and palaeosol samples spanning 22 Myr of accumulation on the Chinese Loess Plateau, *Geophys J Int*, *191,* 64–77