ROCK MAGNETIC CHARACTERIZATION OF THE MINE TAILINGS IN
PORTMAN BAY (MURCIA, SPAIN) AND ITS CONTRIBUTION TO THE
UNDERSTANDING OF THE BAY INFILLING PROCESS

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Abstract

The Portman Bay located in the SW Spain has suffered great changes since the 1950s associated with the mining activity. The direct discharge into the sea of mining waste has caused the silting of the bay in a few decades. In this study the magnetic properties of recent sands from a set of 52 samples from the bay and 16 samples from an opencast mine are magnetically analyzed. In particular, we have measured magnetic susceptibility, hysteresis loops, IRM-acquisition, SIRM-
IRM and back-field-coercivity spectra, thermomagnetic curves and FORC diagram and took SEM micropictures. Data are correlated with classical magnetite content estimations derived from X-ray diffraction (XRD) in three separated grain sized (coarse, medium and fine grain) and heavy metal derived from X Ray Fluorescence (XRF) in samples from a parallel study at the same sampling sites and the same sampling campaign. The results indicate high concentrations of magnetite (up to 28%) compared to magnetically hard minerals that have not been quantified. Higher concentrations of magnetite are recorded in the central part of the beach, as indicated by $M_s$, SIRM and $K_{int}$. Coercivity, however, indicates smaller values in the center of the Bay, suggesting a larger size of the magnetic particles. The S-ratio or high coercivity fraction is higher in older samples. Correlation of the magnetic properties with magnetite grain size indicates a positive correlation between $M_s$ and medium and fine grain size fraction, determined by X-ray diffraction. In addition, magnetic properties show a direct relationship between magnetite content and the heavy metals Pb, Cu and As. Our results indicate that the deposition of magnetite was fast and properties has not been modified in depth. However, spatial location in the Bay is significant when we examine distribution of grain sizes. Also, results suggest that magnetite acts as captor of heavy metals.

Keywords: Iron ore, beach placer deposit, magnetite, Portman Bay, magnetic properties, hysteresis loops, environmental magnetism

1 Introduction

The Portman Bay is located in southeast Spain and belongs to the Cartagena - La Unión Mining District. The Bay is at the foot of the Cartagena range mountain, named “Sierra Minera”, which crosses the Mining District from west to east, parallel to the Mediterranean coast (Conesa et al., 2008). The Cartagena – La Unión district covers an area of about $10 \times 5$ km in the northeast-southwest direction and includes one of the largest Pb - Zn ore deposits in Spain (López-García et al., 2011) (Figure 1a).
The mining industry has been the most important economic activity in this region for more than 2000 years. The ore mining extraction around the Bay started before the Roman Empire, first by the Iberians, followed by the Phoenicians and Carthaginians, and ended definitely in 1991. The wastes generated by the first miners was then used as a source of minerals in later centuries when the extraction activity decreased. This continued until the mid-nineteenth century when the large-scale mining development of the region took place (Conesa et al., 2008; Martínez-Sánchez et al., 2008; Oyarzun et al., 2013).

Mining activity throughout the centuries in the region has produced large geomorphological changes, particularly at the Portman Bay. In the 1950’s the multinational Peñarroya España S. A. started opencast mining and built a mineral processing plant “Lavadero Roberto”. This mineral processing plant dumped over 57 million tons of wastes into the Mediterranean Sea, through the Portman Bay, from 1957 to 1990 (Martos-Miralles et al., 2001; Manteca Martínez et al., 2005). As a result, the Portman Bay was completely filled in a few decades affecting significantly the shoreline, which receded about one kilometre. The mineralogical composition of the beach iron concentrates has been determined to be 17% of quartz, up to 35% of magnetite, 12% of hematite and 36% of siderite (Manteca et al., 2014). Furthermore, the Bay, presently, shows high concentrations of metals such as lead, copper, zinc, cadmium and mercury as well as sulfur and iron oxides (Martínez Orozco et al., 1993; García et al., 2003). In particular, Zn has been shown to be the most mobile cation with respect to Pb and As (Martínez-Sanchez et al., 2008). Heavy metal concentration has already been found to be anomalously high in several biotic elements of the area (e.g., Auernheimer, C. and S. Chinchon, 1997; Cesar et al, 2009; Benedicto et al., 2008). High concentration of pollutants seems to be related to accumulation of metals in multitude of life elements suboptimal health status of fish in the area (e.g., Martinez-Gomez et al., 2012).

Because of significant exposed changes occurred in the Bay within few decades as a result of filling processes, several remediation actions have been proposed. All of these require a complete quantification of the material deposited, reliable physical control on the sand
composition and associated geophysical properties (Peña et al., 2013). In this particular aspect, the tailing has been estimated to contain up to $444 \times 10^3$ t of magnetic iron concentrate in the form of magnetite, hematite and siderite. Finally, if the present beach black sands represent approximately 1/6 of the total bay infilling, the actual amount of iron in Portman Bay’s could be much larger, at least on the order of $1 \times 10^6$ t (Manteca et al., 2014).

The use of magnetic properties to evaluate iron resources has been gaining importance in exploration and mineral prospecting in the last decades (e.g., Clark, 1999; Clark, 2014 and references therein). The work presented here aims to study the magnetic properties of recent sands from the Portman Bay area. The concentration of magnetic minerals deposited is also analyzed and we will discuss their spatial distribution along the Bay and the temporal distribution as a function of the time of deposition. Also, the magnetic parameters will be compared with estimations of heavy metals derived from a parallel spectrometric analysis in the same sampling sites (Carmona Manzano, 2012).

It is particularly important to highlight that recently there is a rising interest in the regional community to environmentally regenerate the Portman Bay and recover the iron-bearing waste as economic resource (Murcia Today, 2014). Therefore, the findings from this study are significant not only in relation to the Portman Bay itself, and future remediation and sustainable development of the area but also for coastal areas with similar concerns.

### 2 Geological-Environmental context

Sierra Minera is located at the eastern end of the Betic Ranges. It is characterized by an overlaid layer structure of tectonostratigraphic complexes. The basement is formed by the Nevado-Filábride (Paleozoic to Triassic) and Alpujárride (Permian to Triassic) complexes (Figure 2), which emerge as superimposed thrust sheets of Alpine age and are affected by metamorphism decreasing from bottom to top. In the Late Miocene, these basal units suffered a gravitational collapse accompanied by a significant high-K calc-alkaline volcanism and marine sedimentation in extensional basins of Miocene to Pliocene age. After the Neogene, there was an important
phase of fracturing followed by volcanic events and uplift of the Sierra, and the currently erosive dismantling (Manteca Martínez and Ovejero Zapino, 1992; Vera, 2004; López-García et al., 2011).

The following types of mineralization can be described in the Sierra Minera the following types of mineralization (Oen et al., 1975; Manteca Martínez and Ovejero Zapino, 1992): (i) mantos: masses and stratabound bodies found in Nevado - Filábride (second manto) and Alpujárride (first manto) complexes. Both manto units have two sets of different minerals: (a) greenalite - magnetite - sulphide - carbonate - silica (silicate manto) and (b) chlorite- sulphide-carbonate-silica (pyrite manto). Most of the lead and zinc produced in the district were extracted from these manto-type deposits. (ii) Disseminations in the Miocene: irregular bodies elongated in a NW – SE direction, with respect to the fracturing. They were the most important mineral resource after the majority of mantos was used up. This is sphalerite-rich mineralization with pyrite, marcasite and galena as minor phases. (iii) Veins and stockworks associated with vulcanites and (iv) Monteras or Gossans type deposits are also developed. However the stockworks (iii) and Gossan (iv) type were not subject to mining by the Peñarroya Company. The main minerals that have been described are goethite, hematite, silica and, to a lesser proportion, mineral of the jarosite group and alunite along with carbonates and clayey minerals (López García, 1985; Carmona Manzano, 2012).

3 Materials and methods
A total of 52 samples of recent sands of the Portman Bay (labeled as “PP samples”) have been analyzed. Nine sampling sites have been selected, distributed along the Portman bay coastline placer and one site at the interior of the bay (Figure 1b). Samples from sites PP1, PP1 - B, PP2, PP2 – B y PP3 – B have been taken at several depths. The PP3 - A samples and a fraction of PP5 samples (the PP5 - D) are hardpan-type or duricrust. Hardpan term refers to a dense layer of that is normally found in the topsoil layer, using here the duricrust term meaning no soil
development is necessary happening. Moreover, the PP4 samples are sulphated facies. In total, 26 samples were collected from the Bay. Furthermore, for each sampled point, two specimens were taken to check their homogeneity.

A small specimen of rock material was sampled from an open cast mine, the Emilia open pit in the vicinity of the town El Llano del Beal, 4 km north of Portman (Figure 2). This was divided into 16 small fragments, due to it being highly heterogeneous in composition (M samples) and represents the original mined material. This material is made to have a statistical sampling of the magnetic properties of the original magnetic signal with respect to the mining processed tailing.

Measurements include magnetic and non-magnetic techniques. Among the first, the magnetic susceptibility of 25 PP samples was determined in a constant low-field (300 A/m) using a Kappabridge KLY-4 manufactured by AGICO (Advanced Geoscience Instruments Co.) (Hrouda et al., 2006). Also, low-field susceptibility has been measured at two frequencies for 52 PP samples using a Bartington Instruments MS2 Magnetic Susceptibility System. The frequency dependence indicates the presence of ferromagnetic grains that are possessing superparamagnetism (Tauxe, 2009).

Hysteresis loops have been measured up to 0.5 T with a spectrometer of coercivities developed by the University of Kazan (Coercivity Spectrometer J-meter) (Jasonov et al., 1998) for 52 PP samples and 16 M samples. Data have been corrected for paramagnetic/diamagnetic contribution, to characterize the magnetic parameters in the studied area: paramagnetic susceptibility ($\kappa_{\text{para}}$), saturation magnetization ($M_s$), remanent magnetization saturation ($M_{\text{rs}}$), coercive force ($B_c$) and initial susceptibility ($\kappa_{\text{ini}}$).

The magnetic characterization also includes acquisition of Saturation of Isothermal Remanent Magnetization (SIRM) up to 0.5 T and further demagnetization by static fields in the opposite direction (back-field IRM) in a Coercivity Spectrometer J-meter. The coercivity of remanence ($B_{cr}$) and total value of SIRM have been computed for all PP and M samples. Also, the amount
of high coercivity fraction has been estimated computing the S-ratio as the difference is
remanence acquired between 100mT and 500mT (Evans and Heller, 2003). Also, the IRM -
acquisition curves were modeled by a series of log-normal distributions of the IRM gradient in
order to infer the coercivity distribution associated to magnetic fractions. The mathematical
fitting has been modeled by the method outlined by Kruiver et al., (2001) and the associated
software.

Thermomagnetic curves were generated through a Petersen Instruments Variable Field
Translation Balance (VFTB) in order to determine the Curie/Neél temperature of the
ferromagnetic phases. Curie/Neél temperatures were determined for a selection of 26 PP
samples and 5 M samples by the maximum in second derivative method (Moskowitz, 1981;
Tauxe, 1998).

Magnetic parameters have been summarized in a Day plots attempting to discriminate domain
state of the magnetic particles (Day et al., 1977; Dunlop, 2002). First-Order Reversal Curve
(FORC) diagrams were measured in material from site PP1 in order to achieve knowledge about
particles interaction and/or domain state (Pike et al., 1999; Roberts et al., 2000). Sand material
was consolidated using non-magnetic glue into a gel cap. FORC diagrams have been processed
with the software and methodology described by Harrison and Feinberg (2008) using a
smoothing factor, SF-6.

Physical characterization and pseudo-compositional estimations have been achieved also by
scanning electron microscopy (SEM), helping in the identification of size and morphology of
the magnetic grains. The SEM was carried out in 6 PP samples (PP1B-A (30-38), PP2-B (25-
30), PP3B–A SUP, PP4-A, PP5P-B y PP6C-B) for the study of the physical structure, particle
size, morphology and location within the sandy material of the ferromagnetic particles.

Magnetic properties have been compared with magnetite content estimated in grain size
fractions run in a parallel study, specific details can be found elsewhere (Carmona Manzano,
2012). Recent sand samples have been physically classified into three fractions, Coase grain size
(C > 0.40 mm), medium (0.40<M<0.20 mm) and fine (F<0.20 mm). Magnetite content in the different particle sizes has been evaluated by X-ray diffraction. The most relevant heavy metal and metaloids concentration has been measured by X-ray Fluorescence (XRF), finding significant concentrations of Pb, Zn, Cu, As, Cd and Hg.

### 4 Results

#### 4.1 Low-field susceptibility

Values obtained for the magnetic susceptibility defined in low-field (300 A/m) are summarized in Figure 3a for sample PP and Figure 3b for M samples. They both show a large variability of values between $0.74 \times 10^{-5}$ and $14.70 \times 10^{-5}$ m$^3$/kg in the case of PP samples and from $-0.07 \times 10^{-5}$ to $6.35 \times 10^{-5}$ m$^3$/kg in M samples. Magnetic susceptibility of the sand samples are characterized by two relatively equal maxima centered at $1.7 \times 10^{-5}$ m$^3$/kg and $12 \times 10^{-5}$ m$^3$/kg, which suggests a bimodal distribution of the low field susceptibility (Figure 3a). The low field susceptibility of the mine sample, however, is characterized by one maximum value centered at $1.12 \times 10^{-5}$ m$^3$/kg (Figure 3b).

Measurements of the magnetic susceptibility in low-field with two frequencies indicate that there is almost no frequency dependence. Values vary between 0.01% and 1.66%, therefore the presence of superparamagnetic material (SP) is considered not to be significant (Hrouda, 2011).

#### 4.2 Hysteresis loops

The hysteresis loops all have very similar shapes for the PP samples (Figure 4a) and M samples (Figure 5a). Magnetization reaches the reversible state at a saturating field of about 250 mT, with no indications of a high coercivity fraction in the induced magnetization. Hysteresis derived parameters, however, show slight differences depending on the source (PP and M samples), as well as sampling site (PP1 to PP6) (Table 1). Remanence parameters ($M_s$ and $M_r$), display large variability, even recorded between twin samples from the same level and site, indicating a highly heterogeneous concentration of magnetic minerals (Evans and Heller, 2003).
Magnetic coercivity is less variable. The largest differences can be found associated to the sample source, with values between 10.28 and 12.72 mT from the sand samples and values between 11.52 and 15.49 mT, from the Emilia open pit samples (Table 1).

### 4.3 IRM-acquisition and back-field SIRM

SIRM acquisition up to 0.5 T and subsequent back-field SIRM curves of PP (Figure 4b) and M samples (Figure 5b) present a very similar shape. The beach sand samples do not have an initial remanence (Figure 4b) while samples from the mine have an original remanence magnetization, which is observed by an initial value of the SIRM at low fields (Figure 5b). Samples approach to saturation at about about 200 mT and asymptotically reach an almost constant value at 500 mT. Values of the S-ratio range between 11.72 and 4.15 % in sand beach samples and 7.49 and 2.19 in M samples (Table 1). Subsequent back-field SIRM shows $B_{cr}$ values between 24.8 and 30.4 mT for samples PP and 22.5 and 32.4 mT for samples M (Table 1).

Both SIRM and back-field SIRM show one inflection point (Figure 4b, Figure 5b) which suggests the presence of a single significant magnetic mineral responsible for the remanence within the soft coercivity fraction.

### 4.4 IRM-coercivity spectra

IRM acquisition curves and first derivative have been mathematically modeled following the procedure proposed by Kruiver et al. (2001). Figure 4c and Figure 5c show the example of the derivative of the IRM acquisition curve (Gradient Acquisition Plot, GAP) and its corresponding fitting using a series of log-normal distribution curves (Kruiver et al., 2001). All the analyzed samples have a similar behaviour, the gradient of the IRM acquisition curve is characterized by a main distribution that carries most of the magnetization (about 90% of the total SIRM) which has been named as Component 1. It has been necessary to include two additional components of low and high coercivity labeled Component 2 and Component 3, respectively, in order to reduce the residual of the GAP curve. The low coercivity component (Component 2) provides an average of 7% to magnetization and, at such low fields, its presence has been attributed to
thermal activation of magnetic particles (Heslop et al., 2004). Component 3 contributes only 3% to the total SIRM, but suggests the presence of a higher coercivity phase.

The field at which the SIRM acquisition curve reaches its inflexion point ($B_{1/2}$), or maximum value of the GAP, is used as an estimation of the average coercivity of the corresponding magnetic population carrying the remanence. Table 1 summarizes the values of the $B_{1/2}$ together with the associated dispersion parameter (DP) of the coercivity distribution.

Both samples PP and M have a very similar coercivity, with a mean $B_{1/2}=38.4\pm2.9$ mT for the samples collected from the Bay and $B_{1/2}=36.2\pm8.4$ for the samples belonging to the Emilia open pit. The results confirm the well-constrained coercivity found in the samples derived from the infilling process with the detachment having a larger variability of the magnetic properties (Table 1).

### 4.5 Thermomagnetic curves

Thermomagnetic curves for PP samples have very similar characteristics (Figure 4d) during heating and subsequent cooling magnetization processes. The Curie/Neél temperature ranged between 550 °C and 580 °C. This Curie/Neél temperature indicates the presence of either magnetite (Curie temperature is 580 °C), or titanomagnetite with low Ti content (Dunlop and Özdemir, 1997). The decrease found above 580 °C suggests the presence of a magnetic mineral that loses magnetization at 680 °C, i.e., hematite (Figure 4d). Since the susceptibility of hematite is lower than that of magnetite, the observation of the magnetization tail attributed to hematite suggests it contains large concentrations of it (Evans and Heller, 2003).

A closer analysis to the heating curve reveals two minor changes in the curve slope, one between 250 °C and 350 °C, approximately, and the second minor change around 450 °C and 550 °C, which might indicate the very mild transformation in the samples (Henry et al., 2005). These two features might be indicative of the presence of iron hydroxides and/or jarosite, that display a breakdown at about 250-300°C and often transforms into maghemite-hematite (Hanesch et al., 2006). The presence of goethite and jarosite has been confirmed by XRD.
measurements (Carmona, 2012) and it is also supported by the lower intensity of the cooling with respect to the warming curve.

The Curie/Neél temperature in M samples (Figure 5d) is also around 580 °C. However, the relationship between heating and cooling tracks has the opposite behavior. The heating curves show lower magnetization than the cooling track of the curve. Also, there is no clear evidence of a change in the slope of the curve for the 250-350 °C range (Figure 5d). The high temperature range does not suggest the presence of hematite (Figure 5d).

4.6 Domain state summary-plots: Day plot and FORC diagram

The also called Day plot is a good estimation of the domain state for magnetite and magnetite-like particles (Day et al., 1977). This representation discriminates the domain state separating in different areas of the diagram the coercivity ratios ($H_{c}/H_{c}$) as a function of magnetization ratios ($M_{r}/M_{s}$). Results from this study for samples PP and M are presented in Figure 6a. Both sets are clustered in the pseudosingle domain state (PSD) of the classical interpretation of the plot (Day et al., 1977) or a mixture of about 50% singledomain (SD) and 50% multidomain (MD) mixing curve 2 in the model proposed by Dunlop (2002).

The sand samples deposited on the Bay are magnetically softer with data getting closer to the MD state than samples from the mine (Figure 6a). Moreover, there is no significant shift toward the superparamagnetic mineral fields (Dunlop, 2002). Considering only the PP samples in the Day plot values are grouped according to the sampling site and spatial distribution within the Bay (Figure 6a).

The FORC diagram for PP sample suggests a distributed particle size in the PSD to SD range, as can be seen by the spread of the contour lines along the y-axes of the diagram (Pike et al., 1999; Roberts et al., 2000).
4.7 SEM

SEM micropictures using the secondary electrons method have been taken for every sampling site. This technique allows a quick identification of the large metallic fraction, visible as bright areas in the image (Reed, 2010). Figure 7 shows the images obtained for the six sampling sites. Big sand grains appear partially covered by smaller bright zones in their corners and edges in all samples (Figure 7a-f). A closer look into the morphological information of the grains shows hexagonal structures and planar crystals suggested to be jarosite grains (Figure 7b and 7c). Pseudocompositional analysis based on spectral identification of scattered electrons reveals these bright zones are related to the presence of magnetite intergrowths with quartz grain (Figure 7e-f). No heavy metals have been identified as single grains at this resolution level, indicating their sizes are smaller than the detection limit of the technique.

5 Discussion

The magnetic results provide information needed to answer three key questions in the study of mining debris: (i) are there a distinct difference in the physical-magnetic properties of samples from the Bay sands (PP samples) and original samples from the mine (M samples), (ii) is there a correlation between PP and M samples; and (iii) is there a correlation of the magnetic parameters with heavy metals content from the same sampling sites.

In order to study the spatial distribution along the Portman Bay, mean values and their corresponding uncertainties from hysteresis and remanence parameters (M_s, M_r, H_c, H_Cr, K_int, K_para, SIRM, B_{1/2} and S-ratio) of the PP samples have been computed. An arithmetic mean and standard deviations are graphically displayed in Figure 8. Sampling sites located at the edges of the Bay (PP1, PP1 – B or PP6) are significantly and statistically different from those sites located at the central part of the Bay. With these two spatial distributions (ends or central parts of the Bay) we have a uniform trend for every parameter that is broken by the values of the PP3 – B sample: this sample has widely scattered values with a large error bar that includes values within the general trend.
The results are consistent because there is a lower content of paramagnetic material (Figure 8a) in the central part of the Bay where the ferromagnetic contribution is greater (Figure 8b). Besides, \( \kappa_{im}, M_s, M_r \) and SIRM show the same spatial distribution (Figure 8b, c, d and g). \( B_{cr} \) has the same distribution that these parameters but with a very small variation range of its values (Figure 8f). \( B_c \) seems to show higher values at the ends of the Bay and lower in the central parts though, the PP3 - B and PP4 areas have higher values than their adjacent (Figure 8e). However, differences between sampling sites are small and their statistical significance is limited. \( B_{1/2} \) has its maximum for the PP4 area and the minimum for the PP1 area (Figure 8h). The S-ratio seems to display a similar trend as that observed for \( B_{cr} \) and \( B_{1/2} \) (Figure 8i). Indeed, S-ration statistically correlates to \( B_{cr} \) and \( B_{1/2} \) (Figure 9). The correlation between S and \( B_{cr} \) indicates the higher coercivity might be related to the presence of a high coercivity mineral (Figure 9a) while a correlation with the \( B_{1/2} \) might be related to variations in the magnetite grain size (Figure 9b). Results are not conclusive, but statistically, the correlation seems to be stronger with respect to \( B_{1/2} \), therefore a grain size dependence is expected between different sampling sites.

We can establish three different classifications according to the variability of the parameters in the Bay: (a) variation with depth, (b) spatial variation along the Bay and (c) temporal variation based on the age of the sediments that have been deposited in the Bay by considering its distribution.

(a) Taking into account the samples that have been collected at different depths in the Bay (PP1, PP1 - B, PP2, PP2 - B and PP3 - B), the parameters obtained do not vary with respect to depth (Table 1), at least for the studied depths, which did not exceed 80 cm. This suggests that alterations, diagenetic processes or transformations due to the sedimentary aging are not important (Evans and Heller, 2003). One should note, however, that the infilling was very rapid, so that the upper most layers have not yet started to undergo alteration; this does not preclude alteration of deeper strata, considering the total thickness of the mineral deposits which is estimated to be 10 m (Martinez-Sanchez et al., 2008; Manteca et al., 2014).
Figure 8 illustrates the spatial distribution of the hysteresis and remanence parameters but these may also be related to temporal effects, since the filling of the bay was earlier in some areas than others. Consequently, minerals have accumulated in some places for longer than in others.

The filling of the Bay began at the western edge of the bay (next to the discharge point where the wastes were poured into the sea) (Martínez Orozco et al., 1993), then the next stage was the waste infilling the bottom of the Bay from the south towards the north. Marine currents affected the way in which sediments have been deposited and distributed since they play a key role in differential particles sedimentation processes depending on their grain size. The coarsest grains have remained on the beach while the finest ones have been deposited at sea bottom. In addition, there is a dynamic mobility: in good weather conditions, the material has accumulated in deposits that are partially or totally destroyed during storms, and they are reformed in another place under more favorable weather conditions. Therefore, the coastline is constantly being modified and where the emerged beach is considered as unstable (Martínez Orozco et al., 1993).

In view of bathymetric maps (Martínez Orozco et al., 1993) we assume that the minerals in PP4 and PP3 samples are the oldest ones because that sampled area is the farthest from the coastline and this is observed in the similarities between parameters in PP4 and PP3A. Some of the magnetic parameters for the PP3 – B samples are significantly different from those measured in the adjacent PP3 –A area. Although we do not know the reason for this difference and the error bars associated with PP3 – B samples cover the general trend, perhaps the different geological properties that may present both samples have some influence: PP3 – A samples are duricrust while PP3 - B samples are not. It should be noted that the PP3 – B samples also contain sphalerite and abundance of jarosite (Carmona Manzano, 2012). Although these phases are paramagnetic at room temperature (Hunt et al, 2013; Majzlan et al., 2000), they may be associated with ferromagnetic intergrowths, which have not been observed under SEM.
The magnetite content determined by classical XRD has been correlated to the estimation derived from magnetic hysteresis. Because magnetization curves are mainly controlled by magnetite, Ms values from hysteresis can be transformed into percentage of magnetite dividing by the tabulated value of 90 Am²/kg (Dunlop and Özdemir, 1997). Values from each level depth have been averaged and standard deviation computed from Table 1. Estimations of magnetite by both methods are recorded in Table 2. The concentration of magnetite in PP samples varies between 21.83% and 0.97% by magnetic methods and 34.04 and 7.78% by X-ray diffraction (Table 2). M samples were only studied by magnetic methods, giving a variation range of magnetite from 5.8% to 0.02% (Table 1).

Magnetite content derived from hysteresis is correlated to κ_{ini} and M_r parameters (Figure 10a and b). The Pearson p-parameter for these two magnitudes gives a “strong correlation” with respect to the magnetite content according to the classification given by Evans (1996) with values higher than 0.8. Anthropogenic action constrains the range of values of the coercive field since what we find in Portman Bay (such as the PP samples) are the products of the mine extraction (such as M samples) (Figure 10c). Correlations are not conclusive, because the magnetite concentration of M samples is much lower than in PP samples.

Hysteresis and remanence results can be correlated with the magnetic granulometry of the PP samples and with the heavy metals content that was obtained by X-ray diffraction analysis (Table 2) (Carmona Manzano, 2012).

Magnetite has been fractioned into three grain-sizes and quantified by XRD: coarse (C), (> 0.40 mm), medium (M), (0.40 to 0.20 mm) and fine (F) (<20 mm) grains. Bulk M_s derived from magnetic hysteresis has been compared with the grain-size content in Figure 11a-c. The coarse-grain fraction is directly correlated with M_s while the opposite happens with the medium-grain fraction (Figure 11 b). Fine particles do not exhibited a good agreement with M_s (Figure 11c).

Because magnetite is known to be an effective heavy metals captor (Biswal et al., 2013; Mayo et al, 2007), M_s was compared with heavy metals content, specifically lead, zinc, iron, copper,
arsenic, cadmium and mercury determined by XRF (Carmona Manzano, 2012) (Table2). We obtained the best correlations for lead, copper and arsenic (Figure 11d,e and f). Copper and arsenic (Figure 11e-f) can not be correlated linearly, but we have few samples to try another fit.

Table 2 depicts the correlation found between the magnetite content by X-ray diffraction and magnetic methods. We observe that the slope of the correlation is nearly 1 and the determination parameter is high. In view of the results we can say that magnetic methods are faster and very effective for studies of Portman Bay (Figure 12). Particularly, magnetic methods are more suitable for low concentrations of magnetite, when XRD is known to have poor resolution.

6 Conclusions
We can conclude related to the study of the rock magnetic characterization of the Portman Bay in four main points:

a) The study of the magnetic properties of the PP samples has shown high magnetite content. Predominantly high concentration of magnetite in all samples with concentrations up to 21.8%.

b) Magnetically hard mineral phases such as hematite are detected by magnetic methods but quantification is not possible. The magnetite is relatively hard with saturating fields higher than 0.2 T. Despite having strong indications of the presence of iron hydroxides in the system, they do not contribute significantly to the remanence.

c) We have also observed that the magnetic properties of the PP samples correspond to a characteristic spatial distribution in the bay, and this distribution may be closely related to how sediments were deposited in the Bay depending on marine currents.

d) We do not observe significant variations in the magnetic properties with depth, up to values of about 80 cm, therefore diagenetic alterations, superficial transformations in maghemite and / or aging alterations can be excluded.
From the results, we observed agreement between the PP samples and M samples, despite the
differences attributed to the transformation in the processing plant.

In view of future research, a much more comprehensive bay sampling would be necessary, with
more samples of the coastline and especially from inside the Bay. Having a dense spatial
distribution of samples from the bay would allow for a better understanding of the interaction
between deposition and latter reworking from currents, including depth effects. It would also
allow for a better statistical evaluation. This would further develop the theory of spatial
distribution along the Bay of the parameters of the magnetic properties, test to a greater extent
the use of magnetite as captor heavy metal, clarify the formation of magnetic minerals,
determine the oxidized phases found in the thermomagnetic curves, etc.

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**Figure Caption**

**Figure 1.** Location of the Portman Bay in the Iberian Peninsula (white dot in the upper and right panel) and the collected samples along the coastline of the Bay (lower and left panel. Source: Google Earth).

**Figure 2.** Geology and mineral deposits of the Cartagena-La Unión Mining District (simplified after Manteca-Martínez and Ovejero Zapino (1992)).

**Figure 3.** Histograms of the low field magnetic susceptibility, $\kappa$ at (300 A / m) for PP (a) and M (b) samples.

**Figure 4.** Summary of analyzes with PP1B – A (0.20 – 0.30) sample. (a) Measured hysteresis loops (black) and after correction of the paramagnetic/diamagnetic contribution (red). (b) SIRM acquisition (up to 0.5 T) and SIRM back-field curves. (c) Gradient Acquisition Plot (GAP) for the raw data, the computed 1, 2 and 3 components and the sum of components. (d) Thermomagnetic curve with the warming-up (red) and cooling-down (blue) values. Arrows indicate the direction in which the process occurs. The inset shows a zoom into the higher temperature range of the warming up curve.

**Figure 5.** Summary of analyzes with M11 sample. (a) Hysteresis loops without paramagnetic/diamagnetic correction (black) and with such contribution (blue). (b) SIRM acquisition (up to 0.5 T) and SIRM back-field curves. (c) Gradient Acquisition Plot (GAP) for the raw data, the computed 1, 2 and 3 components and the sum of components. (d) Thermomagnetic curve with the warming-up (red) and cooling-down (blue) values. Arrows indicate the direction in which the process occurs. The inset shows a zoom into the higher temperature range of the warming up curve.

**Figure 6.** (a) Day plot (Day et al., 1977) of PP and M samples and the corresponding theoretical mixing curves proposed by Dunlop (2002). The inset shows zoom of PP samples (b). FORC diagram of material from site PP1.

**Figure 7.** Selection of images from PP samples obtained by SEM. Detection method of secondary electrons for a, b, c and f panels and backscattered electrons method for d and e panels. The samples were in each case: PP1B-A (30- 38), PP2-B (25-30), PP3B-A SUP, PP4-A-B and PP6C PP5P-B. The scales are at the lower and right part of each panel.

**Figure 8.** Spatial distribution along the Bay of the hysteresis parameters $\kappa_{para}$ (a), $\kappa_{ini}$ (b), $M_s$ (c), $M_r$ (d) and $B_C$ (e) and the parameters related with IRM acquisition $B_{cr}$ (f), SIRM (g), $B_{1/2}$ (h) and S-ratio (i). Red dots represent mean values for clustered samples in the Bay. Black bars represent the standard deviation.

**Figure 9.** Correlation between the S-ratio (%) and $B_{cr}$ (a) and $B_{1/2}$ (b). Red squares represent mean values for PP samples and blue diamond represents mean value of the M samples, all with their corresponding standard deviation.
Correlation has been computed only for PP samples and the figures display the $R^2$ is the coefficient of determination and $p$ is the Pearson correlation coefficient.

**Figure 10.** Comparison and correlation between hysteresis parameters $\kappa_{\text{ini}}$ (a), $M_r$ (b) and $B_c$ (c) of PP (red) and M (blue) samples. Black lines indicate the linear regression, $R^2$ is the coefficient of determination and $p$ is the Pearson correlation coefficient. PP samples represent mean values for clustered samples in the Bay. Black bars represent the standard deviation. Red dots represent mean values for clustered samples in the Bay. Black bars represent the standard deviation.

**Figure 11.** Comparisons and correlations for $M_s$ of PP samples. Comparisons with coarse (a), medium (b) and fine (c) fractions, in percentage, and with Pb (d), Cu (e) and As (f) contents in parts per million. Black lines: linear regression, $R^2$: coefficient of determination and $p$: Pearson's correlation coefficient.

**Figure 12.** Correlation between the two methods used to calculate the concentration of magnetite in PP samples. Black line: linear fit. $R^2$: coefficient of determination and $p$: Pearson's correlation coefficient.

**Table Caption**

| TABLE 1: Summary of the rock magnetic properties and magnetic characterization of samples from the Portman Bay Area (PP samples) and Mina Emilia (M samples). This includes saturation magnetization ($M_s$), saturation magnetization of the remanence ($M_r$), coercivity ($B_c$), coercivity of remanence ($B_{cr}$), initial low field susceptibility ($\kappa_{\text{ini}}$), saturation of isothermal remanent magnetization (SIRM), median destructive field of the main modelled coercivity spectra ($B_{1/2}$) and its corresponding dispersion parameter (DP) and S-ratio (%). |
| TABLE 2: Percentage of magnetite (Mt) derived from magnetic measurements and comparison with the estimation derived from XRD in the total fraction and the grain sized fraction (coarse, medium and fine). Heavy metal content when measured |
(a) $y = 0.666x + 22.18$
$R^2 = 0.8376$
$p=0.8373$

(b) $y = 1.7427x + 23.861$
$R^2 = 0.8647$
$p=0.9299$
(a) $R^2 = 0.7154$

(b) $R^2 = 0.5016$

(c) $F\%$

(d) $R^2 = 0.6287$

(e) $M$%

(f) As (ppm)

$p = -0.8458$

$p = 0.7082$

$p = 0.7929$