Discerning the major environmental processes that influence the magnetic properties in three northern Iberia mountain lakes

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Abstract

In the Iberian Peninsula, magnetic proxy investigations in continental environments are increasing but still scarce. Paleoenvironmental reconstructions from three mountaineous lakes located in northern Iberia are compared and completed with classical magnetic analyses in order to detect the influence of different processes on the record and preservation of magnetic properties. The lakes are located in the Cantabrian Mountains, Enol Lake, and in the Pyrenees, the Marboré Lake and Basa de la Mora Lake and share a similar composition of their catchment areas, dominated by limestones. They present other different characteristics, such as in the organic matter content, being Enol the one with the highest organic carbon values. Redox indicator (Mn/Fe) is higher and more variable in Basa de la Mora Lake, whereas in Enol and Marboré Lakes steadily increases towards the top of the sequences. New and revisited results unravel the significance of the magnetic changes respect to the geochemical and sedimentological variations found in the geological record. These results suggest that diagenesis and changes in the redox conditions alter the concentration of magnetic minerals during the Late Pleistocene and Holocene and underlines their value as environmental and paleoclimate archives.

Keywords: paleolimnology, northern Spain, magnetic properties, mountain lakes

1. Introduction

Lacustrine sediments represent extraordinary and useful sources of information about past environmental and climatic changes all over the world throughout the analyses and interpretation of their sedimentological, geochemical and biological composition (Cohen, 2003). Particularly, mountain lakes are especially sensitive to changes in their environment as a consequence of their location in extreme settings in terms of low temperatures, days with ice cover and/or amount of snow precipitation. Those lakes act as sentinels, reacting rapidly after an environmental change and storing that information in their sediments (Catalán et al., 2013). Most of their sediments are even laminated, with a seasonal deposition of the different layers: organic-rich one associated to the ice-free season (summer) and clayish one when the lake is ice-covered (winter) (eg. Blass et al., 2007). Unfortunately, not the same environmental change is recorded in the same way under different lacustrine settings due to local processes that influence the deposition of sedimentary facies. For example, a temperature rise may be observed as an increase in the precipitation of carbonate in a particular setting while in other lake is the lacustrine organic matter the sediment fraction that experiences an increment (eg. Kelts and Talbot, 1990). To be able to unravel the past environmental history from the succession of facies in a lacustrine sequence a thoughtful understanding of the present-day behavior of the specific system is necessary together with a multi-proxy study of the lake sediments. One of those proxies that store environmental information is the magnetic content of the sediments, usually – but not always – associated to the detrital input arriving to the lake by runoff processes.

The magnetic properties of lacustrine sediments have been increasingly used to decipher erosion, transportation, deposition, postedepositional alteration and/or new formation, of magnetic minerals related to environmental changes (Evans and Heller, 2003; Liu et al., 2012). Due to the wide array of processes that a specific concentration, grain size or type of magnetic mineral can reflect in a terrestrial environment, it is necessary to understand the catchment evolution and the variability recorded by the sedimentary sequence before interpreting the environmental processes that led to changes in the magnetic properties. Thus, additional proxies such as geochemical (organic and inorganic carbon content, qualitative and quantitative analyses of major element), sedimentological observations (smear slides, grain size), biological (i.e., chironomids, diatoms) are a requirement. In part, the main problem to interpret the magnetic properties, particularly magnetic susceptibility, of lacustrine sediments, relates to the fact that, magnetic susceptibility reflects the content of all magnetic minerals: ferromagnetic minerals *s.l.* (i.e., magnetite, goethite), which contribute with high positive values, paramagnetic minerals (i.e., phyllosilicates), which contribute with medium positive values, and diamagnetic minerals (i.e. quartz, calcite), which, contribute with low negative values (Jackson and Borradaile, 2004). Therefore, higher content of ferromagnetic minerals will increase the magnetic susceptibility value. Usually, the magnetic minerals are more abundant when there is more detrital input to a particular lake and thus often related to runoff processes (i.e., when phyllosilicates or ferromagnetic are abundant), however, not always the type or concentration of those minerals is strictly related to allochthonous (exogene) processes. Sometimes, the abundance of organic remains in the sediments controls the diagenetic processes affecting ferromagnetic minerals through methanogenesis, first with the neoformation of oxi-hydroxides such as magnetite, maghemite or hematite in the aerobic respiration zone (near the interface water-sediment), whereas pyrite or greigite (iron sulphides) occur in deeper parts of the sediment during the anaerobic oxidation of methane (Roberts, 2015 and references therein). The neoformation of strong magnetic magnetite increases magnetic susceptibility and the laboratory induced remanence (ARM: anhysteretic remanence magnetization). The iron reduction occurring in deeper parts of the sediment dissolves magnetite, creating the environment for the anaerobic oxidation of methane and if sulphate is available, for example, due to weathering of rocks containing pyrite, sulphate reduction occurs and then, pyrite (paramagnetic mineral) and greigite (ferromagnetic mineral) can form (Roberts, 2015 and references therein). Other times, lake depth and lake water mixing characteristics will also control the amount of oxygen in the lake bottom favoring changes in the redox properties that may lead to diagenetic processes altering the type, size or concentration of magnetic minerals (Roberts, 2015 and references therein). The study of lakes with different characteristics, such as – for example - a distinct organic matter concentration, may help to unravel the environmental meaning of observed changes in the magnetic properties.

The Iberia Peninsula, and particularly the high mountains such as the Pyrenees or the Cantabrian mountains, are ideal locations to reconstruct past environmental changes over the last glacial cycle due to the demonstrated sensitivity and rapid response to climate variability in the North Atlantic area (González-Sampériz et al., 2006; Moreno et al., 2012; Bartolomé et al., 2015). During the last years, several new high-resolution multi-proxy studies were developed on mountain lakes in the Pyrenees and Cantabrian Mountains allowing describing the last deglaciation and Holocene climates (e.g. Moreno et al., 2011; Oliva-Urcia et al., 2018) and the local responses in the environment, such as changes in the vegetation cover (Pérez-Sanz et al., 2013; Leunda et al., 2017) or fire frequencies (Gil-Romera et al., 2014). Magnetic properties are often misrepresented on those multi-proxy studies and, unfortunately, information about the concentration, variability and type of magnetic minerals is not usually integrated with sedimentological, geochemical and biological indicators.

In this study, we benefit from the previous investigation of three mountain lakes in northern Iberia to evaluate the influence of different environmental processes on the magnetic properties of lacustrine sediments. Thus, the multi-proxy study of Enol Lake (Cantabrian mountains) and Marboré Lake and Basa de la Mora Lake (central Pyrenees) is here complemented by the analyses of magnetic indicators (magnetic susceptibility, and the magnetic signal due to “soft”, as for example magnetite, and “hard” as for example goethite, ferromagnetic minerals) thus providing an excellent opportunity to (1) integrate magnetic properties as additional tools to reconstruct past environmental changes in northern Iberia and (2) investigate the subjacent processes that influence on the record and preservation of magnetic properties in lacustrine sediments from high altitude areas.

2. Setting

The three selected lakes are located in northern Iberian mountains (Figure 1, Table 1).

<u>Enol Lake</u> (43º16’N, 4º59’W, 1070 m asl; Figure 1; ENO) is located in the Western Massif of the Picos de Europa Mountains. From a geological point of view, this area is located in the Eastern part of the Cantabrian Zone in a catchment dominated by Carboniferous limestones, (Alba, Barcaliente, Valdeteja and Picos de Europa Formations) and Carboniferous detrital formations, mainly composed by lutites. The study area is characterized today by temperate oceanic climate, with high annual precipitation (above 1000 mm) due to the proximity to the ocean. Winters are mild and summers are cool with a annual temperature of ca. 13°C. Rainfall mostly occurs in winter, associated with mid-latitude storms from the Atlantic Ocean. The region is

located within the phytogeographical Eurosiberian region. The mentioned mild-humid climatic characteristics favour the development of dense deciduous forest formations, mainly in oceanic wind slopes where, in addition, peatlands are abundant. Lake waters are oligotrophic (total phosphorus 8 μg l^{-1}, moderately hard and carbonate and calcium - rich ($[HCO_3^{2-}] > [Ca^{2+}] > [SO_4^{2-}]$) with a conductivity of 202 μS cm^{-1}. Calculations of mineral speciation indicated that present-day bottom water is undersaturated in calcite, at least seasonally (Moreno et al., 2010).

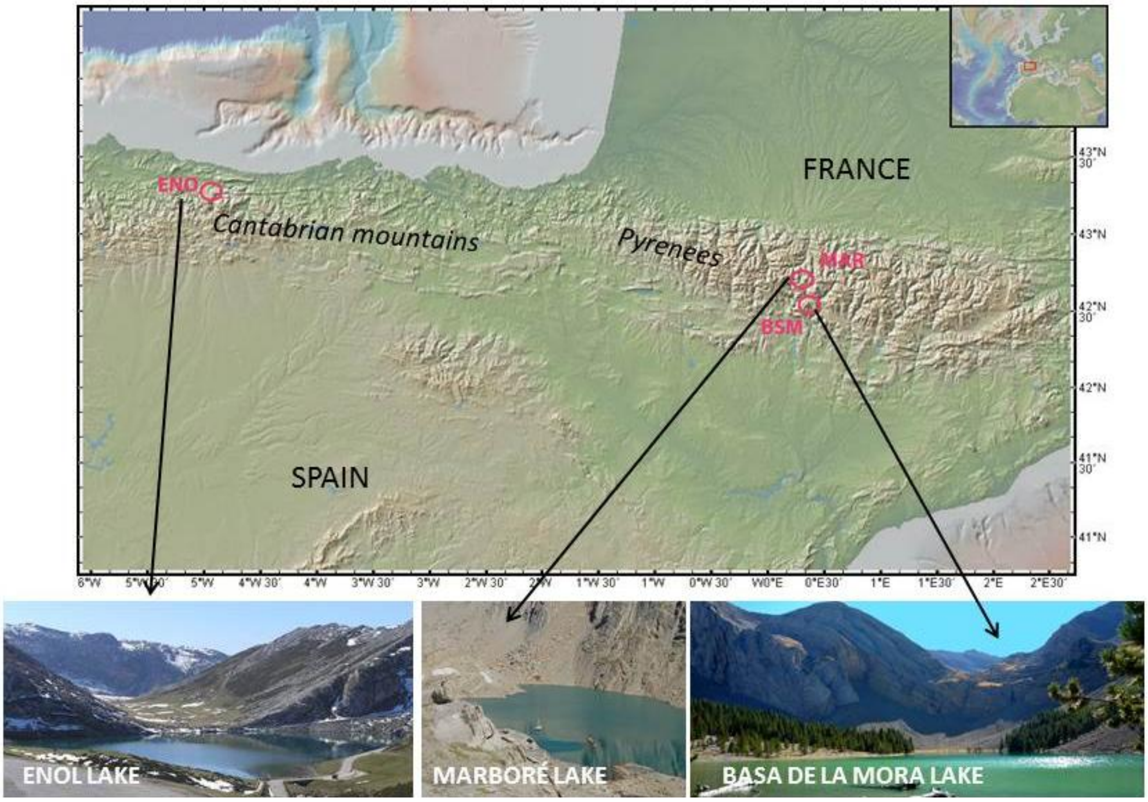

Figure 1. Location in northern Spain of the three studied lacustrine sequences. ENO for Enol Lake; MAR for Marboré Lake and BSM for Basa de la Mora Lake.

<u>Marboré Lake</u> (42º 41’44.27’’N; 0 º20’24.07’’E; 2612 m asl, Figure 1; MAR) is located in the central part of the Pyrenean Internal Sierras (Figure 1), a range composed of carbonaceous Meso-Cenozoic rocks and characterized by south vergent thin-skin thrusts and folds that bound the Axial Zone towards the south (Mattauer and Seguret, 1971). Glacier activity and karstic processes have determined the unique relief of this area, the largest high-altitude carbonate massif in Europe. Marboré Lake is located in a syncline and its watershed lies above the Cretaceous (Campanian-Maastrichtian) Marboré Sandstone formation, constituted by carbonatic limolites (siltstones) from marine

platform environments (Souquet, 1967). The Central Pyrenees encompasses the transition between Mediterranean and Atlantic climate regimes and vegetation regions in a relatively small area. The mean annual temperature during 1982–2001 from Góriz, the nearest meteorological station, located 3 km south of the lake at 2220 m asl, was 4.9 ± 0.5 º C. The coldest month was January (-0.7 º C) and the warmest July (13 º C), with mean annual precipitation around 2000 mm. The vegetation cover around the lake is very scarce, with only some patches of alpine herbaceous rocky species. Nowadays, the tree-line in this valley (mainly formed by *Pinus uncinata* communities) is located around 2000 m asl, and consequently no woody vegetation is present in the cirque or nearby area. Limnological properties are summarized in Sánchez-España et al., (2018), highlighting here it is an ultraoligotrophic, cold dimictic lake with alkaline waters. From November to July, ice and snow up to several meters thick cover Marboré Lake, with water-column temperatures ranging from 0 to 3ºC. Preliminary geochemical modeling indicates that the physico-chemical conditions in the water column are favorable to calcite dissolution.

<u>Basa de la Mora lake</u> (42º32’ N, 0º19’ E, 1914 m asl; BSM) is a small, shallow glacial lake located on the north-facing slope of the Cotiella Peak (2912 m a.s.l.), the highest summit of the Cotiella Massif in the central southern Pyrenees (Figure 1). The Cotiella Massif belongs to the homonymous nappe, located in the western part of the South Pyrenean Central Unit (Séguret, 1972). The landscape surrounding the lake results from intense karstic and glacial activity. The catchment consists of Mesozoic limestones and sandy limestones affected by several thrust sheets (reverse faults). Triassic ophite formations in the watershed are the source of highly characteristic sediments (magnetite, Fe-oxide with high magnetic susceptibility) within the lake deposits. The climate of the study area is sub-Mediterranean with continental features. Rainfall (annual average is 1360 mm) peaks during spring and autumn, following the Mediterranean pattern. However, summers are not as dry as is typical of the Mediterranean because of frontal and convective precipitation which affects the mountainous areas in July and August. Mean air temperatures range from 0.5 to 15ºC between the coldest (January) and warmest (July) months, respectively. The vegetation cover shows a characteristic contrast between south and north facing slopes: the southern slopes are characterized by Mediterranean-type components with sclerophyllous shrubland and evergreen Quercus communities, while the northern

slopes have mixed conifer/deciduous taxa forests. BSM is located in the subalpine belt, near the treeline, so the vegetation surrounding the lake is alpine grassland, *P. uncinata* forest and *J. communiseR. Ferrugineum* shrublands.

3. Material and methods

3.1. Coring and multi-proxy methodology

<u>3.1.1. Enol Lake.</u> The lake was cored in 2008 during LIMNOCLIVER field expedition using a modified Kullemberg platform (see details in Moreno et al., 2011, 2010) and the sedimentary sequence (6 m) recovered in its totality reaching glacier till at the base of the cores. Chronology of the studied core was determined based on 12 ^{14}C AMS dates and a detailed multi-proxy study allowed describing the paleoenvironmental variability of last 38 ka BP in northern Spain (Moreno et al., 2010). Physical properties (including magnetic susceptibility and Gamma Ray Attenuation – GRA - bulk density) were measured every cm with a standard GEOTEK Multi-Sensor Core Logger (MSCL). The cores were split, imaged with a DMT core scanner and analyzed for optical properties. Total Carbon (TC) and Total Inorganic Carbon (TIC) contents were determined every 5 cm by a UIC model 5011 CO_2 Coulometer at the LRC and Total Organic Carbon (TOC) was calculated by subtraction. X-Ray Fluorescence (XRF) data used in Moreno et al., (2010) were produced by the ITRAX XRF core scanner from the Large Lakes Observatory (Duluth) of the University of Minnesota (USA) using 30 seconds count time, 30 kV X-ray voltage, an X-ray current of 20 mA, a step size from 1 cm to 2 mm and a Molybdenum anode x-ray tube to obtain significant data of the following elements: Si, K, Ca, Ti, V, Cr, Mn, Fe, Rb, Sr, Y, Zr, Ba, Pb. Sedimentary facies and units were previously described in Moreno et al., 2010 and 2011 in base of sedimentological, geochemical, and biological data allowing to describe glacial and environmental evolution since last deglaciation (Figure 2).

<u>3.1.2. Marboré Lake</u>. The lake was core in 2011 using an Uwitec platform in the deepest part of the lake (Oliva-Urcia et al., 2018). The studied sequence, finely laminated to banded silts, is composed by the combination of long core MAR11-1U-1A (7 meters) and short core MAR11-1G-1A-4 (20 cm), correlated by Pb concentration values, covering last 14.6 ka. The cores were opened, photographed and sampled at the

laboratory of IPE-CSIC in Zaragoza, Spain. Sedimentological analyses, i.e. measures of composition and texture of the sediment, were done by optical microscopy observation of smear slides, following the method proposed by Schnurrenberger et al. (2003). Chronological framework is based on the 210Pb model (with the AD1963 137Cs peak), 13 AMS 14C dates and three tie points (beginning of the spread of Abies and Tilia and the spread of Olea). The multi-proxy study for this research includes the determination of mineral assemblages by X-ray diffraction, analyses of TOC and TIC at 2-cm resolution in a LECO SC144DR analyzer at the IPE-CSIC and X-ray fluorescence (XRF) analyses performed with an AVAATECH XRF II core scanner at the CORELAB laboratory (University of Barcelona) at 0.5 cm resolution. All data together allow to define four sedimentary units as indicated in Figure 2.

3.1.3. Basa de la Mora Lake. The lake was core in summer 2008 with an Uwitec coring system and platform from the Pyrenean Institute of Ecology (IPE-CSIC). Using the combination of long core (BSM08-1A-1U) and short gravity cores (BSM08-1B-1G) the studied sequence is 12.1 m long. The cores were split lengthwise into two halves, imaged with a DMT Core Scanner and analysed with a Geotek Multi-Sensor Core Logger (MSCL) at 5 mm intervals to characterize the sediment physical properties at the Limnological Research Center at the University of Minnesota (USA). Elemental geochemical composition was analysed using the Itrax XRF Core Scanner at the Large Lakes Observatory (LLO) at the University of Minnesota (USA) at 0.5 cm resolution using 30-s count times, 30 kV X-ray voltage, and an X-ray current of 20 mA. The cores were sub-sampled at 2 cm resolution for TOC and TIC and analysed with a LECO144DR elemental analyser at the IPE-CSIC laboratory of Zaragoza (Spain). Sedimentary facies were defined by macroscopic characteristics including colour, grain-size, sedimentary structures, fossil content and by microscopic smear slide observations (Schnurrenberger et al., 2003). Sedimentary units were defined after the multi-proxy study (Figure 2).

3.2. Magnetic properties

Sampling for the measurements of environmental magnetism was done by means of u-channels embedded in one half of the core. Previous magnetic measurements of the Marboré Lake are presented in (Oliva-Urcia et al., 2018), they were carried out at every

2 cm at the at the Archeomagnetic Laboratory of the Spanish National Research Centre for Human Evolution (CENIEH, Burgos, Spain). New magnetic measurements (except magnetic susceptibility) from Enol (ENO) and Basa de la Mora (BSM) Lakes are presented here. The new measurements were done every 1 cm in a 2G cryogenic with and automated alternating field (AF) demagnetizer in the Institute for Rock Magnetism of the Department of Earth Sciences, at the University of Minnesota (USA). Stepwise demagnetization was done up to 100 mT. Subsequently, anhysteretic remanent magnetizations (ARM) were performed with a DC field of 50 nT under an AF of 100 mT and then stepwise demagnetized. In addition, isothermal remanent magnetizations (IRM) were performed with a pulse magnetizer (2G Enterprises) at 100 and 300 mT after applying 1000 mT in the opposite direction (Opdyke and Channell, 1996). In Basa de la Mora Lake, IRMs measurements saturated the cryogenic, therefore, no reliable results are available.

The variations with depth of the magnetic signal are represented by the χ_{ARM}, the IRM_{150mT} or IRM_{100mT}, the IRM_{1T} and IRM_{1T}/χ_{ARM}. The χ_{ARM} is the ARM normalized by the applied DC and also represents the concentration of low coercivity minerals, called “soft” in Fig. 4 (i.e., magnetite), whereas the IRM_{1T} reflect the concentration of the antiferromagnetic minerals (minerals with high coercivity: hematite, goethite) and the total of ferromagnetic *s.l.* minerals respectively (Hunt et al., 1995; Oldfield, 1991; Ortega et al., 2006; Wang et al., 2010), it is called “hard” in Fig. 4. The $SIRM/\chi_{ARM}$ ratio indicates the magnetic domain or “magnetic grain size” (Peters and Dekkers, 2003). Bi-plots of these analyses will help to characterize the magnetic signal of the sediments. Special attention was paid to parameters potentially indicative of magnetic mineralogy (IRM_{1T}/χ), concentration (χ, χ_{ARM}, IRM_{1T}), and grain size ($SIRM/\chi_{ARM}$) (Thompson and Oldfield, 1986; Verosub and Roberts, 1995; Peters and Dekkers, 2003; Liu *et al.*, 2012).

In addition, samples (20 in BSM and 14 in ENO) were analyzed in the Magnetic Property Measurement System (“old blue” MPMS, Quantum Designs) at the Institute for Rock Magnetism (Minnesota), to characterize the magnetic mineral present. Measurements comprise: i) remanence on cooling: at 20K sample is subjected to a 25,000 Oe field, then it is turn off and sample warms up to 300K while measuring the remanence. ii) Remanence on warming: at 300K sample is subjected to a 25,000 Oe field, then turned off and the remanence is measured applying field cooling and zero field cooling while measuring the remanence. The decrease of remanence in the first curve may be due to superparamagnetic unblocking, crystalographic transitions (i.e., Verwey, Morin transitions), changes in magnetocrystaline anisotropy or spontaneous magnetization (Dunlop and Özdemir, 1977). The decrease of remanence in the second curve is mostly due to crystallographic transitions (diagnostic of ferromagnetic minerals). iii) Field cooling- a 25,000 Oe field is applied at 300K and is kept on while cooling, then sample is warm up while remanence measured. iv) Later, sample is cool down in zero field to 20K, and warm up while measured the remanence. Rapid decrease of remanence before 50K usually marks the presence of superparamagnetic (SP) grains (Sun and Jackson, 1994; Xu *et al*., 1998).

In Burgos University (Spain), 18 BSA and 6 ENO samples were analyzed in the Curie Balance (MMAVFTB, Petersen Instruments) to measure saturation magnetization (Ms); remanent magnetization, (Mrs); coercivity (Hc); and remanence coercivity (Hcr) together with isothermal remanent magnetization (IRM) acquisition curves, back-field curves, and thermomagnetic curves to determine the magnetic mineral present. Discrete Marbore Lake samples were analyzed in the Curie Balance and some of them presented in the supplementary material of Oliva-Urcia et al. (2018).

First-order reversal curve (FORC) diagrams were obtained for 8 samples in Marboré and Basa de la Mora Lakes in order to discriminate magnetic interactions and the coercivity of ferromagnetic minerals. Analyses were performed at the CENIEH in a MicroMag 3900 vibrating magnetometer (VSM - Princeton Measurements Crop.).

4. Results

4.1. Sedimentological characterization of three mountain lakes

Enol Lake is a proglacial lake formed at ca. 38 ka BP once the glacier started to retreat and the melting waters were dammed by a frontal moraine. The chronology for the lowest part of the sequence was not easy to determine due to the extremely low organic content as a consequence of a barren landscape with a nearby glacier until ca. 26 ka BP.

At that time, the sediments change from clayish laminated sediments (Unit 3) to silty-clay slightly organic sediments (Unit 2) (Figure 2). Thus, Unit 3 results from the alternation of gray banded to laminated siliciclastic silts with few intervals of light gray banded carbonate silts, both facies with very low TOC content while, after 26 ka BP, TOC values show a slight increase along Unit 2. In a previous study (Moreno et al., 2010) it was proposed that from 38 to 26 ka BP the lake behaved as a proglacial lake while, after 26 ka BP, we could consider a glaciolacustrine environment. The catchment area is made of limestones but, surprisingly, carbonate is not present in the sediments in a significant amount until Unit 1 (ca. 18 ka BP) with the dominance of Facies 5, when climate conditions improved and permitted a forest development surrounding the lake. The Holocene sedimentary sequence, formed by light gray carbonatic silt with higher organic content, is described in Moreno et al. 2011 where diatoms, ostracods, pollen and geochemical indicators point to a benign climate, warm and wet enough to maintain a mesophilious forest in the area. The last 4500 years were characterized by the first evidences of human activities, mainly grazing and mining in this region (presence of species such as *Juglans* and *Rumex*). Therefore, the sedimentary facies and the rest of proxies, represented in Figure 2 by Ca/Ti as an indicator of carbonate, TOC% as organic productivity proxy, Zr/Rb as a grain size proxy and Mn/Fe as an oxidation indicator, clearly define three stages in the lake evolution that correspond with the three sedimentary units.

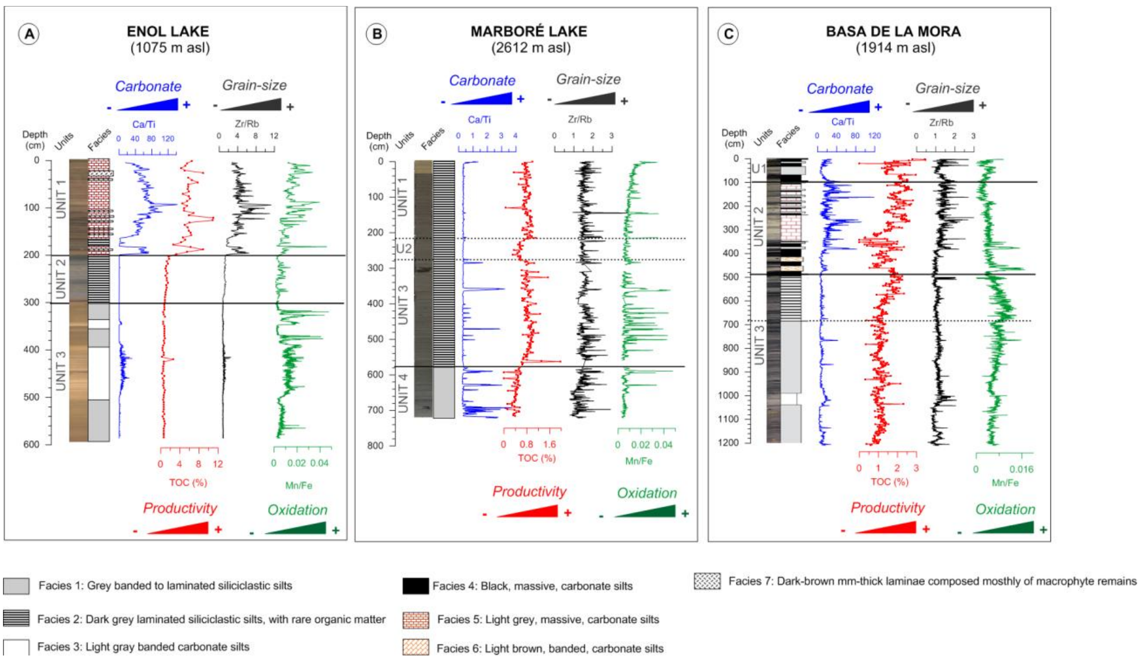

Figure 2. Sedimentology and geochemical ratios of the three lacustrine sedimentary

sequences. A. Enol Lake. B. Marboré Lake. C. Basa de la Mora Lake. The three sequences are represented versus depth and four proxies are shown: Ca/Ti as an indicator of carbonate in the lake (authigenic or detrital); Total Organic Carbon (TOC) percentage as a proxy for productivity (in-lake or transported from the catchment), Zr/Rb ratio as grain-size information and Mn/Fe ratio as a redox indicator. Sedimentary facies and units are indicated. Noted that facies 1 to 7 are shown in the Legend. For more information refer to text and previous references.

Marboré Lake was also a proglacial lake fed by the melting waters of a small glacier located in the NW edge of the lake as demonstrated by historical documents and photographs from the nineteenth and early twentieth centuries (García-Ruiz et al., 2014). The sequence recovered cover the last 14.6 ka indicating that at that time the glaciers were already retreating at high altitude (2600 m asl). The sediments in the Marboré Lake sequence are laminated fine silts and silty clays, characterized by the occurrence of mm-thick brown, white and grey laminae with some cm-thick laminae (bands) in a few intervals (Figure 2). Mineralogical composition is homogenous, mainly dominated by clay minerals (illite and muscovite/biotite, chlorite and minor kaolinite) and, as secondary minerals, feldspars, quartz and sporadic calcite of detrital origin (Oliva-Urcia et al., 2018). The lowest unit (Unit 4) is the one with the lowest values of TOC but the highest of carbonate, particularly in some intervals, represented in Figure 2 by the peaks in the Ca/Ti ratio (Facies 1). As in Enol Lake, the catchment is dominated by limestones but the extremely cold conditions seem to have favored dissolution of carbonate particles once arriving to the lake. The available petrographic, textural and compositional data, all suggest that the origin of laminations in Marboré Lake is similar to that in previously studied varved sediments, thus pointing to a seasonal origin: the calcite-rich, coarse silt/sandy brownish laminae deposit during warmer periods (melting season, summer) and the fine-grained, clay-rich greyish laminae form during colder periods when the lake is ice-covered (Blass et al. 2007). The preservation of calcite is, thus, conditioned to long and/or warmer summers of last deglaciation while other intervals such as GS-1 are marked by clayish sediments without TOC (Oliva-Urcia et al., 2018). Unit 3, characterized by a slight increase in the sedimentation rate and in the organic content in the lake sediments, represents the Early Holocene period, with warmer and more humid conditions after 10.5 ka BP, as also pointed out by a detailed palynological study (Leunda et al., 2017). After 7500 years BP (500 cm depth), the occurrence of brownish and whitish laminae (summer) and the higher frequency of TIC peaks, suggest conditions more conducive to carbonate preservation (higher temperatures and alkalinity) and Mn oxide formation (oxic conditions). The highest TOC values also indicate that the best conditions for lake productivity at this high elevation occurred during the Mid Holocene. Unit 2 is characterized by a decrease in TOC values and sediments with no well-defined laminations and interpreted as an interval of increased clastic delivery to the lake, maybe associated with the end of the Neoglacial and the changes in surface hydrology caused by glacial retreat (Oliva-Urcia et al., 2018). Well defined laminations, relatively higher TOC and the occurrence of two Pb peaks characterized Unit 1 (220–0 cm depth).

Basa de la Mora Lake occupies a glacial overdeepened basin enclosed by a frontal moraine (Belmonte-Ribas, 2014) and surrounded by steep limestone walls. Six sedimentary facies were identified in the sedimentary sequence based on visual description, microscopic observations, grain-size data and mineralogical and geochemical composition (Pérez-Sanz et al., 2013). The sediments consist of either: i) carbonate-poor (<2% TIC), with lower TOC and high κ (Facies 1 to 3 in Figure 2), organized in laminated or banded intervals, or ii) carbonate-rich with variable, but higher organic matter content and low magnetic susceptibility, arranged in massive to banded deposits (Facies 4 to 6). The studied sequence has been divided into three main sedimentary units (Figure 2) covering last 10 ka BP. Unit 3 is characterized by banded carbonate-poor sediments, low Ca/Ti ratio values and relatively low TOC percentages while Si, K, Ti values (and particularly Fe and Mn) – not shown - are high (Facies 1, 2 and 3). This unit allows interpreting a period characterized with permanent and relatively high lake levels with abundant sediment delivery by run-off (10-6 ka BP). Later on, a change occurs and carbonate starts to precipitate in the lake. Unit 2 is made up of carbonate-rich Facies 5 and 6 with intercalations of organic rich Facies 4. TOC percentages are relatively high and are interpreted as an increase in the lacustrine organic matter. This unit represents a drier and probably warmer time interval (6 to 1 ka BP) corresponding to the Mid to Late Holocene. Finally, the last meter of the sequence (Unit 1) corresponding roughly to the last millennium, is characterized by the alternance of carbonate-poor Facies 1 and organic-rich Facies 4, with, in general, high TOC percentages and low Ca/Ti ratio. This Unit corresponds with the Medieval Climate Anomaly and the Little Ice Age, when intensified human disturbance is detected (Pérez-

Sanz et al., 2013).

4.2. Magnetic properties of three mountain lakes

4.2.1. Magnetic minerals

The analyses done in discrete samples (less than 500 mg) reveal the presence of magnetite in all samples by a sharp decrease at 120 K (Verwey crystallographic transition) and 580ºC (Curie temperature of magnetite) in the thermomagnetic curves performed in the MPMS and the Curie balance respectively (Fig. 3, a); b) and c) (Verwey and Haayman, 1941; Dunlop and Özdemir, 1997 and references therein). The decrease at 120K is sharp in some samples, see in Fig. 3 BSA, ~8,900 cal yr BP and ENO, ~24,200 cal yr BP, indicating that magnetite is stoichiometric (Smirnov et al., 2002). In addition, the thermomagnetic curves at low temperature (MPMS analyses) reveal in Enol Lake sediments the presence of goethite, due to the large increase in magnetization upon cooling of the room temperature IRM (Guyodo et al., 2006) (b) in Fig. 3. The FC-ZFC analyses show two different behaviors, in Enol Lake, all samples show a larger ZFC remanence than the FC remanence, whereas in Basa de la Mora Lake, more magnetic variability is present, with a behavior that show little difference in the remanence at low temperatures between FC and ZFC curves. The first behavior relates to a large presence of superparamagnetic (SP) grains of magnetite (nm), that at room temperature have short relaxation times and show a continuous reorganization of their magnetic moment, therefore remanence is zero. However, at low temperatures, relaxation time increases and then the SP grains contribute to the remanence. In addition, at room temperature and under a magnetic field, all magnetic moments of SP grains align and they present a high magnetic susceptibility. The decrease of remanence in warming at very low temperatures (under 50 K) is indicative of SP grains, which is observed in all diagrams (a) of Fig. 3 (Dunlop and Özdemir, 1997, Xu et al., 1998). No indication of neither pyrrhotite (phase transition at 35 K) nor siderite (Néel temperature of 38 K) is observed (Smirnov et al. (2000) and references therein). The high temperature thermomagnetic analyses (Fig. 3 (c)) show the presence and creation of magnetite during heating, see an increasing of induced magnetization forming a broad peak above 450ºC in the heating curve. In addition, a subtle change in the induced magnetization is observed at around 300ºC (the Curie temperature of pyrrhotite is

325ºC; Deckers, 1989).

All analyses related with coercivity (Fig. 3, diagrams d and e) indicate the predominance of low coercitive minerals (“soft”) as magnetite is. The isothermal acquisition of remanence –IRM– and the back-field –BF– curves at room temperature, are shown in diagrams (d) in Fig. 3, IRMs usually saturate above 150-200 mT, and back fields (coercivity of the remanence) are lower than 100 mT. The hysteresis loops (diagrams e in Fig. 3) show saturation of the magnetization at very low fields (less than 200 mT).

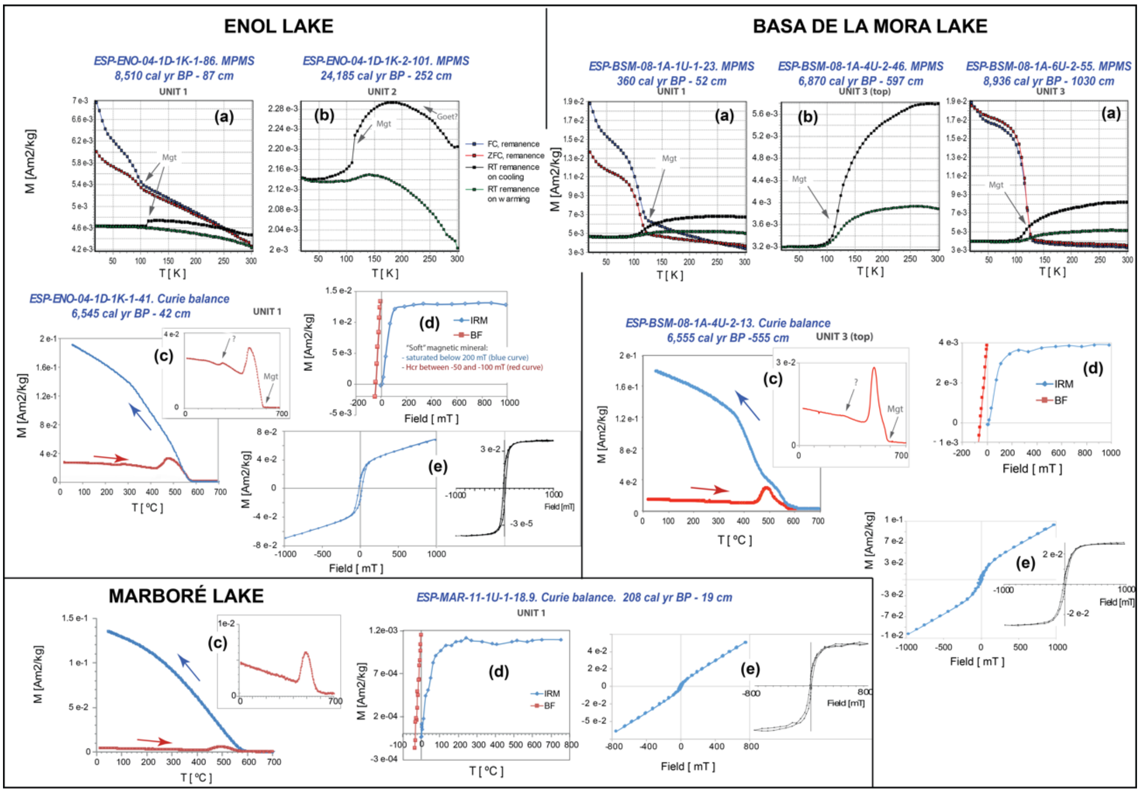

Fig. 3. Selected discrete samples analyzed in the MPMS and Curie balance, age and composite depth are shown. (a) remanence on cooling (black), remanence on warming (green), field cooling –FC– (blue) and zero field cooling –ZFC– (red); (b) remanence on cooling (black), remanence on warming (green); (c) thermomagnetic curve; (d) IRM acquisition and back-field; (e) hysteresis loops, uncorrected (blue) and corrected (black). Results from from Marboré Lake sample (c and d) were presented in the Supplementary material in Oliva-Urcia et al. (2018). Mgt: magnetite, Goet: Goethite.

In summary, the main ferromagnetic mineral present is magnetite in all facies and ages in the three lakes. In addition, SP magnetite grains are revealed by the low temperature measurements in Enol Lake and in some samples of Basa de la Mora Lake (Marboré Lake has no such analyses). Goethite seems to be present in Enol Lake samples. It is worth mentioning that strong magnetic magnetite tends to dominate the magnetic signal, for example, respect to weak magnetite goethite (Guyodo et al., 2006).

4.2.2. Magnetic properties

Magnetic properties with depth, shown in Fig. 4 and Table 2 (and Supplementary Material), correspond to variations of magnetic susceptibility (κ), the ARM normalized by the DC field (χ_{ARM}) and the isothermal remanent magnetizations. Magnetic susceptibility measures the content of all magnetic minerals: ferromagnetic *s.l.* (i.e., magnetite, goethite, which contribute with high positive values to the total), paramagnetic (i.e., phyllosilicates, which contribute with medium positive values to the total) and diamagnetic (i.e. quartz, calcite, contribute with low negative values to the total) minerals (Jackson and Borradaile, 2004). The (χ_{ARM}) measures the content of "soft" ferromagnetic minerals (i.e., magnetite, maghemite) and the IRMs, particularly the one acquired after an application of a magnetic field of 1T measures the content of "hard" ferromagnetic minerals (i.e., hematite, goethite).

In Enol Lake, Unit 3 shows almost null ferromagnetic mineral content whereas Unit 1 shows locally the higher values. In Marboré Lake, the magnetic signal increases progressively towards the top and in Basa de la Mora Lake, the magnetic signal varies largely along the core. The magnetic susceptibility values show large variations from 214 e-5 SI to diamagnetic (negative) values -0.4 e-5 SI in Basa de la Mora Lake, whereas in Enol, magnetic susceptibility is more homogeneous, varying from 11.6 e-5 SI at the bottom to 29 e-5 SI near the top of the section.

Almost concomitant variations of the magnetic properties: magnetic susceptibility, ARM and IRMs are mainly due to variations in the concentration of magnetite grains, therefore they are neither related to changes in magnetic mineralogy nor to changes of the magnetic grain size. There are, however, high values of magnetic susceptibility at 300-350 cm (top Unit 3 and bottom of Unit 2) in Enol Lake unrelated to the SD-MD ferromagnetic content. Similarly, in Basa de la Mora Lake, peaks present in the χ_{ARM}

related to facies 4, black carbonate silts at the bottom of Unit 2, are unrelated to the magnetic susceptibility values. In addition, higher values of IRM_{1T} – IRM_{100mT} are found in Unit 1 (~110 cm depth) of Enol Lake, coeval with a peak in the organic content and in Uni1 1 of Marboré Lake, which also show the highest values of the redox indicator (Oliva-Urcia et al., 2018). This is an indication of the possible presence of hematite, although no Morin transition at 250 K (-23 ºC) (Morin, 1950) is observed in the thermomagnetic curves (Fig. 3).

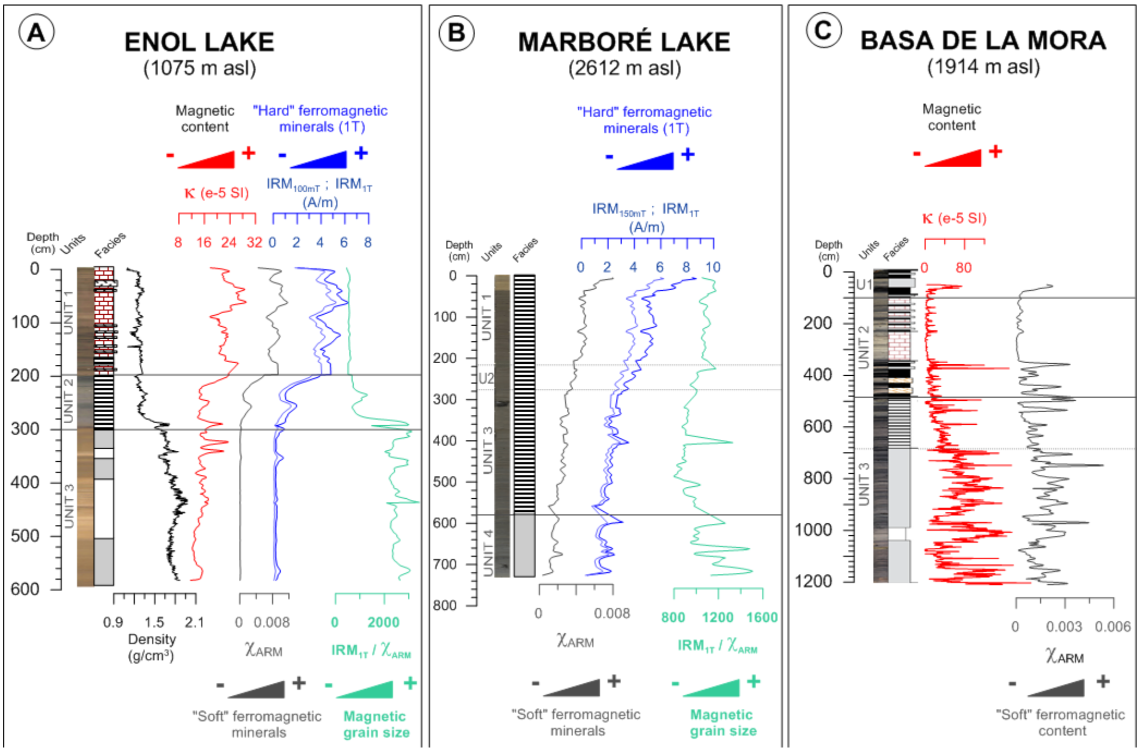

Figure 4. Physical properties of the three lakes. Legend of facies as in Fig. 2. From left to right: A) in Enol Lake: density (g/cm^3), magnetic susceptibility (κ) in e-5 SI, and ARM normalized by the DC fiel (χ_{ARM}) "soft" magnetic mineral content, isothermal remanent magnetization at 100 mT and 1T in A/m ("hard" magnetic mineral content) and IRM_{1T}/ χ_{ARM} ratio. B) Marboré Lake: ARM normalized by the DC field (χ_{ARM}), isothermal remanent magnetization at 150 mT (light blue, left) and 1T (dark blue, right) in A/m and IRM_{1T}/ χ_{ARM} ratio. C) Basa de la Mora Lake: magnetic susceptibility (κ) in e-5 SI, and ARM normalized by the DC field (χ_{ARM}).

When magnetic mineralogy is homogeneous along the core, variation of the magnetic properties such as IRM_{1T}/ χ_{ARM} ratio informs about the magnetic grain size. This ratio is quite homogeneous in Enol Lake (Units 1 and 2, since Unit 3 has very low magnetic content), whereas in Marboré Lake, the $IRM_{1T}/\ \chi_{ARM}$ ratio is high at the bottom of Unit 4 (which also has very low magnetic content) and, later, increases progressively towards the top of the sequence. The Day diagram also represents magnetic grain size when no mixture of different ferromagnetic grain types occurs (Fig. 5), although recent studies find the diagram ambiguous for the definition of domain states (Roberts et al., 2018) .

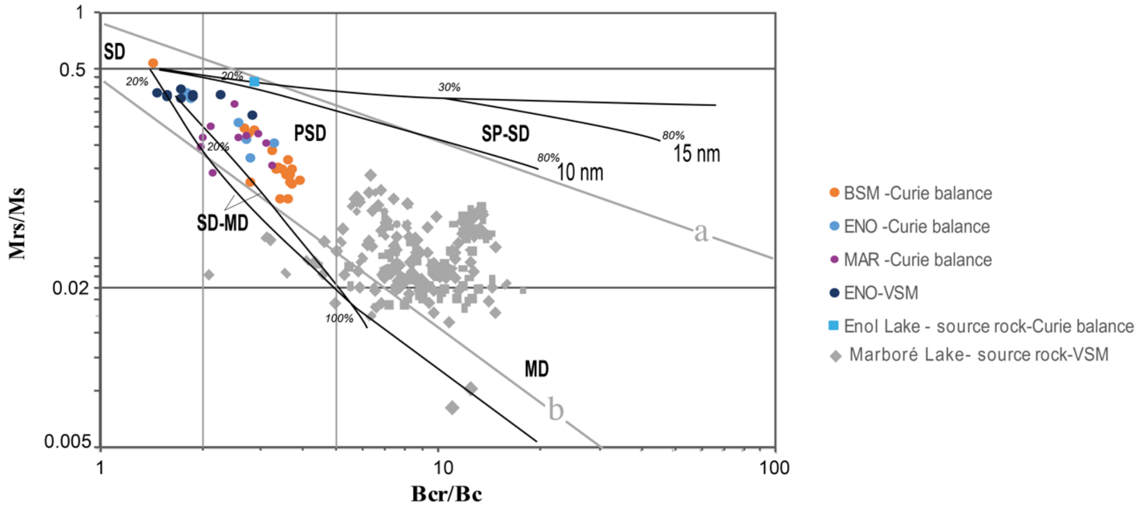

Fig. 5. Sediment samples from Enol (ENO), Marboré (MAR) and Basa de la Mora (BSM) Lakes and source rock (blue box) from Enol Lake and Marboré Lake (grey box), plot on the theoretical Day diagram (Dunlop, 2002). SD: single domain, PSD: pseudo-single domain (usually mixture of SD and MD), MD: multi-domain. Line: a remagnetized carbonates in North America (Jackson, 1990); line b: mixture of SD and MD grains (Parry 1982). Numbers along curves are volume fractions of the soft component (SP or MD) in mixtures with SD grains.

Magnetic property values can be modified when ferromagnetic particles are abundant and close enough to produce magnetic interactions (i.e., ARM values as seen in Sugiura 1979). These magnetic interactions, represented in the vertical axis of the FORC diagrams, seem to be more common in Basa de la Mora lake than in Marboré Lake. In addition, different coercivity clusters (magnetic grain sizes) occur in Basa de la Mora Lake for the same sample, as seen in the horizontal axis of the FORC diagrams of figure 6.

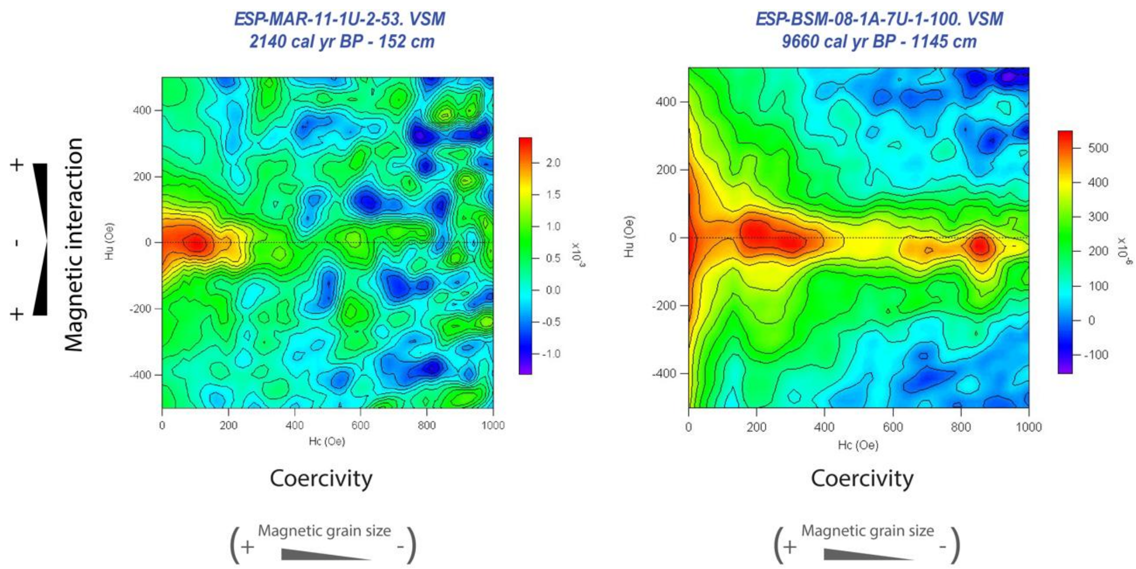

Fig. 6. First-order reversal curve (FORC) diagrams from Marboré and Basa de la Mora Lakes.

5. Environmental factors influencing magnetic properties in lacustrine sediments

The different facies of the three studied mountain lakes have a different expression of magnetic properties thus pointing to a close connection with the sedimentary composition and early diagenetic processes. One clear example is the fact that in Enol Lake, Unit 3 shows almost null ferromagnetic mineral content whereas Unit 1 shows locally the higher values (Figure 4). Unit 3 and Unit 1 are very different in terms of facies, being fine siliciclastic silts at the bottom and organic-rich and carbonate-rich sediments towards the top. In this case, in spite the sediments of Unit 3 are formed by runoff processes and are composed mostly by clay minerals, the ferromagnetic content in Enol Lake may be dominated by the formation of new minerals in relation to redox processes favored by the higher presence of organic matter in Unit 1. This should be possible since the organic content in Enol is 6% in average along Unit 1 and changes in Mn/Fe ratio are also significant (Figure 2). Still, in general, magnetic susceptibility is rather homogeneous in Enol lake, varying from 11.6 e-5 SI at the bottom to 29 e-5 SI near the top of the sequence (Table 2) indicating that the type, size and concentration of magnetic minerals are quite stable and significant changes are more related to post-sedimentary processes (eg. redox changes). Similarly, in Marboré Lake the magnetic signal increases progressively towards the top, being maxima along the uppermost 30 cm where the oxidation increases (see Mn/Fe ratio in Figure 2). However, the extremely low organic content in this ultra-oligotrophic lake prevents the association of redox changes to changes in the organic matter concentration and, more likely, the length of the ice-cover period is definitive in altering the mixing regime in the lake, with more oxic environment at the lake bottom during the last few millennia that would have favored both magnetite preservation and Mn-oxide formation and preservation (Oliva-Urcia et al., 2018).

On the contrary, in Basa de la Mora Lake, the magnetic signal is not homogenous but varies largely along the core. The magnetic susceptibility values show large variations from 214 e-5 SI to diamagnetic (negative) values -0.4 e-5 SI in Basa de la Mora Lake (Figure 4) being the highest values associated to Unit 3 (siliciclastic silts) and the lowest one associated to Unit 2 (carbonatic and organic rich). Surprisingly, Unit 3 with the highest magnetic values (Figure 7D) is composed by the same facies - Facies1 - than Unit 3 in Enol Lake and Unit 4 in Marboré Lake, which are the ones that have the lowest magnetic signal. We defined Facies 1 as gray banded to laminated siliciclastic silts with very low organic content (below 2%) but the detailed composition may differ from Enol, Marboré and Basa de la Mora lakes. In addition, in Basa de la Mora sequence, Facies 1 with high magnetic susceptibility values, show concomitantly high values of $\chi_{ARM,}$ related to the presence of ferromagnetic minerals eroded from the ophite outcrops in the southern boundary of the lake which are emplaced in the Triassic marly rocks with gypsum (Keuper facies). Those ferromagnetic minerals – likely magnetite and hematite – the latter detected by smear slide observations, are not present in high concentration in Facies 1 of the other two Lake sequences, therefore, a difference in the lithology of the catchment area produces significant changes in the magnetic properties. Abundance of those minerals in Basa de la Mora Lake is higher than in Enol or Marboré Lakes as it is discussed below.

Therefore, this is a good example that similar facies may have distinct magnetic properties as a response to different processes, underlining the importance of combining geochemical and sedimentological information with the magnetic data to properly interpret the variations of the latter.

The relationships between the magnetic parameters related to concentration are better discussed with the bi-plot diagrams (Fig. 7). In Enol and Marboré Lakes there is a linear correlation between the different parameters indicating that variation of concentration of magnetic minerals (mostly strong magnetic magnetite) is the main cause for the magnetic values in all sedimentological Units, Figures 7A and 7B. The linear correlation has R^2 values of 0.9 in Enol Lake and varying from 0.9 to 0.8 and 0.6 from Unit 1 to Unit 4 in Marboré Lake. These linear relationships confirm that it is the variation in the concentration the factor controlling the magnetic parameters variations with depth. However, such relationship is not as clear in Basa de la Mora Lake, where magnetic susceptibility values are much higher, approximately between two to six times the magnetic values of Enol-Marboré Lakes, whereas the χ_{ARM} values are slightly lower than in Enol and Marboré Lakes (Fig. 7). The linear correlation has R^2 values of 0.7, 0.3 and 0.4 for Unit 1, 2 and 3 respectively. This facts requires another process besides an increase in the concentration of magnetic minerals to explain the observed variability in the magnetic properties in Basa de la Mora Lake.

The content of "soft" magnetic grains seems to be lower in Basa de la Mora Lake, however, the higher values of the magnetic susceptibility and the saturation of the magnetometer cryogenic during IRM analyses suggest otherwise. Values of χ_{ARM} are sensitive to magnetic interactions of SP/SD grain sizes, therefore ARM can decrease with increasing concentration due to interactions among magnetic particles (Sugiura, 1979; Liu et al., 2012). A negative relationship between ARM/κ and magnetic concentration values indicate magnetic interactions (Yamazaki and Ioka, 1997). In the case of Basa de la Mora Lake, no correlation between ARM/κ and χ_{ARM} or κ is observed. From models, it is known that interactive SD particles behave like MD (softer, magnetically speaking), in contrast, interacting SP or PSD particles behave like SD (Muxworthy, 2001; Muxworthy et al., 2003). On the contrary, non-interacting SD particles will have larger χ_{ARM} values respect to magnetic susceptibility, since χ_{ARM} values are larger (up to ten times) in magnetite grains less than 0.1 μm, compared to grains larger than 0.5 μm, as seen in Fig. 2.c of Peters and Dekkers (2003) and references therein, whereas magnetic susceptibility is constant for magnetic grains of different sizes (Fig. 2.a of Peters and Dekkers (2003).

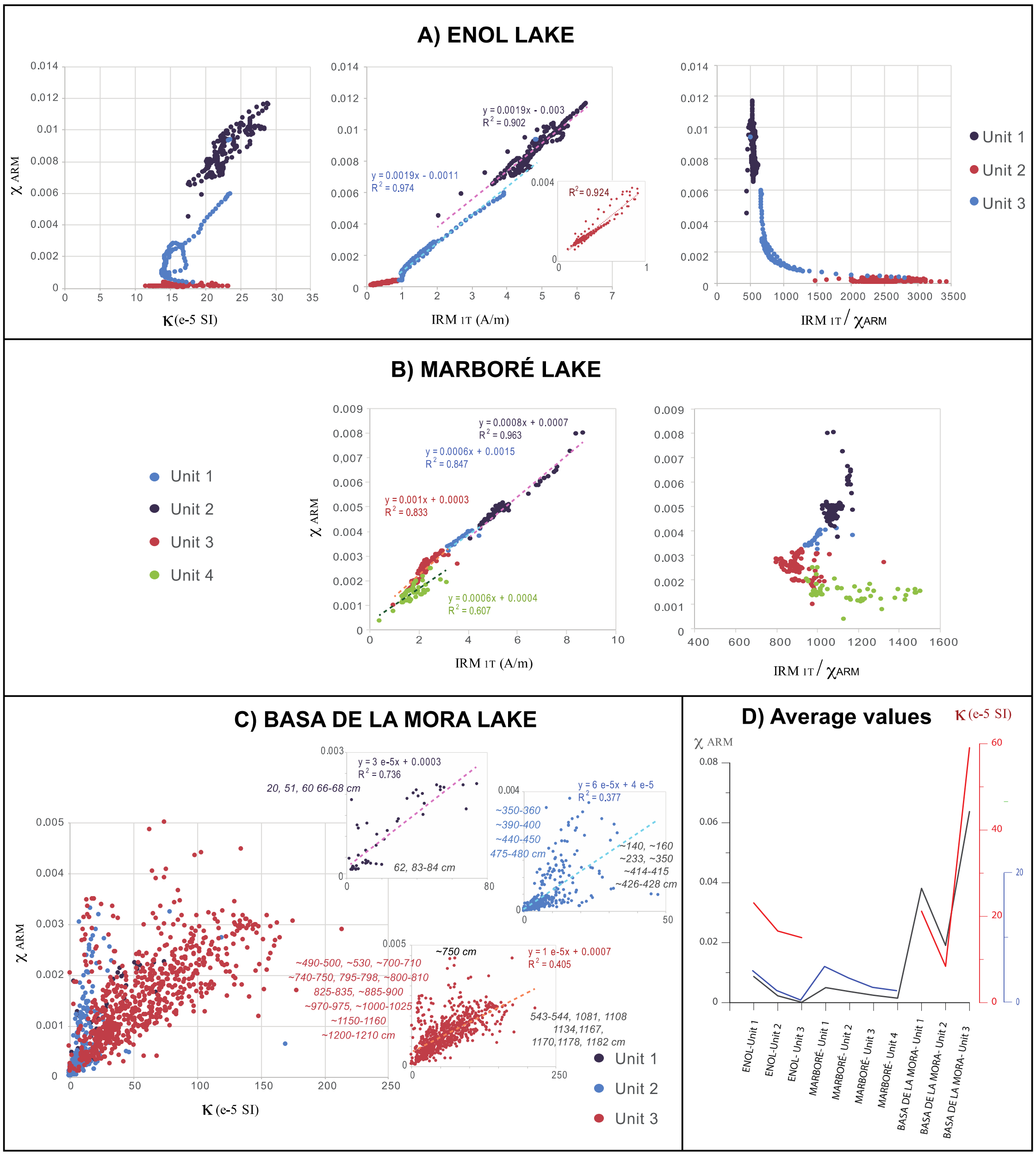

Fig. 7. Bi-plots of the magnetic properties for A) Enol Lake, B) Marboré Lake and C) Basa de la Mora Lake, in italics depths where values are higher (coloured) and lower (grey) respect to the linear trend-line. D) Average values of the magnetic properties for each sedimentological Unit.

Therefore, with the analyses performed in this investigation, we can suggest that the magnetic values in Basa de la Mora Lake seem to be related to, mainly, interacting SP-SD grains. The interacting SP-SD particles will produce high κ but low χ_{ARM} (coloured depths in Fig. 7C). The grey outliers in the same figure may be related to MD grains since they show low χ_{ARM} values (Maher et al., 2003; Liu et al., 2012). The presence of

SP grains has been noticed in Basa de la Mora Lake with the thermomagnetic curves at low temperature measurements (Fig. 3) but also larger grains have been found when plotting the modified Day diagram (Dunlop, 2002) see Fig. 5. There is also evidence of SP grains in Enol Lake (Fig. 3a). Different domain states seem to be present in some samples of Basa de la Mora Lake, as seen Fig. 6, where different coercivity groups are found in the same sample.

The depths at which magnetic properties do not vary concomitantly, for example at 300-350 cm (the top Unit 3 and bottom of Unit 2) in Enol Lake, where the high values of magnetic susceptibility are unrelated to the SD-MD ferromagnetic content (values of χ_{ARM} are very low), might be related to new formation of paramagnetic Mn-oxides, since the susceptibility increase coincides with an increase in the redox proxy (Mn/Fe ratio). The singular new formation of paramagnetic Mn-oxides will explain the high values of magnetic susceptibility in this siliciclastic facies (facies 1 and 2) in addition to the presence of the detrital paramagnetic phyllosilicates at the time the lake become proglacial with some preservation of laminated and rhythmite-type intervals (from 38 to 26 kyr) (Moreno et al., 2010).
On the contrary, in Basa de la Mora Lake, peaks present in the χ_{ARM} related to facies 4 (black massive, carbonate silts) at the bottom of Unit 2, are unrelated to the magnetic susceptibility values.

In summary, Enol and Marboré Lakes show similar magnetic behavior whereas Basa de la Mora show a more variable magnetic signal, probably due to magnetic interactions and different coercivity groups. Higher values in Enol and Marboré Lakes are associated to redox changes in relation to higher organic content (Enol Lake) and/or different water column mixing regime (Marboré Lake). In addition, the magnetic signal in Basa de La Mora is larger than in Enol/Marboré Lakes due to different lithologies in the source rock area. Whereas in Enol and Marboré Lakes the source area is mostly carbonatic rocks (Carboniferous in age in Enol Lake and Upper Cretaceous-Paleogene in Marboré Lake), in Basa de la Mora there are also ophites, which have higher content of ferromagnetic minerals than the limestones.

6. Conclusions

The combination of geochemical and magnetic analyses reveals their importance to show how the different processes and rocks of the catchment area affect the information stored on the magnetic minerals in mountainous lakes.

The almost concomitant variation of the magnetic properties with depth in the three northern Iberian lakes and the bi-plot information reveal that the concentration of strong magnetic magnetite, which is a “soft” magnetic mineral, is the main cause for those variations. Goethite may be present in Enol Lake (thermomagnetic curves) and “hard” magnetic minerals (hematite, goethite) are also deduced at certain depths in Enol and Maboré Lakes thanks to the IRM analyses (1T-100mT), probably linked to high oxidant conditions at the bottom of the lake. Hematite is also observed in Unit 3 of Basa de la Mora Lake by smear sections. Their presence is not detected by the thermomagnetic curves.

To infer the origin of such strong magnetic magnetite grains in the three lakes we have deduce the presence of SP grains (by the thermomagnetic curves) that suggest new formation of magnetite. The similarities between Marboré and Enol Lakes in facies and rocks of the catchment area allow us to extrapolate the low temperature analyses done in Enol Lake but not in Marboré Lake. Therefore, aerobic conditions are inferred for the three lakes, in Enol connected to high organic content and in Marboré Lake due to ice cover variations and mixed waters in the lake. The presence of PSD/MD grains can be related to the detrital source.

However, the different magnetic signal in Facies 1, particularly at the bottom of the three lakes, indicates that rocks of the catchment area play an important role. This is reinforced by the high magnetic susceptibility values, relatively low χ_{ARM} values and the saturation of the cryogenic magnetometer of the Basa de la Mora Lake during IRM analyses indicating more abundance of ferromagnetic minerals and more magnetic interactions than in the other two lakes. In the case of Basa de la Mora lake, detrital input of ferromagnetic minerals is probably the main source for the observed magnetic values.

The new and revisited data reinforce the necessity of provide geochemical information together with the magnetic properties in order to proper interpret the variations of the latter.

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Table

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Table 1. Physical, hydrological and limnological characteristics of the three studied lakes.

Lake	**Coordinates**		**Size** (surface area and water depth)	**Catchment**	**Hydrology - Limnology**			**Climate**		**Vegetation around the lake**
	Latitude and Longitude	*Altitude (m asl)*			*Input/output*	*Mixing regime*	*Nutrients / Ph / alkalinity / oxygen*	*Temp (°C) (coldest /warmest month)*	*Annual precip (mm)*	
Enol	43°16'N, 4°59'W	1070	12.2 ha and 22m depth	Carboniferous limestones	Laminar runoff, groundwater, permenent outlet (no inlet)	Dimictic	Oligotrophic (Total P= 8 µg/l); pH=7.7-8.2, moderately hard (alkalinity 2.4 meq/l; 29mgCa/l)	Annual mean =13	>1100 mm	forested areas with scrub extensions within a Poaceae herbaceous composition.
Marboré	42°41'N, 0°20'E	2612	14.3 ha and 30 m depth	Cretaceous carbonatic limolites	Precip - evap balance with an inlet and an outlet	Dimictic	(ultra)oligotrophic (Total P 2-4 µg/l; TOC < 0.3-1.2 mg/l); pH=7-7.8; alkaline (alkalinity < 0.8 meq/l)	-0.7 – 13 (anual mean=4.9)	1850 mm	patches of alpine herbaceous rocky species (treeline around 2000 m asl)
Basa de la Mora	42º32'N, 0º19'E	1914	3 - 5.5 ha and 2.5 – 4.5 m depth (varied seasonally)	Mesozoic limestones and ophites (Triassic)	Precipitation and surface run-off with ephemeral inlets and a surface outlet	Holomictic	Oligotrophic (Total P=9.2µg/l; TN=918µg/l); pH=8.96; conductivity of 200 µS/cm; DOC=3.5mgC/l	0.5 - 15	1360 mm	alpine grassland, *P. uncinata* forest and shrublands (located near the treeline).

Table

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Lake	κ e-5 SI	χ_{ARM}	$IRM_{100mT\ or\ 150mT}$ (A/m)	IRM_{1T} (A/m)	IRM_{1T}/χ_{ARM}	Mineralogy
Enol	11.6 – 29 (17.8; 4.3)	5.8 E-5 – 1.1 E-2 (3.1 E-3; 3,9E-3)	3.9 E-2 – 5.2 (1.4; 1.7)	0.1 – 6.6 (1.9; 2.1)	458.3 – 3437.7 (1658.3; 952.4)	Mgt (SP, SD, MD), Goet?
Marboré	–	3.6 E-4 – 8 E-3 (3.2 E-3; 1.4 E-3)	0.28 – 6.2 (2.5; 1.1)	0.4 – 8.7 (3.3; 1.7)	800.2 – 1507.6 (1028.1; 133.5)	Mgt
Basa de la Mora	-0.4 - 214 (40.8; 39.8)	8.2 E-6 – 5.3 E-3 (1.2 E-3; 9.7 E-4)	–	–	–	Mgt (SP, SD, MD)

Table 2. Minimum-maximum values of magnetic properties. In brackets: average; standard deviation. Mgt: magnetite, Goet: Goethite, SP: superparamagnetic grain, SD: single domain, MD: multi domain.

Figure 1

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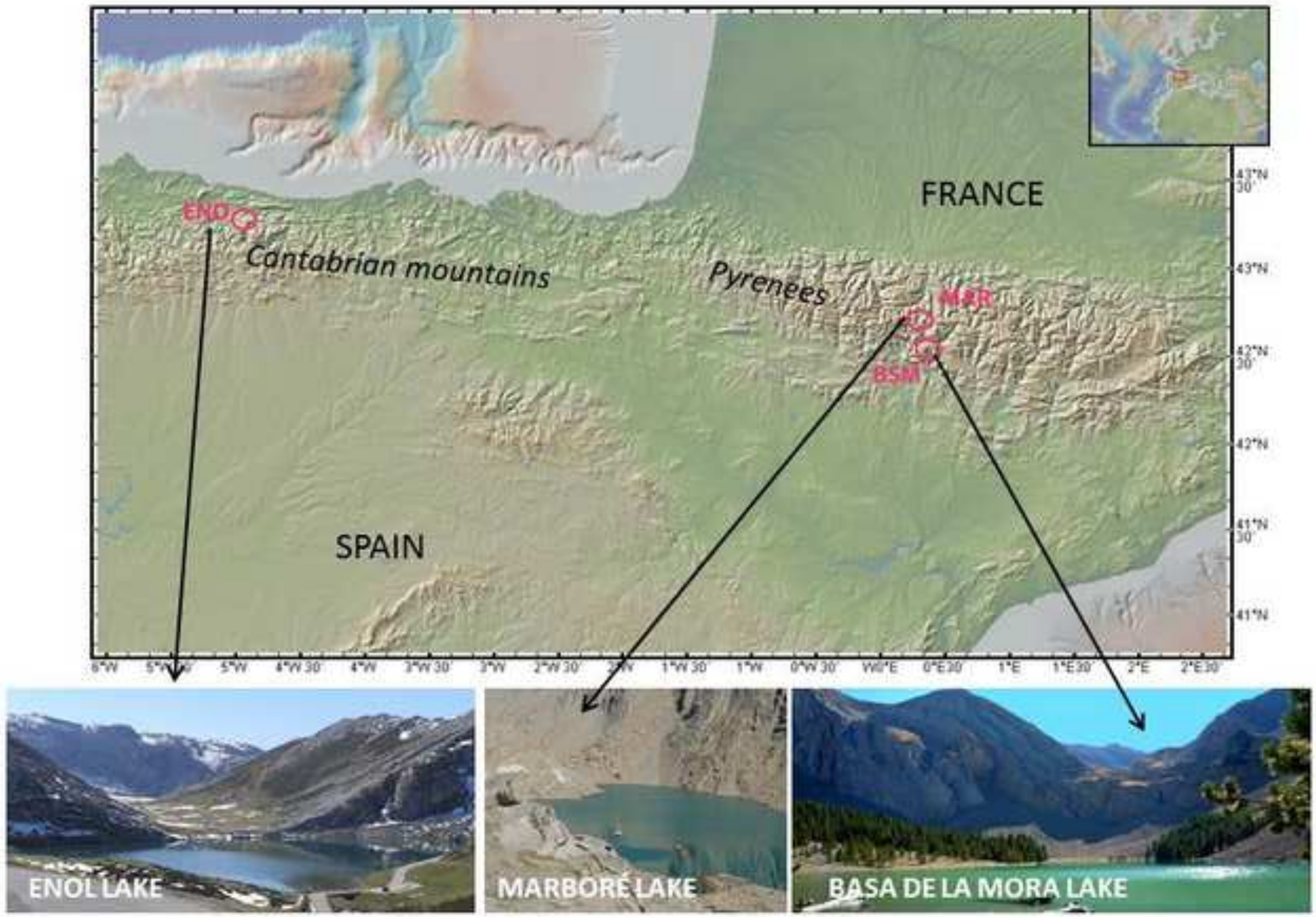

Figure 2

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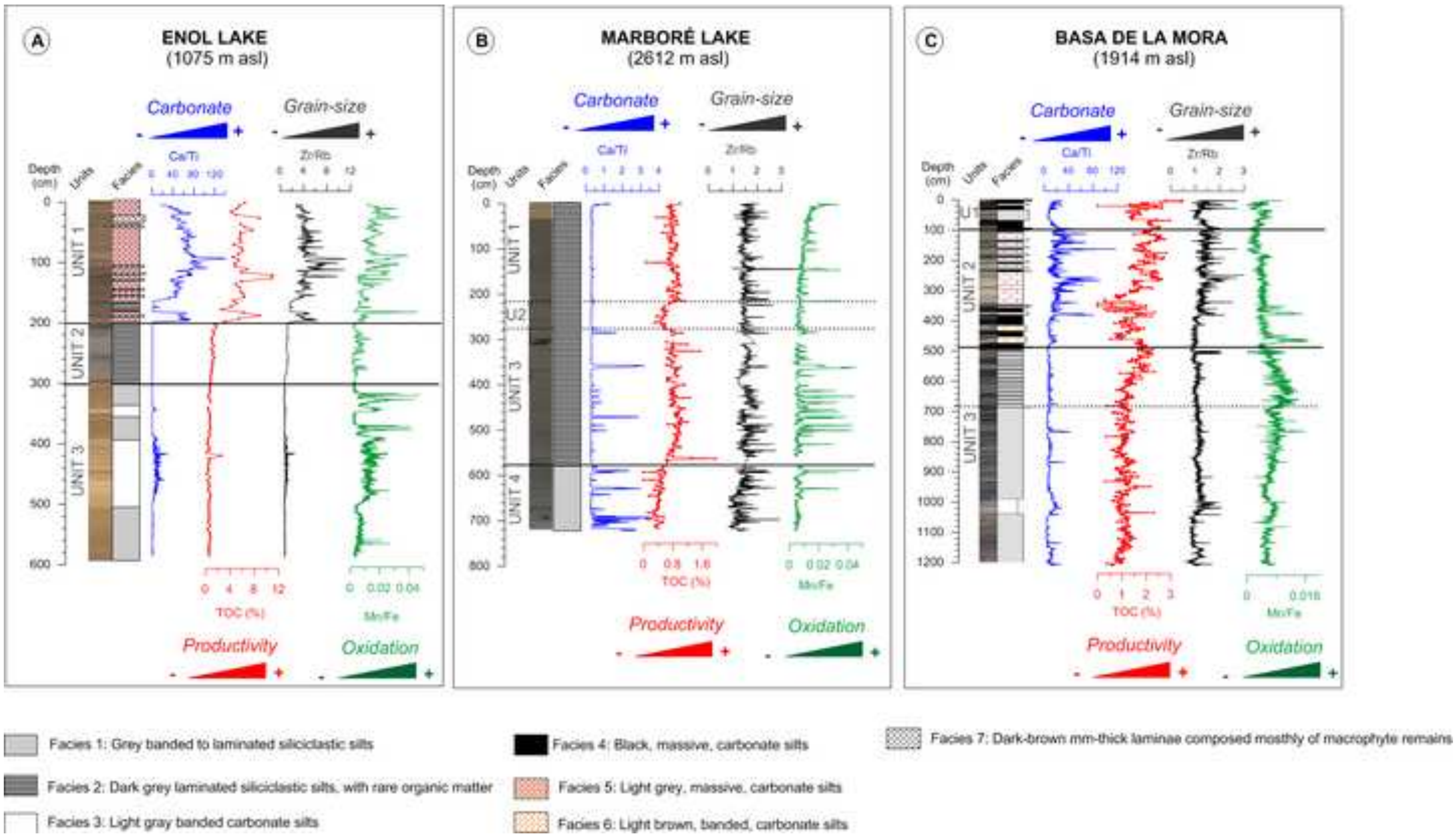

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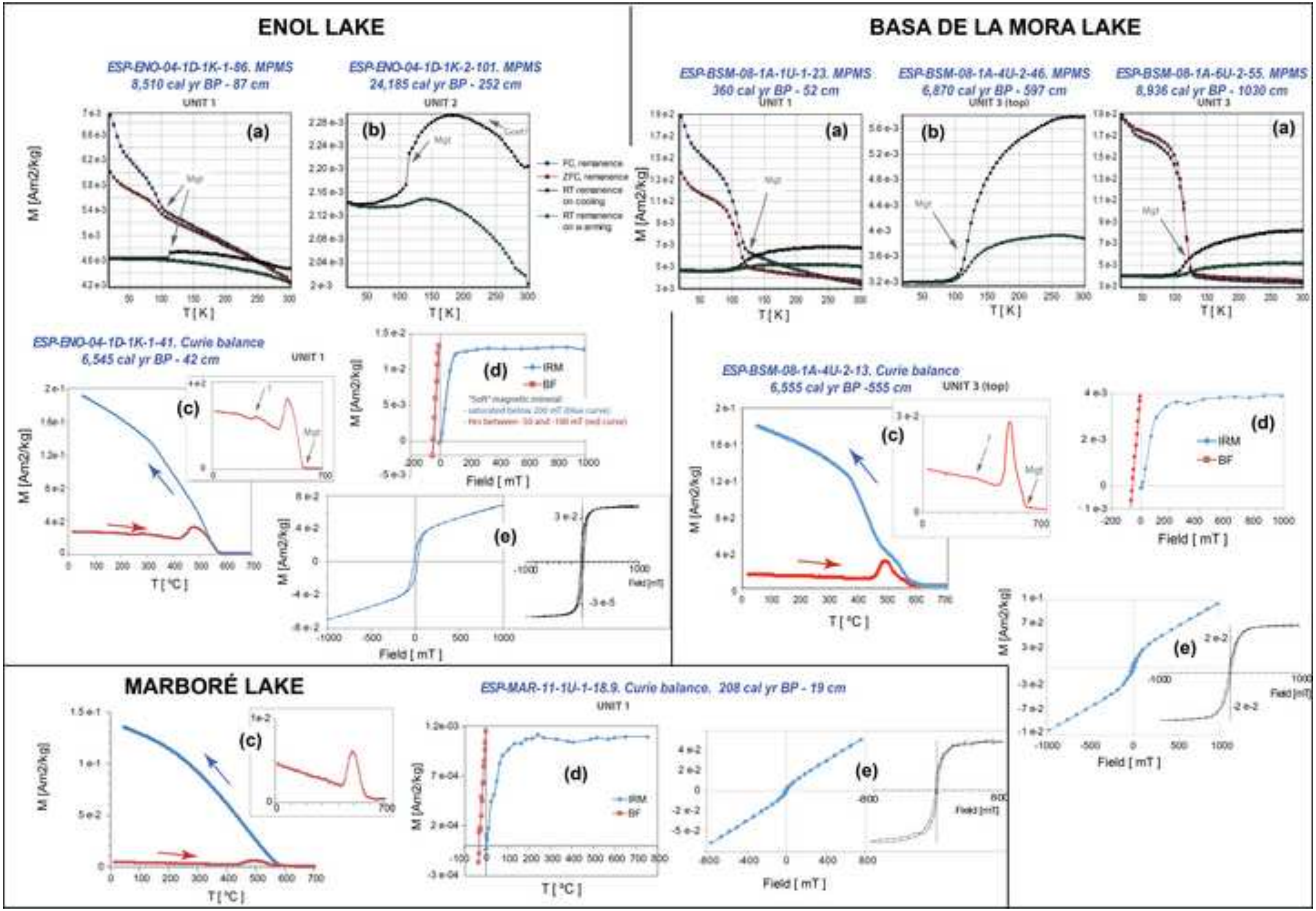

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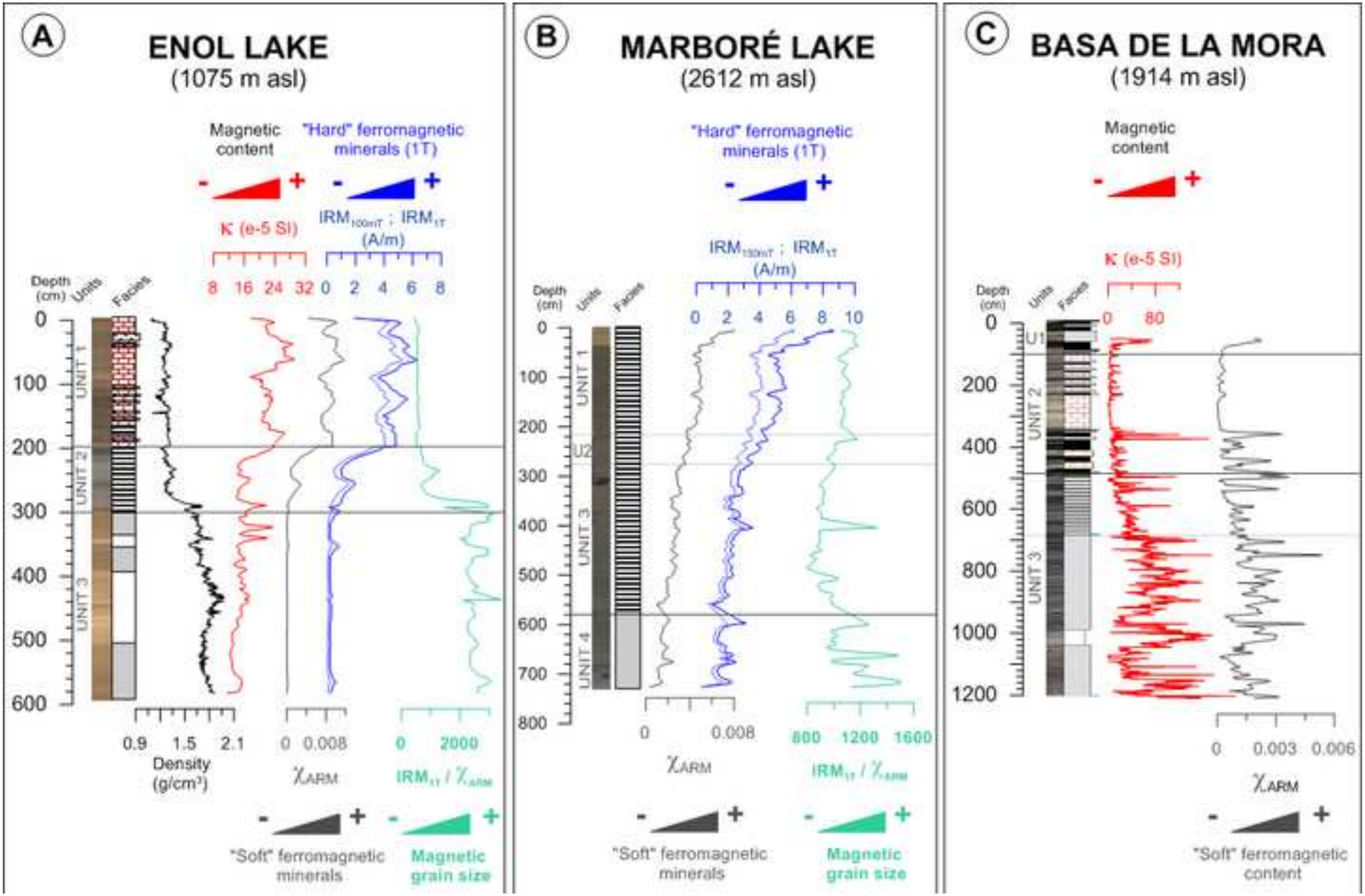

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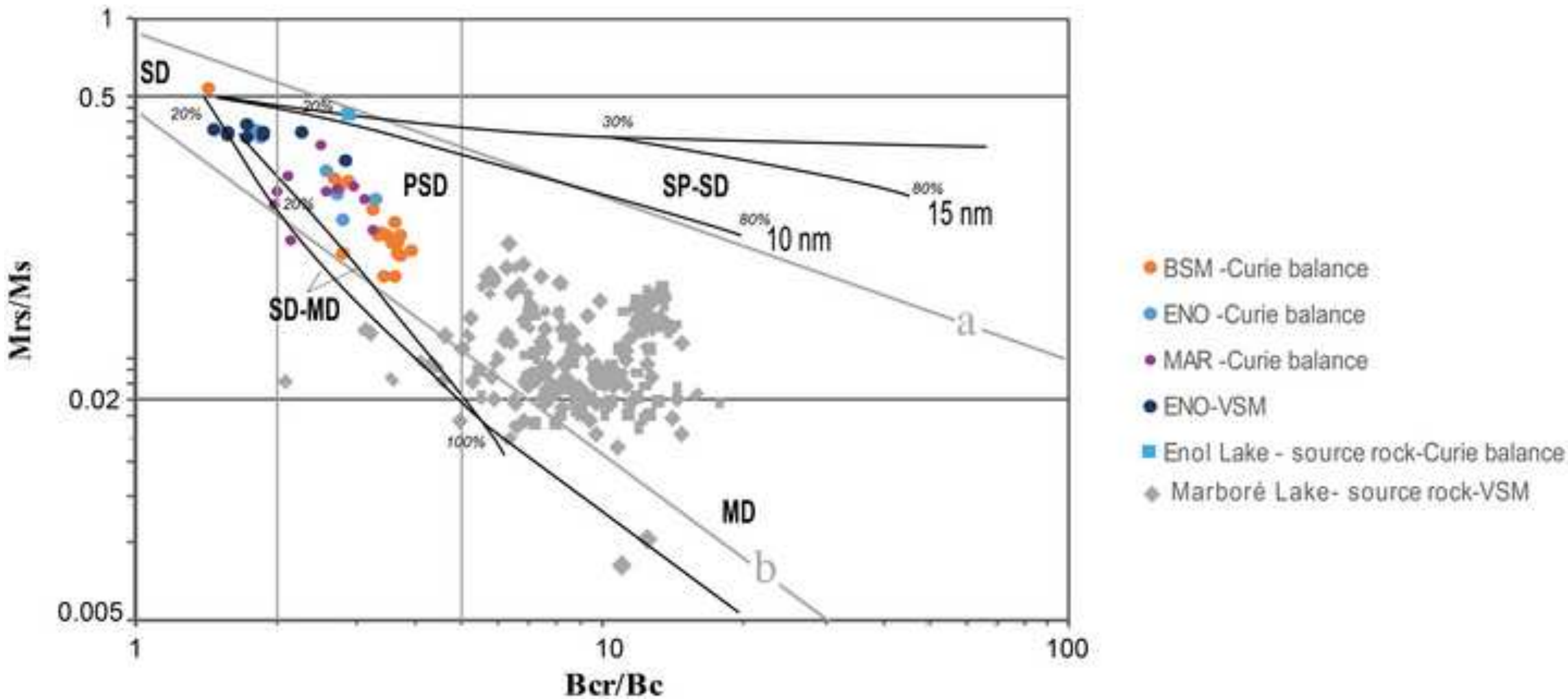

Figure 6
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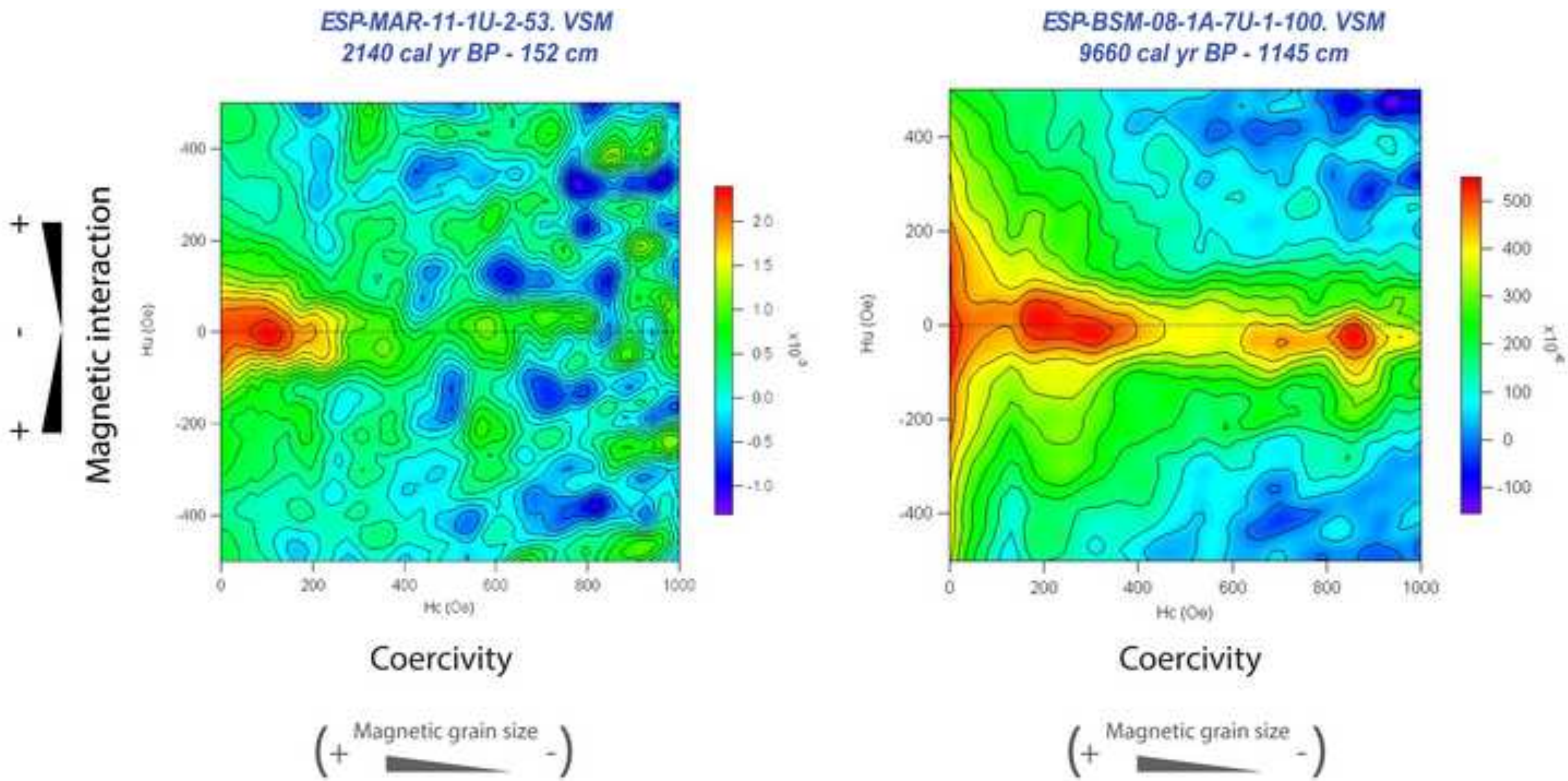

Figure 7

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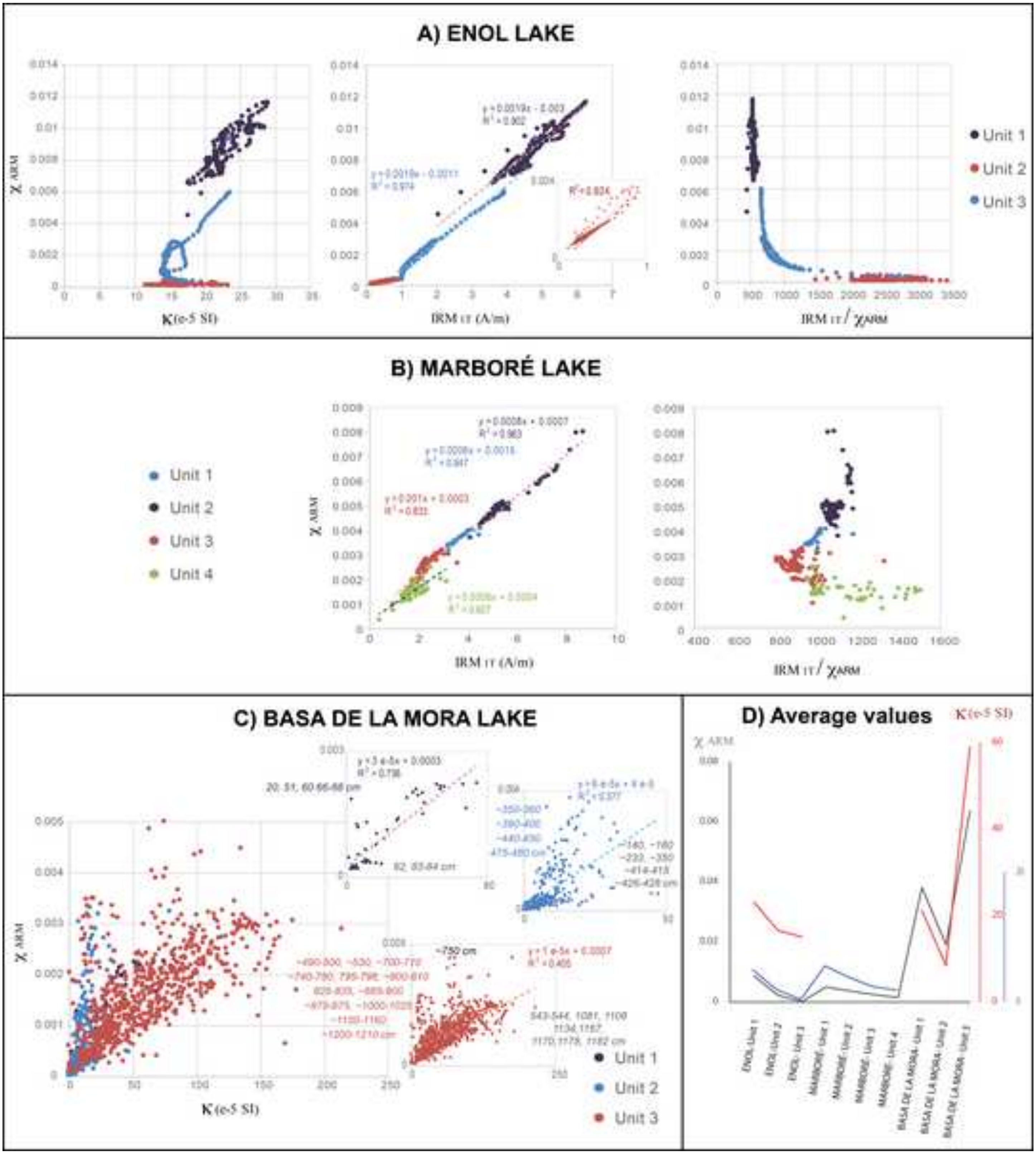

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