The origin of the magnetic record in Eocene–Miocene coarse-grained sediments deposited in hyper-arid/arid conditions: Examples from the Atacama Desert

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The origin of the magnetic record in Eocene-Miocene coarse-grained sediments deposited in hyper-arid/arid conditions: Examples from the Atacama Desert

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ARTICLE INFO

Keywords: Atacama paleoclim ate Magnetic proxies Atacama gravels Paleo environment Wetland deposits Paleosols

ABSTRACT

Magnetic proxies for paleoclimate are tools widely used to understand climate variability, yet current proxies focus on loess-derived soils in humid to temperate climate zones, whereas coarse-grained sediments in arid-hyperarid climate zones remain poorly investigated. To test the potential paleoclimatic-environmental significance of the magnetic record of coarse-grained sediments deposited in a region with a mean annual precipitation (MAP) < 200 mm yr⁻¹, we selected three previously studied sedimentary sequences from the Atacama Desert (Centinela area) and explored their magnetic properties, pedogenic features, salt chemistry and mineralogy. These sequences were deposited under different climate-environmental conditions from the Eocene to the Miocene, and correspond, from oldest to youngest, to the Atravesados II gravels (AtII), the Arrieros gravels (Arr) and the Ratones sediments (Rat). The magnetic susceptibility values (k) obtained in the stratigraphic record of the gravels are mainly controlled by the concentration of detrital (titano)magnetite, which is concentrated in the finest fraction (< 0.5 mm) of sediments. The values decrease in the coarse sediments from AtII to Arr following a climatic transition from arid to hyperarid conditions, an interpretation that is supported by the transition from carbonate-rich (MAP ~ 40 mm yr⁻¹) to sulfate-rich paleosols (MAP < 10 mm yr⁻¹), and changes in the tectonic conditions and/or sedimentary source. In contrast, the Rat fine-grained sediments record changes in paleo-wetland dynamics. The high frequency-dependent magnetic susceptibility (kfd%) values obtained from these layers are mainly controlled by the concentration of authigenic magnetite-maghemite and/or hematite crystals of superparamagnetic/single magnetic size. The increase in kfd% is linked to an increase in the authigenic degree, which is related to variations in the depth of the local water table. These results demonstrate the potential of magnetic proxies to reveal climatic/environmental signals in coarse-grained sediments deposited under desert climate conditions.

1. Introduction

Magnetic proxies for paleoclimate are tools widely used to understand climate variability (e.g., Maher and Thompson, 1999; Evans and Heller, 2003; Liu et al., 2012). In continental domains, magnetic studies mainly focus on archives from lake sediments and loess-derived soils in humid to temperate climate zones. The Chinese loess-derived soils, developed under a mean annual precipitation (MAP) range of ~200 to 1000 mm yr⁻¹, have provided a rich quaternary paleo-precipitation dataset that directly complements the marine oxygen isotope obtained record (e.g., Wang et al., 2006; Geiss and Zanner, 2007; Maher, 2016). Magnetic proxies obtained from fluvi-lacustrine and aeolian deposits also have been used to unravel aridification histories, such as that of the Tibetan plateau uplift (e.g., Xie et al., 2009; Zhang et al., 2015), and to

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infer climatic constraints as far back as the Paleozoic (USA and Antarctica, Retallack et al., 2003; Tramp et al., 2004). However, despite the widespread distributions of these proxies, the connection between magnetic proxies obtained from coarse-grained sediments (especially those developed under a MAP < 200 mm yr$^{-1}$) and environmental/climatic conditions remains poorly investigated (e.g., Pimentel, 2002; Dunai et al., 2005; Lü et al., 2010).

Continental coarse-grained sediments consist of clasts and matrices, and their overall composition greatly depends on the rock types exposed in the source areas. The magnetic components of the matrix may be of a detrital and/or authigenic origin. The terrigenous fraction is controlled by water transportation, wind processes and/or gravitational...
processes, all of which are ultimately controlled by the climatic and/or tectonic conditions (e.g., Arche, 1992). The magnetic authigenic fraction forms during diagenesis and/or soil formation and depends on environmental conditions such as relative atmospheric humidity, underground water circulation, evaporation rate, temperature, geomorphology and bacterial activity (e.g., Maher and Thompson, 1999; Retallack, 2008; Roberts, 2015; Liu et al., 2012). The authigenic magnetic fraction is often associated with the existence of fine-grained minerals in superparamagnetic (SP) and/or single-domains (SD) states (Evans and Heller, 2003; Torrent et al., 2007; Xie et al., 2009). The detrital fraction is commonly composed of coarser grains associated with pseudo-domains (PSD) and/or multi-domains (MD) states (e.g., Dunlop and Özdemir, 2001). Although there is a general consensus that MD/PSD magnetic minerals are enriched in soils by detrital inputs from the disintegration of parent rock (e.g., Evans and Heller, 2003), there is no general agreement about the mechanism by which soils are enriched in SP/SD ferromagnetic minerals (Dearing et al., 1996a, 1996b; Roberts, 2015; Hrouda, 2011). The most likely mechanism is the weathering of Fe-bearing minerals during soil wetting and drying cycles (Dearing et al., 1996a, 1996b; Cornell and Schwertmann, 2003; Maxbauer et al., 2016). Despite these complexities, it has been shown that magnetic proxies can qualitatively record paleoenvironmental conditions (e.g., Orgeira et al., 2011; Maher, 2011; Maxbauer et al., 2016).

The Atacama Desert contains numerous hydrographic basins mainly filled with gravel deposits derived from the erosion of the Precordilleras (e.g., Blanco, 2008) in response to tectonic episodes and/or changes in climatic conditions (Maksay and Zentilli, 1999; Riquelme et al., 2007, 2018). The Atacama Desert is, at present, the driest location on Earth (Jordan et al., 2014). Arid conditions have prevailed since at least the Mesozoic (Suárez and Bell, 1987; Clarke, 2006). The onset of hyper-aridity in the Atacama Desert is linked to the establishment of the Andean rain shadow, which resulted from the uplift of the Andean Cordillera (Rech et al., 2006, 2016; Oerter et al., 2016) and the upwelling of the ancestral Humboldt Current (Shackleton and Kennett, 1975; Alpers and Brimhall, 1988). A variety of methodologies have been used to elucidate the timing of the onset of hyper-aridity in the Atacama Desert. Such methodologies include (a) the use of cosmogenic nuclides (Dunai et al., 2005), (b) dating of fluvioc-lacustrine and alluvial sediments and evaporate formation (Hartley and Chong, 2002; Hartley, 2003), (c) dating of supergene minerals in porphyry copper systems (Alpers and Brimhall, 1988), (d) landscape geomorphology and paleosol analyses (Rech et al., 2006; Jordan et al., 2014), and (e) isotopic correlation of δ18O and δ13C signatures from paleosols, lacustrine and palustrine carbonate horizons (Rech et al., 2006; Oerter et al., 2016; Fernández-Mort et al., 2018; Sun et al., 2018). Most of these proxies indicate that the onset of hyper-aridity occurred before 10 Ma (probably in the Middle Miocene). In particular, the stratigraphy varies from carbonate-bearing rich in clay paleosols (MAP > 200 mm yr⁻¹) up to nitrate-sulfate bearing paleosols (MAP < 20 mm yr⁻¹), which has been interpreted as evidence that the climate changed from semi-arid to hyper-arid conditions during the mid-Miocene (Rech et al., 2006). Likewise, in the Centinela area, as described by Oerter et al. (2016), post-22 Ma paleosols and their δ18O and δ13C values are consistent with pre-mid Miocene aridification. However, some authors have also argued that the onset could have occurred as early as 25 Ma (e.g., Dunai et al., 2005) or as recently as 3–4 Ma (e.g., Hartley and Chong, 2002; Hartley, 2003). Investigations of paleoclimatic variations in the stratigraphic record of the Atacama Desert have been conducted in the Centinela area, where this study is also located (Riquelme et al., 2018; Oerter et al., 2016; Fernández-Mort et al., 2018).

In this study, we explore how magnetic proxies derived from the matrix (< 2 mm) of coarse-grained sediments can be used to determine the climatic/environmental processes that controlled the deposition of sediments in the Atacama Desert. To accomplish this, we used the magnetic properties of the minerals (Curie temperatures, magnetic susceptibility and hysteresis loops), coupled with the sedimentological and pedogenetic features, geochemical analyses and scanning electron microscope images (SEM) of lower Eocene to upper Miocene coarse-grained continental deposits from the Centinela area (Fig. 1). These sedimentary deposits host several arid-paleosol horizons and a wetland deposit. Paleosols include carbonate-rich (MAP ∼ 40 mm yr⁻¹) and sulfate-rich paleosols (MAP < 10 mm yr⁻¹) (e.g., Rech et al., 2006). A characterization of the mineralogy of both the clastic and authigenic fractions was used to determine the variations in grain size, composition, concentration, shape and origin of the Fe-rich minerals and their relationship to the paleo climatic-environmental conditions that occurred during the formation of these deposits.

2. The Centinela area

The Centinela area is located in the Region of Antofagasta in northern Chile (∼ 2300 m.a.s.l.), ca. 40 km SSW of the city of Calama (Fig. 1). In this sector, the Precordilleras (or Cordillera de Domeyko) and its surroundings is comprised of outcrops of Upper Paleozoic-Triassic basement, Mesozoic volcanic and sedimentary rocks, Paleocene-Cretaceous intrusive rocks and Paleocene volcanic rocks (Mpdodis and Cornejo, 2012; Fig. 1C). These rocks are intruded by Lower Cretaceous–Upper Eocene diorites and rhyolitic and dacitic porphyry intrusions (Marinovic and García, 1999). The late Cenozoic sediments in the Centinela area comprise ca. 800 m thick unconsolidated coarse-grained sediments and minor volcanic rocks eroded from the Precordillera (Tomlinson et al., 2001). According to Riquelme et al. (2018), based on stratigraphic relationships, sedimentary facies and thickness, the following gravel deposits are recognized within the study area: Esperanza (middle-upper Eocene), Atravesados (upper Eocene-Oligocene), Tesoro (Oligocene-lower Miocene) and Arrieros (lower to middle Miocene) (Figs. 1. 2). Isotopic dating (Ar/At) and U/Pb detrital zircon data indicate the gravel units were deposited by the mid-Eocene to the mid-Miocene (Riquelme et al., 2018). From these deposits, we selected two gravel units that are interpreted to have been deposited under contrasting climate conditions. The Atravesados gravels include carbonate-bearing soil horizons, suggesting they were deposited prior to the onset of the hyper aridification, whereas the Arrieros gravels include sulfate-bearing soils and are more representative of hyper-arid conditions (Fig. 2).

The Atravesados gravels include a ca. 300-m-thick deposit composed of lower (AtI) and upper subunits (AtII). The AtI (ca. 200-m-thick) is composed of consolidated massive conglomerates, with sand and mud beds and minor intercalations of cross-bedded conglomerates and sandstones, whereas AtII (ca. 100-m-thick) is composed of consolidated cross-bedded and horizontally laminated conglomerates and sand beds, with minor intercalations of massive conglomerates, sandstones and mud. Provenance analyses indicate that the sediments were derived from the erosion of the Upper Eocene Cinchado Formation (aphanitic and porphyric andesites and dacites), the Paleocene intrusions (diorites and quartzodiorites) and the interbedded volcanic layers of the Esperanza gravel deposits in the late Eocene.

The Arrieros gravel (Arr) is an up to 100-m-thick series of poorly consolidated horizontally laminated conglomerates and sandstones with minor intercalations of massive sands and silts interbedded within conglomerate beds. Provenance analyses of detrital zircons and clast composition analysis indicate that almost all of the rock units cropping in the Centinela area were already exposed and eroded at the time when Arr was deposited. The gravels were derived from the erosion of Paleozoic basement rocks (granodiorites and granite), Upper Cretaceous volano-clastic rocks from Quebrada Mala Formation (andesitic and dacitic tuff and volcanoclastic sandstones) and intrusives (porphyric rhyolites) and upper Eocene porphyry copper systems (granodiorite porphries), as well as from Jurassic to Lower Cretaceous rocks from the Caracoles Group (limestones and calcareous siltstones). The deposit also includes conglomerate clasts, which are a distinctive
population in this gravel unit that resulted from the erosion of the underlying gravel deposits.

In this paper, we also include samples of a wetland deposit from the Ratones sediments unit (Rat), which is described for the first time here (see Section 4) and was deposited between 9.52 ± 0.05 Ma and 5.7 ± 0.1 Ma (Tapia et al., 2012), after the onset of the hyper-aridification.

3. Methodology

Sampling was conducted at four localities in the Centinela area (Fig. 1). Paleosol samples were collected within AtII at site 1, within Arr at sites 2 and 3, and within the wetland deposit from Rat at site 4 (Fig. 2). Paleosols were described following the criteria of Schaetzl and Anderson (2005) based on paedogenetic features and classification followed Mack et al. (1993). Sedimentary facies from Rat were described following Nalpas et al. (2008) and classified following Rech et al. (2002).

A total of 35 samples were collected from the stratigraphic profiles (Fig. 3) at the different sampling sites for a geochemical analysis of soluble salts, which followed the procedure proposed by Rech et al. (2006). Using an ICP-AES at the Laboratory of Geochemistry of the Universidad Católica del Norte (UCN), the concentrations of Cl, Na, SO₄, Mg, K, Ca, B and Li were measured and the HCO₃ content was calculated (Appendix 1).

We also collected 115 samples (ca. 0.5 kg each) for magnetic analyses at the same sampling sites. Samples were collected from the top down every ~10 cm in the topmost 45 cm of each sampling site. Below this level, samples were collected at 40 cm intervals down along the stratigraphic profile. Samples were sieved and divided into 4 different grain size fractions: (Fa) < 0.5 mm, (Fb) 0.5–1.0 mm, (Fc) 1.0–2.0 mm, and (Fd) > 2.0 mm. In this study, the fraction Fd represents the coarser-clastic portion, whereas fractions Fa, Fb and Fc represent different mixtures of both clastic and matrix components. Fractions Fa, Fb and Fc were mounted into 8 cm³ standard-size paleomagnetic cubes (345 cubes) for magnetic measurements.

The volume magnetic susceptibility ($k$) was measured in SI units at UCN using a Kappabridge MKF1-FA susceptibility bridge (AGICO Co.) under normal ambient conditions (22–24 °C) and a 200 A/m field. Measurements were performed at: (a) 976 Hz ($kf_1$) and (b) 15.616 Hz ($kf_3$) (Appendix 2). This method allowed us to calculate the frequency-dependent magnetic susceptibility ($k_{fd}$ %) (Dearing et al., 1996a, 1996b):

$$k_{fd} = \left( \frac{k_{fd} - k_{f3}}{k_{f3}} \right) \times 100$$

$k_{fd}$ % is widely used as a normalized parameter, and it is interpreted to reflect the content of the particles close to the superparamagnetic/single-domain (SP/SD) boundary (Verosub and Roberts, 1995). Additionally, to constrain the effects of sedimentary-paedogenetic processes on magnetic grain size (e.g., Evans and Heller, 2003), a subset of
73 fraction Fa sub-samples were subjected to hysteresis experiments at room temperature using a MicroMag AGM 2900-2 alternating gradient force magnetometer at UCN (Princeton Measurements Corp., Princeton, NJ, USA; Appendix 3). Magnetic hysteresis parameters were calculated using PmagPy routines (available at https://earthref.org/PmagPy/ cookbook/ Tauxe, 1998, 2005). In addition, a total of 8 fraction Fa sub-samples were used to determine Curie temperatures via thermomagnetic experiments at the Géosciences Environnement Toulouse (GET) using a CS2 KLY3 (AGICO). Powdered samples were heated from room temperature to 700 °C (and then cooled to room temperature) under a weak magnetic field (300 A/m) and 1 atm pressure in a non-inert (oxygen) atmosphere. Curie points were calculated using the

To establish the mineralogical and clastic contents of the analysed samples, we selected 153 sub-samples representative of the Fa, Fb, and Fc size fractions and characterized the fractions using a standard magnifying lens microscope at the Microscopy Laboratory of UCN (Appendix 5). To better constrain the size and composition of the magnetic minerals, 7 fraction Fb sub-samples were used to obtain high resolution microscopic images at the laboratories of the GET for microscopic imaging using a SEM with an Energy Dispersive Spectroscopy (EDS) of 20 keV of primary energy attached to it.

4. Results

4.1. Characteristics of paleosols and wetland deposits

4.1.1. Paleosols in the Atravesados and Arrieros gravels

At site 1 (Fig. 1) we recognized 6 paedogenetic profiles, rich in calcium carbonate (petro-calccic horizons), interbedded within AtII (Figs. 2, 3A). These profiles are light grey-coloured, well consolidated, have exposed, well-defined base and top surfaces, and vary in thicknesses between 0.5 m and 3.5 m. The paleosols show a massive texture resulting from the obliteration of primary sedimentary features by carbonate precipitation. Horizons developed over fine-grained sand or mud deposits rarely expose carbonate nodules, which can be up to several centimetres in diameter. In contrast, horizons developed over coarse-grained gravel deposits exhibit clasts encompassed by carbonates that are often imploded, thus reflecting paedogenic processes (Gile et al., 1966). Field observations and geochemical analyses indicate that the carbonate content tends to increase when paleosols are developed over sand and mud layers (Fig. 3A). Accordingly, these paleosols yield high HCO3 and Cl and relatively low SO4 concentrations (Fig. 3A), consistent with the development of calcite and halite. We observed the latter in low concentrations, probably resulting from precipitation under more hyper-arid conditions that occurred well after calcite precipitation (Fig. 4). These observations and analyses indicate that these paedogenic profiles can be classified as highly developed carbonate-rich paleosols (Retallack, 2008).

At site 2 (Fig. 1), we recognized a ca. 3 m thick grey-coloured, well consolidated paedogenetic profile that is rich in sulfate and interbedded within the Arr (Figs. 2, 3B). Within this profile, two horizons can be identified. The upper horizon consists of pale brown to grey-coloured, massive and well compacted siltstones including either fractured or imploded clasts in the uppermost part of this horizon, indicating a complete vailing of the primary sedimentary fabric. This horizon commonly exhibits V-shaped subvertical joints of a ca. 2 m depth, filled with silt, sand and clay. The lower horizon is less consolidated compared to the upper horizon and partly maintains the texture of the original sedimentary fabric; however, the original fabric is slightly obliterated by the growth of interstitial gypsum. Geochemical measurements of water soluble SO4 and Cl yield high SO4 values that are probably related to the occurrence of gypsum. HCO3 was not identified. The concentration of total dissolved soluble salts (TDSm) is lower in the upper horizon (Figs. 3B, 4). Following the Schaetzl and Anderson (2005) criteria for classification of paleosols, the paleosol in site 2 corresponds to a sulfate-rich paleosol with an upper petrogypsum (Bym) and a lower salic horizon (Bz; Fig. 2).

Directly below the Bz level, we identified a 2 m thick reddish horizon of partially consolidated sediments, which showed small subvertical carbonate-rich veins (1 cm wide, up to 15 cm long), most of which represent conspicuous small root traces as well as subvertical joints. This horizon also included lensoid-shaped, subhorizontal carbonate-veins up to 80 cm thick that might represent gley structures that result from past circulation of groundwater (Schaetzl and Anderson, 2005). Geochemical analyses showed that the Cl and HCO3 content is higher than that of SO4 (Fig. 3B), agreeing with the high concentrations of chlorides and calcite relative to the gypsum content (Fig. 4). These observations and analyses indicate that this paleosol can be classified as a low-developed carbonate-rich paleosol (Retallack, 2008).

At site 3 (Fig. 1), we observed a grey-coloured paedogenetic profile, ca. 1 m thick, developed in the uppermost part of Arr (Figs. 2, 3C). This paleosol exhibits an upper horizon of ca. 60 cm thickness that is well compacted and contains pervasive gypsum crystals between clasts and a set of V-shaped joints filled with sand and gypsum in the topmost portion. The lower horizon is a ca. 30 cm thick paleosol that partly preserves the primary sedimentary fabric and contains clasts encompassed by gypsum. Despite the feeble recovery of soluble salts from this horizon, high concentrations of Cl and SO4 were measured, with a minor HCO3 content (Fig. 3C). We interpret the upper horizon as a Bym horizon and the lower part as a Bz horizon, suggesting this paleosol can be classified as a sulfate-rich paleosol.

4.1.2. Wetland deposit in the Ratones Sediments

At site 4 (Fig. 1), we observed a greenish-brown unit that is restricted to the head of the Quebrada Los Arrieros, reaches ~20 m in thickness and corresponds to the Ratones Sediments (Rat). The deposits are mainly composed of poorly consolidated clays and silts, sands and massive gravel with minor intercalations of horizontally laminated sands and conglomerates. Thin gypsum layers are commonly interbedded along the entire stratigraphic section analysed. Carbonated silts and marls are typically associated with silt and clay beds (Figs. 2, 3D). When this unit was deposited, most of all the rock units outcropping in the Centinela area were already exposed. The provenance analyses of clay compositions indicate that the gravels are mainly derived from the erosion of Paleozoic basement rocks and from the Quebrada Mala Formation. The deposition of Rat sediments occurs post-10 Ma (Tapia et al., 2012). In this unit, we measured a high amount of soluble salts (TDSm), accompanied by high concentrations of SO4, HCO3 and Cl (Fig. 3D). The analyses thus agree with the concentration of chlorides, sulfates and carbonates in this deposit (Fig. 4). Following the Rech et al. (2002) criteria, this deposit is interpreted to be a paleo-wetland.

4.2. Mineralogy of sedimentary deposits and paleosols

4.2.1. Optical microscopy observations

A variable mixture of quartz, feldspars, carbonates, chlorides and/or sulfates species dominate the content of the matrix and the mineralogy of sediments observed in the Centinela area (Fig. 4, Appendix 5). The mineral composition of the sedimentary deposits and paleosols is similar, showing only slight differences in concentration, especially in the carbonate and gypsum content. We observed lithic fragments of igneous rocks accompanied with minor amounts of eroded sedimentary rocks. Carbonates are mainly present in the carbonate-rich paleosols, AtII, Arr and the clay and silt layers from Rat (Fig. 4); gypsum is mostly present within the sulfate-rich paleosols, the Arr and sand and gravel layers from Rat (Fig. 4, Appendix 5).

The mineralogical observations of the size fractions (Fa, Fb and Fc) suggest silt and undifferentiated clays are mainly present in fraction Fa and gradually decrease in fractions Fb and Fc (Appendix 5). In this fraction, we also identify Fe-oxides, including magnetite (> 1%), hematite (< 1%) and Fe-oxyhydroxide (< 1% < mainly as goethite and limonite) (Fig. 4). Fe-bearing minerals are abundant in fraction Fc and tend to decrease (or are absent) in the other size fractions. In fraction Fa, we observed magnetite in all the paleosols and in the sedimentary deposits analysed; it was mainly found in the form of single crystals, whereas in fractions Fb and Fc it appears as crystals disseminated on clasts. Additionally, hematite occurs as single crystals in the fraction Fa, whereas it occurs as crystals disseminated on clasts in fractions Fb-Fc and commonly its concentration is increased in samples from carbonate-rich paleosols. Fe-oxyhydroxides (e.g., goethite, limonite), abundant in the fraction Fa of sulfate-rich paleosols, are in the form of crystals or patinas covering clasts in fractions Fb-Fc (Fig. 4, Appendix 5).
4.2.2. Identification of Fe-bearing minerals via scanning electron microscope (SEM)

SEM/EDS analyses of the fraction Fa sub-samples selected from all stratigraphic units (samples distribution; Fig. 3) indicated the presence of carbonate-rich paleosol horizons in AtII (site 1; Fig. 5A) and sulfate-rich paleosols in Arr (site 2; Fig. 5B), with subhedral rounded (Ti-poor) titanomagnetite crystals of approximately 20 μm in size. Additionally, these analyses indicated that all samples contained euhedral to subhedral rounded crystals of magnetite larger than 20 μm in size (site 2; Fig. 5C). In addition, we identified the presence of laminated crystals of hematite in the sulfate-rich paleosol in Arr (site 3; Fig. 5D) and in the carbonate-rich paleosol in Arr (site 2). At first approximation, the shape and particle size of the observed Fe-bearing minerals suggest a detrital origin for these minerals (Maher and Thompson, 1999).

Samples from the basal clay and silt layers from Rat contain subhedral maghemite and/or magnetite crystals of ca. 2 μm in size (site 4; Fig. 6E). In addition, we identified several titanomagnetite crystals with low sphericity and with rounded shapes (> 2 μm). In addition, in samples from the top clay and silt layers, we identified subhedral hematite crystals, ca. 1 μm in size (site 4; Fig. 6F). Magnetite and titanomagnetite crystals larger than 20 μm were found only in gravel and sand layers. The difference in shape and particle size between the fine-grained and coarse-grained layers from Rat may suggest these minerals have different origins (Maher and Thompson, 1999).

4.3. Magnetic properties of sedimentary deposits and paleosols

4.3.1. Bulk magnetic susceptibility (k)

Fig. 3 shows the variation in magnetic susceptibility with respect to the stratigraphic columns of the different sedimentary deposits. In all profiles, k values are higher and more variable in fraction Fa, whereas in the fractions Fb andFc they tend to be lower and less variable. k values are only similar in all fractions at site 1 (Fig. 3). Magnetic minerals selectiveness, related to decreasing dilution of the sedimentary flows, may explain this pattern. AtII corresponds to stream-flow deposits (more diluted), whereas Arr and the gravel-sand layers from Rat corresponded to hyper-concentrated debris-flows and sheet-flows (less dilute) (Tapia et al., 2012; Riquelme et al., 2018). The k values varied from 1.45 × 10−2 (SI) in the gravel layers of site 1 (AtII), to 1.08 × 10−4 (SI) in the silt-clay layers from site 4 (Rat) (Appendix 2), with an average value of ca. 4.00 × 10−3 (SI). We measured the largest k values in the subsamples from fraction Fa at AtII (6.34 × 10−3 SI on average; Fig. 3A, Appendix 2). Relatively average k values were obtained from the Rat’s gravel and sand layers (4.74 × 10−3 SI on average; Fig. 3D, Appendix 2), whereas the lowest values were obtained from the Arr sites (3.21 × 10−3 SI on average; Fig. 3B, Appendix 2) and from the clay and silt layers from Rat (on the order of 1.08 × 10−4 and 2.08 × 10−3 SI; Fig. 3D, Appendix 2). In the deposits, the k values (from fraction Fa) tended to be higher in the layers in which no soil development has occurred or the degree of pedogenesis is less intense (see Section 4.1; Fig. 3).
4.3.2. Frequency-dependent magnetic susceptibility (kfd%)

The largest kfd% values were measured in samples from clay and silt layers at site 4, yielding a maximum value of approximately 10 to 12% (Appendix 2); in contrast, at all other sites, the kfd% values were low with an average of ca. 2%, except for the gravel and sand layers from site 4 in which the kfd% values were slightly higher, ca. 3%. These kfd% values are similar among the Fa, Fb and Fc fractions (Fig. 3) for all samples. This parameter is used to qualitatively estimate the presence and concentration of small ferromagnetic particles that have magnetic sizes near the SP/SD limit (Maher and Taylor, 1988; Dearing et al., 1996a, 1996b). We propose that the number of very small ferromagnetic particles is only significant in the clay and silt layers from Rat. We also propose that it reflects the presence of authigenic processes over magnetic minerals due to the wet environmental conditions (Dearing et al., 1996a, 1996b; Evans and Heller, 2003; Hao et al., 2008).

4.3.3. Identification of Fe-bearing minerals via thermomagnetic experiments

Measured thermomagnetic experiments show irreversible behaviour for all samples analysed (Fig. 6), probably linked to a change in the mineral phases during heating in a non-inert atmosphere (oxygen) (Tauxe, 1998, 2005). Similar behaviour is observed in all curves: a) an increase of approximately 200–400 °C in the heating curve, probably associated with the presence of a metastable mineralogical phase, such as maghemite (e.g., Özdemir, 1990) b) a progressive decrease in susceptibility from 550 to 580 °C, probably associated with the presence of Ti-poor titanomagnetics (Tc2) (e.g., Evans and Heller, 2003), c) a drastic change in the slope of the curve ca. 580 °C, suggesting the presence of nearly-pure magnetite (Tc1), and d) the progressive decrease indicated by a gentle slope between 580 and 680 °C, suggesting a mixture of Ti-rich and Ti-poor titanohematites-titanomaghemite (Tc3; Tauxe, 1998).

The analyses of the second derivative (Tauxe, 1998) confirmed the presence of maghemite, titanomagnetite and magnetite in samples from the carbonate-rich paleosols from AtII (site 1; Fig. 6A, B, Appendix 4). The presence of titanomaghemite and/or titanohematite is also suggested by Curie temperatures above 580 °C (e.g., Evans and Heller, 2003), although a significant peak in the second derivative was not observed (Appendix 4), probably due to the smooth slope present after ca. 580 °C. The same behaviour was observed on the second derivative for samples from Arr; however, these samples displayed a more abrupt decreases in their susceptibility values between 575 and 582 °C (Tc1), suggesting the presence of (nearly-pure) magnetite (site 2; Fig. 6C, D, and site 3; Fig. 6E, F). Arr samples (site 2 and 3) were collected from the sulfate-rich paleosols (site 2; Bz horizon, and site 3; Bym horizon) and from the gravel horizons. Additionally, in Fig. 6E the decrease in susceptibility at approximately 120 °C suggests that goethite is present. Samples from Rat (site 4; Fig. 6G, H) were only collected from gravel layers and yielded thermomagnetic curves with clear magnetic
susceptibilities that decreased at approximately 548 °C (Tc2), between 571 and 586 °C (Tc1), and between 649 and 654 °C (Tc3), which indicates the presence of titanomagnetite, magnetite and titanomaghemites and/or titanohematites, respectively (e.g., Tauxe, 1998).

4.3.4. Magnetic hysteresis

Similar behaviours in the hysteresis curves calculated in this paper can be observed in all samples (Appendix 3). These samples mainly exhibit strong ferromagnetic behaviour and weak paramagnetic behaviour, which is evident by the shape of the curves, the high low-field susceptibility (χlf) and magnetization (Ms and Mr) values, and the low (or negative high-field susceptibility (χhf) values. The samples also have low coercive force values (Hc), except those from the fine-grained sediments from Rat (Appendix 3). The hysteresis values were plotted in the Theoretical Day Plot (Fig. 7; cf. Dunlop, 2002a) to discriminate the magnetic size (and possible mixtures of sizes) of the Fe-bearing minerals. Values measured from sub-samples of the clay and silt layers from Rat plot within the pseudo-single-domain (PSD) field, between the single-domain (SD) + multi-domain (MD) mixing curves and the SD + superparamagnetic (SP) (10 nm) domain mixing curve. This finding might be the result of a mixture of PSD and SP magnetic grains or a ternary mixture of SP + SD + MD (i.e., Dunlop, 2002b); however, in the latter case, it could be inferred that there is a large percentage of small particles (SP/SD) that result from authigenic processes linked to wetter environmental conditions, which is supported by the high values of kfδ% (> 5%). In contrast, values from the sub-samples from...
paleosols and sediments without pedogenesis or authigenesis plot mainly between the MD curve and the SD + SP (10 nm) domain mixing curve (e.g., Dunlop, 2002b). This observation might be the result of a SP + MD mixture dominated by MD magnetic grains. Such magnetic grains, seen in the SEM analyses and consistent with the low \( k_{fd}\% \) values (< 3%) obtained, likely indicate a detrital origin (magnetite and titanomagnetite \( > 20 \mu m \)).

5. Discussion

5.1. Magnetic proxies in paleosols and sediments deposited \(< 200 \text{ mm yr}^{-1}\)

As mentioned above, the fraction \( F_a \) of all samples has more variable and higher \( k \) values compared to the \( F_b \) and \( F_c \) fractions. The \( k_{fd}\% \) values are relatively low, with an average of < 4%, regardless of the sampling site and fraction, except for in the clay and silt layers of the Ratones sediments (Rat). Microscopic (Fig. 4) and SEM/EDS (Fig. 5) observations and thermomagnetic experiments (Fig. 6) from fraction \( F_a \) sub-samples indicate that the Fe-bearing minerals from all sites, except for those from the clay and silt layers from Rat, are rounded subhedral magnetite (\( > 20 \mu m \), Figs. 4 and 5A, B) and titanomagnetite crystals (Fig. 5C). The AtII and Arr also include, to a lesser extent, laminated (\( > 20 \mu m \)) hematite crystals (Fig. 5D). Maghemite appears to be present in all deposits, according to the results of the thermomagnetic experiments. In the thermomagnetic experiment and microscopic observation of the Arr sample CT0201A (Fig. 6E), we interpreted the goethite present to be a product of erosion of the supergene alteration of the surrounding copper porphyry (e.g., Riveros et al., 2014) rather than an authigenic product, since other proxies suggest restricted pedogenesis processes. The Day plot (Fig. 7) indicates that the Fe-bearing minerals in coarse-grained sediments are mostly PSD/MD. The dataset obtained here allows the possibility that the stratigraphic variations in magnetic susceptibility (\( k \)) values for the AtII, Arr and Rat gravel and sand sediments are mainly controlled by the concentration of Fe-bearing minerals. These minerals correspond to detrital material derived from the erosion of rock outcrops in the vicinity, as also has been suggested by Sáez et al. (2012, for the Quillagua Basin).

Carbonate-rich paleosols are common within the AtII and Arr, indicating that these units were deposited under arid climate conditions (Rech et al., 2006). Carbonate-rich paleosols within the Arr are covered by a several metres thick sulfate-rich paleosol. The field observations and the presence of root traces in the carbonate-rich paleosols suggest that they formed at the surface; the well-developed sulfate-rich paleosol formed later under distinctly more arid climatic conditions (Rech et al., 2006; Jordan et al., 2014; Sun et al., 2018). The superposition of similar pedogenic features observed in the gravel deposits in the Calama basin and chronologically correlated with the Arr are interpreted to be evidence of the mid-Miocene climate hyperaridification (Rech et al., 2006, 2010). Consistent with these results, early to mid-Miocene climate desiccation also has been determined from the paleosol content of the Arr exposed at the Tesoro mine open pit (Oerter et al., 2016) and from the sulfate-rich paleosols that occur within the gravel deposits exposed at the Spence mine area, 30 km north of the Centinela area (Sun et al., 2018).

The \( k \) values tend to slightly decrease in the sulfate-rich Bym and carbonate-rich paleosol horizons relative to the \( k \) values from the
sedi-ments with no or poor (Bz) paleosol development (Fig. 3). This slight variation in k values and the low kfd% values (< 4%) contrast with values reported for paleosols formed under conditions of higher rainfall (> 200 mm yr⁻¹). In these conditions, authigenesis of Fe-bearing minerals (i.e., magnetite, hematite or maghemite of SP/SD magnetic grain size) mainly results in the enhancement of k and kfd% values of the host sediments (e.g., Dearing et al., 1996a, 1996b; Maher and Thompson, 1999; Evans and Heller, 2003; Geiss and Zanner, 2007; Hao et al., 2008; Xie et al., 2009; Maxbauer et al., 2016). Due to the limited Fe-mineral authogenesis (evidenced by the low kfd% values of other proxies), the small decrease in magnetic susceptibility relative to that of the sediments with no or poor (Bz) paleosol development (Fig. 3) found in sulfate and carbonate rich paleosols can be related to dissolution processes that are potentially linked to light chemical reactions between the Fe-bearing detrital minerals and the carbonate/sulfate-rich solutions (e.g., Bustillo, 2010; Ewing et al., 2006). In this case, the released Fe³⁺ minerals may reprecipitate to form higher coercivity minerals such as maghemite, hematite or goethite (Orgeira et al., 2008). Indeed, microscopic observations show a slightly higher hematite content and the presence of maghemite in these horizons (Appendix 5). Alternatively, changes in the concentrations of Fe-bearing minerals due to mechanical weathering or the growth of salt crystals (e.g., Retallack, 2008) could be invoked. However, these variations are small compared to the variability in susceptibility along the profiles and therefore these limited pedogenetic processes cannot account for the variations observed. The magnetic signature of sediments in arid/hyper-arid climates is likely derived from detrital sources or variations in the input linked to climate and/or tectonic conditions of the catchment.

Among the different sedimentary units, AIff shows larger k values than those of the Rat coarse sediments, which have larger k values than the Arr (Fig. 8). Following the interpretation discussed above, the increased k values are probably linked to an increased detrital input (e.g., Sáez et al., 2012); the similar behaviour observed in the thermomagnetic curves suggests that a major change in the sediment source among different sedimentary units is unlikely. One possibility is that variations in the k value relate to variations in the climatic conditions in which these units were deposited; the climatic variations are indicated by the presence of different paleosols (carbonate-rich and sulfate-rich paleosols) and by variations in the content of the sedimentary facies (Riquelme et al., 2018; Fernández-Mort et al., 2018). The facies of AIff suggest it was deposited under wetter conditions than the Arr and Rat coarse sediments (gravel and sand layers). The AIff sedimentary facies indicate relatively permanent stream-flows that do not occur under the hyper-arid conditions that currently prevail in the Atacama Desert. Currently, these facies are only observed at the bottom of the main canyons that are fed by runoff from precipitation in the high Andes Cordillera (e.g., Nalpas et al., 2008). In contrast, the Arr and Rat coarse sediments are almost completely composed of hyper-concentrated debris-flow and sheet-flow deposits, similar to those observed during recent torrential rain episodes in the Atacama Desert (Riquelme et al., 2018). Diminished k values in the AIff to the Arr and Rat coarse sediments, could be related to the decreased precipitation rates and dilution of the sedimentary flows from which these sediments were deposited. Indeed, the AIff deposition occurred during more humid climatic conditions and more diluted flows than did deposition of the Arr and Rat coarse sediments. Additionally, the AIff and Arr- Rat coarse sediments differ in their sediment provenances (although this is not obvious from the thermonagnetic experiments) and in the tectonic conditions under which they were deposited (Riquelme et al., 2018).

Riquelme et al. (2018) showed that AIff mainly includes clasts rich in magnetic minerals that originate from Paleocene andesitic and dacite volcanic rocks, whereas clasts from Cretaceous and Paleocene granitoïds are subordinate. The Arr and Rat formations are sourced from a wider range of lithologies and include important contributions from Mesozoic calcareous and Paleozoic metamorphic basement rock fragments (Riquelme et al., 2018). Tectonic conditions also differed during the deposition of the sedimentary units. AIff coincides with a time of relatively rapid exhumation and denudation, as suggested by modelling of thermochronological data from the Centinela Mining District (Sanchez et al., 2018), whereas the deposition of the Arr and Rat coarse sediments coincides with a time of relatively slow rock erosion and denudation and landscape pediplanation (Maksav and Zentilli, 1999; Riquelme et al., 2018). Therefore, some of the decrease in the susceptibility may have arisen from variations in the source and the tectonic context.

In these arid/hyper-arid contexts, we show that variations in the magnetic susceptibility correspond to changes in the concentrations of Fe-bearing minerals, which are linked to both the source and the tectonic/climatic context. Since variations in source are easy to track, sections of continental gravels can be used to unravel the tectonic/climatic history of a region and therefore continuous, longer records are now needed.

5.2. Magnetic proxies in wetland deposit

Sedimentary deposits entrenched within incised valleys that include silt, clay and marl beds, such as those exposed in Rat, are common in the Atacama Desert and have been related to wetland environments (Betancourt et al., 2000; Rech et al., 2002, 2003; Quade et al., 2008; Grosjean et al., 2005). Two opposing models have been proposed for the origin of the fine-grained deposits in these environments; these two models suggest that the deposits either result from high or low water-tables. In the first model, fine-grained sediments are deposited when the water-table reaches the ground surface and the dense vegetation and humidity content of the sediments allows fine sediments to be trapped, making them relatively resistant to erosion (Quade et al., 1995; Rech et al., 2002). In the second model, fine-grained sediment deposition occurs during dry periods when the water-table drops and hillslopes are de-vegetated, allowing the stripped soil to erode and sediments to accumulate in channels (Grosjean, 2001). Both models used to interpret the wetlands deposits are concerned with environmental fluctuations that have a higher frequency and shorter time-scale (10-100 kyr) than those registered by paleosols within AIff and Arr (Fig. 9).

The clay and silt layers from Rat show higher kfd% values (> 5%) and lower k values in the coarse-grained layers of this sedimentary unit (Fig. 3). Additionally, the hysteresis parameters indicate that the Fe-bearing minerals mainly correspond to SP/SD magnetic grain sizes (Fig. 7). These observations indicate a diagenetic or/and authigenetic origin for Fe-bearing minerals in clay and silt layers from Rat (Dearing
et al., 1996a, 1996b; Maher and Thompson, 1999; Evans and Heller, 2003; Maxbauer et al., 2016). In addition, small size hematite grains (ca. 2 μm, Fig. 5F) are observed in the upper part of Rat, whereas small crystals of maghemite/magnetite are observed in the lower part of this deposit (Fig. 5E), which would indicate the oxidation state increases upwards in the stratigraphic record.

Authigenesis of Fe-bearing minerals in the wetland deposits could be linked to redox oscillations during wet/dry cycles and the fermentation process related to soil formation in wetland environments. The production of nanocrystalline magnetite could result from the partial reduction of ferricydrite or detrital (titanio)magnetite when the water-table reaches the ground surface and reprecipitation when the water table drops and the wetlands dry out (this occurs periodically through the Rat unit) in an extreme oxidizing medium due to the hyper-arid conditions of the desert (Navarro-González et al., 2003; Fig. 9). Fermentation processes are widely related to bacterial activity, although they have also been proven to occur abiotically (e.g., Maher, 1998; Hu et al., 2013; Maxbauer et al., 2016). In our case, no magnetotactic bacteria were observed under the SEM. The partial destruction of paedogenic magnetite in an active soil by maghemitization processes (e.g., Orgeira et al., 2008, 2011; Maxbauer et al., 2016) linked to wet/dry cycles could contribute to the low k values and could explain the maghemite and hematite crystals observed in these layers (Fig. 5F, E). Another means of forming maghemite and hematite is through the oxidation of authigenic/detrital magnetite during early diagenesis, which is caused by the circulation of post-formation shallow groundwater (Pimentel et al., 1996; Pimentel, 2002); this process cannot be discarded in our case and may partially account for the signal observed. An aging pathway of ferricydrite to hematite is an alternative way to produce hematite (e.g., Maxbauer et al., 2016). However, in this process, there is no pathway for the production of magnetite/maghemite, which are observed in the samples; therefore, we favor the process described in Fig. 9. To test the validity of this hypothesis, a quantitative model of magnetic enhancement could be tested on the current wetland deposits from the Atacama Desert, where the annual precipitation and evapotranspiration potential rates are known (e.g., Orgeira et al., 2011).

The clay and silt layers from Rat showed increased kfd% values. Allowing us to propose that this value can be used as a proxy for characterizing the increase in diagenetic and/or authigenic modifications linked to local water-table variations associated with local climatic fluctuations. This finding also allows us to substantiate the hypothesis that fine-grained deposition likely occurs when the water-table reaches the ground surface (e.g., Quade et al., 1995; Rech et al., 2002).

6. Conclusions

The present study seeks to establish a relationship between magnetic proxies – i.e., magnetic susceptibility and frequency-dependent magnetic susceptibility – measured on continental coarse-grained sediments and paleosols developed under low-precipitation (MAP < 200 mm yr⁻¹) climatic conditions. For this work, we selected a sedimentary sequence of coarse-grained sediments resulting from Eocene-Miocene erosion of the Centinela area of the Precordillera of northern Chile. Our conclusions can be summarised as follows:

- The k signal obtained along the stratigraphy in the Centinela area, except from the clay and silt layers from Rat, is controlled by the concentration of detrital Fe-bearing minerals (i.e., mainly magnetite and titanomagnetite), which are concentrated in the finest fraction (< 0.5 mm) of the coarse-grained sediments.
- The impact of paedogenic processes on magnetic minerals in paleosols developed under arid to hyper-arid climate conditions on coarse-grained sediments is small compared to that on paleosols developed on fine-grained deposits during wetter climates.
- The decreasing of k values from the AtII to the Arr and Rat coarse sediments is linked to a decrease in the input of detrital Fe-bearing minerals, which could be related either to tectonics or to a regional trend in climate aridification that changed the provenance of the sediments. Longer records are needed to resolve this uncertainty.
- The high kfd% values in the clay and silt layers from Rat are linked to an increase in the authigenic degree, which could be related to local water-table variations associated with local, high-frequency, short time scale climatic fluctuations (10–100 kyr).
- The integration of different datasets (magnetic proxies, mineralogy, geochemistry, and field-based stratigraphic data) demonstrates the feasibility of using magnetic proxies to uncover climatic/environmental signals in coarse-grained sediments.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.palaeo.2018.12.009.
Acknowledgments

This work was funded by CONICYT (the Chilean Commission on Science and Technology), by means of a Doctorados Nacionales scholarship No. 21150393 and FONDECYT Project No. 1170992, and by the IRD (Institut de Recherche pour le Développement, France) by means of grant ARTS-IRD No. 862271K and the Laboratoire Mixte International (LMI) Cuivre et Pediments (COPEDIM). We thank Antofagasta Minerals for providing access to the study area and for support during fieldworks campaigns. We gratefully acknowledge the editor Professor Thomas Algeo and two anonymous reviewers for their useful reviews, which have greatly improved this work.

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