Magnetic susceptibility application: a window onto ancient environments and climatic variations: foreword

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Abstract: Magnetic susceptibility (MS) is a powerful tool, which is being applied increasingly on sedimentary rocks to constrain stratigraphic correlations, or as a palaeo-environmental or palaeoclimatic tool. The origin of the magnetic minerals responsible for the variations in MS can be linked to various phenomena such as detrital inputs, pedogenesis, bacterial precipitation or diagenesis. Therefore, it is critical to improve our knowledge of the origin of the MS signal in order to apply it for correlations or as a proxy. Here, we present a synthesis of the techniques that can be applied to get a better understanding of the origin of the MS signal, through comparison with other palaeo-environmental proxies, through magnetic measurements or through dissolution and direct observation of the extracted minerals. We also propose an overview of the different techniques applied in order to use MS as a correlation tool, and we show various examples of successful applications of MS as a recorder of change in past sea-level and climate. We also present the main results and activities of the IGCP-580 project 'Application of magnetic susceptibility as a palaeo-climatic proxy on Palaeozoic sedimentary rocks and characterization of the magnetic signal'.

Understanding palaeo-environment changes, including changes in climate, requires identification of reliable proxies that can be efficiently documented within a short time frame and at relatively low cost, in order to obtain the types of high-resolution time series data required for such research. Magnetic susceptibility (MS) measurements readily meet these criteria. MS records commonly are relatively robust and can be correlated within and between different sedimentary basins. MS measurements are bulk, non-oriented measurements, and represent the sum of all individual susceptibility contributions of various magnetic minerals present in the sample. The origin of these main magnetic minerals is generally assumed to result from detrital inputs, from fluvial or aeolian sources (Ellwood *et al.* 2000; Stage 2001; Rey *et al.* 2008; Hladil *et al.* 2010*a*; Maher 2011). In some case, magnetic minerals are also related to soil formation (Tite & Linington 1975; Dearing *et al.* 1996) or are of bacterial origin (Kirschvink & Chang 1984; Hladil *et al.* 2004; Kopp & Kirschvink 2008). In Quaternary marine

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sediments, magnetofossils are locally relatively common, compared with the pre-Quaternary magnetofossil records (Kopp & Kirschvink 2008).

The use of MS as stratigraphic tool was originally developed during the 1970s, with studies on Mesozoic and Cenozoic deep-marine (Radhakrishnamurty et al. 1968; Amin et al. 1972) and lake sediments (Oldfield et al. 1978). The climatic influence on the MS evolution was comprehensively documented in Pleistocene marine sediments, through the link between MS and oxygen isotope evolution (Robinson 1986). In this respect, MS was used for correlation and as a palaeo-environmental proxy (e.g. Foubert & Henriet 2009). Furthermore, spectral analysis of MS records was also used to demonstrate the presence of orbitally driven climatic cycles in Cenozoic sediments (Mead & Tauxe 1986; Shackleton et al. 1999), which significantly improved the precision of the Cenozoic Time Scale (Hinnov & Hilgen 2012). More recently, the use of MS has been widespread in the analysis of lithified Palaeozoic (mostly marine) sedimentary rocks (Crick et al. 1997; Da Silva & Boulvain 2002; Racki et al. 2002; Hladil et al. 2006; Da Silva et al. 2009a; Whalen & Day 2010; Koptíková 2011). However, deciphering the ultimate origin of the magnetic minerals carrying the MS signal is of crucial importance for meaningful interpretation of the MS signal in terms of palaeo-environmental evolution. In lithified sediments, the primary origin of the magnetic minerals is often partly constrained. Key questions that need to be considered include: what the source of the primary minerals is; and whether they are of aeolian or riverine sources or formed during pedogenesis or by bacteria. Furthermore, secondary processes, such as diagenesis, remagnetization and metamorphism, can influence, complicate or completely erase the primary signal.

This Special Publication was initiated to gather and present results from the IGCP-580 UNESCO project (2009-2015) on the 'Application of magnetic susceptibility as a palaeo-climatic proxy on Palaeozoic sedimentary rocks and characterization of the magnetic signal'. The volume includes contributions related to MS data from Silurian rocks to Recent sediments, with material from Europe, Middle East, North Africa, China, North America and Russia. The book is divided in three parts: the first part concerns the control exerted by sedimentary setting on MS evolution; the second part comprises contributions that focus on the origin and nature of the minerals carrying the MS signal; and the final part deals with the identification of climatic/ astronomic cycles in magnetic susceptibility signals.

In this introductory paper, we will present the different techniques that can be applied in order to identify the nature and the origin of the magnetic minerals, with examples for each technique. We then present some examples of the application of MS, including methods and precautions for correlations and palaeo-environmental and palaeoclimatic applications. Some of the techniques and applications described in this introduction are used in papers included in this volume (given in bold at first mention). The main results and activities of the IGCP-580 project are also described.

Origin of the MS signal

Since the MS signal can be related to primary origins (mostly fluvial or aeolian detrital inputs, bacterial or pedogenetic precipitation) or can be transformed through secondary processes (diagenesis, remagnetization, metamorphism), it is important to assess the origin of the minerals carrying the MS signal. Demonstration of a primary detrital origin of the magnetic component is indeed crucial in order to effectively use MS for correlations or as a palaeoenvironmental and palaeo-climatic proxy.

Different techniques have been developed in order to assess the origin of minerals that influence the MS signal including: (1) comparison with other proxies influenced by palaeo-environmental parameters; (2) magnetic property measurements to obtain information on the magnetic mineralogy and grain size; and (3) direct observation of the magnetic minerals via dissolution.

Comparison with other proxies

Comparing the MS signal with other palaeoenvironmental proxies or detrital proxies permits inferences about the carriers of the MS signal. A positive correlation between MS and independent palaeo-environmental proxies is the first indication that the primary signal is preserved. These non-magnetic palaeo-environmental proxies include the following:

- *Clay or quartz content or insoluble residues in carbonate rocks* are typically of detrital origin and are classical parameters to be compared with MS in order to infer a primary, detrital origin of the MS signal (Ellwood *et al.* 1999; English 1999; Mabille & Boulvain 2008; Hladil *et al.* 2009). For example, Mabille & Boulvain (2008) showed that the MS increased with increasing quartz content on two Middle Devonian sections from Belgium (Fig. 1a).
- Geochemical elements such as Zr, Th, Ti and Al are proxies for changes in source or amount of detrital material or type of weathering (Tribovillard et al. 2006; Calvert & Pedersen 2007) and have been compared with MS in order to highlight a detrital origin of this MS signal (Riquier et al. 2010; Da Silva et al. 2012, 2013; Śliwiński

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Fig. 1. Comparison of magnetic susceptibility signal with other proxies and magnetic parameters from selected Devonian examples. (a) Average, minimal and maximal magnetic susceptibility values plotted by percentage of detrital quartz for La Couvinoise and Les Monts de Baileux sections from Belgium; Modified after Mabille & Boulvain (2007).
(b) Magnetic susceptibility compared with Zr content in Villers and Tailfer sections from Belgium, modified from Da Silva *et al.* (2013). (c) Comparison of magnetic susceptibility evolution with sedimentary facies from the Villers section (Belgium). Modified after Da Silva *et al.* (2013).

et al. 2012; Alekseev *et al.* 2015; Grabowski *et al.* 2015; Jadot & Boulvain 2015; Pas *et al.* 2015; Whalen *et al.* 2015). An example is provided in Figure 1b, with a comparison of the MS with the Zr content for two Frasnian sections from Belgium (Da Silva *et al.* 2012). The two sections illustrate very different behaviours, with the Villers section indicating a moderate correlation between MS and Zr content (r = 0.6) and a poor correlation on the Tailfer section

(r = 0.3). This suggests that some primary signal was partly preserved in the Villers section, while it was very poorly preserved owing to diagenetic impact at Tailfer (for complete results, see Da Silva *et al.* 2013).

 Gamma-ray spectrometry (GRS) measurements are related to the abundance of the three dominant radioactive elements occurring in sedimentary rocks: K, Th and U. For carbonate rocks, K and Th are interpreted as reflecting clastic content, whereas U is related to bottom-water oxygenation and diagenetic processes involving changes in oxidation-reduction state (Ehrenberg & Svana 2001; Kozłowski & Sobień 2012). GRS curves have often been compared with MS patterns, and differences and similarities can provide insight into detrital and/or diagenetic influences (Bábek *et al.* 2010; Koptíková *et al.* 2010*a*, *b*, Koptíková 2011; Kozłowski & Sobień 2012; Ellwood *et al.* 2013; Grabowski *et al.* 2013; Chadimova *et al.* 2015; Devleeschouwer *et al.* 2015; Mayrhofer & Lukeneder 2015). In Devonian carbonates from the Barrandian area in the Czech Republic (Požáry-3 section), Koptíková *et al.* (2010*a*) showed that there is a relatively good correlation between MS and GRS (Fig. 2).

 The spectral reflectance (SR)/colour index is used as indicator of CaCO₃ content and organic carbon in carbonates and is interpreted in terms



Fig. 2. Stratigraphic framework of the Požáry-3 section: lithostratigraphy, chronostratigraphy and basic outcrop logging patterns – spectral gamma-ray logs (GRS), magnetic susceptibility log (MS), spectral reflectance (SR) and brightness (CIE L^* , the brightness, is a dimensionless number (no units), as it is defined as a ratio between the maximum reflectance or white colour and the measured value). Modified after Koptíková *et al.* (2010*a*).

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of cyclicity and palaeo-climate. The SR allows an estimation of the concentration of minerals such as hematite, goethite and chlorites, which are often interpreted as palaeo-climatic proxies (e.g. Koptíková et al. 2010a). Comparison of MS signal with SR was proposed in Koptíková et al. (2010a), and Devleeschouwer et al. (2015). Koptíková et al. (2010a) also showed that both SR and MS signals, in Czech Barrandian Devonian carbonates, record a marked cyclicity (Fig. 2, Požáry-3 section). The SR log is obscured by zones of elevated brightness, which are associated with minor faults and 'leaching zones' (Fig. 2) with enhanced diagenesis. However, the MS signal in these zones remains relatively unaffected (Fig. 2), which indicates that in this case, local diagenetic alteration has a low impact on the MS data.

- Facies evolution can also be compared with the MS signal to identify a link between sea-level and MS changes (Mabille et al. 2008; Da Silva et al. 2009a; Bábek et al. 2013; Alekseev et al. 2015; Dechamps et al. 2015; Grabowski et al. 2015; Sardar Abadi et al. 2015). The MS signal from the Villers section (Devonian, Belgium), which was previously interpreted as carrying a detrital signal, based on the link with Zr (Fig. 1b), also demonstrates a clear link between MS and facies evolution, with increasing MS correlated with shallowing-upward trends (Fig. 1c; Da Silva et al. 2012).
- Radioactive isotopes: Sr (Frank 2002) and Nd isotopes (Burton & Vance 2000; Burton 2006; Dopieralska et al. 2006) are derived from the weathering of continental material and submarine volcanism, and can be used to investigate continental erosion and oceanic circulation. Application of Sr or Nd isotopes on Palaeozoic sections is still relatively rare and, to our knowledge, no comparison with MS signal has been published yet.

Magnetic property measurements

Magnetic property measurements allow identification of the nature, amount and grain size of the main magnetic minerals. Magnetic grain size is a key parameter because it depends strongly on the forming conditions of the magnetic minerals: diagenetic grains are typically 30–100 nm whereas detrital grains are commonly much coarser (micron size) (Channel & McCabe 1994). Numerous books have offered extended details on all of these techniques (e.g. Walden *et al.* 1999; Evans & Heller 2003; Tauxe 2010). Here we propose a synthesis of the main magnetic techniques and significant outcomes for the application of MS as a palaeoenvironmental tool.

Nature of the magnetic minerals

- (1)Hysteresis measurements allow the quantification of the proportion of ferromagnetic (e.g. magnetite, hematite, goethite, etc.) minerals on one side and of paramagnetic (e.g. most clay minerals, pyrite, etc.) and diamagnetic (e.g. calcite, quartz, etc.) minerals on the other side (Devleeschouwer et al. 2010; Riquier et al. 2010; Da Silva et al. 2013; Blumentritt 2015; Devleeschouwer et al. 2015; Sardar Abadi et al. 2015). Furthermore, parameters extracted from hysteresis loops (parameters such as: M_{rs} , remanence magnetization; M_{s} , saturation magnetization; H_c , coercivity; and $H_{\rm cr}$, remanence coercivity) permit a rough discrimination between high (such as hematite) and low coercivity (such as magnetite) ferromagnetic minerals and provide information on the grain size (see below).
- (2) The isothermal remanent magnetization (IRM) acquisition curve and S-ratio allow a better discrimination of low and high coercivity ferromagnetic minerals by Gaussian function processing (Robertson & France 1994; Kruiver et al. 2001; Egli 2003), which also provides an estimate of their relative proportions (applied by e.g. Egli 2004; Font et al. 2005, 2010; Da Silva et al. 2013; Chadimova et al. 2015; Devleeschouwer et al. 2015; Grabowski et al. 2015).
- (3) Thermomagnetic measurements facilitate identification of the ferromagnetic mineral types based on their respective Curie or Néel temperature, but cannot provide quantification of these minerals (e.g. Nawrocki et al. 2008; Devleeschouwer et al. 2010; Ellwood et al. 2015).

Magnetic grain size indicators

- The Day plot (defined by Day et al. 1977, and improved by Parry 1982, and Dunlop 2002) uses the main hysteresis parameters in an M_s/M_{rs} v. H_c/H_{cr} plot (applied by Devleeschouwer et al. 2010; Riquier et al. 2010; Casier et al. 2011; Sardar Abadi et al. 2015), in order to discriminate between domain state (from the smallest grains to the coarsest: superparamagnetic, SP; single domain, SD; pseudo-single-domain, PSD; multidomain, MD).
- (2) The squareness v. coercivity plot (Tauxe et al. 2002) uses hysteresis parameters in an M_s/M_{rs} v. H_c plot that is also applied to discriminate between domain state (applied by Da Silva et al. 2012, 2013; Devleeschouwer et al. 2015).
- (3) The frequency dependence of susceptibility ($\chi_{\rm fd}$) is the difference in susceptibility

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measured at high and low frequencies and is used to identify the presence of SP particles (Jackson *et al.* 1993; Font *et al.* 2005; Chadimova *et al.* 2015; Devleeschouwer *et al.* 2015).

- (4) Anhysteresic remanent magnetization susceptibility (χ_{ARM}) is used in order to identify SD particles (Evans & Heller 2003; Blumentritt 2015; Chadimova *et al.* 2015; Grabowski *et al.* 2015).
- (5) The anhysteresic remanent magnetization divided by the isothermal remanent magnetization (ARM/IRM), the saturation isothermal remanent magnetization divided by the low field susceptibility (SIRM/ χ_{1f}) and the χ_{ARM}/χ_{1f} ratio are also grain size indicators (Evans & Heller 2003);
- (6) First-order reversal curves (Roberts et al. 2000) are used for magnetic characterization of different populations of magnetite (Roberts et al. 2006) or biogenic magnetite SD particles (Egli et al. 2010);
- (7) The decay of viscous remanent magnetization (Mullins & Tite 1973; Spassov & Valet 2012) indicates the presence of ultra-fine-grained particles (close to the limits between SP and SD grain sizes, i.e. around 30 nm). Nevertheless, this parameter is influenced by the lithology (e.g. difference between clastic and carbonate sediments; Zwing *et al.* 2005) and probably by changes in the concentration or in the grain size population of these nanomagnetic particles.

Direct observations of the magnetic minerals

Direct examination of magnetic grains from a sample is possible when the grains are abundant and large enough. However, it is often necessary to extract the magnetic minerals from the rock. Such processing is extremely time-consuming (full procedure by Hounslow & Maher 1999), but it

may be the only procedure providing precise information about the origin of the magnetic minerals. Figure 3 illustrates iron oxide and pyrrhotite grains extracted from Devonian carbonates (from Koptíková *et al.* 2010*b*; Koptíková 2011).

Applications of MS: a window onto ancient palaeo-environments

After deciphering the origin of the MS signals through one of the previously described techniques, or even better, a combination of different techniques, it is possible to isolate the primary, detrital MS signal. Such MS data, forming long, continuous time series, can then be used as a palaeoenvironmental and palaeo-climatic proxy and for correlations and cyclostratigraphic analyses.

Application of MS as a correlation tool

After the pioneering works of Crick *et al.* (1997), MS has been widely used for correlating Palaeozoic sedimentary sequences. Importantly, these correlations need to be framed in a well-developed biostratigraphic framework. Correlations can then be established through different techniques:

- By visual correlation of MS peaks (Crick et al. 1997; Geršl & Hladil 2004; Da Silva & Boulvain 2006; Bábek et al. 2010; Boulvain et al. 2010; Michel et al. 2010; Dechamps et al. 2015; Grabowski et al. 2015; Mayrhofer & Lukeneder 2015; Whalen et al. 2015).
- The MS curve can also be included in a *sequence stratigraphic* framework (Whalen & Day 2008, 2010; Da Silva *et al.* 2010). Whalen & Day (2010) demonstrated a predictable pattern of relatively low MS in late transgressive and early highstand facies and higher MS in late highstand, lowstand and early transgressive facies at both the sequence and parasequence level.



Fig. 3. SEM images of mineral assemblages in insoluble residues from Devonian. (**a**) Iron oxide, Eifelian in the Prague Synform, from the Cerveny lom Quarry. (**b**) Pyrrhotite, Lochkovian to Emsian in the Prague Synfrom, Požáry-3 section (79.7 m, see log on Fig. 2), modified after Koptíková *et al.* (2010*b*).

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- Ellwood *et al.* (2006) presented the MS curve as *bar-log format*, similar to the presentation of magnetic polarity data. If the MS cyclic trends increase or decrease by a factor of 2 or more, and if the change is represented by two or more data points, then this change is assumed to be significant, and the highs and lows associated with these cycles are differentiated by filled (high MS values) or open (low MS values) bar logs. Whalen & Day (2010), using bar logs delineated from spline-smoothed MS signals, demonstrated very high-level correlation ($R^2 \ge 0.9$) of the MS signature between several sections in western Canada through a modified graphic correlation technique.
- Hladil *et al.* (2010*b*) applied the numerical method of *dynamic time warping* (developed in the field of speech recognition), which computes the most probable correlation(s). This technique is proposed to solve inherent problems related to MS records, such as patterns with different shapes and intensities and the possible incompleteness of the record from individual sections. Chadimova *et al.* (2015) applied dynamic time warping to a Silurian succession in the Czech Republic.
- After identifying Milankovich cycles (see more details in the following section) in target sections, **De Vleeschouwer** *et al.* (2015) and De Vleeschouwer *et al.* (2012*b*), used these as correlation anchors in order to correlate respectively Givetian and Frasnian sections. The construction of a floating time scale permits display of the data as time series in the time domain, rather than in the distance domain. It is then possible to correlate contemporaneous series, since accumulation rate does not have to be taken into account (see also Da Silva *et al.* 2013).

Application of MS records as palaeoenvironmental and palaeo-climatic proxy

Influence of sea-level. If magnetic minerals are of a primary detrital origin, the MS signal may be strongly influenced by sea-level variations. Ellwood et al. (1999) contend that, during times of regression, the base level is lowered, which increases erosion potential, thus increasing the amount of detrital particles transported and distributed into the marine setting. This would cause enhanced MS values during times of low or falling sea-level. In this respect, MS has been often interpreted as influenced by sea-level variations (Zhang et al. 2000; Da Silva et al. 2009a, b; Koptíková et al. 2010a; Whalen & Day 2010). The relationships documented by Whalen & Day (2010) largely support prior assertions about the relationship of MS to sea-level change (Crick et al. 1997; Ellwood et al. 1999,

2000) at the third and fourth order but not during a long-term second-order sea-level event. Therefore, the link between sea-level changes and MS may be more complicated than expected (Mabille et al. 2008; Da Silva et al. 2009a; Bábek et al. 2013). Actually, the record of sea-level changes may differ depending on the sedimentary setting and the morphology of carbonate platforms, which can influence the way magnetic minerals settle in a sedimentary environment (cf. comparison of MS records on different platform types in Da Silva et al. 2009a). On carbonate platform (s.s.), during lowering sealevel, the carbonate production rate decreases, while the detrital input increases, leading to higher MS values (Da Silva et al. 2009a). On carbonate ramp and atoll settings, higher sedimentation rate and water agitation in shallow water facies can hamper the settling of magnetic particles and can result in lower MS values (Mabille & Boulvain 2007; Da Silva et al. 2009a, b; Bábek et al. 2010, 2013; Koptíková et al. 2010a). These findings demonstrate the importance of understanding the depositional setting of facies sampled for MS and the potential pitfalls of comparing MS records from different palaeo-environments (see also Alekseev et al. 2015; Grabowski et al. 2015; Pas et al. 2015; Sardar Abadi et al. 2015).

Influence of climate – cyclostratigraphy. As mentioned above the influence of climate on MS variations in sediments was demonstrated in Pleistocene sediments by coupling variations in MS with the O-isotope curve (Robinson 1986). In Palaeozoic sediments, this influence is often inferred, and the recent application of spectral analysis on MS records provides convincing evidence of the presence of astronomically driven (Milankovich) cycles in Palaeozoic sections (Rodionov et al. 2003; Ellwood et al. 2008, 2011a, b, 2015; De Vleeschouwer et al. 2012a, b, 2015; Da Silva et al. 2013; Devleeschouwer et al. 2015; Grabowski et al. 2015). Identification and counting of climatic cycles of constant duration, identified into MS signals, permit the creation of floating time scales for some parts of the Palaeozoic (Ellwood et al. 2007, 2011a, b, 2015; De Vleeschouwer et al. 2012a, b, 2015; García-Alcalde et al. 2012; Da Silva et al. 2013). These floating time scales improve our knowledge of the timing of different events (De Vleeschouwer et al. 2013), further providing more accurate correlations between different sedimentological sections (see also the previous section). The average spectral misfits method (Meyers & Sageman 2007) can be applied to MS datasets and allows a quantification of the optimal sedimentary rate for a stratigraphic interval (when a orbital signal is preserved). It also provides a statistical test for the rejection of the null hypothesis, that is, no orbital signal.

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IGCP-580 project: application of MS as a palaeo-environmental tool

The IGCP-580 project (UNESCO) entitled 'Application of magnetic susceptibility as a palaeoclimatic proxy on Palaeozoic sedimentary rocks and characterization of the magnetic signal' (synthesis of project activities in Da Silva *et al.* 2014) was initiated to encourage the use of MS data for correlation and palaeo-environmental/palaeoclimatic analysis in deep time. It was launched in 2009 within the framework of the development and acquisition and processing of MS data from Palaeozoic rocks, but also with an awareness of the possible complexity behind this MS signal and the importance of gaining a better understanding of its origin.

The first main objective of IGCP-580 was to compile existing MS data and to collect new material and MS data (about 35 000 samples collected by the different participating teams during the 5 years of the project). During the project, we received all types of contribution related to the application of MS, in all types of setting and lithology and from any time period. However, in order to provide an over-arching framework, we decided to focus the IGCP-580 field work and sampling on the Devonian system. This time period was selected because, for the Palaeozoic, it has a relatively robust biostratigraphic framework, allowing an essential control to frame the correlations through MS. Furthermore, an important amount of MS data had already been published on the Mid-Palaeozoic (Crick et al. 2001; Ellwood et al. 2001, 2007: Da Silva & Boulvain 2002, 2003, 2006; Hladil 2002; Racki et al. 2002; Hladil et al. 2003, 2006; Geršl & Hladil 2004; Whalen & Day 2008; Da Silva et al. 2009b). This permitted insertion of the newly collected material (Devonian from the Czech Republic, China, Carnic Alps and Canada; see Da Silva et al. 2014) into an already extensive database.

This book and introductory chapter are a contribution to the IGCP-580 (UNESCO) project: Application of magnetic susceptibility as a palaeo-climatic proxy on Palaeozoic sedimentary rocks and characterization of the magnetic signal.

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