Review article

Magnetic susceptibility as a high-resolution correlation tool and as a climatic proxy in Paleozoic rocks – Merits and pitfalls: Examples from the Devonian in Belgium

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A B S T R A C T

Low-field magnetic susceptibility ($\chi_{mf}$) measurements are quick and sensitive enabling the creation of high-resolution records; making $\chi_{mf}$ an attractive correlation tool and a proxy for paleoclimate and paleoenvironments. In geologically young material — foremost in Cenozoic sediments — $\chi_{mf}$ belongs to the geoscientist’s toolkit. However, $\chi_{mf}$ is a convolved signal and may reflect other processes than the often implicitly inferred depositional conditions. Diagenesis, remagnetization and low-grade metamorphism, can potentially obscure the original, depositional, $\chi_{mf}$ signal. This aspect is particularly important when interpreting $\chi_{mf}$ records from Paleozoic rocks.

Here, we review data obtained from a large sample collection of Middle to Upper Devonian sections in Belgium. Comparison of $\chi_{mf}$ trends with paleoenvironmental indicators (facies) and with detrital input proxies (Zr, Th, Ti, Al) allowed to assess the persistence of depositional trends. Furthermore, the $\chi_{mf}$ signal was deconvolved into its dominant mineralogical contributions with the help of magnetic-property analysis.

The main results are pointing to a magnetic signal dominated by fine-grained magnetite, of which paleomagnetic analysis indicated a formation during Carboniferous remagnetization. This prompts a potentially strong influence of post-depositional processes and it complicates the interpretation of $\chi_{mf}$ in records from Paleozoic environments. However, in most of the sections, there is a relatively good relationship between $\chi_{mf}$ trends and facies evolution and between $\chi_{mf}$ and geochemical proxies for detrital inputs. This indicates that the newly formed magnetite grains would at least partly remain where they are formed, and this allows a relative preservation of the original signal, despite the strong influence of diagenesis. Two sections show a stronger impact of diagenesis, where for about half of these sections, the primary, depositional information is lost.

The Eifelian–Givetian Monts de Baileux section was selected for time-series analysis of the $\chi_{mf}$ series. The Average Spectral Misfit (ASM) method is applied to explicitly evaluate the null hypothesis of no orbital signal and in this section, there is 99.05% chance that the MS signal is reflecting an orbital imprint.

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1. Introduction

Since the 1980s magnetic susceptibility (labeled $\chi_{mf}$, $\chi_{LF}$, $\kappa$, or MS; in this contribution we opt to use $\chi_{mf}$) has been increasingly used in recent sediment records as a paleoclimatic proxy or as a correlation tool (e.g. Kent, 1982; Mead et al., 1986; Thompson et al., 1980; Soreghan et al., 1997; Vanderaveroet et al., 1999). It is
routinely adopted in the International Ocean Drilling Program (IODP) for correlation purposes since the 1980s as well (e.g. Bloemendal et al., 1988). A close relationship between magnetic susceptibility, lithogenic input and oxygen isotopes led to use of $\chi_{in}$ as a paleoclimatic indicator (e.g. Curry et al., 1995; Robinson, 1986, 1993). Spectral analysis of $\chi_{in}$ records demonstrated the response of the sedimentary system to astronomically driven climate change (e.g. Mead et al., 1986; Shackleton et al., 1999; Bouilla et al., 2008; De Vleeschouwer et al., 2012a, 2012b).

While IODP program work often relates to unlithified sediments, magnetic susceptibility measurements were increasingly retrieved from lithified sediments of Mesozoic and Palaeozoic age since the end of the 1990s (e.g. Crick et al., 1997). This technique called magnetosusceptibility event and cyclostratigraphy (MSEC) is claimed to enable establishing intercontinental correlations which are argued to be facies-independent and of a higher resolution than biozones (Ellwood et al., 1999; Crick et al., 2000). Since the beginning of the 21st century, this technique has become more popular and has been used for correlating Palaeozoic sediment sequences (Bábek et al., 2007, Bertola et al., 2013; Da Silva and Boulvain, 2010; Da Silva et al., 2009a, 2010; Devleeschouwer et al., 2010; Ellwood et al., 2006, 2007; Hladil, 2002; Hladil et al., 2003; Koptíková, 2011; Koptíková et al., 2010; Racki et al., 2002; Whalen and Day, 2010). The present contribution is carried out under the umbrella of the IGGP-580 (UNESCO, 2009–2013) project, which is dedicated to the “Application of magnetic susceptibility as a paleoclimatic proxy on Paleozoic sedimentary rocks and characterization of the magnetic signal”.

The rationale behind the application of magnetic susceptibility to rocks is similar to that in the case of recent sediments. The underlying line of thinking is that the provenance of magnetic minerals is detrital input. Variations in detrital input are driven by climate, sea level or tectonic changes (the latter leading to long-duration ‘base level’ changes). The use of $\chi_{in}$ records is well appreciated because data acquisition is fast and straightforward, providing the high-resolution data required for climatic studies, correlations and paleoenvironmental research. All iron-bearing minerals – silicates, carbonates, sulfides, or oxides – show a positive response when subjected to a magnetic field (this is the free electron spins tend to line up with the applied field). Depending on whether or not the free electron spins of the iron ions in the mineral behave collectively, the minerals are classed as paramagnetic (non-collective spin behavior, small positive response) or ferromagnetic (collective spin behavior, very large positive response). We speak off paramagnetic or ferromagnetic minerals. Examples of paramagnetic minerals are clay minerals or pyrite, etc. While examples of ferromagnetic minerals (sensu lato) include magnetite ($Fe_3O_4$), and the magnetic iron sulfides (greigite ($Fe_3S_4$) and pyrrhotite ($Fe_S$)). Minerals that contain only paired electron spins in their structure like quartz or calcite are in magnetic terminology termed diamagnetic and they have a negative response to an applied field. The ferromagnetic minerals often occur only in trace amounts in essentially all rock types but their contribution to a rock’s $\chi_{in}$ however, is often significant because of the very high specific susceptibility of these minerals (in comparison with paramagnetic and diamagnetic minerals).

Compared to recent sediments, Paleozoic or younger rocks affected by diagenesis have some additional potential complexities that should be considered when interpreting $\chi_{in}$ records. 1) The primary paleoenvironmental setting is often not that well constrained; so the origin of the magnetic minerals is rather poorly constrained as well (e.g. proportion of oolitic and riverine input, influence of biological processes during deposition). 2) After deposition, post-depositional transformations can be relatively strong, from the very early diageneric, to burial, remagnetization and metamorphism (e.g. McCabe and Elmore, 1989; Elmore et al., 1993, 2012; Font et al., 2006, 2012; Rowan et al., 2009). Thus, it was clearly demonstrated that diagenesis can create or destroy magnetic minerals (Channel and McCabe, 1994; Katz et al., 2000; Elmore et al., 2001; Zegers et al., 2003; Zwing et al., 2009). Indeed, the magnetic susceptibility signal can be a convolved expression of detrital, diagenetic and later remagnetization processes; thus, for a meaningful interpretation in terms of paleoenvironment and paleoclimate, the origin of the magnetic susceptibility signal must be fully understood. This implies the untangling of the influence of primary sedimentary processes and secondary processes (i.e. diagenesis, metamorphism, and potential remagnetization). However, only few studies addressed the question of the potential influence of diagenesis and metamorphism on the $\chi_{in}$ signal (Schneider et al., 2004; Devleeschouwer et al., 2010; Riquier et al., 2010; Da Silva et al., 2012).

A remagnetization event was described in the carbonate rocks of the Devonian of the Rhehoercynian fold and thrust-belt (Molina Garza and Zijderveld, 1996; Zwing et al., 2002, 2005, 2009; Zegers et al., 2003). However, a clear link between facies and magnetic susceptibility was also highlighted (Da Silva and Boulvain, 2002, 2006), indicating a possible preserved paleoenvironmental signal. Here, we review a decade of research on the $\chi_{in}$ signal from the Devonian of Belgium. A compilation of various techniques serves to identify these preserved primary trends; the origin of the magnetic susceptibility signal is evaluated and the influence of remagnetization established. As a first approach, the origin of the magnetic susceptibility signal is assessed by comparing the $\chi_{in}$ records with paleoenvironmental proxies, such as facies indicators (Da Silva and Boulvain, 2006). Further elemental analysis is performed on selected sections so that measured $\chi_{in}$ patterns can be evaluated against trends of acknowledged detrital elements such as Zr, Rb, Ti and Al. Comparison with facies allows for the determination of an effective link between $\chi_{in}$ and depositional environment, while the elemental proxies reflect changes in the source, amount or type of weathering (Tribovillard et al., 2006; Calvert and Pedersen, 2007; Riquier et al., 2010). To help explain the origin of the $\chi_{in}$ signal, a more detailed rock-magnetic characterization is performed on selected samples. Measurement of magnetic hysteresis loops enables the distinction of the paramagnetic and diamagnetic contributions to $\chi_{in}$ distinguishing the matrix contribution from the ferromagnetic contribution. With acquisition curves of the isothermal remanent magnetization (IRM) the ferromagnetic minerals are characterized in more detail. This allows to evaluate the influence of diagenesis, remagnetization and (incipient) metamorphism on the $\chi_{in}$ signal by comparison with published data. Finally, after an in-depth assessment of the impact of secondary processes on $\chi_{in}$ trends, we selected a section where the $\chi_{in}$ signal is shown to reflect depositional conditions, for spectral analysis. The imprint of astronomical forcing is discussed.

2. Geological setting

The studied Devonian neritic limestone outcrops from southern Belgium are part of the western zone of the Rhehoercynian fold-and-thrust belt. From the Eifelian until the late Frasnian, southern Belgium was located at 15°–20° south of the equator, with a humid tropical climate (Copper, 2002; Joachimski et al., 2009). These conditions favored the expansion of well-developed reef carbonates during this period. The most distal part of the carbonate platform (‘southern belt’) is located along the southern border of the Dinant Synclinorium (Fig. 1A); what is referred to as the ‘intermediate belt’ is represented in this study by a single section in the Philippeville Anticlinorium. The shallowest facies are exposed along the northern border of the Dinant Synclinorium (“northern
belt” (Fig. 1A and B). For these sections, good palaeontological and stratigraphic control is available (Middle Devonian: Bultynck and Dejonghe, 2001 and Frasnian: Gouwy and Bultynck, 2000, synthesis in Table 1).

During the Eifelian (Fig. 1B) a mixed siliciclastic-carbonate ramp developed, with its maximum development in the southern belt (Mabille and Boulvain, 2007a). The Eifelian starts with biostromes (Couvin Formation) surrounded by shales (Jemelle Formation), and overlain by the Hanonet Formation, a well-bedded argillaceous carbonate unit (Bultynck, 2006). Above the boundary between the Eifelian and the Givetian, a large carbonate platform or ramp (Trois-Fontaines Formation) succeeded the mixed deposits of the Hanonet Formation. During the remainder of the Givetian, the carbonate platform reached its maximum development (Terres d’Hauers, Mont d’Haurs and Fromelesnes Formations), with extended reefal depositions. At the boundary between the Givetian and the Frasnian, the carbonate platform is drowned and replaced by shaly intervals (Nismes and Presles Formations).

Figure 1. Geological setting of the Middle and Upper Devonian in Belgium. A. Geological map with the location of the different outcrops (numbered 1–13) and the different type of analysis provided on each section (χ — magnetic susceptibility measurements). B. South to North Geological cross section of the Middle to Upper Devonian through Southern Belgium, as restored before the Variscan orogeny (double arrow X–Y on the map in Fig. 1A). Yellow rectangles are corresponding to the different sections and the numbers are the same as on Fig. 1A. 1. Villers-le-Gambon; 2. Tailfer; 3. Aywaille; 4. Barbe; 5. Couvin; Villers-la-Tour; 7. Baileux; 8. La Couvinoise; 9. La Boverie; 10. Le Lion; 11. Moulin Bayot; 12. Lompret; 13. Nord. Complete explanation of numbers 1–13 is in Table 1.
During the middle Frasnian, an extensive carbonate platform developed again in Belgium (Fig. 1B; Bouvain et al., 1999). In the more distal part (southern belt), there is a succession of three carbonate mound and atoll packages separated by argillaceous intervals (Arche and La Boverie mounds in the Moulin Liénaux Formation and the Lion mound in the Grands Breux Formation) (Bouvaïn and Coen-Aubert, 2006). In the intermediate part of the basin, argillaceous, crinoidal and biostromal facies (Pont-de-la-Folle and Philippeville formations) are present and in the northern belt (proximal) of the basin, there is a succession of stromatoporoid biostromes and lagoonal facies (Lustin Formation).

The Rhenohercynian fold-and-thrust belt was formed during the Carboniferous to Permian, as a consequence of the collision between Laurussia and Gondwana, during the Variscan orogeny (e.g. Oncken et al., 1999). The main metamorphic event reached a highest temperature of 450 °C in the south, in the early Paleozoic massifs. However, the studied sections have experienced conditions between high diagenesis (<200 °C) and lower anchizone (200–250 °C) (Fiélitz and Mansy, 1999; Han et al., 2000; Table 1). For the interpretation of 14C records, it is important to consider that the Rhenohercynian fold-and-thrust belt was remagnetized during the Variscan orogeny (e.g. Molina Garza and Zijderveld, 1996; Zwingle et al., 2002, 2005, 2009; Zegers et al., 2003). The main remagnetized natural remanent magnetization (NRM) components, the Carboniferous component resides in very fine-grained magnetite (Zwing et al., 2005; Zegers et al., 2003). These particles have a very high 14C that potentially obscures depositional information, even when they are present in the rocks as a trace constituent. The remagnetization mechanism is interpreted to be tied to burial and smectite to illite conversion (Zegers et al., 2003; Zwingle et al., 2009). The transformation of smectite into illite occurs between 2 and 4 km burial depth (Jackson et al., 1988; Katz et al., 1998). Since illite contains less iron than smectite, the liberated iron is the source of the magnetite in which the remagnetization resides. The clay diagenesis and remagnetization in the Rhenish Massif were coeval at 324 ± 3 Ma with respect to the main deformation phase in the Late Carboniferous (Zwing et al., 2009).

3. Methods and techniques

This work integrates data from (Table 1): (A) Frasnian carbonate platform; (B) Eifelian – Givetian mixed siliciclastic-carbonate platform; (C) Eifelian – Givetian ramp and (D) Frasnian carbonate mounds and atolls. Some of these sections are lateral time equivalent (Fig. 1B), allowing direct comparisons of sections from the same setting and sections from different settings. Each level sampled has been subjected to a detailed sedimentological analysis. This has provided environmental interpretations and identification of sea-level variations in the different palaeogeographical contexts (Mabille and Bouvain, 2007a, 2007b; Bouvain, 2007; Da Silva and Bouvain, 2004, 2012). A detailed 14C data base of these 13 sections is available, with 3371 magnetic susceptibility measurements (Da Silva et al., 2009).

3.1. Geochemistry

Out of the 13 sections, we selected 6 sections corresponding to different ages and depositional setting of which samples were selected with a regular stratigraphic interval for geochemical analyses (Table 1 and Electronic supplement Table).

Major and trace element geochemistry were done using X-ray Fluorescence (ARL 9400 XP XRF instrument, University of Liège, Belgium); complete analytical process is described in Duchesne and Bologne (2009). All rock samples were crushed with a Baulknecht crusher and milled in agate mortars. The major elements (in this paper TiO2 and Al2O3) were measured on lithium tetra- and meta-borate fused glass discs, with matrix corrections following the Traill–Lachance algorithm and are expressed in elemental oxide concentration. Trace elements (in this paper Zr and Rb) were measured on pressed powder pellets and data were corrected for matrix effects by Compton peak monitoring and are expressed in elemental concentration. Accuracy is estimated as better than 1% for major elements and 5% for trace elements as checked with 40 international and in-house standards. In order to compare 14C with geochemical results on exactly the same sample, 14C was measured on the crushed sample used for these geochemical analyses. A positive correlation between 14C and geochemical proxies, is also an indication that a primary signal was preserved.

3.2. Magnetic measurements

Initial magnetic susceptibility measurements (χm, n = 3371 distributed over the 13 sections) were performed on a KLY-3S instrument (AGICO, noise level 2 × 10−8 SI) at the University of Liège (Belgium). Magnetic susceptibility is expressed on a mass-specific basis in m3/kg; each data point is the average of three
were extracted from the hysteresis loops: saturation magnetization mounted on a P1 phenolic or P1 silica probe (for magnetically very
laboratory used for hysteresis loop measurements on (Paleomagnetic Labo-
nating gradient force magnetometer MicroMag Model 2900 was
detailed information on the ferromagnetic fraction.
the initial susceptibility. IRM acquisition curves provide more
the different magnetic fractions (dia-, para-, and ferromagnetic) on
Hysteresis data aid to get a better understanding of the in
natural samples fall into the
size but different shapes. In reality, most hysteresis data from
mineralogy, bimodal grain-size distributions or grains of similar
zation direction parallel to the direction in which the subsequent
handler that allows the processing of batches up to 96 samples
quired IRM results. IRM acquisition curves were generated with the
these specimens for most meaningful comparison with the ac-
chromatic, for a broad range of plausible sedimentation rates. In this
need for any time-constraint from biostratigraphy or radiometric
dated orbital component and the closest signi
fluctuation of 0.01 g). Out of this data base, we selected 4 sections for
measurements. Sample mass is at least 10 g (weighed with a pre-
precision of 0.01 g). Out of this data base, we selected 4 sections for
hysteresis and IRM acquisition curve measurements (24 samples for
Tainter and Baileux, 23 samples for Villers-le-Gambon and 12 samples for Moulin Bayot). The selected sections represent
different ages and depositional setting; samples were picked with a
regular stratigraphic interval (Table 1 and Electronic supplement Table).
It is important to note that the magnetic parameters (hys-
teris and saturation (SIRM or \( M_{s} \)) will help to get a better idea of the
proportion of minerals in terms of their magnetic amounts.
Hysteresis data aid to get a better understanding of the influence of
the different magnetic fractions (dia-, para-, and ferromagnetic) on
the initial susceptibility. IRM acquisition curves provide more
detailed information on the ferromagnetic fraction.
A Princeton Measurements Corporation (Princeton, USA) alter-
nating gradient force magnetometer MicroMag Model 2900 was
used for hysteresis loop measurements on (Paleomagnetic Labo-
nary Fort Hoofddijk, Utrecht University (The Netherlands);
strumental noise level 2 \( \times 10^{-11} \) Am², typical signals were at least
two orders of magnitude higher). Small sample chips (5–40 mg
that were weighed before with a semi-micro balance) were
mounted on a P1 phenolic or P1 silica probe (for magnetically very
very samples). The maximum field was 1.5 T, field increment
15 mT during the averaging time 50 ms. The following parameters
were extracted from the hysteresis loops: saturation magnetization
\( M_s \) (Am²/kg); remanent saturation magnetization \( M_r \) (Am²/kg, also
labelled SIRM); high-field magnetic susceptibility \( \chi_{HF} \) (m³/kg) and
coercive force \( B_C \) (mT). \( M_s, M_r \) and \( \chi_{HF} \) were normalized with
respect to sample mass. \( \chi_{m} \) corresponds to the high-field magnetic
susceptibility values and represents the paramagnetic and
diamagnetic contributions. \( M_s \) and \( B_C \) were determined after slope
slope correction based on data points at field values >1.0 T. The ferro-
magnetic susceptibility \( \chi_{term} \) (m³/kg) which corresponds to the
ferromagnetic s.I. contribution, was calculated by subtracting \( \chi_{HF} \)
from \( \chi_{m} \) (e.g. Walden et al., 1999). The parameters extracted from
the hysteresis curves are often interpreted in terms of magnetic
grain size through the classic “Day-plot” of \( M_s/M_r vs B_C/B_0 \) (Day
et al., 1977; Dunlop, 2002). However, the Day-plot is slightly
equivocal concerning the grain size in case of mixed magnetic
mineralogy, bimodal grain-size distributions or grains of similar
size but different shapes. In reality, most hysteresis data from
natural samples fall into the “PSD” box on the Day diagram, which
helps little in term of grain size interpretation (Tauxe et al., 1996).
Furthermore, the exact value of the remanent coercive force \( (B_C) \) is subject to experimental conditions due to time-dependent effects
cased by small magnetic grains (e.g. Fabian and von Dobeneck,
1997). To circumvent these potential biases Tauxe et al. (2002)
proposed to use instead the “squareness versus coercivity field
plot” (SOQ), \( M_s/M_r vs B_C \) to get insight into magnetic domain and
shape regions.

Specimens of 25 mm diameter and ~20 mm height were pre-
pared for the IRM acquisition data. The \( \chi_{m} \) was also measured on
these specimens for most meaningful comparison with the ac-
quired IRM results. IRM acquisition curves were generated with the
robotized magnetometer set-up at the ‘Fort Hoofddijk’ paleomag-
netic laboratory; each curve consists of 55 field steps up to a
maximum field of 700 mT, more or less logarithmically spaced over the
field range. A 2G\textsuperscript{c}-DC-SQUID magnetometer (instrumental
noise level 3 \( \times 10^{-12} \) Am²) with in-line alternating field (AF) and
IRM acquisition facilities is interfaced with an automatic sample
handler that allows the processing of batches up to 96 samples
without operator interference. The magnetic starting state is the
static three-axisial-AF-demagnetized state with the last demagneti-
zation direction parallel to the direction in which the subsequent
IRM is acquired. This ensures minimal deviation from lognormality
for the low levels of magnetic interactions anticipated (Heslop
et al., 2004). They were fitted with cumulative log-Gaussian (CLG)
functions according to Kruiver et al. (2001). Each coercivity distri-
bution is characterized by \( B_{1/2} \) (the field at which half of the SIRM is
reached, indicative of the magnetic mineralogy and grain size),
SIRM (saturation IRM; the magnetic concentration of the respective
phase) and DP (dispersion parameter, provides information on the
distribution of grain sizes and/or crystal defects). Because the
Kruiver et al. (2001) package allows fitting of symmetric compo-
ents in the log-field space, distributions that appear to be skewed at
(low) low applied fields need to be fitted with an extra
component with no physical meaning. It is a consequence of the
magnetic behaviour of fine ‘semi-SP’ particles (magnetic interac-
tion is irrelevant for the low concentrations here) (cf. Heslop et al.,
2004). Its SIRM is added to that of the dominant low-coercivity
component.

3.3. The Average Spectral Misfit methodology

If the assumption that the magnetic minerals that drive the \( \chi_{m} \)
signal are related to detrital inputs is valid, one can expect to
recognize the influence of climate, sea-level and/or tectonics in a
\( \chi_{m} \) series (tectonic processes commonly influencing the magnetic
susceptibility at a longer time scale than the other parameters). As
astronomical forcing is known to strongly affect both runoff and
weathering rates and thus detrital input (e.g. Beckmann et al.,
2005; Tuenter et al., 2007; Wehausen and Brumsack, 2002),
testing the presence of an orbital signal in a \( \chi_{m} \) series might help to
assess the importance of climate (mostly through regional precip-
itation intensity) and sea level (mostly through mean global tem-
perature) in determining the \( \chi_{m} \) signal.

The Average Spectral Misfit (ASM) methodology, designed by
Meyers and Sageman (2007), allows for such a test, without the
need for any time-constraint from biostratigraphy or radiometric
dating. Indeed, in the Devonian, such time-constraints are very
limited and often lack the necessary resolution. The ASM bypasses
this problem, by quantifying the discrepancy between a target
orbital spectrum, and the measured peaks in a stratigraphic spec-
trum, for a broad range of plausible sedimentation rates. In this
way, the method yields an optimal sedimentation rate and provides
a formal statistical test for rejecting the null hypothesis (no orbital
signal). The metric is measured in cycles/kyr and represents the
average distance (or “misfit”) between the target and measured
spectrum peaks, while explicitly accounting for the resolution
limitations inherent in the analysis. ASM is defined as (Meyers
and Sageman, 2007)

\[
ASM = \frac{1}{N} \sum_{k=1}^{N} a_k
\]

\[
a_k = \begin{cases}
0 & \text{if } |f_s*f - f_{pred}| \leq 0.5\Delta f_s \\
|f_s*f - f_{pred}| > 0.5\Delta f_s & \text{otherwise}
\end{cases}
\]

\( N \) = number of orbital periods in the analysis
\( f \) = spatial frequency peak location (cycles/m)
\( s \) = sedimentation rate (m/kyr)
\( f_{pred} \) = predicted orbital frequency (cycles/m)
\( \Delta f_s \) = spatial frequency resolution bandwidth (cycles/kyr)
\( a_k \) = distance (in cycles/kyr) between the location of the
predicted orbital component and the closest significant peak in the
spectrum.
The ASM is conducted using all significant spectral power peaks and harmonic components with ≥95% probability. The target orbital spectra for the Middle Devonian (388 Ma) is predicted by Berger et al. (1992), and all three orbital parameters are used for fitting.

Significance levels for rejection of the null hypothesis (no orbital signal) are estimated with 100,000 randomly organized Monte Carlo spectra simulations. The simulated spectra have the same resolution limitations (Nyquist frequency and Rayleigh resolution) as the measured spectrum, but contain randomly distributed frequencies. The ASM probability distribution for each temporal calibration is constructed using the simulated spectra. The null hypothesis \( H_0 \) significance levels indicate how frequently a particular ASM value should occur by chance, given a spectrum with randomly distributed frequencies. Detailed information on the method can be found in Meyers and Sageman (2007).

Orbital terms that lie above the Nyquist frequency or below the Rayleigh frequency are not evaluated, as they cannot be robustly detected. To identify significant spatial frequencies \( f \), two methods for spectral estimation are used.

1. The multitaper method (MTM) spectral analysis was conducted using 3 discrete prolate spheroidal sequences (DPSS) as data tapers to compromise between spectral resolution and side-lobe reduction. Small variations in accumulation rate behave like phase modulations, and introduce multiple spurious spectral peaks (Muller and MacDonald, 2000). MTM spectral analysis is chosen because it averages these sidelobes into the main peak and thereby gives a superior estimate of the true spectral power. To assess whether or not the strongest spectral peaks are statistically different from the red noise spectrum, the 95% confidence level \( (\text{CL}) \) is calculated (robust AR(1) estimation, median smoothing window width = \( 10\Delta t \), LogFit, \( f_{\text{nyquist}} = 2/\Delta t \)).

2. The MTM harmonic test (Thomson, 1982) is used to identify the line components corresponding to a periodic or quasi-periodic signal. This method is selected because it is able to detect low-amplitude harmonic oscillations in relatively short time series. This feature is an important advantage over standard spectral methods, which yield spectral peaks whose width and height depend strongly on the length of the time-series.

4. Results, interpretation and discussion

4.1. Magnetic susceptibility and depositional proxies

4.1.1. Magnetic susceptibility and facies

In this section, the results of magnetic susceptibility measurements have been compared with microfacies evolution for the different sections and settings. These results were published before in different papers and are summarized here (Boulvain and Coen-Aubert, 2006; Boulvain et al., 2005; Da Silva and Boulvain, 2002, 2006; Da Silva et al., 2012, 2009a; 2009b, 2010; Mabille and Boulvain, 2007a, 2007b). In the classical carbonate platform, in the mud mounds and in the ramp, there is a relationship between magnetic susceptibility trends and microfacies but this link is different in the three settings as detailed below. Magnetic susceptibility is compared with microfacies but also with the degree of water agitation (DWA, obtained through the texture: from mudstone to grainstone implies an increasing water agitation) and with the sedimentation rate (obtained through comparison with literature for each main setting), but also through direct observations of condensed levels and occurrence of bioturbations, perforation or encrustation (characteristic of lower sedimentation rate) (Fig. 3).

The median magnetic susceptibility for all the sections is 2.09 × 10^{-8} m^3/kg which is slightly lower but in the typical \( \chi_m \) range of the marine sediments. Their median \( \chi_m \) value is 5.5 × 10^{-8} m^3/kg as established for 11,000 lithified marine sedimentary rocks, including siltstone, limestone, marl and shale samples (Ellwood et al., 2011).

- Shallow carbonate platform: Frasnian and Eifelian–Givetian sections provide carbonate platform deposits (Table 1). Frasnian sections are dominated by biostromal and lagoonal deposits and all the sections are divided into two parts, a lower part dominated by distal facies (biostromal unit) and an upper part dominated by proximal facies (lagoonal unit). In these sections, different trends are observed (a more complete description is in Da Silva and Boulvain, 2006; Da Silva et al., 2009a): (1) The \( \chi_m \) profiles are clearly divided in two distinct parts, with low \( \chi_m \) in the biostromal unit and high values in the lagoonal unit (Fig. 2A and B). (2) In both units, fourth-order shallowing upward cycles are identified and each regressive trend corresponds to a peak in the \( \chi_m \) records (Fig. 2A and B). A similar pattern observed in most of the sections has been used to propose correlations between the Frasnian platform sections (Da Silva and Boulvain, 2006). (3) A strong relationship between magnetic susceptibility \( \chi_m \) and microfacies was determined, with increasing mean \( \chi_m \) with increasing proximally (Fig. 3A). In the Eifelian–Givetian sections, the biostromal-reefal and internal facies show similar trends as observed for the Frasnian platforms (Figs. 3B and 4A). This increasing of \( \chi_m \) toward a distal-proximal transect could be interpreted in terms of detrital input coming from the main land and increasing with reduced distance from the source.

- Carbonate mounds and atolls: In the mound examples, a clear link between \( \chi_m \) and microfacies is also observed (Figs. 2C and 3D), but this correlation is opposite to what was observed in the carbonate platforms. \( \chi_m \) is lower for shallower facies and decreases during regressive trends; it is higher for the deepest facies and increases during transgressive trends (Fig. 2C). Since the trends observed in all mounds are similar, \( \chi_m \) application allowed to find correlative patterns between mounds that are several tens of kilometres apart (Boulvain and Coen-Aubert, 2006). These trends observed in carbonate mounds were interpreted (Da Silva et al., 2009a) as related to strong variations of sedimentation rate and water agitation during deposition. The deep mound facies, deposited below the storm wave base (Boulvain, 2007) and showing some condensed levels, had a low sedimentation rate and water agitation during deposition, allowing magnetic particles to settle and increasing the \( \chi_m \) signal. Water agitation and sedimentation rate were the highest in the atoll crown facies (rudstones and algal-bacterial carbonate precipitation enhanced). This could have prevented the magnetic particles to settle down and lead to minimal \( \chi_m \) values (Fig. 3D). In the lagoon inside of the atoll crown, \( \chi_m \) values are still relatively low which could be related to the protection by the atoll, preventing magnetic particles to enter into the lagoon. Because this evolution is opposite to what is observed in the shallow water platform outcrops, it is not possible to perform correlations between the Frasnian shallow water outcrop and mud mounds (Fig. 2, magnetic susceptibility trends are inverse).

- Carbonate ramp — external/fore-reef platform: The ramp and fore-reef platform Eifelian–Givetian deposit successions show a similar evolution to that of the mud mound setting. The \( \chi_m \) records show peaks at the top of transgressive units and mean \( \chi_m \) values are decreasing following a distal to proximal trend (Fig. 4B and C). These trends were interpreted as also related to
strong variations of sedimentation rate and water agitation during deposition. In the deepest facies of both models, water agitation (mudstones) and sedimentary rate are minimal, allowing a concentration of magnetic minerals and leading to high \( \chi_m \) values (Fig. 3B and C). In the mid-ramp, characterized by shoals with crinoidal grainstones, water agitation was maximal, as well as sedimentation rate and it leads to low magnetic susceptibility. Since the process of accumulation of the magnetic minerals is similar in both models, some correlations between the fore-reef platform and ramp Eifelian–Givetian sections were proposed (Mabille and Boulvain, 2007b; Fig. 4B and C).

4.1.2. Magnetic susceptibility and geochemical proxies

To assess the influence of detrital input on \( \chi_m \), we compare the magnetic susceptibility with some geochemical proxies such as Ti, Al (both expressed as their oxide), Rb and Zr; which are classically interpreted as proxies for detrital input (Tribovillard et al., 2006; Calvert and Pedersen, 2007; Riquier et al., 2010). In the six sections selected for geochemical analysis the TiO\(_2\), Al\(_2\)O\(_3\), Zr or Rb trends are relatively similar. We will focus in the following on TiO\(_2\), other elements (Al\(_2\)O\(_3\), Zr and Rb) are listed in Table 2 (mean value and coefficient of determination). The table in the electronic supplement provides the complete set of data. Results from the Tailfer and Villers-le-Gambon sections were previously published (Da Silva et al., 2012). Here, they are integrated, with the results from Baileux, Moulin Bayot, La Couvinoise and Aywaille which have not been published yet.

To constrain how we can interpret \( \chi_m \) in terms of detrital input variation, we plot \( \chi_m \) against TiO\(_2\), Al\(_2\)O\(_3\), Zr or Rb. The plot of TiO\(_2\) (Fig. 5) indicates very good correlation for the Moulin Bayot \((r = 0.89)\) and moderate correlation for Villers-le-Gambon, Baileux and La Couvinoise sections \((r \) around 0.65). However, for the entire Tailfer section, including the biostromal and lagoonal units, there is essentially no correlation between \( \chi_m \) and detrital proxies \((r \) between 0.13 and 0.32, Table 2). Furthermore, there is a strong difference between the behaviour of \( \chi_m \) versus detrital proxies in the biostromal and lagoonal units. In the biostromal unit, the TiO\(_2\) content is low (mean value of 0.07%) and the correlation between \( \chi_m \) and TiO\(_2\) is high \((r \approx 0.85)\). For the samples from the lagoonal unit, TiO\(_2\) concentrations are higher (0.17%) and the correlation between \( \chi_m \) and TiO\(_2\) is distinctly lower \((r \approx 0.25)\). For the Aywaille section which was deposited in a similar setting as Tailfer (Da Silva et al., 2012), the results are very similar to those observed in Tailfer. For the entire section, there is a moderate correlation...
4.2. Rock magnetic information — separation of ferromagnetic and paramagnetic plus diamagnetic contributions to \( \chi_{in} \)

In this section, we will first consider some magnetic parameters individually: \( \chi_{\text{Ferro}} \), \( \chi_{\text{HF}} \), \( M_s \), \( B_r \), and \( M_{HF}/M_s \). We will then compare these parameters with \( \chi_{in} \) to identify the main magnetic parameters controlling the initial susceptibility. Results from the Tailfer and Villers-le-Gambon sections were previously published in Da Silva et al. (2012) and are integrated here, with new results from Baileux and Moulin Bayot. In the Tailfer, Villers-le-Gambon, Baileux and Moulin Bayot sections, after slope correction, all loops appear to be wasp-waisted (three samples from Baileux have a goose-necked shape). The wasp-waistness results from two distinct coercivity populations either due to different mineralogy or due to different grain size (e.g. Wasilewski, 1973; Jackson et al., 1993; Roberts et al., 1995; Tauxe et al., 1996). The goose-necked shape is related to a magnetic mineralogy that consists of two (or more) magnetic minerals with a notably varying coercivity (such as a mixture of hematite and magnetite, Roberts et al., 1995; Tauxe et al., 1996).

The contribution of the ferromagnetic susceptibility (\( \chi_{\text{Ferro}} \)) and \( M_s \) is between \( 0.18 \times 10^{-8} \) and \( 1.74 \times 10^{-8} \) m³/kg and between \( 0.85 \times 10^{-4} \) and \( 5.64 \times 10^{-4} \) Am²/kg respectively. \( M_s \) data are relatively well correlated with \( \chi_{in} \) for all sections (Tailfer, Villers-le-Gambon and Baileux, correlation coefficient \( r = 0.75 \); Moulin Bayot, \( r = 0.96 \); Fig. 6A and Table 2). The correlation is even higher between \( \chi_{\text{Ferro}} \) and \( \chi_{in} \) (Tailfer and Moulin Bayot \( r = 0.99 \); Villers-le-Gambon \( r = 0.998 \) and Baileux \( r = 0.94 \); Fig. 6B, Table 2). These correlations indicate that the variation in \( \chi_{in} \) is driven by varying contents of ferromagnetic minerals despite their low concentrations.

Measured \( B_r \) values (slope corrected) are in the range of 2.5—25 mT (Fig. 6C) which is low but common for carbonate platform sediments (Borradaile et al., 1993; Riquier et al., 2010). The occurrence of two grain-size populations could explain the relatively large coercivity distribution (e.g. Borradaile et al., 1993). In the Baileux section, three goose-necked samples have higher \( B_r \) values (40.1, 56 mT and 184.3 mT). They are interpreted as related to a mixture of low coercivity (such as magnetite) and high coercivity (such as hematite) minerals.

\( \chi_{HF} \) quantifies the contribution of the paramagnetic and diamagnetic minerals to the bulk magnetic susceptibility. Most of the samples have a low or negative \( \chi_{HF} \) (\( \chi_{HF} \) between \( 0.28 \times 10^{-8} \) and \( 2.21 \times 10^{-8} \) m³/kg, Fig. 6D), indicative of a low content of the paramagnetic fraction (because the contribution of the paramagnetic fraction easily outweighs that of the diamagnetic carbonate fraction). There is no clear correlation between \( \chi_{HF} \) and \( \chi_{in} \) for Tailfer \( (r = 0.12) \) and Villers-le-Gambon \( (r = 0.34) \) and a moderate correlation in the cases of Baileux \( (r = 0.50) \) and Moulin Bayot \( (r = 0.58) \). This absence or low correlation means that the diamagnetic and paramagnetic fractions do not have a major control on the variations in \( \chi_{in} \).

The shape of the hysteresis loops, \( B_r \) and \( M_{HF}/M_s \), provide information concerning the magnetic grain size of the ferromagnetic fraction. The squareness vs coercivity plot (Fig. 7B) is used in order to interpret the grain size and their shape (Tauxe et al., 2002). Most of the samples plot on the ‘vortex’ trendline (Tauxe et al., 2002). Williams and Dunlop (1995) suggested that grains whose remanent state is a vortex are responsible for PSD behavior.

4.2.2. IRM acquisition curves

Using the Kruiver et al. (2001) software three ferromagnetic components could be distinguished. Component-1 represents the main part of the IRM acquisition curve (commonly >80%); SIRM of component-1 ranges between \( 0.50 \times 10^{-4} \) Am²/kg and 79.50 \( \times 10^{-4} \) Am²/kg (Fig. 8A). \( B_{1/2} \) values (\( B_{1/2} \) values ranging between 48.98 and 89.13 mT, Fig. 8B) are generally compatible with magnetite, pyrrhotite and greigite. Greigite, however, is highly unlikely given the high-temperature diageneric conditions that extend regionally to very low grade metamorphism. For a reasonably large grain-size range pyrrhotite and magnetite have similar coercivity properties and therefore, no single room-temperature magnetic parameter can reliably differentiate these two minerals (Peters and Thompson, 1998). Component-2 represents components between 5 and 20% of the IRM signal, but can reach higher values (maximum 87%) in some cases, mostly in Baileux section (4 samples on 23 for the Tailfer section, 5 on 24 for the Villers section, 9 on 24 for the Baileux section and 2 on 10 for the Moulin Bayot section) and is responsible for the non-saturating IRM curve type. SIRM of component-2 is between \( 0.03 \times 10^{-4} \) Am²/kg and 18.61 \( \times 10^{-4} \) Am²/kg (Fig. 8C) with the lowest values observed in Moulin Bayot. Component-2 is interpreted as a high coercivity mineral (\( B_{1/2} \) between ~160 and ~1000 mT, Fig. 8D), likely hematite. DP of component-1 is between 0.25 and 0.41 log mT and DP of component-2 is between 0.12 and 0.47 log mT.
Figure 4. Magnetic susceptibility ($\chi_m$ in m³/kg) trends compared with facies evolution for selected sections from the Eifelian (Villers-la-tour, corresponding to section 6 on Fig. 1) and Eifelian–Givetian boundary (La Couvinoise and Baileux, corresponding to sections 8 and 7 on Fig. 1). Magnetic susceptibility trends are indicated by dashed arrows and facies trends by solid arrows. For the carbonate shallow-water platform (A), $\chi_m$ is directly related to facies trends and sequences, with an $\chi_m$ increase during shallowing-upward trends. For the Ramp and External platform sections (B and C) mean $\chi_m$ increases during transgressive trends and decrease during shallowing-upward trends. This parallel evolution allows relatively good correlations (dashed lines) between the Ramp and external platform sections (B and C). Legend is on Figure 2D.

Table 2
Mean value (mean) for each parameter and correlation coefficient ($r$) between each parameter and initial susceptibility ($\chi_m$ in m³/kg). NM – Not measured. For a definition of each parameter, refer to the main text.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hysteresis</th>
<th>Geochemistry</th>
<th>SIRM acquisition curve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_r$</td>
<td>$B_1$</td>
<td>$\chi_{HF}$</td>
</tr>
<tr>
<td></td>
<td>Am³/kg</td>
<td>mT</td>
<td>m³/kg</td>
</tr>
<tr>
<td>TAILFER</td>
<td>Mean</td>
<td>1.47</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$r$</td>
<td>0.75</td>
<td>0.23</td>
</tr>
<tr>
<td>VILLERS</td>
<td>Mean</td>
<td>6.76</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$r$</td>
<td>0.75</td>
<td>0.41</td>
</tr>
<tr>
<td>BAILEUX</td>
<td>Mean</td>
<td>5.94</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$r$</td>
<td>0.75</td>
<td>0.23</td>
</tr>
<tr>
<td>MOULIN BAYOT</td>
<td>Mean</td>
<td>6.84</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$r$</td>
<td>0.96</td>
<td>0.11</td>
</tr>
<tr>
<td>LA COUVINOISE</td>
<td>Mean</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td></td>
<td>$r$</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>AYWAILLE</td>
<td>Mean</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td></td>
<td>$r$</td>
<td>NM</td>
<td>NM</td>
</tr>
</tbody>
</table>
The SIRM of component-1 is highly correlated with $\chi_{m}$ in (Fig. 8A; Tailfer and Villers-le-Gambon $r = 0.89$, Baileux $r = 0.98$ and Moulin Bayot $r = 0.99$), showing again that the variation in $\chi_{m}$ is driven by concentration variations of the ferromagnetic minerals. There is also a high correlation between SIRM of component 2 and $\chi_{m}$ in Tailfer (Fig. 8C, $r = 0.79$); the correlation coefficient is higher in the lagoonal unit than in the biostromal unit ($r = 0.81$ in the former and $r = 0.49$ in the later). In the Villers-le-Gambon section, the correlation coefficient is relatively low ($r = 0.49$) (biostromal unit $r = 0.79$ and lagoonal unit 0.52). In the Baileux ($r = 0.18$) and Moulin Bayot ($r = 0.32$) sections, correlation is low, confirming the small influence of hematite on the initial susceptibility in such rocks.

4.3. Origin of the magnetic susceptibility signal and implications on its application as a correlative tool and paleoenvironmental proxy

All the sections studied here show relatively similar characteristics. Indeed, for the different sections, the hysteresis, IRM acquisition curve parameters and geochemistry results are pointing to: (a) a minor influence of diamagnetic and paramagnetic minerals (Fig. 6D); (b) a major influence of ferromagnetic minerals, despite their low amount (Fig. 6A and B); the ferromagnetic mineral with the strongest influence on $\chi_{m}$ being magnetite or pyrrhotite (cf. coercivity values, Figs. 6C–8B) and a minor contribution of hematite in most of the samples (Fig. 8C and D); (c) the ferromagnetic grains are mostly in the range of PSD grain size (Fig. 7B); (d) There is a relatively good link between geochemical proxies for detrital inputs ($\text{TiO}_2$, $\text{Al}_2\text{O}_3$, $\text{Zr}$, $\text{Rb}$) and $\chi_{m}$ (Fig. 5). Only in the lagoonal units from the Tailfer and Aywaille sections, the behavior is different: there is no clear relationship between geochemical proxies and $\chi_{m}$ (Fig. 8A) and there is a slightly higher content of ferromagnetic minerals (Fig. 6B). So for these two parts of section, the primary magnetic susceptibility signal was distorted by diagenesis.

Remagnetization events were recognized in the Paleozoic rocks of the Rhenish Massif (e.g. Molina Garza and Zijderveld, 1996; Zwing et al., 2002, 2005, 2009; Zegers et al., 2003). Zwing et al. (2005) have studied platform carbonates, biohermal carbonates and siliciclastic rocks from the northeast Rhenish Massif (Germany). The hysteresis ratio from siliciclastic rocks fall in or close to the field of MD magnetite (Fig. 7C, Parry, 1982), indicative of detrital magnetite. The hysteresis parameters of biohermal rocks fall in the field of SD-SP magnetite of remagnetized rocks (Fig. 7C, Jackson, 1990). Some fine grained clastic rocks and the platform...
carbonates have hysteresis properties between the biohermal carbonates and coarse clastic rocks (SD–MD mixture, Fig. 7C). The presence of ultrafine grained magnetic material in carbonates and fine clastic rocks support the evidence of remagnetization, mostly in carbonate rocks. In siliciclastic coarser rocks, the fine grained magnetic fingerprint gets increasingly disguised with increasing amount of MD magnetite of detrital origin (Zwing et al., 2005). Zegers et al. (2003) focused on the Devonian carbonates of Belgium and identified two main remagnetization events: the Carboniferous C-component, carried by SP to SD magnetite and the Late Permian P-component carried by pyrrhotite.

On a squareness vs coercivity plot (Tauxe et al., 2002), the Devonian Belgian samples from this study are compared to the remagnetized carbonates from the Rhenohercynian fold-and-thrust-belt studied in Zegers et al. (2003) and in Zwing et al. (2005). They all follow a similar trend (Trend 1, Fig. 7C) but to cubic magnetite grains. The 115 nm, 70 nm, and 20 nm are represented by the labels USD/SP, CSD-USD transition, and CSD-USD transition, respectively. The CSD-USD transition in Devonian Belgian samples from this study are compared to the biohermal carbonates from Zwing et al. (2005) and data from Devonian carbonates of Belgium studied by Zegers et al. (2003).

The two components identified in Zegers et al. (2003) are interpreted as a result of different mechanisms. The C-component, carried by SP–SD magnetite, is interpreted as formed during the smectite to illite transition. Zwing et al. (2009) reached similar conclusions and dated the clay diagenesis and remagnetization in the Rhenish Massif at 324 ± 3 Ma. This smectite to illite transformation and related remagnetization process does not need the presence of an external fluid. It could have been enhanced by pressure solution and it is considered as relatively ubiquitous in the Rhenish Massif. The P-component most likely resides in pyrrhotite and is spatially correlated with barite bearing Mississippi Valley-type (MVT) ore districts and would be the result of the circulation of external high salinity fluids. The P-component is more geographically restricted than the C-component.

Concerning the P-component, its influence is rather prominent in the two main MVT districts recognized in Belgium (Zegers et al., 2003), the northern Namur-Verviers district and the more southern Dinant district (Dejonghe, 1998). So the presence of pyrrhotite is possible, mostly in the sections located inside of these MVT domains. As mentioned earlier, pyrrhotite and magnetite have similar coercivity properties and are difficult to differentiate when based on coercivity properties alone (Peters and Thompson, 1998). However, the occurrence of pyrrhotite in a substantial amount, produced by external fluid would completely transform the original detrital magnetic susceptibility signal. The Tailfer, Barse, Aywaille, Couvin, Villers-la-Tour, Baixeux and Lompret sections are outside of
both MVT districts. The La Couvinoise, Le Lion and Nord sections are located at the southern edge of the Dinant MVT district and Villers-le-Gambon at its northern edge. So in all these sections, the formation of an appreciable pyrrhotite mineralization was unlikely (Zegers et al., 2003). The Moulin Bayot and La Boverie sections are located inside of the perimeter of the Dinant MVT. However, both sections show a link between $\chi_{in}$ and facies (Boulvain and Coen-Aubert, 2006) and in Moulin Bayot, the $\chi_{in}$ and Ti are clearly correlated ($r = 0.89$), so it seems that the influence of pyrrhotite is not significant.

Geochemistry, hysteresis and IRM acquisition curve data from the measured sections, pointing to a $\chi_{in}$ mostly carried by ferromagnetic grains in PSD range, are in agreement with a main remagnetization C-component carried by fine-grained magnetite. The iron produced during the smectite to illite conversion would precipitate along interconnected voids (e.g. Weil and Van Der Voo (2002) in a study on the Devonian of the Cantabrian mountains). For the Villers-le-Gambon, Baileux, La Couvinoise, Moulin Bayot sections and for the biostromal units of Tailfer and Aywaille sections, the good correlation between magnetic susceptibility and proxies of detrital input points to a relative conservation of the primary detrital signal despite the remagnetization event. This indicates that even under the conditions that led to the C-component formation, the newly formed magnetite remained probably in situ or closely associated with the detrital clay minerals, without strongly affecting the primary depositional trends related to detrital input.

In the lagoonal units in the Tailfer and Aywaille sections, however, the link between $\chi_{in}$ and detrital input is not observed anymore. As mentioned before, the Tailfer and Aywaille sections are located outside of the Namur-Verviers MVT district and so this perturbation of the depositional signal cannot be explained by pyrrhotite formed through fluid circulation. In the framework of the C-component, three processes may have modified potentially primary trends (Da Silva et al., 2012): 1) the originally present clay mineral suite contained a considerably varying amount of smectite (unfortunately this remains hard to test); 2) in the very restricted lagoonal setting as observed in the Tailfer and Aywaille lagoonal unit (Da Silva and Boulvain, 2012), early reductive diagenetic processes could have already influenced the magnetic mineral composition and 3) during the smectite to illite transition, prolonged reaction could have blurred the original lithological expression. Indeed, if a portion of the released iron had migrated over a larger distance, say up to several decimeters (under the action of fluid that is considered to be buffered by the nearby lithology), this could lead to a partially hidden primary signal. The loss of detrital information in the lagoonal units of the Tailfer and Aywaille sections highlights the importance of checking the link between geochemical proxies and detrital input before using $\chi_{in}$ for correlation purposes or as a paleoenvironmental proxy.

5. Application of magnetic susceptibility as a paleoclimatic proxy – the search for orbital forcing

In search for the imprint of astronomical forcing, the fore-reef platform setting of the Hanonet Formation at the Monts de Bailleux section was selected (Fig. 1B; Table 1). The obtained results will be compared with the results from the Hanonet Formation’s...
stratotype at the La Counvinoise section, where astronomical imprint on $\chi_{in}$ signal has already been identified (De Vleeschouwer et al., 2012a). A detailed sedimentological comparison between the two sections was already described (Mabille and Boulvain, 2007b). The Monts de Baileux section, as well as the La Counvinoise section, are suitable for the detection of orbital signals, since the geochemical analysis for those sections demonstrate a correlation between $\chi_{in}$ and elemental proxies for detrital inputs (r around 0.65 for both sections, see Table 2). Since $\chi_{in}$ is correlated to detrital input, $\chi_{in}$ can potentially be related to climate-driven changes in weathering, runoff and sea-level. Furthermore, the conodont biostratigraphy (Bultynck, 2006; Mabille and Boulvain, 2007b) is well-known and the stratigraphic interval is relatively well constrained. The section partly contains the ensensis and hemiansatus conodont zones (Table 1). Hence, according to Kaufmann (2006) the studied section was deposited in only a few hundreds of thousands of years.

The 108.1 m thick Mont de Baileux section consists of clayey levels, argillaceous limestones and limestones. The Eiffelian — Givetian boundary occurs in the lowermost part of the section (Fig. 1). The fore-reef environment is characterized by a relatively high carbonate input coming from proximal settings, and thus by rather fast accumulation. The absolute rate at which sedimentation took place in this stratigraphic interval is determined objectively by applying the Average Spectral Misfit (ASM) method.

The MTM harmonic test was carried out on the $\chi_{in}$ series from Les Monts de Baileux section ($N = 278$, 108.1 m stratigraphic thickness) after detrending and linear interpolation to an equally-spaced (0.4 m) series. Figure 9A demonstrates that the MTM harmonic test yields 21 significant ($>$95%) harmonic components. Each of these 21 frequencies explains significantly more of the series' variance than would be expected if the series were composed of red noise. MTM spectral analysis on the same series (Fig. 9B), identifies 7 significant spectral peaks exceeding the 95% confidence level. As both methods estimate the spectrum of the same $\chi_{in}$ signal, one expects similar results. Indeed, both methods suggest the same frequency intervals to contain important cyclic components of the signal (e.g. 0.4–0.6 cycles/m, 0.7–0.75 cycles/m, 0.9–1.1 cycles/m). Average Spectral Misfit analysis of these 28 periodic components is conducted across a broad range of sedimentation rates from 1 to 25 cm/kyr (0.25 cm/kyr increment). This broad range is chosen to contain all accumulation rates can be considered realistic from a 25 cm/kyr (0.25 cm/kyr increment). This broad range is chosen to re

Figure 9. Multitaper method (MTM) spectral analysis and Average Spectral Misfit (ASM) H0 significance level results for the Hanonet Fm. (Monts de Baileux) $\chi_{in}$ series. A: MTM harmonic analysis probability results. B: MTM power spectrum estimate. C: Null hypothesis significance levels for sedimentation rates from 1 to 25 cm/kyr, calculated with 0.25 cm/kyr increment. The dotted line indicates the critical significance level of 1%. D: Null hypothesis significance levels for sedimentation rates from 10 to 15 cm/kyr, calculated with 0.05 cm/kyr increment. The dotted line indicates the critical significance level of 1%. E: MTM harmonic analysis probability results (vertical bars) and power spectrum estimate (solid black line), using the optimal accumulation rate of 12.10 cm/kyr. Expected locations of the Givetian eccentricity (E1: 404 kyr, E2: 124 kyr, E3: 95 kyr), obliquity (O1: 39 kyr, O2: 32 kyr) and precession (P1: 20 kyr, P2: 17 kyr) periods are displayed as red shaded bars. Eccentricity (E3, E2 and E1) and precession-related (P1 and P2) bars seem to correspond to peaks in the power spectra, while around the obliquity-related bars (O1 and O2), no elevated spectral power is suggested. See Table 3 for the expected periods of the astronomical parameters.

associated to an astronomical parameter. This astronomical interpretation is given in Table 3. The strong low-frequency spectral peak at 0.01845 cycles/m (Fig. 9B and E) corresponds to a periodicity of 447.93 kyr, when an accumulation rate of 12.1 cm/kyr is considered. Therefore, this frequency is associated with long-eccentricity (E1: 404.18 kyr). At first sight, this match seems to be suboptimal. However, the rather limited duration of the studied section entails that only 2 long-eccentricity cycles are fully contained in the studied section. Therefore, its periodicity can only be approximated by any spectral approach. The imprint of the short-
and Loutre, 1991). At the predicted frequency of obliquity (O1 and O2 in Fig. 9E), no significant periodic components are observed. Consequently, this analysis confirms the negligible influence of obliquity at the equatorial palaeolatitude of the Dinant Synclinorium during the Middle Devonian. Also, Figure 9E indicates two important harmonic components in the $\chi_m$ series at frequencies 0.1123 and 0.1208 cycles/kyr (8.91 and 8.28 kyr period resp.). They are designated as the result of half-precessional climate forcing. Indeed, these cycles have already been observed in the Hanonet Fm. stratotype at the La Couvinoise section (see De Vleeschouwer et al., 2012a). In the latter study, the importance of half-precessional climate forcing in an equatorial Mid-Devonian climate setting is discussed from a palaeoclimatological point of view.

The results of the above described time-series analyses provide a floating time frame for the Monts de Baileux section. The main advantage of displaying time-series in the time domain, rather than in the distance domain, is that contemporaneous series (Bultynck and Dejonghe, 2001) can be easily compared, since differences in accumulation rate do not have to be taken into account anymore. De Vleeschouwer et al. (2012a) proposed a floating time scale for the Hanonet Fm. stratotype at the “La Couvinoise” section. The $\chi_m$ series of both sections can thus be compared in detail despite the considerable differences in paleoenvironment, sedimentology, and accumulation rate (Fig. 10). The cyclostratigraphic framework allows for correlations between both sections, palaeoenvironmental settings were significantly different. The lower part of the La Couvinoise section was deposited in the open marine environment of a multiclinal ramp, while the lower part of the Monts de Baileux corresponds to a fore-reef environment. The difference in palaeoenvironmental model between the two sections explains the considerable lower $\chi_m$ values in the Monts de Baileux section. The upper part of both sections, on the other hand, was deposited in a fore-reef setting. In this part, it is evident that $\chi_m$ patterns and amplitude are highly similar between both sections. These results clearly illustrate that astronomically interpreted $\chi_m$ series can be used for quite detailed (regional) correlations, as well as for palaeoclimatological interpretations.

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**Table 3**

<table>
<thead>
<tr>
<th>Observed frequency (cycles/m)</th>
<th>MTM harmonic probability</th>
<th>MTM spectral analysis confidence level</th>
<th>Observed periodicity (kyr)</th>
<th>Astronomical interpretation (kyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01845</td>
<td>&gt;99%</td>
<td></td>
<td>447.93</td>
<td>E1: 404.18 kyr</td>
</tr>
<tr>
<td>0.07322</td>
<td>&gt;99%</td>
<td></td>
<td>112.84</td>
<td>E2 &amp; E3: 123.82 &amp; 94.78 kyr</td>
</tr>
<tr>
<td>0.4150</td>
<td>&gt;95%</td>
<td></td>
<td>19.91</td>
<td>P1: 19.85 kyr</td>
</tr>
<tr>
<td>0.4956</td>
<td>98.54%</td>
<td></td>
<td>16.68</td>
<td>P2: 16.79 kyr</td>
</tr>
<tr>
<td>0.9277</td>
<td>99.64%</td>
<td></td>
<td></td>
<td>Half-Precession: 8.91 kyr</td>
</tr>
<tr>
<td>0.9985</td>
<td>99.66%</td>
<td></td>
<td></td>
<td>Half-Precession: 8.28 kyr</td>
</tr>
</tbody>
</table>

---

**Figure 10.** Magnetic Susceptibility floating time-series of the La Couvinoise section (black) and Monts de Baileux section (red). The relative time-axis for the La Couvinoise section is from De Vleeschouwer et al. (2012a). The relative time-axis for the Monts de Baileux section was constructed using the optimal accumulation rate of 12.30 cm/kyr. Grey/white shaded bars indicate the short 100-kyr eccentricity cycles. $\chi_m$ values in the lower part of both sections differ because of a different palaeoenvironmental setting (open marine in La Couvinoise vs fore-reef in Monts de Baileux). In the upper part of both sections, $\chi_m$ trends and amplitude are similar because both sections are characterized by a fore-reef palaeoenvironment.
6. Conclusions

Magnetic susceptibility ($\chi_m$) has been used for a long time as paleoenvironmental proxy and correlation tool on recent rocks, because the data acquisition is fast and straightforward, providing high-resolution data required for this type of research. Magnetic susceptibility is now more and more frequently applied on Paleozoic sediments. However, it is essential to check the origin of the minerals responsible of the magnetic variations to determine whether the primary detrital signal has been preserved that is biased by secondary diagenetic signals. Here we review an important set of data from the middle and upper Devonian carbonate sequence of the Monts de Baileux section, Belgium. From ramp, platform and mound and atoll settings.

Hysteresis measurements and IRM acquisition curves are pointing to a $\chi_m$ signal distinctly influenced by fine-grained PSD magnetite particles which have been formed during the Variscan orogeny as a consequence of remagnetization (Zegers et al., 2003; Zwing et al., 2002, 2005) related to the smectite to illite transition, whereby liberated iron precipitates as magnetite. So, diagenetic and low grade metamorphic processes can potentially have a strong influence on $\chi_m$ trends.

When comparing the variations in the magnetic susceptibility signal with facies evolution, it appears that $\chi_m$ is influenced by proximality but also by the main depositional setting. This constitutes a first argument that a primary $\chi_m$ signal was at least partially preserved. A comparison of $\chi_m$ with elemental detrital proxies such as Ti, Zr, Rb and Al also reveals a relatively good correlation. This also indicates that the primary detrital signal is reasonably well preserved in the $\chi_m$ trends. Thus, primary trends could have been retained despite diagenetic or very low grade metamorphic imprints related to burial and remagnetization. The persistence of the primary signal is interpreted as follow: smectite to illite transition, the newly formed magnetic minerals are not transported over a meaningful distance and are remaining more or less in situ. However, in the lagoonal deposits from the Tailfer and Aywaille sections, $\chi_m$ and TiO$_2$ (Zr, Rb and Al), are not correlated, pointing to a much stronger influence of diagenesis with the concomitant loss of depositional paleoenvironmental information.

The $\chi_m$ record from an Eifelian-Givetian section (Hanonet Formation; Monts de Baileux section; mixed platform sediments), with well preserved depositional information as inferred from correlation between detrital proxies and magnetic susceptibility has been chosen to test for the imprint of astronomical climate forcing. Average Spectral Misfit analysis was carried out to test the null-hypothesis of no orbital signal preserved in the selected $\chi_m$ signal. ASM yields an optimal sedimentation rate of 12.1 cm/kyr for the studied signal and successfully rejects the null hypothesis, with only 0.952% chance that the null hypothesis is wrongly rejected. In other words, ASM demonstrates that the MS signal of the Hanonet Fm. at the Monts de Baileux section carries an imprint of astronomical climate forcing. Precession and eccentricity are the dominant astronomical drivers, as could be expected for a tropical setting.

The results presented here were acquired on a large data set from the Middle to Upper Devonian carbonate sediments in Belgium. Importantly, data have been gathered from notably different carbonate or mixed sediment platform morphologies and paleoenvironmental settings. A measured $\chi_m$ record is a primary environmental signal potentially convolved with, or even overprinted by a secondary diagenetic (or metamorphic) signal. It appears that magnetic susceptibility can be used as a paleoenvironmental and climatic proxy also on Paleozoic rocks, under the proviso that its primary character is verified on a case-by-case basis. Parts of the sections investigated did not fulfill this criterion and should therefore not be used for this purpose. This implies that the depositional character of any $\chi_m$ record should be assessed before further inferences are being made. The origin of the magnetic susceptibility can be evaluated by a combination of rock-magnetic and geochemical approaches.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.marpetgeo.2013.06.012.

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