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PAPER

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Magnetite-out and pyrrhotite-in temperatures in shales and slates

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Abstract

Clay-rich basins have undergone varying degrees of magnetic transformation during burial, affecting their ability to retain accurate records of Earth's dynamic magnetic field. We propose to bracket the magnetite-out and pyrrhotite-in temperatures in shales and slates from Taiwan and the Pyrenees by using a combination of low-temperature magnetic transitions and geothermometers. For T_{burial} < 340°C, the magnetic assemblage is dominated by magnetite. Gradually with increasing burial temperature, the concentration of magnetite decreases to a few ppmv. We observe the magnetite-out isograd at T_{burial} ~350°C. At T_{burial} >60°C and T_{burial} >340°C respectively, fine-grained and coarse-grained pyrrhotite develop. In the course of burial, a clay-rich basin gradually loses its capability to retain a record of Earth's magnetic field. It is only during basin uplift, that coarse pyrrhotite might acquire a thermo remanent magnetization. Our results point out therefore highly contrasted magnetic properties and palaeomagnetic records between deeply buried basins and exhumed ones.

1 | INTRODUCTION

Shales are of broad interest in the geosciences as integrated representations of the geochemistry of the upper continental crust (McLennan, 2001). They and their metamorphic counterparts, slates, have strong economic importance because of their high capability to retain liquids and gas. Shales and slates are also important natural magnetic archives: they contain fine particles of ferrimagnetic minerals with the capability to acquire and retain nearly continuous high-fidelity records of Earth's restlessly varying magnetic field (e.g., Kodama, 2012).

Among the most important of these magnetic constituents are magnetite (Fe_3O_4) and monoclinic pyrrhotite (Fe_7S_8), which are respectively common in shales and slates (Aubourg et al., 2012). During diagenesis and metamorphism, minerals are continuously produced, altered and dissolved, and both the presence and content of magnetite and pyrrhotite change radically, with dramatic impacts on the palaeomagnetic records of shales in sedimentary basins. In this study we track the sequence of magnetic mineral transformations as a function of burial depth/temperature in two sedimentary basins, based on observations of diagnostic low-temperature (10–300 K) magnetic mineral transitions and two geothermometers, and show how the magnetic memory of the materials evolves. The calibration established here will also allow these same magnetic phases to be used for geothermometry in other basins.

Roberts (2015) provided a comprehensive review of biological and chemical processes that control the magnetic assemblage in sediments during early diagenesis in hemi-pelagic marine environments (T_{burial}<50°C). In a sulphidic environment, the content of inherited iron oxides declines drastically for depths ranging from tens of centimetres to a few metres due to reductive dissolution. This is in effect a partial-to-full reset of inherited magnetic minerals, permanently removing their stored palaeofield records.

For higher burial temperatures, in the range 50–250°C, studies from different basin settings reported that the dominant magnetic mineral in shales is fine-grained magnetite, in concentrations on the order of tens of ppmv (Kars, Aubourg, & Suárez-Ruiz, 2015). The identification of a magnetically irreversible Verwey transition at ~118 K, indicates that magnetite is nearly stoichiometric (Dunlop & Özdemir, 2018). This suggests that some of the magnetite is a secondary product. Two main mechanisms are generally invoked to form magnetite diagenetically (Elmore & McCabe, 1991; Van der Voo & Torsvik, 2012). Magnetite can form at the expense of pyrite, with the cooperation of organic matter (Brothers, Engel, & Elmore, 1996). Magnetite can also result from the diagenetic smectite-to-illite transformation (Katz, Elmore, Cogoini, Engel, & Ferry, 2000). In both cases, the driving parameter is the burial temperature. Widespread fluid circulation at the scale of the basin or local fluid circulation near veins, are also likely mechanisms to produce magnetite (Elmore, Muxworthy, & Aldana, 2012). It is then likely that some magnetite is authigenic in shales buried at modest depth (<10 km). This diagenesis is however dependent of the lithology as documented by Moreau and Ader (2000) who observed the preservation of fine-grained magnetite in carbonates.

At greater depth (>10 km), the presence of monoclinic pyrrhotite has been widely reported in slates as the result of metamorphism. Carpenter (1974) reported a pyrrhotite isograd close to the biotite isograd (~375°C). Ferry (1981) observed the occurrence of pyrrhotite and pyrite in the chlorite zone up to the staurolite/andalusite zone (T_{burial}~700°C). Although the breakdown of pyrrhotite into magnetite has been reported for temperatures higher than 500°C (Bina, Corpel, Daly, & Debeglia, 1991), pyrrhotite can be stable as long as carbon is present (Poulson & Ohmoto, 1989). It is generally considered that pyrrhotite formation starts for T_{burial} > 200°C (Carpenter, 1974). Below ~180°C, Horng and Roberts (2006) suggested that the process of pyrrhotite formation must be very slow. However, Aubourg and Pozzi (2010) documented fine-grained pyrrhotite in shales which experienced T_{burial} near 100°C. This occurrence of low-temperature monoclinic pyrrhotite is in agreement with thermodynamic calculations by Gillett (2003), who showed that pyrrhotite might form at very mild temperatures (<200°C) in reducing conditions when pyrite is present.

In the Dauphinois zone, Rochette and Vialon (1984) proposed that the magnetite-out isograd occurred at the anchizone-epizone limit (T_{burial}~250°C). In the Jurassic Helvetic shales, Rochette (1987) mapped the pyrrhotite-in isograd, resulting from the breakdown of pyrite, very close to the stilpnomelane-out isograde.

All these pioneering works suffered from relatively poorly constrained estimates of burial temperature to bracket the magnetite-out and pyrrhotite-in isograds. Vitrinite reflectance is a proven technique in shales but it is strongly anisotropic for metamorphic rocks (Komorek & Morga, 2003), leading to difficulties in the estimation of burial temperature. A geothermometer based on Raman Spectroscopy on Carboniferous Materials (RSCM) in the range of T_{burial} 200–650°C has provided a breakthrough in the establishment of peak burial temperatures in slates (Beyssac, Goffé, Chopin, & Rouzaud, 2002; Lahfid et al., 2010).

Different scenarios of the magnetization process may be envisaged with respect to burial temperature and Curie temperature (e.g., Appel, Crouzet, & Schill, 2012). When T_{burial} < T_{Curie}, the resulting magnetic record is a combination of chemical remanent magnetization (CRM) and thermo-viscous remagnetization (Fabian, 2009). CRM is acquired at the time of the growth of pyrrhotite above the blocking volume (~17 nm diameter). (Clark, 1984). However, when T_{burial} > T_{Curie}; the resulting magnetic record is a thermo remanent magnetization, acquired during the cooling of metamorphic units. In this case, the onset of magnetization is much younger than for a growth CRM. It is therefore essential to accurately constrain the magnetite-out and pyrrhotite-in temperatures to understand the magnetic recording process in slates.

In this study, we propose to define the magnetite-out and pyrrhotite-in temperatures in shales and slates by using rock magnetism and the RSCM and vitrinite geothermometers. To that purpose, we will study shales from the Taiwan belt and slates from the Western Pyrenees.

2 | RESULTS

A total of 48 shales and slates have been sampled in the Taiwan and Pyrenean belts. Sixteen Miocene shales have been sampled in the fold-and-thrust belt of the Western Foothills, North of Taiwan (Table S1, data repository). These shales are weakly deformed and present no evidence of fluid circulation. Late Cretaceous slates have been collected in the Western Pyrenees, in both the North and South parts of the Belt. 20 and 12 slates come from the "Nappe des Marbres" and the "Chainons Béarnais" respectively. The peak metamorphic conditions in these two areas are contemporaneous with extreme thinning of the lithosphere during the late Cretaceous (Clerc & Lagabrielle, 2014; Ducoux, 2017). These slates display cleavage parallel to bedding, and overall, they are moderately deformed with no evidence for fluid circulation.

We measured the reflectance of vitrinite (Ro) for the Taiwan shales and RSCM for the Pyrenean slates. In the Taiwan shales, Ro is obtained by the mean of a minimum of 20 readings. It ranges from 0.4% to 2.4%. When using the empirical calibration of Barker and Goldstein (1990), the corresponding range of burial temperature is ~55–265°C. The RSCM geothermometer is based on the degree of graphitization, which is assumed to be irreversible during burial (Beyssac et al., 2002). The RSCM is composed of first-order (1,100–1,800 cm^{-1}) and second-order (2,500–3,100 cm^{-1}) regions. Decomposition of the graphite band (1,580 cm^{-1}) and graphite defect bands (D1, D2, D3, D4) shows an excellent correlation with peak burial temperature, apparently not dependent on temperature gradient or origin of the organic matter. We analysed 34 samples and applied the Beyssac et al. (2002) and Lahfid et al. (2010) calibrations depending on the pattern of graphite bands. Peak burial temperature, obtained by the mean of a minimum of 20 readings, ranges from ~340 to ~420°C in slates from the Chainons Béarnais and from ~250 to ~590°C in slates from the Nappe des Marbres. Overall, the range of studied peak burial temperatures of the Taiwan shales and Pyrenean slates is 55–590°C.

Because magnetite and monoclinic pyrrhotite have been commonly, if not exclusively, identified in shales and slates, our approach is designed to document these two minerals using low-temperature magnetic remanence properties. The advantage of the low-temperature technique is that it limits magnetic transformations. The disadvantage is that it does not allow observation of all magnetic phases such as maghemite or hexagonal pyrrhotite. Using a SQUID magnetometer (MPMS; Magnetic Property Measurement System), we monitored the cooling and warming from 300 K to 10 K of an artificial remanent magnetization. The room-temperature saturation isothermal remanent magnetization (RT-SIRM) is imprinted with a DC magnetic field of 2.5 T. During cycling, the RT-SIRM displays non-reversible magnetic changes at the Verwey transition at ~118 K (Özdemir, Dunlop, & Moskowitz, 1993) and reversible to non-reversible changes at the Besnus transition at 30–34 K (Dekkers, 1989; Rochette, Fillion, Mattéi, & Dekkers, 1990). These are diagnostic signatures of, nano-to-micron sized magnetite and micron-sized monoclinic pyrrhotite respectively. In our experiments, we often observed a magnetic transition at temperatures below 80 K, which has been termed "P behavior" (Kars, Aubourg, & Pozzi, 2011). This P-behaviour is an induced magnetization due to the trapped magnetic field (~5 μT) inside the MPMS magnetometer. Its origin is thought to be due to the presence of pyrrhotite in the superparamagnetic (SP) state. Aubourg and Pozzi (2010) have shown that it is possible that very small magnetic changes due to the Besnus transition were masked by the P-behaviour. This suggests that P-behaviour is a marker of fine-grained pyrrhotite in SP and potentially SD (single-domain) particle sizes. The link between P-behaviour and SP pyrrhotite is consistent with Gillett (2003) who predicted the existence of pyrrhotite at burial temperature <200°C.

Demonstrative examples are shown in Figure 1. For the less deeply buried sample (Figure 1a), only stoichiometric magnetite is detected. For samples buried at ~77 and ~128°C (Figure 1b–c), we see both the Verwey transition and P-behaviour, suggesting that magnetite and superparamagnetic pyrrhotite coexist. For a sample buried at ~295°C (Figure 1d), the weakest magnetization is observed, barely detectable using a MPMS. It nevertheless clearly shows both non-reversible changes in magnetization across the Verwey transition and reversible behaviour across the Besnus transition. This suggests the co-existence of multi-domain (MD) magnetite and single-domain (SD) pyrrhotite (Dekkers et al., 1989). This assemblage has been observed only for samples at burial temperatures between ~300 and 350°C (repository data, Table S1). For samples buried at ~347 and ~589°C (Figure 1e–f), only a non-reversible Besnus transition is detected, indicating that pyrrhotite is multi-domain, and that magnetite is absent.

The evolution of RT-SIRM intensity vs. peak burial temperature is shown in Figure 2. There is a general decrease of RT-SIRM from 10^3 to 10 $\mu Am^2/kg$ over the T_{burial} range from ~55 to ~340°C. It is in the range 250–350°C that RT-SIRM reaches a minimum of <100 $\mu Am^2/kg$. For T_{burial} in the range 340–350°C, samples display a very large (two orders of magnitude) range of RT-SIRM (10–10^3 $\mu Am^2/kg$). For T_{burial} > 350°C, there are a 4-orders of magnitude range of RT-SIRM (10–10^5 $\mu Am^2/kg$) without a systematic relationship between burial temperature and RT-SIRM.

In this evolution, we distinguish magnetite and pyrrhotite occurrences on the basis of our rock magnetic analysis. When T_{burial} ranges from ~50 to 350°C, stoichiometric magnetite is detected. In addition, fine-grained pyrrhotite in SP-SD states is suggested by the P-behaviour magnetic transition (Figure 1b–c) and reversible Besnus transition (Figure 1d). Taking magnetite as the main magnetic mineral, and knowing its saturation remanent magnetization

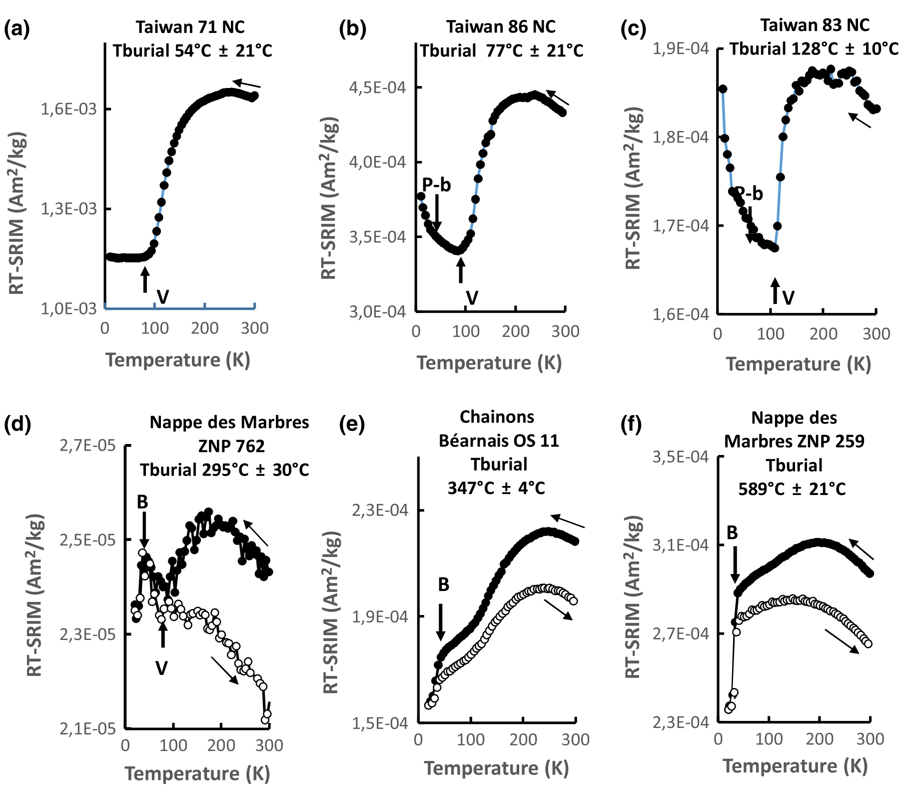

FIGURE 1 Low-temperature (10 K–300 K) monitoring of saturated isothermal remanent magnetization acquired at room temperature (RT-SIRM), measured on an MPMS at the Institute of Rock Magnetism (Minneapolis). (a–c) cooling of RT-SIRM. (d-f) cooling and warming (cycling) of RT-SIRM. P–b, V, B stand for P-behaviour (~80 K), Verwey (~118 K) and Besnus (~32 K) magnetic transitions. During the experiment, a trapped field of 5 μT is oriented upward, to accentuate the P-behaviour. The Besnus transition, pointing downward, is either magnetically reversible (d) or non-reversible (e–f). Location of samples is indicated as well as burial temperature derived from vitrinite reflectance (a–c) and Raman spectroscopy on carboniferous materials (d–f) [Colour figure can be viewed at wileyonlinelibrary.com]

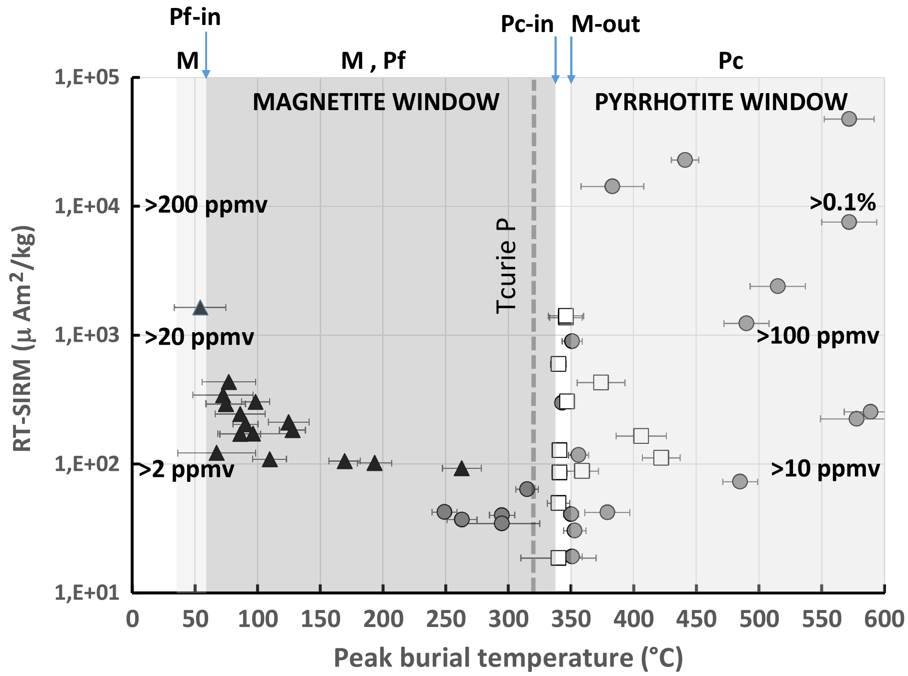

FIGURE 2 RT-SIRM versus Peak burial temperature. Peak burial temperature is estimated from vitrinite reflectance (Taiwan samples) and RSCM (Pyrenean samples), with error bars corresponding to the standard deviation (95%) of at least 20 readings. Error bars for RT-SIRM are of the order of 1%. M, Pf, Pc stand for magnetite, fine pyrrhotite (SP, SD) and coarse pyrrhotite (SD, MD). Approximate volumetric concentrations of magnetite (left) and pyrrhotite (right) are indicated. Black triangles: Taiwan shales. Open squares: Chainons Béarnais slates. Grey circles: Nappe des Marbres slates [Colour figure can be viewed at wileyonlinelibrary.com]

at room temperature (SIRM <20 Am^2/kg) (Maher & Thompson, 1999), a value of SIRM at 10^{-3} Am^2/kg gives a magnetite volumetric concentration of >20 ppmv (Figure 2). This content decreases by one to two orders of magnitude as T_{burial} increases up to 350°C. It is worth noting that in the range of T_{burial} ~250–350°C, magnetite content is very low (>1 ppmv), and even less if a portion of the remanence is carried by fine-grained pyrrhotite. We propose to place the magnetite-out isograd at ~350°C. This isograd is indicative of magnetite concentration lower than a few ppmv. We propose the existence of a fine-grained pyrrhotite isograd (Pf-in) at T_{burial}~60°C with a rather large temperature uncertainty (Figure 2). This isograd is based on the first observation of the P-behaviour magnetic transition at ~60°C (Figure 2). This fine-grained pyrrhotite probably results from the breakdown of magnetite and pyrite (Gillett, 2003). In any case, the content of fine-grained pyrrhotite capable of retaining a remanence in the range 60–340°C is very small, and barely detectable. Aubourg and Pozzi (2010) initially proposed to use the onset of P-behaviour as a marker of shallow-depth burial in shales.

At T_{burial} >340°C, coarse-grained pyrrhotite is characterized by non-reversible magnetization changes across the Besnus transition (Figure 1e–f) and high concentration (Figure 2). We suggest therefore the existence of a coarse-grained pyrrhotite isograd, named Pc-in, at T_{burial} ~340°C. From our dataset, it seems that there is a narrow band between 340–350°C where pyrrhotite and magnetite coexist (Figure 2). The abrupt jump of pyrrhotite content is likely due to the breakdown of pyrite (Rochette, 1987). The content of pyrrhotite displays a large range (Figure 2) from ppmv to 0.1%, when its SIRM is taken as <6 Am^2/kg (Dekkers, 1988). This content is apparently not driven by burial temperature. We define the coarse-grained pyrrhotite window, for T_{burial} from 350°C up to 600°C at least. To better

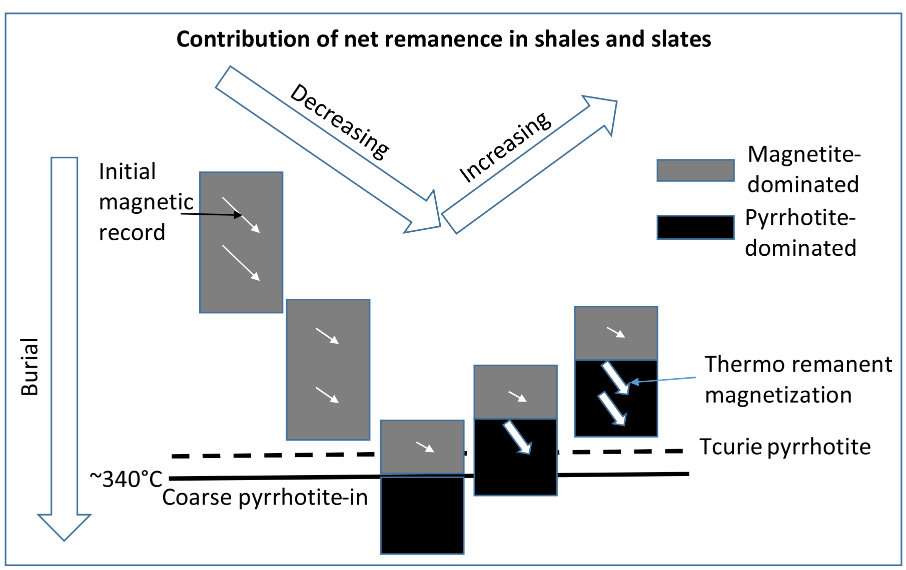

FIGURE 3 Schematic of basin remanence evolution during burial and uplift. An initial remanence in clay-rich basin is gradually lost during burial. For burial temperatures near 340°C, it is suggested that only a small contribution of initial remanence survives. On uplift, the contribution to remanence is increasing again when crossing the Curie temperature of pyrrhotite isotherm at ~320°C [Colour figure can be viewed at wileyonlinelibrary.com]

quantify the contribution of pyrrhotite and magnetite, it could be useful to investigate the thermal demagnetization of remanence at high temperature as proposed by Schill, Appel, and Gautam (2002).

3 | CONCLUSION: A MODEL FOR THE EVOLUTION OF MAGNETIC PROPERTIES AND PALAEOMAGNETISM OF CLAY-RICH BASINS

We propose a scenario of changing magnetic mineralogy in shales and slates during progressive burial (Figure 3). In this scenario, the coarse-grained pyrrhotite-in temperature is above the Curie temperature of pyrrhotite. The net remanence in shales should decrease regularly with burial depth because magnetite concentration drops by two orders of magnitude. For T_{burial} in the range 50–340°C, we suggest a dynamic interplay between the formation of magnetite from pyrite degradation and smectite-to-illite transformation, and its destruction to the profit of fine-grained pyrrhotite. For T_{burial} in the range ~250–340°C, magnetite and fine-grained pyrrhotite are barely detectable, making the shale-to-slate transition almost invisible magnetically. By T_{burial}~340°C, coarse-grained monoclinic pyrrhotites form above their Curie temperature, and hence slates are magnetically disordered, and have no remanence. It is then suggested that a clay-rich basin buried >10 km should almost no longer have a magnetic memory of burial or its previous history. It is only during the uplift of the metamorphic unit, that slates can become strongly magnetic, with the acquisition of thermo remanent magnetization when crossing the isotherm ~320°C, which corresponds to the Curie temperature of pyrrhotite.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Table S1. Shales and slates sample label and geological age. Latitude. Longitude. RT-SIRM is the Room Temperature Saturation Isothermal Remanent Magnetization (10^{-6} Am^2/kg). Occurrence of Magnetic transition. Verwey (~118 K) indicates presence of magnetite. P–b (<80 K) P-behaviour indicates the presence of superparamagnetic particles, likely fine-grained pyrrhotite. Besnus transition (~34 K) indicates the presence of monoclinic pyrrhotite. Vitrinite reflectance RO in %. s: standard deviation at 95% level of RO from > 20 readings. Tburial is the peak burial temperature calculated from RO and Raman Spectroscopy of Carboniferous Materials data (*n*>20 readings). s is the standard deviation at 95% level

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