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Magnetic properties of sedimentary greigite (Fe₃S₄)

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Abstract

New data are presented here that document the previously poorly known magnetic characteristics of sedimentary greigite (Fe₃S₄). Several diagnostic magnetic properties can be used in conjunction to rapidly screen sediments to detect the presence of greigite. Such discriminants are necessary because greigite displays a similar (or higher) range of coercivities compared to most ferrimagnetic minerals and the commonly used method of alternating field demagnetization cannot be used to distinguish between palaeomagnetic remanence components due to greigite and other ferrimagnetic minerals. Sedimentary greigite has high ratios of the saturation isothermal remanent magnetization to magnetic susceptibility (M_{rs}/χ), which are accompanied by hysteresis ratios of $M_{rs}/M_s \approx 0.5$ and $B_{cr}/B_c \approx 1.5$ (M_s is the saturation magnetization, B_c is the coercive force and B_{cr} is the coercivity of remanence). Greigite has no low-temperature phase transition, whereas the ferrimagnetic iron sulphide pyrrhotite undergoes a major phase transition at about 34 K, and unoxidized magnetite displays the Verwey transition at 118 K. Low-temperature measurements may therefore prove valuable in distinguishing between magnetite, pyrrhotite and greigite, although the absence of a low-temperature transition cannot be taken as definitive evidence for the presence of greigite. Greigite also displays characteristic high-temperature behaviour, with a major drop in magnetization between 270 and 350°C. Determination of the M_{rs}/χ ratio is an excellent means of rapidly screening sediments to identify stratigraphic intervals that may contain greigite. Subsequent low-and high-temperature analyses can then provide unambiguous identification of greigite and enable the evaluation of the presence of other magnetic minerals.

1. Introduction

Greigite (Fe₃S₄) is a ferrimagnetic iron sulphide mineral that forms in sulphate-reducing sedimentary environments as a precursor to pyrite [1–4]. Most marine sediments and sedimentary rocks contain at least traces of pyrite because a major proportion of the world's mud is, and was, buried under anoxic, sulphate-reducing conditions [3]. Greigite is widely considered to be of minor importance in most sedimentary sequences because of its metastability with respect to pyrite. However, it is being increasingly identified in a wide range of depositional environments, with many occurrences in rocks of Pleistocene and older age [4–9].

Sedimentary rocks are an important source for palaeomagnetic studies of geomagnetic field behaviour (including directional (e.g., [10–12]) and relative palaeointensity (e.g., [13,14]) studies) and for environmental magnetic studies of palaeoclimate [15,16]. Such studies are often critically dependent on the extraction of a detrital magnetic signal. If greigite is preserved in a sedimentary sequence, its presence will have major implications for the palaeomagnetic record. The principal effect is that iron sulphide minerals form at the expense of detrital iron-bearing minerals, with dissolution of detrital magnetite being the most common manifestation [4,17–20]. A chemical remanent magnetization (CRM) due to greigite will also compete with, and

possibly obscure, the detrital magnetic signal [5]. Discrepancies in the timing of acquisition of remanence of different magnetic minerals can also have adverse effects on high-resolution studies of palaeosecular variation, relative palaeointensity (which depend on the sole presence of detrital magnetite [13]), geomagnetic polarity transitions [12] and high-resolution magnetostratigraphy (which tie sedimentary records of Earth orbital cycles to magnetostratigraphy to calibrate the magnetic polarity timescale (e.g., [21])). Unwarranted assumptions about the nature of the detrital magnetic record could jeopardize the validity of such studies. It is therefore necessary to be aware of the possible presence of diagenetic/authigenic phases, such as greigite, and to detect their presence in order to take diagenetic factors into account in the interpretation of palaeomagnetic records. It should be noted that in many occurrences the CRM held by greigite is strong and stable [4-6,9,22]. The presence of greigite therefore does not necessarily suggest that palaeomagnetically useful information cannot be determined, but nevertheless care must be taken in interpreting records that contain this mineral.

In recent years, greigite has been identified in an increasing number of sedimentary environments that range from Holocene to Cretaceous in age [4–9,22–26], with significant numbers of these occurrences in strata of Miocene through to Pleistocene age. These findings demonstrate that greigite can persist for long periods in the sedimentary record and that it should not be assumed to be an unimportant ferrimagnetic mineral. Furthermore, the discovery of magnetotactic bacteria that produce greigite magnetosomes [27–31] provides additional evidence for a potentially widespread source of sedimentary greigite.

In this paper, new data are presented from a range of natural greigite samples as well as from two synthetic greigite samples. The natural samples were extracted from rapidly deposited Plio-Pleistocene marine sediments from southwestern Taiwan [8], Miocene coal measures in the Czech Republic [7], Cretaceous marine sediments from northern Alaska [5], and Mio-Pliocene lacustrine sediments from near the greigite type locality in California [32]. The synthetic samples were precipitated using a hydrothermal method that involves mixing ammonium

ferrous sulphate (Mohrs salt) with a sodium sulphide solution, as described by Uda [33] and Snowball [24].

2. Methods

All of the magnetic studies were performed on magnetic separates, most of which were obtained by pumping a slurry of disaggregated sediment between the poles of an electromagnet by means of a peristaltic pump. All of the magnetic separates were subjected to X-ray diffraction (XRD) analysis to ensure that greigite is the only detectable magnetic mineral present. Thermomagnetic analyses were conducted using a Princeton Applied Research Corporation vibrating sample magnetometer (VSM) with heating at 10°C/min at the Institute for Rock Magnetism at the University of Minnesota or with a Kappabridge KLY-2 susceptibility meter with a CS-2 high-temperature attachment at the Palaeomagnetism Laboratory at the University of California-Davis. Thermomagnetic measurements provided additional evidence for the magnetic purity of the separates. Hysteresis measurements, acquisition of a saturation isothermal remanent magnetization (M_{rs}) and backfield demagnetizations of M_{rs} were performed on a Princeton Measurements Corporation alternating gradient magnetometer up to maximum fields of 1 T at UC-Davis. For some samples, hysteresis loops were measured on a VSM at different temperatures between 77 and 600 K (at the Institute for Rock Magnetism). Low-temperature remanence analyses were made on all of the samples by imparting a saturation remanence with an applied field of 2.5 T at 5 K, followed by measurements of M_{rs} at regular intervals from 5 K to room temperature. These lowtemperature measurements were made with a Ouantum Designs magnetic properties measurement system at the Institute for Rock Magnetism.

3. Results

3.1. Magnetic purity of samples

Greigite was positively identified in all of the samples by XRD analysis (Fig. 1). The magnetic

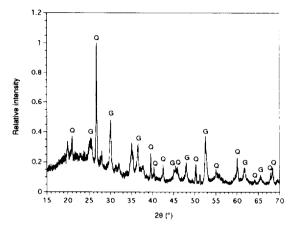


Fig. 1. X-ray diffractogram showing characteristic peaks for greigite from sample EJEM 12. The sample contains a mixture of greigite (G) and quartz (Q) grains which could not be adequately separated during the extraction process. No other ferri-of ferromagnetic minerals were detected in any of the samples.

purity of the samples is attested to by the observation that no other magnetic minerals are evident in XRD and in high-and low-temperature analyses (see discussion below). Much of the sedimentary greigite occurs as small concretions in which non-ferrimagnetic impurities, particularly quartz (Fig. 1), pyrite and feldspar also occur. These impurities do not affect the magnetic properties reported here. Mass-independent parameters are discussed throughout this paper because of the difficulty in estimating the mass of the greigite with respect to the non-ferrimagnetic impurities. The concretions were not disaggregated in order to avoid mechanically altering the grain size of the particles. Electron microscopic observation of the size of the grains was attempted by obtaining polished thin sections through some of the greigite-rich concretions. However, the polishing process may have caused smearing of the relatively

Table 1 Selected mineral magnetic properties of the greigite samples studied

Sample ¹	N ²	B _c (mT)	B _{cr} (mT)	M _{rs} /M _s	B _{cr} /B _c	f _{SP} ³
EJEM 07	1	58.0	80.6	0.510	1.39	0.34
EJEM 08	2	54.0	81.5	0.443	1.51	0.35
EJEM 09F	2	48.6	71.0	0.446	1.46	0.43
EJEM 09I	1	35.8	68.4	0.366	1.91	0.26
EJEM 09C	5	53.4	71.6	0.515	1.34	0.30
EJEM 10F	2	47.9	67.5	0.482	1.41	0.38
EJEM 10I	2	53.2	68.1	0.536	1.28	0.24
EJEM 10C	2	46.0	63.0	0.497	1.37	0.29
EJEM 11	2	57.1	81.7	0.505	1.43	0.25
EJEM 12	2	42.4	68.3	0.410	1.61	0.28
EJEM 13	2	36.3	62.8	0.369	1.73	0.29
EJEM 14	2	45.4	71.2	0.429	1.57	0.25
EJEM 15	3	41.0	68.9	0.397	1.68	0.26
EJEM 16	2	50.9	77.4	0.459	1.52	0.26
EJEB $375 + 376$	2	59.6	77.5	0.572	1.30	0.28
EJEB 380	4	71.3	94.8	0.591	1.33	0.21
Krs	2	20.2	44.8	0.238	2.22	0.28
Simpson	2	46.4	60.3	0.535	1.30	0.35
Saddleback	1	39.4	70.2	0.442	1.78	
SYN90B	3	24.0	51.6	0.300	2.15	0.66
SYN93A	3 2	11.4	58.0	0.183	5.08	0.89

¹ EJEM and EJEB samples are from Taiwan [8]; Krs is from the Czech Republic [7]; Simpson is from Alaska [5]; Saddleback is from near the greigite type locality [32]; SYN samples are synthetic [24].

 $^{^{2}}$ N = Number of subsamples from which hysteresis measurements were made.

 $^{^3}$ $f_{\rm SP}$ = Superparamagnetic fraction, defined as [(SIRM (4.2 K)) - (SIRM (300 K))]/(SIRM (4.2K)).

soft greigite particles and no reliable grain-size determinations were obtained. Direct grain-size observation awaits further work which will enable elucidation of the magnetic properties of greigite within a grain-size-dependent framework. Such work should be done on high-purity synthetic samples to avoid the presence of non-ferrimagnetic impurities, which are difficult to remove from natural samples.

3.2. Coercivity of remanence and coercive force

The measured values of the coercivity of remanence (B_{cr}) , as shown in Table 1, lie in the range 44.8-94.8 mT. This range is consistent with values reported previously for greigite by Roberts and Turner [4] and Reynolds et al. [5] and is also consistent with values reported from a range of compositions of ferrimagnetic iron-nickel sulphides by Van Velzen et al. [34]. The range of B_c values reported in Table 1 is also consistent with those reported for natural and synthetic greigite samples by Snowball [24]. An important initial observation from Table 1 is that all of the greigite samples have B_{cr} values that are higher than those of magnetite with grain sizes in the $0.012-200 \mu m$ range [35,36]. This observation suggests that greigite will display a greater resistance to alternating fields than magnetite and some other ferrimagnetic minerals. Despite the high values of B_{cr} , all of the greigite samples analysed display isothermal remanent magnetization acquisition curves that are similar to those for magnetite, with saturation occurring between 200 and 300 mT. Caution must therefore be exercised in interpreting results based on alternating field demagnetization or M_{rs} acquisition curves. This result highlights the need for a rapid means of detecting sedimentary greigite.

3.3. High-temperature behaviour

Thermomagnetic behaviour typical of greigite is shown in Fig. 2. When heated in air, greigite is characterized by a major decrease in magnetization between 270 and 350°C. Rather than continuously decreasing, the magnetization increases above 440°C until it peaks at temperatures above 500°C, then decreases again to approach zero at 580°C. Previous attempts to determine precisely the thermal stability field, including the Curie temperature, for greigite

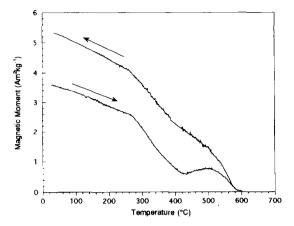


Fig. 2. Typical thermomagnetic analysis for greigite (heated in air). Arrows indicate heating and cooling curves. See text for description. All of the thermomagnetic curves obtained for the studied samples indicate the sole presence of greigite.

have failed, however, due to kinetic problems associated with rate of reaction [37]. Skinner et al. [32] showed that greigite is stable up to 282°C and that it begins to break down to form minor pyrrhotite plus sulphur vapour above 282°C, and then to form pyrrhotite and pyrite at temperatures above 320°C. This breakdown may account for much of the major decrease in magnetization between 270 and 350°C. Nevertheless, it is unlikely that significant amounts of pyrrhotite have formed between 282 and 320°C because no pyrrhotite Curie temperature is evident at 320–325°C (cf. [38]) in Fig. 2 or in the thermomagnetic curves that have been published for greigite in other studies [4,5,22,24].

Krs et al. [7] conducted detailed XRD studies of the thermal breakdown products of greigite and found that the intensities of greigite diffraction peaks decrease after heating between 250 and 300°C, at which point pyrite and marcasite begin to form (consistent with the decrease in magnetization seen above 270°C in Fig. 2). Pronounced changes take place at 320°C with the generation of pyrrhotite along with the continued formation of pyrrhotite and marcasite. The concentrations of these three phases increases until 360°C. The presence of pyrrhotite is not detected in the thermomagnetic results because the 320–360°C temperature range, over which significant pyrrhotite forms, is above the Curie tempera-

ture for pyrrhotite [38]. Krs et al. [7] note that these sulphide phases decompose above 360°C and are not detectable above 400°C. The increase in magnetization observed in this study above 440°C (Fig. 2) is attributed to the formation of magnetite, as indicated by the Curie point at about 580°C. Magnetite apparently continues to form during heating to 600°C because the magnetic moment observed in the cooling curve is higher than that of the heating curve.

Given the difficulty of determining the Curie temperature of greigite, a different approach was attempted in this study. Hysteresis loops were measured (in air) at discrete temperature steps for sample EJEB 380 from 77 K to 614 K in order to determine whether any significant break points occur in the hysteresis parameters that could delineate the thermal blocking point of greigite (Fig. 3). The thermal blocking point will be lower than the Curie temperature, but it provides an excellent minimum estimate for the Curie temperature. All of the measured hysteresis parameters (including M_s , M_{rs} , B_c , B_{cr} , M_{rs}/M_s and B_{cr}/B_c) show a significant break at 595 K (322°C). This break must mark the lower limit of the unblocking temperature range at which thermal energy begins to overcome the magnetocrystalline anisotropy (see below) of greigite. The observation that the M_{rs}/M_s ratio is greater than 0.5 until 322°C also indicates that magnetocrystalline anisotropy is dominant throughout the blocking temperature range of greigite. The estimate of 322°C for the maximum unblocking temperature of greigite is close to the estimated Curie temperature of 606 K (333°C) given for synthetic greigite by Spender et al. [39]. The estimate of Spender et al. [39] is based on the extrapolation of a steeply decreasing part of a thermomagnetic curve and is not particularly well determined. Nevertheless, the present minimum estimate of 322°C is reasonable and is consistent with the interpretation of Spender et al. [39]. Van den Berghe et al. [40] made Mössbauer measurements on greigite samples up to 480 K (207°C) and extrapolated their data to obtain a Curie temperature estimate of 800 K (527°C). This result appears to be highly unrealistic given the evidence presented above which indicates that sedimentary greigite decomposes completely at 400°C [7].

Despite the uncertainty concerning the Curie temperature of greigite, the thermomagnetic behaviour is

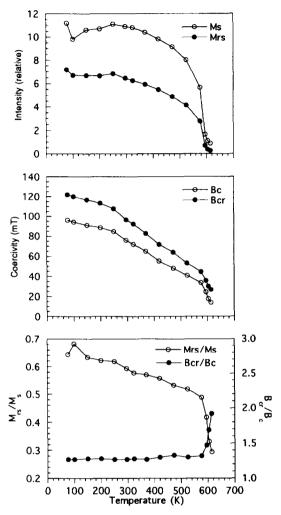


Fig. 3. Temperature dependence of hysteresis parameters for sample EJEB 380 (see text). The major break in slope at 322°C indicates that this temperature is close to the maximum unblocking temperature of greigite. The small break in slope at around room temperature may be an artifact of the meaurement. Low-temperature measurements were made with a liquid nitrogen cooling sleeve and the high-temperature measurements were made in an oven; both were attached to the vibrating sample magnetometer for the appropriate measurements. The switch between the two attachments may be responsible for the minor difference in slope in the values measured below and above room temperature.

distinct and easily recognizable (cf. [4,5,22,24]). Therefore, thermomagnetic analysis is an excellent means of detecting the presence of greighte in sediments. Many workers use nitrogen atmospheres dur-

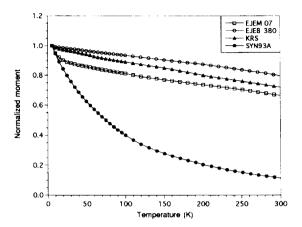


Fig. 4. Low-temperature analysis of $M_{\rm rs}$ applied with a field of 2.5 T at 5 K for four samples, with measurements made during warming in zero field. See text for description. No low-temperature transitions were detected in any of the greigite samples measured. This indicates that it is unlikely that other minerals such as pyrrhotite or magnetite, both of which display low-temperature phase transitions, are present in the samples.

ing thermomagnetic analyses. It should be noted, however, that this procedure does not elucidate the thermomagnetic properties of greigite [5,22]. Reynolds et al. [5] obtained widely variable thermomagnetic curves simply by using different flow rates of nitrogen. This may be because oxygen impurities commonly occur in bottled nitrogen. Nevertheless, the important point is that thermomagnetic curves that are diagnostic of greigite are attainable with air environments and they can be easily compared with thermomagnetic curves from the literature [4,5,22,24].

3.4. Low-temperature behaviour

Measurement of M_{rs} , acquired in an applied field of 2.5 T, was made as samples were heated from low temperatures (5 K) to room temperature to determine whether greigite undergoes a low-temperature phase transition during zero-field warming of the sample to room temperature, as is observed at 30–34 K for pyrrhotite [41,42]. As demonstrated by the continuous and smooth curves in Fig. 4, significant variability exists in the superparamagnetic (SP) content of the different samples, as indicated by the different degrees of remanence drop between low and room

temperatures. The SP fraction can be estimated by the relationship (cf. [43]):

$$f_{\rm SP} = \frac{M_{\rm rs} (4.2 \, K) - M_{\rm rs} (300 \, K)}{M_{\rm rs} (4.2 \, K)}$$

This relationship will overestimate the SP fraction because it does not take into account temperature-dependent changes in $M_{\rm rs}$ due to changes in $M_{\rm s}$ between 4.2 K and 300 K. Despite this limitation, $f_{\rm SP}$ is a useful parameter for obtaining a comparative estimate of the SP content of a suite of samples (Table 1).

No low-temperature phase transition is evident in any of the greigite samples (Fig. 4). This result is in agreement with limited work on synthetic samples by Spender et al. [39]. Low-temperature analysis therefore provides an excellent means of distinguishing between the two most commonly occurring ferrimagnetic iron sulphide minerals, pyrrhotite and greigite. The lack of a low-temperature phase transition is also important because greigite is a cubic spinel and is isostructural with magnetite [32], which exhibits a Verwey transition at 118 K (unless the magnetite is surfically oxidized [44]). Low-temperature work may therefore prove valuable in distinguishing between magnetite, pyrrhotite and greigite, although the absence of a low-temperature transition cannot be taken as definitive evidence for the presence of greigite or the absence of (oxidized) magnetite.

3.5. High-field behaviour

Magnetic hysteresis parameters, including M_s , M_{rs} , B_c and B_{cr} , were determined at room temperature for multiple subsamples of each sample, up to maximum fields of 1 T. The distribution of points on a bilogarithmic plot of M_{rs}/M_s vs. B_{cr}/B_c (Fig. 5) is indicative of a mixing line due to mixtures of SD and SP grains that extends from M_{rs}/M_s values of 0.6 to 0.2 and B_{cr}/B_c values of 1.25 to 2.5. The two outliers on the far right of Fig. 5 represent two subsamples of synthetic sample SYN93A. Measurements from the other synthetic sample (SYN90B) lie near the lower right of the main mixing line indicated in Fig. 5. The low M_{rs}/M_s ratios for the synthetic samples is consistent with a mixture of SD

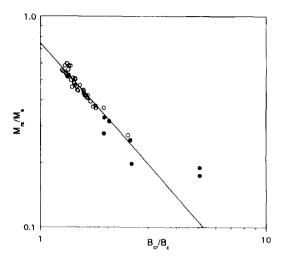


Fig. 5. Bilogarithmic plot of $M_{\rm fs}/M_{\rm s}$ vs. $B_{\rm cr}/B_{\rm c}$ for all of the greigite samples subjected to hysteresis analysis. The data cluster along a mixing line near single-domain-like values of $M_{\rm rs}/M_{\rm s} \approx 0.5$ and $B_{\rm cr}/B_{\rm c} \approx 1.5$, except for samples from coal beds and synthetic samples (closed symbols; see text for description and Table 1 for average values of each sample).

grains with a much larger fraction of SP grains than is evident in the natural samples (Fig. 4 and Table 1). The large SP fraction, mixed with SD grains, in the SYN93A subsamples contributes to 'waspwaisted' hysteresis loops, the details of which are described elsewhere [45]. The two values to the left of, and below, the main mixing line are from two subsamples from coal beds in the Czech Republic (Krs; [7]). Low-temperature data from these samples (Fig. 4 and Table 1) indicate an SP fraction similar to the other natural greigite samples, and therefore it is unlikely that the M_{rs}/M_s and B_{cr}/B_c values are due to mixtures of SD and SP grains in this case. It is more likely that the Czech coal beds contain larger (pseudo-single-domain) greigite grains than those in the other natural greigite samples which are derived from marine and lake sediments. The distinct geochemical conditions in the coal beds may enable growth of much larger greigite grains than is the case in other environments. The major difference in depositional environment makes the coal beds a poor analogue for greigite from marine and lacustrine sedimentary environments which display a much different hysteresis behaviour.

Data from the synthetic samples, the coal sample (Krs) and other samples that displayed irregular hys-

teresis loops (shown with closed symbols in Fig. 5) were omitted when calculating the best-fit mixing line through the hysteresis data shown in Fig. 5. The M_{rs}/M_{s} values for data points on the upper left-hand side of the mixing line in Fig. 5 range between 0.5 and 0.6. These room-temperature values are higher than those expected for a random assemblage of SD grains with shape anisotropy [46]. Extrapolation of the mixing trend of Fig. 5 to $B_{cr}/B_{c} = 1$ gives a maximum $M_{\rm rs}/M_{\rm s}$ value of 0.75. The $\langle 100 \rangle$ crystallographic axis was determined to be the easy axis of magnetization in synthetic greigite samples by Yamaguchi and Wada [47]. This determination is supported by electron microscopic observations of greigite crystals, produced by magnetotactic bacteria, that are aligned in chains with the $\langle 100 \rangle$ crystallographic axis parallel to the direction of the chain [28,29,31]. Alignment of the magnetosomes along the easy axis of magnetization presumably optimizes the ability of the microorganisms to navigate along geomagnetic field lines. If the $\langle 100 \rangle$ axis is the easy axis of magnetization and if magnetocrystalline anisotropy controls the hysteresis behaviour of greigite, it would be expected that M_{rs}/M_s would approach 0.83 as B_{cr}/B_c approaches unity [48]. The value of 0.75 determined here is lower than expected, although it is well above the value expected for shape anisotropy (0.5). The particle size and shape and magnetic interactions between particles were not considered in the theoretical calculations [48] and the M_{rs}/M_s ratio of 0.75 is most nearly consistent with the expected behaviour of SD grains with magnetocrystalline anisotropy.

With the exception of the greigite from the Czech coal beds (Krs), all of the natural samples studied display SD-like hysteresis behaviour (Fig. 5 and Table 1), with $M_{\rm rs}/M_{\rm s}\approx 0.5$ and $B_{\rm cr}/B_{\rm c}\approx 1.5$. This observation is consistent with those of Snowball and Thompson [22], Roberts and Turner [4] and Reynolds et al. [5], who all report substantially higher $M_{\rm rs}/\chi$ ratios for greigite-bearing samples than for magnetite-or titanomagnetite-bearing samples. The $M_{\rm rs}/\chi$ ratio is largely a measure of magnetic grain size: fine grains have high ratios while coarser grains have lower ratios.

While high values of $M_{\rm rs}/\chi$ and SD-like hysteresis parameters are possible from other materials, typical sediments that are dominated by magnetite

and titanomagnetite grains usually yield hysteresis values that fall well within the pseudo-single-domain size range (cf. [49]), with M_{rs}/M_s values of about 0.10-0.30 (e.g., [13,50]). M_{rs}/M_s ratios of about 0.40-0.50 have been reported for a wide range of natural pyrrhotite samples in grains up to 20 µm in size [51,52]. It is not clear, however, if pyrrhotite occurs commonly in sulphate-reducing sedimentary environments, although some cases have been documented [8]. Regardless, low-and high-temperature measurements provide a powerful means of distinguishing between sedimentary greigite and pyrrhotite. High ratios of M_{rs}/χ and M_{rs}/M_s of natural greigite samples can therefore be a highly useful guide for detecting the presence of sedimentary greigite. Recognition of high values of M_{rs}/χ in greightebearing sediments has been a major factor that led to the increased incidence of the identification of sedimentary greigite in recent years [22,24].

A probable explanation for the observation of high M_{rs}/χ ratios and SD-like M_{rs}/M_s ratios is that a much wider range of grain sizes falls within the SD range for greigite than is the case with magnetite. For magnetite, the range of grain sizes that displays SD behaviour is rather restricted (0.025–0.08 μ m; [53]). The saturation magnetization of synthetic greigite at room temperature is estimated at ~ 25 A m² kg⁻¹ (cf. [39]). This value is less than one-third of that for magnetite. The lower value of M_s for greigite suggests that SD behaviour can be maintained at larger grain volumes than is possible in magnetite because larger volumes would be required before it became energetically favourable to nucleate a domain wall. This hypothesis is supported by calculations of the threshold size for the SD to two-domain boundary in which this size is estimated to be several times that of magnetite for grains with width/length axial ratios of unity [54]. Hoffmann [55] used the Bitter method and magneto-optical Kerr effect to optically observe domains in greigite and estimated that the SD to two-domain boundary occurs at $0.7-0.8 \mu m$. If this is true, the relatively large range of sizes over which SD behaviour is maintained provides a physical explanation for why SD-like hysteresis ratios and high M_{rs}/χ ratios are commonly observed for greigite-bearing sediments. As stated above, the occurrence of SD-like hysteresis ratios and high M_{rs}/χ ratios is not necessarily restricted to greigite, although it does provide a first step in identifying sediments that might contain greigite.

4. Conclusions

Based on the data described above, several distinct magnetic properties can be used to identify sedimentary greigite. First, natural greigite usually has high M_{rs}/χ ratios that are accompanied by hysteresis ratios of $M_{\rm rs}/M_{\rm s} \approx 0.5$ and $B_{\rm cr}/B_{\rm c} \approx 1.5$. Second, greigite undergoes no low-temperature phase transitions, and thus it can be distinguished from pyrrhotite, which displays a phase transition at 30-34 K [41,42], and magnetite, which displays the Verwey transition at 118 K [44]. Third, greigite undergoes a major drop in magnetization between 270 and 350°C. Rapid screening of sediments can be achieved by determination of the M_{rs}/χ ratio. Subsequent lowand high-temperature measurements should then enable unambiguous identification of greigite as well as the evaluation of the presence of other magnetic minerals. Widespread application of this method should lead to the recognition of the presence of greigite and to a more complete understanding of the effects of diagenetic sedimentary greigite formation on the palaeomagnetic record in a wide range of geological settings.

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