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HYSTERESIS PROPERTIES OF SIZED DISPERSED MONOCLINIC PYRRHOTITE GRAINS

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Abstract. Monoclinic pyrrhotite (Fe_7S_8 with 4C superstructure) was magnetically separated from a massive pyrrhotitic ore for preparation of nine grain-size fractions ranging from ~ 80 μm (large multidomain grains) to < 3 μm (single-domain grains). Grains smaller than 100 μm were found to be magnetically hard with coercive forces ranging from 135 oe for 83 μm grains to 920 oe for < 3 μm grains. For grain sizes between 83 μm and 7 μm the coercive force is given by $H_c \propto d^{-0.79}$. Variations in hysteresis properties with grain size appear to be gradual, with no evidence of sudden changes associated with domain structure transitions.

Introduction

The crystallography, mineralogy and magnetic properties of pyrrhotite group minerals, with the general formula $Fe_{1-x}S$ ($0 < x < 0.125$), have been reviewed by Ward [1970], Schwarz [1974], Power and Fine [1976] and Vaughn and Craig [1978]. Monoclinic 4C pyrrhotite is the only ferrimagnetic pyrrhotite phase which is stable at room temperature.

Soffel [1977, 1981] has investigated the domain structure of small natural pyrrhotite grains in a diabase using the Bitter pattern technique. Extrapolation of the empirical relationship between grain size and number of domains yields a value of 1.6 μm for the critical single-domain size, d_c. A theoretical calculation [Clark, 1983] gives 2.9 μm for d_c. Examination of Soffel's data reveals that grains up to ~ 3 μm have single-domain structure. The preferred estimate for d_c is thus 3 μm. On the other hand 80 μm grains contain approximately 20 domains and can therefore be considered large multidomain grains, although pseudo-single-domain effects associated with non-magnetic inclusions can be observed in grains of this size [Soffel, 1977].

Although many investigations of the intrinsic magnetic properties of pyrrhotite have been carried out, very little has been published on fine particle rock magnetism of pyrrhotite, particularly with regard to grain size dependence of magnetic properties.

Results

Massive pyrrhotite ore from Mt Bonnie, Northern Territory (Australia), was selected for preparation of magnetic separates from which distinct grain size fractions were produced. This ore was chosen because thermomagnetic analysis indicated monoclinic pyrrhotite as the only magnetic mineral present and because of the near-perfect reversibility of the thermomagnetic curves, even after heating in air to above 300°C, indicating that the sample was not prone to oxidation. Details of sample preparation and characterization are given by Clark (1983). The mean and standard deviation of the grain size distributions and the pyrrhotite content of the prepared synthetic specimens are given in Table 1.

For an initially demagnetized specimen of a ferromagnetic or ferrimagnetic material the Rayleigh relationships are obeyed, provided the applied field remains small compared to the coercive force [Chikazumi and Charap, 1978, p. 296]. The magnetization is then quadratic in applied field:

$$J = \chi H + \eta H^2 \qquad (1)$$

where χ is the initial or reversible susceptibility and η is the Rayleigh parameter.

Values of χ and η for the dispersed pyrrhotite specimens are given in Table 2. Initial susceptibility values ranged from ~ 0.025 G/oe for 83 μm grains to ~ 0.01 G/oe for the finest fractions (< 15μm), and η/χ ratios varied between ~ 3×10^{-2} oe^{-1} and ~ 3×10^{-3} oe^{-1}.

The following coercivity parameters are given in Table 3: bulk coercive force, H_c (the back field required to reduce the magnetization of a saturated specimen to zero); coercivity of

TABLE 1. Synthetic Dispersed Pyrrhotite Specimens

Specimen	Mean grain length (s.d.) (μm)	Pyrrhotite content Mass (mg)	Pyrrhotite content Volume (%)
NRC1	83(38)	33.7	0.07
NRC2	83(38)	192.0	0.39
NRC3	83(38)	113.4	0.23
NRF	44(12)	38.0	0.08
R4	42(12)	71.1	0.14
R8	32(8.5)	89.6	0.18
R12	20(6)	88.1	0.18
R14	15.5(5.7)	193.2	0.39
R16	11.1(3.4)	71.0	0.14
R17	6.9(1.7)	64.8	0.13
R18	<3(-)	22.0-25.6	0.04-0.05

Specimen mnemonics refer to ring numbers in the Bahco dust analyser, except for NRC (no ring coarse fraction) and NRF (no ring fine fraction). The mass of pyrrhotite in each specimen was determined from the saturation magnetization (J_s). Uncertainty of J_s for R18 leads to a range of values for pyrrhotite content. The volume (%) of pyrrhotite was calculated from the mass, assuming a density of 4.6 g/cm^3 and a specimen volume of 10.8 cm^3

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TABLE 2. Initial Susceptibility (χ) and the Rayleigh Parameter (η)

Grain length (μm)	$\chi \times 10^2$ (G/oe)	$\eta \times 10^4$ (G/oe^2)
83*	2.46	6.7
44	1.57	3.3
42	1.75	3.3
32	1.50	2.7
20	1.29	1.8
15.5	1.26	0.78
11.1	1.08	0.35
6.9	1.04	0.71
<3	1.02-1.19$^+$	1.1-1.4$^+$

* Hysteresis properties for the 83 µm fraction given in Tables 2-4 are averages of values for the three NRC specimens.

$^+$ The range of values quoted reflects uncertainty in the pyrrhotite content of the <3 µm specimen.

TABLE 3. Coercivity Parameters

Grain length (μm)	H_c	H_{cr}	H_{cr}'	$H_{1/2}$	$H_{1/2}'$
83	135	185	270	100	55
44	210	285	400	185	105
42	230	300	400	195	115
32	280	340	440	235	130
20	375	415	520	340	205
15.5	510	520	630	490	270
11.1	665	715	790	700	350
6.9	825	855	940	740	525
<3	920	1245	1340	1120	630

All coercivity parameters are in oersteds. H_c = bulk coercive force; H_{cr} = coercivity of remanence; H_{cr}' = coercivity of remanence acquisition; $H_{1/2}$ = median destructive alternating field (single-axis); $H_{1/2}'$ = median destructive alternating field (tumbling)

remanence, H_{cr} (the back field required to reduce the remanence of a saturated specimen to zero); coercivity of remanence acquisition, H_{cr}' (the field required to impart isothermal remanence equal to half the saturation remanence to an initially demagnetized specimen); and the median destructive alternating fields of saturation remanence, $H_{1/2}$ (for single-axis demagnetization) and $H_{1/2}'$ (for tumbler demagnetization).

Table 4 lists the hysteresis properties: saturation remanence (J_{rs}), relative remanence (J_{rs}/J_s), H_{cr}/H_c, susceptibility/saturation magnetization ratio (χ_m/J_s), and $(H_{cr}' + H_{1/2})/2H_{cr}$.

Discussion

The data of Table 2 indicate that the initial magnetization curves up to ~ 5 oe are reasonably linear and that measurements in fields of this order, or less, are satisfactory for estimation of susceptibility in the Earth's field (~ 0.5 oe).

The variation in susceptibility with grain size is more pronounced for pyrrhotite than for magnetite of equivalent grain size. This is because the intrinsic susceptibility of pyrrhotite is not controlled to the same extent by self-demagnetization of the grains. The observed susceptibility of pyrrhotite is $\leq$ 0.025 G/oe for $<$ 80 µm grains, but ranges up to ~ 0.1 G/oe for very coarse-grained material [Kropacek, 1971; Clark, 1983].

The coercivity parameters (Table 3) indicate that $<$ 80 µm grains are magnetically hard, the coercivity (sensu lato) increasing markedly with decreasing grain size. The bilogarithmic plot of bulk coercive force versus grain size (Figure 1) shows that the relationship $H_c \propto d^{-n}$ is obeyed for 7 µm $<$ d $<$ 83 µm, where $n \approx 0.79$.

The parameter n is related to domain structure and the distribution of crystal defects which impede domain wall motion [Stacey and Banerjee, 1974, pp. 66-69].

The high coercivity of medium-to fine-grained pyrrhotite is consistent with the intensity and stability of natural remanent magnetization carried by many pyrrhotite-bearing rocks [Kropacek, 1971; Clark, 1983].

The grain sizes studied are characterized by high relative remanence values ($0.23 < J_{rs}/J_s < 0.58$) and low values of H_{cr}/H_c ($<$ 1.38). For the finer grains, J_{rs}/J_s approaches the upper limiting value of 0.637 for uniaxial stable single domain grains with magnetic moments confined to the basal plane [Dunlop, 1971].

A remarkable feature of the data in Tables 2 and 4 is that trends in various hysteresis properties with decreasing grain size are reversed for the finest grain size fraction. The ratios η/χ, H_{cr}/H_c and, probably, χ/J_s increase for the $<$ 3 µm grains, and J_{rs}/J_s decreases. The presence of superparamagnetic grains in the finest fraction can explain these observations. It is believed that particles below the superparamagnetic threshold size (~ 0.017 µm [Clark, 1983]), which can have susceptibility up to ~ 0.2 G/oe, are clinging to larger grains and influencing the hysteresis properties.

The susceptibility of stable single-domain pyrrhotite grains is estimated by Clark [1983] to be 4.8×10^{-3} G/oe, which is less than half the observed susceptibility of the $<$ 3 µm fraction.

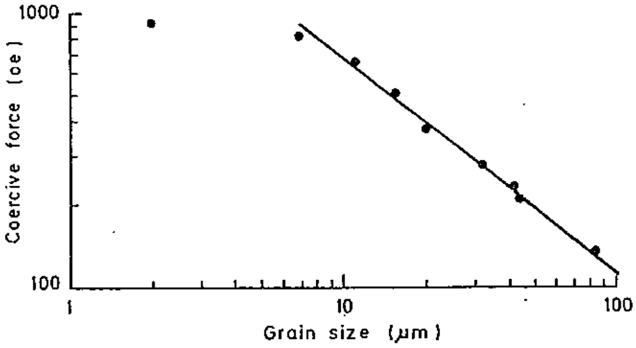

Fig. 1. Coercive force versus grain size for the synthetic dispersed pyrrhotite specimens. The straight line corresponds to the relationship $H_c = 4310\ d^{-0.79}$.

TABLE 4. Saturation Remanence and Hysteresis Property Ratios

Grain length (μm)	J_{rs} (emu/g)	J_{rs}/J_s	$(\chi_m/J_s)\times 10^4$ (oe^{-1})	H_{cr}/H_c	$\frac{H_{cr}'+H_{1/2}}{2H_{cr}}$
83	3.66	0.230	3.36	1.38	0.99
44	4.95	0.311	2.15	1.36	1.02
42	5.51	0.346	2.39	1.30	1.00
32	6.59	0.413	2.05	1.21	1.00
20	7.60	0.477	1.76	1.11	1.04
15.5	9.31	0.584	1.72	1.02	1.08
11.1	8.43	0.529	1.47	1.08	1.04
6.9	9.19	0.58	1.42	1.04	0.98
<3	6.49-7.56	0.407-0.474	1.39-1.62	1.35	0.99

J_{rs} = saturation remanence, normalized to unit mass of pyrrhotite;
J_s = apparent saturation magnetization (taken to be 15.9 emu/g);
χ_m = mass susceptibility of pyrrhotite fraction. Other symbols as for Table 3. The range of values given for the finest grain size reflect uncertainty in the pyrrhotite content of this specimen

This fact, together with the anomalous approach to saturation of this grain size fraction, lends support to the hypothesis of a superparamagnetic component.

Dankers [1981] established the following empirical relationship for dispersed magnetite, titanomagnetite and haematite grains:

$$H_{cr}' + H_{1/2} \simeq 2\, H_{cr} \qquad (2)$$

It can be seen from Table 4 that this relationship also holds, over the size range studied, for dispersed pyrrhotite grains. Although Dankers [1981] invoked grain interactions as an explanation for the relationship $H_{1/2} < H_{cr} < H_{cr}'$, self-demagnetization of multidomain grains provides a more natural explanation of this phenomenon. Bailey and Dunlop [1983] demonstrated that the observed coercivity of a multidomain grain in an alternating field is reduced from the intrinsic value by self-demagnetization. A quantitative explanation of the relationship given by equation (2) [Clark, 1983] suggests an empirical method for determination of self-demagnetizing factors of multidomain grains. This is important because earlier methods for determination of the internal field of multidomain grains have been shown by Smith and Merrill [1982] to be inadequate.

Conclusions

The data of Tables 2-4 indicate systematic, but gradual, grain-size dependence of the magnetic properties of pyrrhotite. As in titanomagnetites no sudden changes of properties associated with domain structure transitions are observed.

The results indicate that monoclinic pyrrhotite grains smaller than 100 μm are magnetically hard, with H_c ranging from 135 oe for 83 μm grains to 920 oe for < 3 μm grains. Between 83 μm and 7 μm the coercive force is given by $H_c \propto d^{-0.79}$. The high coercivity is in accord with the observed high intensity and stability of remanence carried by rocks containing fine-to medium-grained pyrrhotite.

The empirical relationship $H_{cr}' + H_{1/2} = 2H_{cr}$, which has been found by Dankers [1981] to hold for magnetite, titanomagnetite and hematite, has been extended to pyrrhotite.

These data provide input to theoretical investigations of the rock magnetism of monoclinic pyrrhotite, with relevance to fine particle rock magnetism generally. The results also suggest the applicability of hysteresis property measurements to magnetic granulometry of pyrrhotite-bearing rocks.

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