31. ROCK MAGNETIC PROPERTIES OF HYDROTHERMALLY FORMED IRON SULFIDES FROM MIDDLE VALLEY, JUAN DE FUCA RIDGE¹

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ABSTRACT

Hydrothermally formed sulfide samples recovered from the Juan de Fuca Ridge during Ocean Drilling Program Leg 139 were investigated to determine the carrier of remanent magnetization and to study rock magnetic properties. The samples were examined by isothermal remanent magnetization acquisition, alternating field demagnetization, back field measurements, thermomagnetic and hysteresis measurements, X-ray diffraction, and ore microscopy. Grain sizes for magnetite and pyrrhotite particles were estimated from hysteresis parameters on samples containing only one magnetic phase. Magnetomineralogical analyses made on whole-rock samples show that massive sulfides recovered from Holes 856G and 856H are composed predominantly of pyrite, pyrrhotite, magnetic, and minor amounts of sphalerite and chalcopyrite. Magnetite together with two types of pyrrhotite determines the magnetic properties of these rock samples. The first type of pyrrhotite is ferrimagnetic up to 320°C. X-ray diffraction data are in good agreement with those for monoclinic pyrrhotite. The second type of pyrrhotite is antiferromagnetic at room temperature and ferrimagnetic between 200°C and 270°C. X-ray diffraction data show typical peaks for hexagonal pyrrhotite. Thermomagnetic analyses indicate that samples from Hole 856G contain mainly magnetite, whereas parameters from Hole 856H were also influenced by pyrrhotite. Pyrrhotite and magnetite were distinguished by the large J_{rs}/J_s and the small B_c/B_c ratios for pyrrhotite compared with those for magnetite, and through direct methods such as ore microscopy and X-ray diffraction.

INTRODUCTION

The sedimented spreading center at the northern end of the Juan de Fuca Ridge provides ideal conditions for creating sulfides because the relatively impermeable sediment limits the recharge and discharge of hydrothermal fluids and thermally insulates the underlying crust. Where discharge of hydrothermal fluids does occur, large sulfide deposits can be produced (Davis, Mottl, Fisher, et al., 1992). Three well-studied sediment-covered spreading centers are located in the Eastern Pacific Ocean: Middle Valley on the Juan de Fuca Ridge, Escanaba Trough on the Gorda Ridge, and Guaymas Basin in the Gulf of California. High-temperature hydrothermal discharge and sulfide deposits have been observed and sampled at all three locations (Lonsdale and Becker, 1985; Davis et al., 1987; Koski et al., 1988). Ocean Drilling Program (ODP) Site 856 is located in the eastern part of Middle Valley (48°26'N, 128°41'W) and comprises a transect of holes extending from the top of a small, sediment-covered hill southward to a low ridge of massive sulfide, which protrudes 60 m above the surrounding seafloor. The investigated samples from Holes 856G and 856H contain predominantly magnetite and pyrrhotite as magnetic phases. Pyrrhotite rarely has been found to carry a useful paleomagnetic record of the ancient geomagnetic field, but the strong ferrimagnetism, high susceptibility, and high electrical conductivity of pyrrhotite and its common occurrence in sulfide ore deposits make the mineral of considerable interest in exploration geophysics (Clark, 1983). The knowledge of the magnetic properties and thereby the mineral identification is also useful in magnetic fabric determinations for investigating the genesis and tectonic history of the deposit and for aiding the interpretation of the associated magnetic anomalies (Schwarz, 1975; Rochette, 1987).

Iron sulfides, particularly pyrrhotites, along with iron oxides, are the most important magnetic components in natural rocks, although the magnetic properties of the former presently are not well understood. During recent decades numerous rock and paleomagnetic investigations of iron oxides and iron-titanium oxides have been made, but there have been relatively few magnetic investigations of pyrrhotite and other iron sulfides. This is surprising because a great variety of different types of iron sulfides exist in nature, formed by various processes. Aside from their economic importance (sulfides occur in paragenesis with gold, platinum, nickel, copper, lead, and zinc ores), there is a rising scientific interest in these minerals. It appears that iron sulfides are more abundant in marine sediments than was previously assumed (e.g., Freeman, 1986). Many different types of iron sulfides are also found in metamorphic formations (Rochette, 1987).

Phase relations of the troilite-pyrrhotite-pyrite system (FeS-Fe_{1-x}S–FeS₂) have been studied extensively, but still are not understood in detail. In the FeS–FeS₂ system, pyrrhotite is the major phase that is of significance to rock magnetism. The term pyrrhotite is used collectively for hexagonal and pseudohexagonal (monoclinic) iron sulfides of composition Fe_{1-x}S, where the crystal structure is similar to that of Niccolite (NiAs). The parameter x accounts for vacancies at iron locations in the crystal structure, which cause an apparent increase in oxidation state from Fe²⁺ to Fe³⁺. The common range of x for naturally occurring samples is $0 < x \le 0.125$ (Kissin and Scott, 1982). Based on the magnetic properties the sulfides are classified into three series:

1. $0 < \times < 0.07$: metastable pyrrhotites (Fe-content ≥ 48 atomic percent). [Atomic percent iron = $100 \times m/(m+n)$ for the compound Fe_mS_n (e.g., Power and Fine, 1976).] These iron-rich pyrrhotites have nearly the same properties as troilite (FeS). At room temperature the crystal structure of their composition is hexagonal and their magnetic behavior is antiferromagnetic (Schwarz and Vaughan, 1972).

2. 0.07 < x < 0.11: intermediate iron/sulfur content (iron content between 48.0 and 47.3 atomic percent). In this range we find Fe₁₁S₁₂, Fe₁₀S₁₁, and Fe₉S₁₀. Magnetic behavior at room temperature is antiferromagnetic but a small ferrimagnetic moment may exist (Nakazawa and Morimoto, 1971). According to Haraldsen (1941) the saturation magnetization increases suddenly at the γ -transition (antiferromagnetic-ferrimagnetic transition point). The γ -transition occurs between $T_{\gamma} = 210^{\circ}$ C (Lotgering, 1956; Bennett and Graham, 1981) and $T_{\gamma} = 220^{\circ}$ C (Schwarz and Vaughan, 1972). Curie temperatures of the intermediate pyrrhotites depend on the composition and range between $T_c = 200^{\circ}$ C and 230°C for 0.07 < x < 0.09 (Fe₁₁S₁₂) and between $T_c = 260^{\circ}$ and 270°C for 0.09 < x < 0.11 (Fe₁₀S₁₁, Fe₉S₁₀).

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Table 1. Summary of Curie temperatures and lattice	parameters of samples from Holes 856G and 856H.
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Core, section, interval (cm)			Lithologic unit	Curie temperature and transition temperature (°C)									Cell edge of	
	Piece	Depth (mbsf)		Τ _γ	T _{c1}	T _{e2}	T _{c3}	T _{c4}	T _{c5}	T _{c6}	T'c2	T'c6	Type of curve	magnetite determined by X-ray analyses (Å)
139-856G-														
3R-1, 100-102	10	18.60	3				448	499	516	579	228	546	A	8.412
4R-1, 60-62	8	27.60	3							572	333	565	A	8.410
4R-1, 122-124	17	28.22	3					484		544	307	554	A	8.396
4R-2, 2-4	1	28.46	1	209			414			570	309	555	A/B	8.413
5R-1, 34-36	5	37.04	2	243			382		528	582	300	549	A/B	8.396
6R-2, 80-82	13	48.60	3					457	524	563	364	551	A	8.410
6R-4, 5-7	1	50.75	3			313	443		524	576	313	558	A	8.423
7R-1, 23-25	3	56.03	3					470?		583	462	576	A	
7R-4, 31-33	4	60.41	5							580	477		A	8.392
139-856H-														
2R-1, 32-34	5	13.82	2	207						573	328	548	A/B	8.422
3R-1, 87-89	8 B	22.97	4							555	305/336	548	A	8.400
3R-2, 121-123	4A	24.47	4							559	309	546	A	8.410
3R-3, 61-63	6	25.32	4							559	298	546	A	8.405
4R-1, 13-15	3	26.73	4					488		564	302	547	A	8.392
4R-2, 8-10	2	28.18	4						502	553	308/350	542	A	8.402
4R-3, 2-4	1	29.58	4	221						551	309	553	A/B	8.390
5R-1, 46-48	8	32.86	2	185	273	321					279/321	551	C	
6R-1, 22-24	4	37.62	2	229/255		326/371					281	555	D	
7R-1, 103-105	16	44.13	2							549	294	537	A	8.385
8R-1, 121-123	18	49.21	5							586	302	470	A	8.406
9R-1, 18-19	3	52.68	4					473		575	306	552	A	8.410
13R-1, 37-39	5	71.27	2				414			593	324	558	A	8.409
14R-1, 72-74	12	76.42	1	214	244	306				581	302/326	533	в	8.397
15R-1, 109-111	17	81.59	1	219	261	302				569	309/381	556	в	_
16R-1, 84-86	17	86.04	1			323				570	298	543	D	

Notes: T_{Y} = temperature of γ -transition of hexagonal pyrrhotite, T_{c1} = Curie temperature from hexagonal pyrrhotite, T_{c2} = Curie-temperature from monoclinic pyrrhotite, T_{c3} , T_{c4} , T_{c5} = converting temperatures from pyrite to a ferromagnetic mineral and the Curie temperature of this phase, T_{c6} = Curie temperature of magnetite, T'_{c2} , T'_{c6} = Curie temperature of the builded minerals estimated from cooling cycle. A, B, C, D are explained in text. — = no magnetite detected.

3. 0.11 < \times < 0.125: high sulfur content, low iron content (47.0– 46.5 atomic percent). The sulfides with high sulfur content show a spontaneous magnetization. The most interesting mineral in this group is the monoclinic Fe₇S₈. The monoclinic pyrrhotite is a stable phase below about 230°C. Between 230°C and about 300°-350°C it is metastable and tends to convert slowly to pyrite and hexagonal pyrrhotite (Ward, 1970). Graham et al. (1987) showed that the environment (e.g., fugacity of O₂) is an important factor in mineral change. The Curie temperature is between 300°C (Lotgering, 1956) and 350°C (Brodskava et al., 1976) for Fe₇S₈ and decreases with decreasing sulfur content. Saturation magnetization is reported to be 20 Am²/kg (Schwarz and Vaughan, 1972; Halgedahl and Fuller, 1981). At room temperature the (001) plane is that of easy magnetization, and the [001] direction is the hard direction of magnetization. According to Bin and Pauthenet (1963), crystal anisotropy is high. Soffel (1977, 1981) investigated the domain structure of natural fine-grained pyrrhotite in a diabase using the Bitter pattern technique (Bitter, 1931). Extrapolation of the empirical relationship between grain size and the number of domains yields a value of 1.6 µm for the critical single-domain to two-domain transition. Clark (1984) calculated a value of 2.9 µm.

METHODS

Holes 856G and 856H were drilled on the top of the sulfide ridge in the presumed center of the hydrothermal sulfide deposit. Nine samples from Hole 856G and 16 samples from Hole 856H from different lithologic subunits were investigated. Sulfide samples from these holes were classified on the basis of macroscopic descriptive attributes of the core. Based on the content of principal minerals, six types were defined in Davis, Mottl, Fisher, et al. (1992). These are as follows:

Type 1: Homogenous, massive, fine-grained pyrrhotite

Type 2: Homogenous, massive, fine-grained pyrite-pyrrhotite

Type 3: Homogenous, medium- to coarse-grained pyrite-pyrrhotite

Type 4: Heterogeneous and veined coarse-grained pyrite-pyrrhotite

Type 5: Massive colloform and vuggy pyrite

Type 6: Sediment with sulfide veining

The classification for the investigated samples is summarized in Table 1.

Samples for rock magnetic investigations were cut from 1-in. drill cores, from 1-in. cubes, or from amorphous rock samples. Natural remanent magnetization (NRM) and acquisition curves of isothermal remanent magnetization (IRM) were determined with a Molspin spinner magnetometer. The IRM was produced with a coil for fields up to 140 mT and with an electromagnet for fields up to 1500 mT. Alternating field (AF) demagnetization of the natural remanent magnetization and of the IRM was done statically in three directions in a 2G demagnetizer. Initial susceptibility was measured with a Jelinek KLY1 susceptibility bridge (Geofysika, Brno, Czech Rep.). Curie temperatures were determined with a horizontal Curie balance by heating small rock fragments, which were cut from the cores and cubes or amorphous samples. Most of the time saturation magnetization as a function of temperature, $J_{e}(T)$, was measured during a heating and cooling cycle in air. Some of the samples were sealed and evacuated in glass tubes. The applied magnetic field of the Curie balance was set to 0.35 T and the heating rate amounted to 50°C/min. A thermal lag between the measured temperature and the temperature of the samples was not observed. To determine the Curie temperature the intersection of two tangents to the J_s(T) curves above and below T_c was used (Grommé et al., 1969). The estimated error in the Curie temperature determinations is <10°C. Transition temperatures for pyrrhotites were determined with the same method. Hysteresis properties determined from hysteresis loop measurements were used to estimate the magnetic mineral content, stability, the domain state of the minerals, and the thus indirectly the grain size of the samples with predominant one magnetic phase. Hysteresis loops were measured with a vibrating sample magnetometer (VSM).

The samples were further characterized with X-ray diffraction. For that purpose, the magnetic particles were separated with a hand magnet from a suspension of the ground sample in water. A powder spectrometer was used with CuK_{α} radiation and Si as an internal calibration standard. The cell edge was calculated for the cubic Feoxides from at least three well-defined peaks. The analysis of pyrrhotite by X-ray diffraction is based on the (102)-spacing (Arnold,

1962; Desborough and Carpenter, 1965; Scott, 1974). This method is acceptable as long as the phases are homogenous and there are not more than two components in the solid solution (Scott, 1974). The interpretation of the powder diffraction pattern depends on the distinction of the hexagonal peak and both monoclinic peaks.

Polished sections were prepared from all 25 investigated samples and were examined by ore microscopy using a reflected light microscope to determine the mineralogy and textural relationships of the sulfides. Monoclinic and hexagonal pyrrhotites were distinguished by applying a thin layer of ferrofluid, which is attracted by the magnetic grains in the samples (Bitter, 1931). The ferrofluid method reveals inhomogeneities in magnetic particles such as those caused by the exsolution of lamellae or shows domain structures in magnetic pyrrhotite grains.

RESULTS AND DISCUSSION

Remanence Properties and Magnetic Susceptibility

In order to obtain information on the types of magnetic minerals present in the samples from Holes 856G and 856H, IRM acquisition and AF demagnetization data were collected for all samples. IRM acquisition curves (Fig. 1) show the different behavior of saturation for samples containing mainly magnetite and samples in which the magnetization is carried by pyrrhotite. Sample 139-856G-5R-1, 34–36 cm, consists of magnetite as the only magnetic phase. This sample saturates in much weaker fields (at about 100 mT) than the samples containing pyrrhotite.

The magnetic susceptibility, χ , of natural materials in weak magnetic fields depends on the kind, abundance, and grain size of ferromagnetic minerals in a complicated manner. Nevertheless there seems to be a correlation between magnetic susceptibility and the concentration of ferro(i)magnetic minerals in rocks (Petersen and Bleil, 1982). Sulfide samples from Holes 856G and 856H show values between 1×10^{-3} and 0.5 (SI units). Thompson and Oldfield (1986) presented the dependence of saturation remanence and susceptibility in a bilogarithmic diagram. Calibration of the parameters was based on 1000 naturally occurring samples. Results from the samples investigated for the present study containing mainly magnetite are plotted in this diagram (Fig. 2). The magnetic grain size of the magnetics is estimated to vary between about 1 and 100 µm.

Hysteresis Properties

Hysteresis parameters determined from rock samples from Holes 856G and 856H are presented in Table 2 and are plotted vs. depth in Figure 3. Samples from Hole 856G and the mainly magnetitecontrolled samples from Hole 856H were saturated at about 500 mT. Samples containing monoclinic pyrrhotite needed higher fields to reach saturation; an acquisition field of 1000 mT was not sufficient. A hysteresis loop for Sample 139-856H-6R-1, 22-24 cm, containing mainly monoclinic pyrrhotite, is shown in Figure 4. The rectangle shape is typical for monoclinic pyrrhotites and has been observed previously (e.g., Menyeh and O'Reilly, 1991). Values of saturation magnetization, J_s, for Hole 856G and 856H samples vary between 90 and 20000 mA \times m²/kg. Most samples have values at about 10000 mA × m²/kg, except for two samples from Holes 856G and three samples from Hole 856H, which have much lower values (Table 2). Saturation remanence varies between about 9 and 4000 mA \times m²/kg. The ratio of saturation remanence to saturation magnetization, J_{rs}/J_{s} , is used as an estimate of the magnetic domain structure or magnetic grain size (Day et al., 1977). Theoretical calculations show that ideally J_{rs}/J_s is 0.5 for single-domain magnetites. Magnetization ratios less than 0.05 are characteristic for multidomain magnetite grains. J_{rs}/J_s values in the present study vary between 0.05 and 0.15 in samples in which magnetite is the only magnetic mineral. Samples that contain predominantly pyrrhotites show Jr./J. ratios between 0.25 and 0.47. This is in good agreement with the results of Rochette et al.



Figure 1. Acquisition curves of the isothermal remanent magnetization normalized to their remanence value at the maximum available field of 1.5 T. Mg = magnetite; mo po = monoclinic pyrrhotite; hex po = hexagonal pyrrhotite.



Figure 2. Bilogarithmic plot of saturation remanence vs. susceptibility for magnetite-bearing samples from Hole 856G (circles) and Hole 856H (squares) (after Thompson and Oldfield, 1986). The concentration and grain size values apply to pure magnetite.

(1989), who showed that the ratio J_{rs}/J_s is greater than 0.2 for pyrrhotite and less than 0.2 for multidomain magnetite. Menyeh and O'Reilly (1991) measured J_{rs}/J_s values between 0.484 and 0.380 on synthetic pyrrhotite for grain sizes between 0.8 and 29 µm.

Coercive force, Bc, and remanence coercive force, Bcr, are used to estimate the stability of magnetization. These parameters are generally correlated with Jrs/Js and magnetic grain size. Higher coercivity is associated with smaller magnetic grains (higher J_{rs}/J_s). Investigated samples from Holes 856G and 856H show a wide range of coercive force values between 2.5 and 40 mT. The samples containing primary magnetite have generally lower coercive forces (Bc between 2.5 and 12.5 mT) than the samples containing mainly pyrrhotites (B_c between 24 and 40 mT). The remanence coercive force ranges between 9 and 27 mT for magnetite-dominant samples and between 39 and 54 mT for pyrrhotite-dominant samples. Bc/Bc is another measure of stability. It increases with increasing grain size. J₁₅/J₅ and B_{cr}/B_c for the magnetite-dominant samples from Holes 856G and 856H are plotted together in Figure 5. Based on the results, the estimated magnetic grain size of the magnetites is between pseudo-single-domain (PSD) and multidomain (MD). The low Ber/Be ratio, which is approximately independent of grain size, is typical for pyrrhotite (Dekkers, 1988).

Table 2. Summary of hysteresi	s parameters and susce	eptibility values of same	mples from Holes	856G and 856H

Core, section, interval (cm)	Piece	Depth (mbsf)	Lithologic unit	Volume susceptibility (10 ⁻³ SI)	J_{rs} (mA · m ² /kg)	J_s (mA · m ² /kg)	J _{rs} /J _s	B _c (mT)	B _{cr} (mT)	B _{cr} /B _c	Dominant magnetic species
139-856G-											
3R-1, 100-102	10	18.60	3	119.5	844	5690	0.148	10.5	21	2.00	mag
4R-1, 60-62	8	27.60	3	470	1500	19540	0.077	7	13.5	1.93	mag
4R-1, 122-124	17	28.22	3	351	1360	15010	0.091	9	19	2.11	mag
4R-2, 2-4	1	28,46	1	48	725	6380	0.114	8.5	23.5	2.76	mag + hex po
5R-1, 34-36	5	37.04	2	100	956	6060	0.158	12.5	25	2.00	mag + hex po
6R-2, 80-82	13	48.60	3	345	801	16140	0.050	4	14	3.50	mag
6R-4, 5-7	1	50.75	3	62.3	436	5180	0.084	6.5	26.5	4.08	mag
7R-1, 23-25	3	56.03	3	4.5	32.1	243	0.132	9	27	3.00	mag
7R-4, 31-33	4	60.41	5	1.35	9.4	92	0.102	6.5	22	3.38	mag
139-856H-											
2R-1, 32-34	5	13.82	2	199	394	5240	0.075	3.5	13	3.71	mag + hex po
3R-1, 87-89	8B	22.97	4	219	724	9870	0.073	5	13	2.60	mag + few hex po
3R-2, 121-123	4A	24.47	4	409	1124	14890	0.075	6.5	17	2.62	mag
3R-3, 61-63	6	25.32	4	326	1325	16710	0.079	6.5	16	2.46	mag
4R-1, 13-15	3	26.73	4	160	541	8520	0.064	5	15	3.00	mag
4R-2, 8-9	2	28.18	4	288	695	1170	0.063	4.5	14	3.11	mag
4R-3, 2-4	1	29.58	4	134	629	5990	0.105	9.5	22	2.32	mag+ po (mono + hex)
5R-1, 46-48	8	32.86	2	32.2	2290	8330	0.275	29	43	1.48	mono po + few hex po
6R-1, 22-24	4	37.62	2	2.64	296	636	0.466	40	54	1.35	hex po + few mono po
7R-1, 103-105	16	44.13	2	265	463	7820	0.059	4.5	16	3.56	mag
8R-1, 121-123	18	49.21	5	3.41	10.9	204	0.053	2.5	9	3.60	mag
9R-1, 18-19	3	52.68	4	472	708	17280	0.041	3	15.5	5.17	mag
13R-1, 37-39	5	71.27	2	162	439	7710	0.057	5	16.5	3.30	mag
14R-1, 72-74	12	76.42	1	47.3	1300	5060	0.257	24	45	1.88	hex po + mono po + mag
15R-1, 109-111	17	81.59	1	48.3	870	2310	0.377	31	41	1.32	hex po + mono po
16R-1, 84-86	17	86.04	1	65.6	3600	10160	0.354	35	39	1.11	mono po + mag

Notes: J_{rs} = saturation remanence; J_s = saturation magnetization; B_c = coercive force; B_{cr} = remanence coercive force; mag = magnetite; mono po = monoclinic pyrrhotite; hex po = hexagonal pyrrhotite.



Figure 3. Depth variation of hysteresis properties of sulfides from Holes 856G (circles) and 856H (squares).

The grain size of pyrrhotite can be estimated from B_c and B_{cr} values. A comparison with the results of samples investigated by Clark (1984), Dekkers (1988), and Menyeh and O'Reilly (1991) points to magnetic grain sizes of pyrrhotites between 10 and 50 μ m.

Thermomagnetic Identification of the Magnetic Minerals

The Curie temperature of iron sulfides depends heavily on the Fe/S ratio. This ratio can be determined from the thermomagnetic curve, which represents the change in magnetization with temperature (Schwarz, 1975). Investigations of samples collected during Leg 139 show that magnetite (for samples from Holes 856G and 856H)

and pyrrhotite (for samples from Hole 856H, monoclinic as well as hexagonal) are magnetically dominant.

Samples from Hole 856G show Curie temperatures mainly between 544° and 583°C with an average value of $572° \pm 12°C$, suggesting the presence of magnetite. Titanomagnetite is unlikely to be present because no titanium was detected in sulfide samples from Holes 856G and 856H. In addition, observed transition temperatures between 443° and 528°C (see Table 1) seem to be transition points where pyrite converts to a ferro(i)magnetic phase, which may be magnetite. Two samples from Hole 856G (-4R-2, 2–4 cm and -5R-1, 34–36 cm) show a small increase in the magnetization at temperatures between 209° and 243°C. This might be an indication of small



Figure 4. Hysteresis loop at room temperature for a whole-rock sample. The maximum available field of 1000 mT fails to saturate the material. Magnetomineralogical methods show that this sample contains mainly monoclinic pyrrhotite (Fe₂S₈).

amounts of hexagonal pyrrhotite in these samples, although typical Curie temperatures of hexagonal pyrrhotites were not observed. Apart from the magnetite Curie point, some samples from Hole 856H (e.g., -4R-3, 2-4 cm; -6R-1, 22-24 cm; -14R-1, 72-74 cm, and -15R-1, 109-111 cm) show transition temperatures for hexagonal pyrrhotite (about 220°C), at which magnetization increases and Curie temperatures between 244° and 273°C are present. In addition, typical Curie points for monoclinic pyrrhotites (Fe₇S₈) are observed between 302° and 327°C. Four characteristic curves are shown in Figure 6. The type of the thermomagnetic curve for Sample 139-856H-7R-1, 103-105 cm (marked as curve type A in Table 1) was found to be common in the samples from Hole 856G and some samples from Hole 856H, indicating that magnetite is the only magnetic phase. The curve for Sample 139-856H-15R-1, 109-111 cm, (marked as curve type B in Table 1) indicates a mixture of monoclinic and hexagonal pyrrhotite plus small amounts of magnetite. During heating the \gamma-transition of Fe₉S₁₀ from antiferro- to ferrimagnetism was observed at 219°C, and the Curie temperatures of Fe_9S_{10} ($T_{c1} = 261^{\circ}C$) and Fe_7S_8 ($T_{c2} = 302^{\circ}C$) were determined. Rapid cooling quenches the high-temperature ferrimagnetic structure of Fe_9S_{10} so that the γ -transition is skipped in the cooling cycle. The increase in magnetization indicates that probably pyrite was altered into magnetite after heating to 600°C. The thermomagnetic curve of Sample 139-856H-5R-1, 46-48 cm, (curve type C in Table 1) shows monoclinic and hexagonal pyrrhotite similar as for type B, although no magnetite was observed before heating up to 660°C. Sample 139-856H-16R-1, 84-86 cm, shows a thermomagnetic curve for monoclinic pyrrhotite plus small amounts of magnetite (curve type D in Table 1). The Curie temperature of the magnetite phase from Hole 856H varies between 551°C and 593°C with an average value of 567° ±14°C (see Table 1). Cation impurities may explain Curie temperatures that are lower than those typical of magnetite. Graham et al. (1987) observed thermomagnetic curves of magnetite, in which the Curie temperature had been lowered (by up to 140°C depending on cooling rates), and suggested that this observation resulted from oxygen solubility in magnetite and pyrrhotite. During cooling every sample from Hole 856H showed at least two Curie temperatures and an increase in magnetization. This increase appears to be due to an increase in magnetite content formed by the oxidation of pyrite during heating in air. The observed Curie temperatures are from the magnetite phase (T'_{c6} in Table 1) and probably from pyrrhotite (T'_{c2} in Table 1). The mean value calculated for all T'_{c2} is about $325^{\circ} \pm 50^{\circ}$ C. Samples that were evacuated in glass tubes show near-perfect reversibility of the thermomagnetic curves. The Curie temperatures visible on the



Figure 5. Plot of J_{rs}/J_s vs. B_{cr}/B_c for samples from Site 856 containing mainly magnetite as magnetic mineral. SD, PSD, and MD denote the range of single-domain, pseudo-single domain, and multidomain grains proposed by Day et al. (1977).

heating curve of the sealed samples do not differ from those of the unsealed samples.

X-ray Diffraction

Magnetite lattice constants for Hole 856G and 856H samples were calculated to be between 8.392 and 8.423 Å, with a mean of 8.404 ± 0.010 Å (Table 1). Compared with the established lattice constant of magnetite (8.396 Å) the determined values are somewhat high, but within the estimated range of error. The lattice constant for these samples may be stretched by cation impurities. Sulfides were identified by comparing d-spacings with the standard ASTM values.

Ore Microscopy

Pyrite, pyrrhotite, and magnetite were identified as major opaque minerals in the massive sulfides by reflected light microscopy. Chalcopyrite, sphalerite, hematite, and traces of marcasite were also observed in some samples. For magnetic investigations magnetite and pyrrhotite are the most significant minerals in massive sulfides. Magnetite was found in nearly every sample from Holes 856G and 856H (except Sample 856H-5R-1, 46-48 cm and 856H-6R-1, 22-24 cm) and is present in amounts up to 12 volume percent (vol%). The observed grain sizes range between 1 and 500 µm. Idiomorphic crystals of magnetite with grain sizes up to 200 µm are present in Sample 139-856H-3R-3, 61-63 cm. Analyzed samples from Hole 856G have pyrrhotite contents up to 2 vol%. Samples from Hole 856H contain up to 75 vol% pyrrhotite with grain sizes of the crystallites up to 50 µm. Some pyrrhotites have grain sizes up to 1000 µm subdivided in crystallites between 20 and 50 µm. Magnetic and nonmagnetic minerals were distinguished with the Bitter pattern technique (Bitter, 1931).

As described previously monoclinic pyrrhotite is ferrimagnetic at room temperature and because of its uniaxial symmetry the multidomain grains have a rather simple domain structure (Soffel, 1977, 1981). An example of monoclinic polycrystalline pyrrhotites covered with ferrofluid and photographed with crossed nicols is shown in Figure 7. The subdivision in crystallites with grain sizes of about 10–50 μ m is visible.

Figure 8 also shows a monoclinic pyrrhotite covered with ferrofluid. The parallel domain structure is the result of the crystal symmetry and the large magnetocrystalline anisotropy. The apparent bend of the easy axis is caused by the subdivision in different crystallites building the big pyrrhotite crystal.



Figure 6. Thermomagnetic curves of magnetization vs. temperature for pyrrhotite-magnetite mixtures from Hole 856H. Samples were measured in air in an applied magnetic field of 0.35 T. The heating rate was set to 50°C/min. T_{γ} is the antiferro/ferrimagnetism transition of Fe₉S₁₀. T_{c1} and T_{c2} are the Curie temperatures of Fe₉S₁₀ and Fe₇S₈. T_{c6} is the Curie temperature of magnetite. T'_{c2} and T'_{c6} are the Curie temperatures during cooling. A. Mainly magnetite as magnetic phase. B. A mixture of monoclinic pyrrhotite, hexagonal pyrrhotite, and magnetite. C. Pyrrhotites (monoclinic and hexagonal). D. Monoclinic pyrrhotite and minor magnetite.



20 µm



20 µm

Figure 7. Photomicrograph of polished section from Sample 139-856H-5R-1, 46–48 cm, covered with magnetic colloid and viewed in reflected light under crossed nicols. The domain structure of the monoclinic pyrrhotite particles is visible. The domain walls appear as dark lines.

Several samples show pyrrhotite grains that are nonmagnetic in the center (hexagonal pyrrhotite) but have magnetic rims with visible domain structures (e.g., Sample 139-856H-4R-3, 2–4 cm; 139-856H-14R-1, 72–74 cm). An example is shown in Figure 9. Bennett and Graham (1980) observed similar occurrences and attributed this feature to a reaction of the sulfides with air. The amount of monoclinic pyrrhotite increases at the expense of the hexagonal variety if the sulfur content is low, whereas monoclinic pyrrhotite gives way to pyrite at higher sulfur contents. This decrease in the metal/sulfur ratio is caused by the removal of iron to form the oxides. Hexagonal pyrFigure 8. Photomicrograph of polished section from Sample 139-856H-5R-1, 46-48 cm, covered with magnetic colloid and viewed in reflected light. The large multidomain pyrrhotite grain (about 130 μ m) has lamellae-shaped domains and long 180° domain walls.

rhotites with oxidized monoclinic rims may homogenize to a completely hexagonal phase.

Remanence Directions

Most of the samples from Site 856 were not oriented, so it was impossible to obtain information on the relative age of the sulfides or structural information from the remanent magnetization. AF demagnetization was used to demagnetize the natural remanent magnetization of the five vertically oriented samples. The AF cleaning technique was used because it has no effect on the magnetic mineralogy.



Figure 9. Photomicrograph of polished section from Sample 139-856H-14R-1, 72-74 cm. The nonmagnetic pyrrhotite grains in the center have rims with visible domain structures.

Three samples containing magnetite as the only magnetic mineral showed stable components with positive inclinations near the expected value of +66°C. Progressive demagnetization of the samples containing pyrrhotite did not show a stable component.

SUMMARY

The magnetic properties of the samples from Hole 856G are controlled mainly by magnetite and small amounts of hexagonal pyrrhotite. Almost all samples from this hole contain a high pyrite content (up to 90%), with magnetite at about 10%, and pyrrhotite (mostly hexagonal pyrrhotite), chalcopyrite, sphalerite, and hematite up to 5%. The high content of magnetite is clearly apparent in the thermomagnetic curves, in rock magnetic parameters determined from the hysteresis loops and in the mineralogical investigations.

Most of the samples from Hole 856H show magnetic behaviors similar to those of samples from Hole 856G. In these samples magnetization is carried only by magnetite; the pyrrhotite content varies from a trace to 5%. Five samples from Hole 856H contain predominantly pyrrhotite (monoclinic, as well as hexagonal pyrrhotite up to 75%) with magnetite between 0% and 8%. These samples (-5R-1, 46-48 cm; -6R-1, 22-24 cm; -14R-1, 109-111 cm; -15R-1, 109-111 cm; -16R-1, 84–86 cm) are characterized by high J_{rs}/J_s (0.25 < J_{rs}/J_s < 0.47), and low B_{cr}/B_c ratios (1.1 < B_{cr}/B_c < 1.9). The pyrrhotite grain size estimated from the coercive force and remanent coercive force of the pyrrhotite-controlled samples was between 10 and 50 µm, which is in good agreement with the observed grain sizes determined by optical microscopy.

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