17. MAGNETIC PROPERTIES OF BASEMENT ROCKS, LEG 37, SITE 332

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INTRODUCTION

Sixty-two (21 semioriented, 41 nonoriented) samples from Holes 332A and 332B were analyzed for paleomagnetic and rock magnetic properties. At least one sample was available from most of the cores. Chemical and, in part, mineral compositions were obtained on the same samples by Flower et al. (this volume). Some of their results have been incorporated for comparison with data from the ore minerals.

Although routine paleomagnetic work was done for all samples, the main emphasis was on a detailed study of the magnetic mineral components. The aim of these measurements is an identification of the ferrimagnetic phases, in particular of their oxidation state. The effects of alteration on magnetic properties of the ore minerals are discussed.

PALEOMAGNETIC MEASUREMENTS

Methods

For the conventional paleomagnetic study of the samples, intensities (J) and directions (I,D) of natural remanent magnetism (NRM) were measured on a Digico Spinner Magnetometer. The samples were cylinders, about 2.4 cm long and with a diameter of 2.2 (Hole 332A) and 2.5 cm (Hole 332B). For the semioriented samples only the inclination (I) of remanence could be determined as the orientation of the core is limited to the vertical direction. The variation of the declination (D) of remanence was measured relative to a fiducial azimuthal mark. For the non-oriented samples, measurements of remanence were also related to an arbitrary marking.

A systematic alternating-field (AF) demagnetization treatment was carried out in a field-compensated space using a two-axis tumbler device. The NRM of seven pilot samples from each hole was measured after every stage of a detailed stepwise demagnetization in fields of 0, 25, 50, 75, 100, 150, 200, 250, 300, 400, 500, 600, 800, 1000, 2000 oe. For all remaining samples a routine demagnetization was performed in 0, 25, 50, 100, 200, 500 oe fields. The volume susceptibility was measured with a Bison magnetic susceptibility bridge. Isothermal saturation remanent magnetizations (J_{SR}) were produced in a 10⁴ oe field. The bulk coercitivity (H_C) and the coercitivity of remanence (H_{CR}) were determined by a progressive reduction of this remanence with magnetic d.c. fields applied in opposite direction. Results

The results of paleomagnetic and bulk rock magnetic measurements are listed in Table 11, Chapter 2 (this volume). Figures 1a and b show downhole plots of the NRM, the susceptibility, the Königsberger ratio, and the medium destructive field.

Discussion

Remanent Magnetization

The NRM intensity varies widely in both holes: 0.4-20 × 10⁻³ emu/cc in 332A and 0.25-10 × 10⁻³ emu/cc in 332B. As for most magnetic properties, there is no apparent downhole trend in the NRM intensity. Systematic variations characteristic of single cooling units (Watkins and Haggerty, 1967; Marshall and Cox, 1972; Petersen, 1976) were not found presumably due to the lack in continuous sampling. The mean (arithmetic) NRM intensity values are (3.325 ± 3.373) × 10⁻³ emu/cc for Hole 332A and $(2.803 \pm 2.604) \times$ 10⁻³ emu/cc for Hole 332B (equal weight given to each sample). These values are substantially lower than the averages found for dredged oceanic basalts, but are quite similar to other DSDP data as summarized by Lowrie (1974).

Magnetic Stability (Intensity)

The following two parameters are used to describe the magnetic stability: the medium destructive field (MDF) and $S_{200} = J_{200}/J_{\rm NRM}$ the ratio between the NRM intensity after AF-demagnetization in a 200-oe field and the original NRM intensity. A significant correlation was found between these two parameters and the bulk coercitivity and the coercitivity of remanence in both holes. The mean MDF of Hole 332A, 374 ± 142 oe, is distinctly higher than the 266 \pm 141 oe observed for Hole 332B. Both values fall into the range reported for other DSDP samples (Lowrie, 1974). These stabilities are high compared to subaerial basalts, reflecting the generally small grain size of ore minerals in ocean floor basalts. In Figure 2 AF-demagnetization curves are shown for some representative samples that are used for a classification (see Table 11, Chapter 2, this volume).

Magnetic Stability (Directions)

The NRM directions measured are generally similar to those reported for these sites by Ade-Hall et al. (1975). A main feature is the abundance of relatively shallow inclinations as compared to a central dipole field for the area (56°). In most cases there is only negligible change of these unusual inclinations during AF-demagnetization; especially no general trend to steeper inclinations was observed. Vector diagram plots (Zijderfeld, 1966) of the horizontal and vertical magnetization component were used to define a stable inclination value.

AF-demagnetization curve types indicating the presence of additional antiparallel softer remanent components (denoted with one or two asterisks, respectively) are abundant in both holes (Table 11, Chapter 2, this volume). They are of special interest regarding the acquisition of secondary remanences. The type (*) is interpreted as a superposition of two antiparallel components, whereas in type (**) at least three different magnetizations must contribute. Type (*) occurs for both normal and reversed remanences; type (**) was only identified for samples carrying a normal magnetization. We argue, therefore, that the secondary components were not only formed during the last 7 · 10⁵ yr of normal Brunhes epoch but also during earlier epochs of reversed polarity. Assuming that the secondary magnetic components reflect an earth magnetic field direction and not intrinsic properties of the magnetic mineral phases like partial self-reversal (Creer and Petersen, 1969; Petersen and Bleil, 1973), we have to resort to a build-up at elevated temperatures or during maghemitization (Butler, 1973). This conclusion is based on two assumptions: (a) a negative secondary component in samples showing a positive overall magnetization must apparently have a higher stability than any viscous remanence acquired during the present field epoch, and (b) a roughly equal length of normal and reversed polarity in the last 3.5 m.y.

Susceptibility

Downhole variation of susceptibility in Hole 332A is much more restricted than in Hole 332B (Figures 1a, 1b). A moderate but significant negative correlation exists between susceptibility and the various stability parameters which may be interpreted in terms of grain size variations (see Table 1). In contrast, no correlations were found for susceptibility and NRM intensity.

Königsberger ratios (Q) derived from the susceptibility values vary between 1.3 and 157; because about 75% of the Q values are higher than 10, induced magnetizations of the rock sequence penetrated at Site 332 will not contribute significantly to the measured anomalies.

ROCK MAGNETIC MEASUREMENTS

Methods

Rock magnetic analysis was done on 10 samples from Hole 332A and 12 samples from Hole 332B. These studies comprise ore microscopic observation including measurement of modal abundance and grain size of the



Figure 1a. Downhole variation of the intensity of natural remanent magnetization (NRM), the volume susceptibility, the Königsberger ratio Q calculated for a magnetic field of 0.45 oe at the drilling sites and the medium destructive field (MDF). Results of several samples from the same core are shown at identical depths. Mean values of individual cores are connected by solid lines. Hole 332A.



Figure 1b. Downhole variation of the intensity of natural remanent magnetization (NRM), the volume susceptibility, the Könisberger ratio Q calculated for a magnetic field of 0.45 oe at the drilling sites and the medium destructive field (MDF). Results of several samples from the same core are shown at identical depths. Mean values of individual cores are connected by solid lines. Hole 332B.

opaque mineral phases, determination of the lattice constant of the ferrimagnetic Fe-Ti spinels, and microprobe chemical analysis (the latter only on two samples from each hole). Furthermore Curie temperatures, saturation magnetization, and the different proportions of ferrimagnetism, paramagnetism, and superparamagnetism were determined by means of a translation balance.

Optical and X-ray Measurements

Polished sections were studied under reflected light using a Leitz microscope. Volume content of the opaque phases and their mean grain size were measured on a Quantimet image analyzing device. Conventional point counting was also done on some samples for comparison. The results deviate systematically, point counting typically giving values higher by a factor of 1.5-2.5 compared to Quantimet data, depending on the total number of grains analyzed per unit area.

Lattice constants of the magnetically separated Fe-Ti spinels were determined using the conventional Debye-Scherrer technique.

Strong Field Magnetic Measurements

A translation balance was used for those measurements, where magnetic fields up to 13,000 oe could be applied. Magnetization was measured in the temperature range between -180° C and $+700^{\circ}$ C, the

samples being in air. For the Curie temperature measurements a magnetic field of 4250 oe was chosen to reduce the influence of paramagnetism. In order to determine the Neel $J_s(T)$ curve type of the Fe-Ti spinel phase, the temperature dependence of magnetization was measured in a field of 10,100 oe. In this case (Figure 3), the paramagnetism of the silicates has to be taken into account. An apparent paramagnetic susceptibility was determined from the linear field dependence of magnetization, obtained after saturation of the ferrimagnetic mineral component and measured at constant temperatures. The $J_s(T)$ curve of the ferrimagnetic phase was then derived by subtraction of the apparent paramagnetism from the bulk magnetization curve.

The temperature dependence of the reciprocal apparent paramagnetic susceptibility thus determined is nonlinear, showing that other contributions to the magnetization exist. As known from the petrographic analysis, antiferromagnetic components cannot be the cause for this nonlinearity. We assume therefore, that superparamagnetism of very fine-grained Fe-Ti oxides is responsible.

This hypothetical superparamagnetism has been determined quantitatively by subtraction of the true paramagnetism from the apparent paramagnetism. The former was measured at 700°C, thus being well above the Curie temperature of any ferrimagnetic phase. A



Figure 2. Alternating-field demagnetization curves. Letter symbols indicate different types of magnetic stability, crosses the presence of antiparallel magnetic components (see text). Δ: Hole 332B, Sample 10-3, 39-41 cm (#2A); ◊: Hole 332B, Sample 9-1, 88-90 cm (#10); Δ: Hole 332A, Sample 23-1, 130-132 cm (#18); □: Hole 332A, Sample 36-1, 21-23 cm (#3); ○: Hole 332A, Sample 34-2, 36-38 cm (#5).

detailed discussion of this method shall be given elsewhere.

Results

Ore Microscopic Investigation

The main opaque minerals are titanomagnetites with minor iron sulfides. The mean modal opaque content is 1.0 vol %, distinctly lower than for an average subaerial basalt. The volume of iron sulfides is always less than 10% of the titanomagnetite phase (highest values were found in Core 44 of Hole 332B) and therefore should not contribute significantly to the magnetization of the rocks.

Titanomagnetite, the main carrier of remanent magnetization, is maghemized to a variable extent, a clear indication for low temperature oxidation (oxidation temperatures below 250°C). In all samples so far studied no sign of high temperature deuteric oxidation was found. Also, neither primary nor secondary ilmenite was observed. With few exceptions the grain sizes of titanomagnetite are much smaller than in subaerial basalts, average grain size for the Hole 332A rocks being 4.7 μ m and for Hole 332B rocks 5.7 μ m. These results are in good agreement with data published by Lowrie et al. (1972). The small grain size and the frequent occurrence of skeletal-shaped titanomagnetite grains are indications for rapid cooling of relatively small rock units.

Curie Temperatures and Lattice Constants

Both parameters are listed in Table 1, and their downhole variation is shown in Figure 4a, b. Curie temperature and lattice constant vary between 237°C to 343°C and 8.369Å to 8.427Å, respectively, in Hole 332A and between 150°C to 467°C and 8.358Å to 8.464Å in Hole 332B. A striking negative correlation exists between both these parameters. None of the analyzed rocks contain stoichiometric titanomagnetites when compared with values measured for synthetic stoichiometric titanomagnetites (Bleil, 1976) and taking into account the influence of impurity ions like Al and Mg (Table 2). In accordance with the ore microscopic observations, we find variable degrees of alteration of the titanomagnetites resulting most likely from halmyrolysis (Hart, 1973).

In order to determine quantitatively the oxidation state defined by the oxidation parameter z (O'Reilly and Banerjee, 1967) the Readman and O'Reilly (1970) $Tc - a_o$ contour lines have been used. Both parameters were corrected for the Al and Mg impurity ions according to Richards et al. (1973). These corrections are based on the microprobe analysis listed in Table 3. For samples where no analysis was available the mean of these values was used. The compositions thus obtained are shown in the ternary system FeO-Fe₂O₃-TiO₂ in Figure 5a, b. Also shown are the corresponding wholerock compositions determined by Flower et al. (this volume).

From these figures it can be seen that the ore component in most of the rocks is highly oxidized. However, there is no apparent correlation between the oxidation state of the ore phase and the Fe^{2+}/Fe^{3+} ratio of the whole rock. Therefore, it seems to us that in the deep ocean environment oxidation effects more rapidly the ore component than the silicate phases.

A downhole plot of the oxidation parameter z(Figure 4a, b) shows a general trend of decreasing zvalues with depth. However, in Hole 332B there are two significant breaks in this trend with very low oxidation at a depth of 350 meters (Core 10) and near 700 meters (Cores 44 and 46). The low z values correlate with large grain sizes but not vice versa; larger grain size may indicate intrusive or thick extrusive bodies. These samples also show anomalous values for most other magnetic parameters (Figure 1b). The very high z values observed between 400 and 550 meters in Hole 332B may tentatively be interpreted as (a) a noncontinuous magma emplacement; i.e., the rocks now below about 400 meters formed the uppermost part of the basement for a relatively long time, or (b) the rock sequence between 400 and 550 meters is highly fractured giving free access to seawater even at this depth.

Assuming that the magnetic ore grains have originally been stoichiometric titanomagnetites and that the original Fe/Ti ratio has not significantly been changed by the oxidation process, the original composition—as expressed by the parameter x (stoichiometric titanomagnetites having the chemical formula Fe₃- $_xTi_xO_4$)—can be determined from Figure 5. The values thus obtained are listed in Table 1. The correlation

Sample (Interval in cm)	Depth (m)	<i>T_C</i> (°C)	a ₀ (Å)	z	x	Initial Curie Temperature (°C)	Vol % Ore	Ore Grain Size	JS (emu/g)
Hole 332A									
6-2, 107-109 (8)	104.57	343	8.378 ±0.002	0.80	0.57	147	0.6	3.9	0.160
8-1, 50-52 (6)	121.50	313	8.369 ±0.002	0.86	0.68	52	1.3	3.0	0.245
12-1, 81-83 (9)	159.81	273	8.388 ±0.003	0.79	0.69	43	1.0	4.3	0.370
17-1. 50-52 (6)	207.00	250	8.391 ±0.001	0.78	0.73	8	1.1	4.8	0.274
29-1, 65-66 (9)	321.15	247	8.406 ±0.002	0.71	0.67	57	1.3	8.3	0.270
30-1, 135-137 (20)	331.35	262	8.403 ±0.003	0.68	0.58	106	1.4	5.7	0.276
32-2, 28-30 (2)	350.78	271	8.425 ±0.02	0.53	0.53	179	0.6	1.7	0.170
36-1, 21-23 (3)	387.21	297	8.388 ±0.002	0.77	0.64	87	1.0	2.9	0.285
37-1, 101-103 (4)	397.51	237	8.427 ±0.001	0.56	0.58	138	1.5	8.2	0.395
40-3, 35-37 (4A)	428.35	282	8.404 ± 0.003	0.68	0.59	129	0.4	4.4	0.160
Hole 332B									
1-5, 57-60 (6)	148.57	393	8.375 ±0.002	0.80	0.47	229	0.2	1.6	0.138
2-4, 122-125 (13)	180.10	467	8.358 ±0.002	0.85	0.38	299	0.2	2.2	0.118
3-1, 27-30 (2B)	199.81	420	8.367 ±0.001	0.82	0.43	259	0.2	2.5	0.120
6-1, 111-114 (12)	287.83	253	8.400 ±0.003	0.74	0.69	46	1.2	2.9	0.225
9-1, 88-90 (10)	333.76	244	8.415 ±0.002	0.65	0.63	95	1.2	6.8	0.280
10-3, 39-41 (2A)	354.39	150	8.464 ±0.002	0.31	0.63	125	1.6	11.5	0.585
15-1, 103-105 (9)	399.53	260	8.410 ±0.003	0.67	0.63	95	1.4	7.3	0.248
16-2, 63-65 (8)	410.13	328	8.366 ±0.001	0.87	0.67	61	0.3	0.8	0.120
25-1, 106-113 (16)	494.56	298	8.379 ±0.002	0.83	0.68	52	0.8	3.0	0.095
31-1, 116-119 (9)	551.66	293	8.377 ±0.001	0.84	0.70	35	1.3	10.1	0.045
44-5, 124-126 (11)	681.24	217	8.452 ± 0.001	0.26	0.51	197	1.3	9.8	0.715
46-2, 58-61 (3B)	695.08	210	8.453 ±0.001	0.32	0.54	187	1.7	10.2	0.790

TABLE 1 Rock Magnetic Data, Site 332



Figure 3. Example of thermomagnetic curve measured at 10,100 oe. Solid circles: total magnetization (heating); open circles: total magnetization (cooling). Solid curve: ferrimagnetic saturation magnetization; dash-dotted curve: superparamagnetic fraction,

between the TiO₂-content of the whole rock and the x values of the titanomagnetites is poor (Figure 4). A direct correlation seems to exist only in the upper part of Hole 332B (Figure 4b). The variation of the x values is remarkably small except for the uppermost and lowermost samples of Hole 332B.

The mean x value of all samples (0.60) is in very good agreement with the four microprobe analyses and also with other analyses from ocean floor basalts (Ozima et al., 1974).

A calculation of the initial Curie temperatures of the postulated primary titanomagnetites (being the carrier of the original thermoremanence acquired during primary cooling) gives values ranging between 8°C and 299°C (mean T_{ci} : 119°C, 36% of the samples having a T_{ci} below 60°C, see Table 1). These values have been corrected for the Al and Mg impurities.

The abundance of low Curie temperatures makes it likely that partial remagnetization may have taken place at only moderately elevated temperatures. In this context it should be mentioned that the blocking temperature of most samples will be close to their Curie temperature, because of the generally very small grain size of the ore phase.

Ferrimagnetism, Paramagnetism, and Superparamagnetism

The $I_s(T)$ curves of the ferrimagnetic mineral phases investigated so far all show the shape of Neel P and L type, which is also evidence for the presence of titanomagnetite (Schult, 1971).

There is a remarkably large contribution of the paramagnetic silicates to the total magnetization even



Figure 4a. Downhole variation of the Curie temperature and the lattice constant of the ferrimagnetic Fe-Ti spinel components, their oxidation parameter z together with the whole-rock FeO/Fe_2O_3 -ratio (dashed line) and the parameter x compared to the whole-rock titanium content (wt %, dashed line). The parameter z gives the proportion of Fe^{2+} oxidized to Fe^{3+} in titanomagnetites, while x gives their titanium content.

at room temperature in strong magnetic fields: roughly 40% of the total magnetization measured at 10,100 oe are due to the paramagnetism of the silicates (Figure 3). In the basalts studied here only 10% of the total iron content of the rock is present as ore mineral as compared to about 50% in average subaerial basalts (Hargraves and Petersen, 1971). The former value is determined from a comparison of ore content and Fe content of the whole rock and independently from the thermomagnetic measurements.

All samples show an irreversible thermomagnetic curve characteristic of ocean floor basalts (Schaeffer and Schwarz, 1970). An example is shown in Figure 3. When heating the sample beyond 400°C, a typical secondary maximum in magnetization is observed. This is generally interpreted as a decomposition of titanomaghemite into a nonmagnetic titanium-rich phase and a strongly magnetic titanium-poor spinel phase (O'Reilly and Readman, 1971). Because the temperature dependence of reciprocal strong field susceptibility is nonlinear, superparamagnetic effects are likely to contribute, amounting to about 20% of the saturation magnetization of the ferrimagnetic mineral phase at room temperature in a magnetic field of 10,100 oe. This indicates a fairly high content of very small ore grains which cannot be detected microscopically (these submicroscopic ore grains thus are not accounted for in the value of mean grain size given in Table 1).

CONCLUSIONS

At present we restrict our conclusions to a discussion of the NRM which is the most important parameter for an interpretation of marine magnetic anomaly patterns. Our data together with the results recently published by Ade-Hall et al. (1975) show that the nature of NRM of ocean floor basalts differs significantly from earlier assumptions used for interpretation and modeling of the anomaly pattern. The average NRM intensity is too low by at least a factor of 2 in order to fit the previously accepted model of a magnetic layer 2A with a thickness of only 500 meters (Talwani et al., 1971). In addition, the presence of shallow inclinations and mixed polarities further complicates a simple magnetization model of the upper oceanic crust.

The following two arguments led us to the conclusion that the NRM of the rocks studied is of a composite



Figure 4b. Downhole variation of the Curie temperature and the lattice constant of the ferrimagnetic Fe-Ti spinel components, their oxidation parameter z together with the whole-rock FeO/Fe₂O₃-ratio (dashed line) and the parameter x compared to the whole-rock titanium content (wt %, dashed line). The parameter z gives the proportion of Fe²⁺ oxidized to Fe³⁺ in titanomagnetites, while x gives their titanium content.

TABLE 2 Electron Microprobe Results, Ti-magnetite ^a									
	33	2A	332B						
	29-1-9	30-1-20	10-3-2A	46-2-3B					
SiO ₂	0.26	0.54	0.12	0.45					
TiO ₂	22.42	20.59	21.65	20.72					
Al203	1.98	2.32	1.73	1.82					
Fe2O3b	76.16	75.51	78.18	78.62					
Cr ₂ O ₃	0.10	0.07	0.09	-					
MnO	0.46	0.45	-	0.49					
MgO	0.40	0.57	0.69	0.25					
CaO	0.16	0.25	0.06	0.24					
к ₂ о	0.01	0.02	-	0.01					
Sum	101.95	100.32	102.52	102.60					

^aAnalysis: K. Abraham, Institut für Mineralogie, Ruhr-Universität Bochum, West Germany.

nature, the primary thermomagnetic magnetization being overprinted by other magnetization processes during later periods due to remagnetization, chemical magnetization, and viscous components:

1) There exists no correlation between NRM intensities and any of the other magnetic parameters measured so far, in particular saturation remanence, saturation magnetization, or magnetic stability. If the NRM is of a single type, any of these parameters should correlate as there is no great variation neither of the ore composition nor of the amount of opaque grains. Equivalent studies of the variation of magnetization within single lava flows and dikes show distinct correlations in most cases—for example, with saturation remanence (Watkins and Haggerty, 1967; Ade-Hall et al., 1968; Wilson et al., 1968; Petersen, 1976).

2) The carriers of remanent magnetization are very fine grained titanomaghemites. These cation-deficient spinels have been formed by low temperature oxidation (temperatures not exceeding 250°C) of originally stoichiometric titanomagnetites. A recalculation of the initial Curie temperatures of these primary ore components (being the carrier of the original thermoremanence acquired during the initial cooling) yields a mean T_{ci} of 119°C with 36% of the T_{ci} values being below 60°C. These low Curie temperatures make it likely that partial remagnetization may have taken place at only moderately elevated temperatures.

In regard to the acquisition of a chemical remanence, Marshall and Cox (1971) have shown that the direction of an original remanent magnetization of titanomagnetite is not destroyed by oxidation, if the oxidation occurs below the original Curie temperature of the titanomagnetite. On the other hand, Butler (1973) gives



Figure 5. Composition of the ferrimagnetic ore components (open symbols) and the corresponding whole-rock compositions (full symbols) within the ternary system FeO-Fe₂O₃-TiO₂. Numbers refer to cores; different symbols to magma groups as defined by Flower et al. (this volume). (a) Hole 332A. (b) Hole 332B.

arguments that low-temperature oxidation of oceanic basalts will cause a significant portion of the originally stable carriers of the remanence to become superparamagnetic and thus lose their initial magnetization.

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