## On the compositional field of self-reversing titanomaghemite: Constraints from Deep Sea Drilling Project Site 307

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[i] In 1956, Verhoogen proposed that ionic reordering during low-temperature oxidation of titanomagnetite could result in self-reversal of natural remanent magnetization. Later, in 1966, O'Reilly and Banerjee concluded that (1) the compositional field of self-reversing titanomaghemite was restricted to very high oxidation states and (2) that high oxidation temperature (>250°C) would be required to reach these oxidation levels, which would in turn be inconsistent with stability of the cation-deficient structure of titanomaghemite in nature. However, an example of the process has been reported, in some altered pillow basalt lavas of Late Cretaceous age from Detroit Seamount (Ocean Drilling Program (ODP) sites 883, 1203, and 1204) in the northwestern Pacific Ocean. Here we present new paleomagnetic, rock magnetic and compositional data from mid-ocean ridge tholeiitic basalts of Late Jurassic age collected at Deep Sea Drilling Project (DSDP) Site 307. Although severely oxidized, the DSDP Site 307 basalt samples lack the clear self-reversed magnetizations seen in some samples from Detroit Seamount. These data constrain the compositional field of self-reversing titanomaghemite to extremely high oxidation states (z > 0.95), consistent with the first conclusion of O'Reilly and Banerjee. The comparison of results from ODP sites 883, 1203, and 1204 on Detroit Seamount and those from the DSDP Site 307 basalts suggests that the presence of self-reversed magnetizations may signify unusually vigorous and sustained fluid flow that resulted in very efficient removal of Fe from titanomaghemite producing the extremely high oxidation states required for self-reversal.

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### 1. Introduction

[2] An assumption commonly made in analyzing paleomagnetic data from weathered submarine basalts is that the process of low-temperature oxidation of titanomagnetite creates a chemical remanent magnetization (CRM) which pseudomorphs the parental thermal remanent magnetization (TRM). It is believed that the development of CRM contributes to the decrease of the intensity of natural remanent magnetization (NRM) in oceanic basalts, but does not affect the NRM direction [e.g., *Marshall and Cox*, 1971; *Dunlop and Ozdemir*, 1997].

[3] Titanomaghemite, a cation-deficient ferrimagnetic spinel produced as a result of low-temperature oxidation of titanomagnetite ( $Fe_{3_r}Ti_xO_4$ , 0 < x < 1), can be represented by its chemical formula as

$$\operatorname{Fe}_{[2-2x+z(1+x)]R}^{3+}\operatorname{Fe}_{(1+x)(1-z)R}^{2+}\operatorname{Ti}_{xR}^{4+}\Box_{3(1-R)}O_4^{2-}$$

where R = 8/[8 + z(1 + x)], the box denotes a lattice (cation) vacancy, and z ( $0 \le z \le 1$ ) is the oxidation parameter

[O'Reilly, 1984]. The above formula assumes oxidation by the addition of oxygen; in submarine conditions it is more likely that oxidation occurs by iron removal [O'Reilly, 1984; *Dunlop and Ozdemir*, 1997; *Furuta*, 1993]. In the remainder of this paper we will use the *x* and *z* parameters as "compositional variables" defined by O'Reilly [1984], irrespective of the mechanism of oxidation.

[4] Data from natural and synthetic titanomaghemites show that the assumption that the secondary CRM carried by titanomaghemite pseudomorphs a primary TRM is well justified for slight to moderately high oxidation states when titanomagnetite grains carrying the initial TRM are in the single- or pseudosingle-domain state [Marshall and Cox, 1971; Ozdemir and Dunlop, 1985; Brown and O'Reilly, 1988]. On the other hand, it was suggested on theoretical grounds from the consideration of cation distribution in titanomaghemite that the NRM may undergo a self-reversal due to the process of ionic reordering [Verhoogen, 1956, 1962; O'Reilly and Banerjee, 1966; O'Reilly, 1983].

[5] The concept of ionic reordering in titanomaghemite was introduced by *Verhoogen* [1956,1962] and consequently refined by *O'Reilly and Banerjee* [1966], *Readman and O'Reilly* [1972] *and O'Reilly* [1983], who restricted the self-reversal field of titanomaghemite to oxidation states higher

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than in Verhoogen's original model. The term "ionic reordering" refers to a process of preferential incorporation of cation vacancies created on tetrahedrally coordinated cites (A sites) of the inverse spinel structure of titanomaghemite into the octahedral positions (B sites) at high oxidation stages. Reordering is accomplished by the migration of iron cations from B to A sites, which may eventually shift the balance between the antipodal magnetizations of A and B magnetic sublattices ( $M_A$  and  $M_B$ , respectively) so that a self-reversal of spontaneous magnetization ( $M_s = MB - MA$ ) takes place. Primary remanent magnetization (e.g., TRM of basalts), if controlled by a contribution from single-domain grains, may thus evolve into a self-reversed CRM as a result of ionic reordering.

[e] An important consequence of ionic reordering was recognized by *Schult* [1968, 1971], who showed that low-temperature oxidation of titanomagnetite and attendant ionic reordering should be accompanied by a Q —» P —> L —\*N —> Q' transition of  $M_s(T)$  curve types [*Neel*, 1948]. Titanomagnemites which undergo self-reversal due to ionic reordering should exhibit either N-type thermomagnetic behavior with compensation points above room temperature or Q'-type behavior.

[7] The possibility that the low-temperature oxidation of titanomagnetite can produce a self-reversal of NRM in altered basalts was of great interest in the 1960s and 1970s, but no clear evidence was found, except for two studies of oxidized alkali basalts: one of Miocene age from Steinberg at Meensen, Germany [Schult, 1976], and another of Oligocene age from New South Wales, Australia [Hoffman, 1982], (the latter example was presented only in abstract form). Ozima and Sakamoto [1971] also reported a self-reversal in synthetic titanomaghemites, but the relevance of this study was questioned later because of the presence of multiphase oxidation products in the synthetic material, originally considered to be single-phase titanomaghemite [e.g., Dunlop and Ozdemir, 1997]. As pointed out by O'Reilly and Banerjee [1966], it was thought that the high oxidation stages required for self-reversal in titanomaghemite are unreachable in nature because the cationdeficient structure would not be stable and instead would invert to Fe-rich and Ti-rich phases.

[8] Recent studies on basalts recovered by the Ocean Drilling Program (OOP) and its predecessor, the Deep Sea Drilling Project (DSDP), suggested that highly oxidized nonstoichiometric titanomagnetics (titanomaghemites) exhibit N-type thermomagnetic behavior [Doubrovine and Tarduno, 2002; Matzka et al, 2003; Carvallo et al., 2002; Doubrovine and Tarduno, 2004]. In most cases, the temperature of magnetic compensation and N-type self-reversals of remanent magnetization were observed below room temperature, and hence considered irrelevant for the self-reversal of NRM by ionic reordering. Similar behavior had also been documented earlier in continental basalts [Schult, 1968] and basalts associated with subduction zones [Nishida and Sasajima, 1974]. There is, however, a notable exception.

[9] Recently we showed that titanomaghemites from some samples of oxidized basalt drilled at Detroit Seamount of the Emperor seamount chain in the northwestern Pacific (OOP sites 883, 1203 and 1204) exhibit N-type thermomagnetic behavior with compensation points distributed above and below room temperature [Doubrovine and Tarduno, 2004]. Thermal and alternating field (AF) demagnetization experiments performed on these samples revealed the two antiparallel components of NRM suggesting a partial self-reversal of magnetization. Through a series of rock magnetic, scanning electron microscopy, energydispersive X-ray spectrometry and X-ray powder diffraction analyses, we were able to demonstrate that the NRM component with unblocking temperatures up to ~250-350°C is a self-reversed CRM carried by the titanomaghemites with N-type behavior above room temperature. The compositions of self-reversing titanomaghemite were constrained to 0.65 < x < 0.86, z > 0.8. In this paper, we will present new paleomagnetic, rock magnetic and compositional data obtained from highly oxidized Late Jurassic midocean ridge basalt (DSDP Site 307), which provide further constraints on the conditions needed for self-reversal of remanent magnetization carried by titanomaghemite.

#### 2. Basalts From DSDP Site 307

[10] DSDP Site 307 (28°35.26'N, 161°00.28'E) is located on Mesozoic magnetic anomaly M21 (148.3-149.4 Ma [Ogg, 1995]) of the western portion of the Hawaiian magnetic lineations, ~280 km southeast from the southern flank of Shatsky Rise and ~130 km northwest from Busch Seamount (Figure 1).

[11] Site 307 was drilled during DSDP Leg 32 [Larson et al., 1975]. The drill hole penetrated 18.5 m into the basaltic basement and a 4.5-m-thick sequence of altered, tinegrained basalts intercalated with hyaloclastite beds was recovered. Six cooling units (which are probably basaltic pillows [Marshall, 1975]) were identified in the recovered cores based on the presence of altered glass selvages and hyaloclastite beds. Throughout the entire section, basalts show the signs of severe alteration due to seafloor weathering. In the most altered intervals, plagioclase and pyroxene are completely replaced by clays (montmorillonitc, celadonite and chlorite). In the least altered parts of the sequence, plagioclase appears largely unaltered. Basalt is highly fractured, fractures are filled with calcite and ankerite. Many fractures are bordered by the ~1-cm-thick bands of more highly altered basalt.

[12] Pervasive alteration of the basalts from Site 307 made it difficult (virtually impossible) to determine whether their original compositions were tholeiitic or alkalic from a conventional major and minor element analysis of whole rock samples [Marshall, 1975]. However, trace element (Sr, Nb, Zr) contents, together with a petrographic evidence (presence of plagioclase microphenocrysts and plagioclase-pyroxene glomerocrystic clots in the least altered samples) and geomorphology (location presumed to be Late Jurassic ocean floor), suggest that the Site 307 basalts are altered mid-ocean ridge tholeiites [Marshall, 1975].

#### 3. Paleomagnetic Data

[13] An early paleomagnetic study of the basalt samples from Site 307 [Larson and Lowrie, 1975] suggested that the NRM carriers are maghemitized titanomagnetites, which was consistent with reflected light microscopy observations [Larson et al., 1975]. Alternating field demagnetization (up



Figure 1. Map showing location of DSDP Site 307.

to 40 mT with 5 mT steps) showed a single NRM component of normal polarity with an average inelination of  $11^{\circ} \pm 4^{\circ}$ . However, the overall high degree of alteration of the Site 307 basalts as well as a 270-410°C range of Curie temperature observed by Larson and Lowrie [1975] are similar to those from the Detroit Seamount basalts (OOP sites 883, 1203, and 1204) which show a partial self-reversal of NRM due to ionic reordering in titanomaghemite [Doubrovine and Tarduno, 2004]. This raises a concern that a small self-reversed CRM component might have been overlooked in the total NRM of the Site 307 basalts. Comparison of the thermal and AF demagnetization data from OOP Site 883 basalts [Doubmvine and Tarduno, 2004] suggests that a small self-reversed CRM can be easily masked by a prominent CRM pseudomorphing the parental TRM owing to overlapping coercivity spectra of the two NRM components. In that case, thermal demagnetization is a proper way to resolve and isolate magnetization components. This provides the motivation for reexamining the paleomagnetic data from Site 307 using thermal demagnetization.

[14] Azimuthally unoriented samples of Site 307 basalt were collected at the West Coast Core Repository of the Ocean Drilling Program. Fifteen samples were selected for thermal demagnetization experiments. Samples (cut as 1 cm cubes) were taken at irregular intervals throughout the basalt section so that the entire rock sequence was adequately represented. Samples were demagnetized at 25°C steps within a 50-625°C range using an ASC TD-48 thermal demagnetization device at the University of Rochester. A few sister samples of the samples subjected to thermal demagnetization were demagnetized by alternating field treatment at 3, 5 and 10 mT increments up to a 150 mT maximum applied field using a Sapphire Instruments SI-4 AF demagnetizer. Measurements of remanent magnetization after each demagnetization step were done with a 2G DC SQUID rock magnetometer.

[15] Thermal demagnetization showed that for most samples (// = 11), the NRM direction of normal polarity remained remarkably stable at all thermal treatment levels. The NRM is assigned normal polarity following the magnetic anomaly identifications of Larson and Lowrie [1975], and the assumption that the Site 307 basalts are of the same age as the bulk oceanic crustal profile. The NRM intensity decreased after treatment to ~200°C, then increased between 200 and 250-275°C, and thereafter decreased to ~550-600°C, where samples were demagnetized (Figures 2a and 2c). This behavior could be formally described as three antiparallel magnetization components: two of normal polarity with unblocking temperatures below 200°C and above 275°C, respectively, and one of reversed polarity with unblocking temperatures between 200 and 275°C. In contrast, AF demagnetization showed no sign of the reversed NRM component; a simple univectorial decay was observed for all AF-demagnetized samples' (Figures 2b and 2d). The directions of remanent magnetization isolated at temperatures above 300°C and at fields above 5-10 mT, fit by principal component analysis [Kirschvink, 1980], were indistinguishable for all sister samples. The remaining samples showed either a univectorial decay of NRM (Figure 2e) or spurious, shallow magnetizations of reversed polarity demagnetized up to ~300°C, and a stable NRM component







S, Down



**Figure 2.** Orthogonal vector plots of (a, c, e, and f) stepwise thermal and (b, d) AF demagnetization of basalt samples from DSDP Site 307. Open squares are projection of magnetization on a vertical plane; solid circles are projection of the magnetization on a horizontal plane (note that ODP samples recovered by rotary drilling are azimuthally unoriented). Numbers next to data represent thermal (°C) or AF (mT) treatment levels. AF data shown in Figures 2b and 2d are from the sister samples of the samples in Figures 2a and 2c, respectively. Samples 307-13R2-023 (Figures 2a and 2b), 307-13R2-059 (Figures 2c and 2d), 307-13R2-139 (Figure 2e), and 307-13R3-135 (Figure 2d).

of normal polarity, isolated above 300°C (Figure 2f). The origin of the spurious magnetization is not clear. However, inclinations of the normal polarity component are consistent with those isolated at high unblocking temperatures for the majority of samples (Figures 2a and 2c).

[16] In the following sections, it will be argued that the magnetization isolated in thermal demagnetization data above 300°C (and from AF demagnetization data) is a CRM pseudomorphing the parental TRM, which can be considered as a characteristic remanent magnetization (ChRM). The average inclination of the ChRM calculated from the analysis of inclination data [McFadden and Reid, 1982] is  $10.4^{\circ} \pm 5.9^{\circ}$  (Table 1), which corresponds to a paleolatitude of  $5.2^{\circ} \pm 3.0^{\circ}$ . These values are indistinguishable from the earlier estimates of Larson and Lowrie [1975] (average inclination,  $11^{\circ} \pm 4^{\circ}$ ; paleolatitude, 5.6°).

[n] Because of large uncertainties in unit-mean inclinations associated with the small number of analyzed samples, no attempt was made to subdivide the Site 307 basalt sequence into the inclination groups by comparing mean inclinations from adjacent lithostratigraphic units through a formal statistical test [e.g., Kono, 1980]. Instead, each lithostratigraphic unit was considered as an independent "inclination unit". The best estimate of the precision parameter for paleomagnetic directions [McFadden and *Reid*, 1982] from this six-inclination group model (k =158.8) was transferred into the pole space using the formulation of Cox [1970], which assumes that the parent virtual geomagnetic poles (VGPs) form a Fisherian distribution [Fisher, 1953]. The estimated precision parameter for VGPs (K = 379.8) was used to calculate a polar angular dispersion  $(S = 4.2^{\circ})$  and a directional angular dispersion  $(s = 6.4^{\circ})$ [Cox, 1970]. The polar angular dispersion is significantly lower than the value predicted from global data on paleosecular variation of lavas for a relevant time window (S =18.9° for 110-195 Ma and paleolatitude of 5.2° [McFadden et ai, 1991]), suggesting that the Site 307 basalt sequence does not average the secular variation of geomagnetic field. This is consistent with the structure of the basalt section, described as a stack of basaltic pillows and hyaloclastites [Marshall, \975], probably erupted over a short time interval, insufficient to average the paleosecular variation. The estimate of paleolatitude of DSDP Site 307 in the Late Jurassic inferred from paleomagnetic data [Larson and Lowrie, 1975; this study] may thus be inaccurate; at the very least the uncertainty of the paleolatitude is an underestimate.

#### **Rock Magnetic and Compositional Data** 4.

#### 4.1. Magnetic Carriers in DSDP Site 307 Basalt

[is] Examination of polished thin sections using reflected light and scanning electron microscopy (using a Leo 982 scanning electron microscope at the University of Rochester) revealed fine (<1 urn to ~10-20 urn), skeletal grains of titanomaghemite (Figure 3a). Large grains exhibit multiple cracks, which make the grains to appear inhomogeneous in backscattered electron (BSE) images (Figure 3a). (Note that the resolution of the BSE imaging signal is determined by the size of the beam interaction volume in titanomaghemite, which is approximately ~1-1.5 um at 15 kV acceleration voltage used for our SEM observations.) Some of the cracks appear to be shrinkage cracks forming to accommodate the

Table 1. Unit-Mean and Site-Mean Inclinations<sup>a</sup>

Unit	n	I deg	Alex deg	k
		.,		
1	1	0.9		
2	4	5.1	4.3	786.2
3	3	12.9	15.2	183.4
4	1	7.0		
5	3	14.9 14.0		217.7
6	3	15.4	20.4	102.2
1 <u>-</u> 6 <sup>b</sup>	6	10.4	5.9	158.8

<sup>a</sup>Here *n* is number of samples or units; *I* is inclination;  $\Delta I_{95}$  is 95% confidence interval; k is best estimate of precision parameter [McFadden and Reid, 1982]. Inclinations in italics are nominal values for units with  $n \leq 2.$ <sup>b</sup>Average.

decrease in lattice parameter as titanomagnetite gets progressively oxidized. Large cracks propagating through the adjacent silicate matrix grains may have been introduced during grinding and polishing of the thin sections. No clear variation in brightness or reflectivity toward the edges of grains and cracks was observed. Titanomaghemite grains in Site 307 basalt appear to be homogeneously oxidized.

[19] Magnetic hysteresis loops measured at room temperature using a Princeton Measurements Corporation alternating gradient force magnetometer (AGFM) show the bulk magnetic properties in the pseudosingle-domain range [Day et al, 1977; Dunlop, 2002] (Figure 3b). For the observed grain sizes, pseudosingle-domain hysteresis properties are consistent with the theoretical estimates of magnetic domain state for titanomaghemite with high oxidation states [Moskowitz, 1980].

#### 4.2. Compositions of Titanomaghemite From Site 307 Basalts

[20] Compositions of titanomaghemites from Site 307 basalts (x and z values) were estimated through a series of energy-dispersive X-ray spectrometry (EDS) and X-ray powder diffraction (XPD) analyses. Three samples were selected for compositional analyses: two samples, which showed prominent increases of NRM intensity upon heating to 200-275°C in thermal demagnetization data (samples 307-13R2-023 and 307-13R2-059), and one sample with a very small, but detectable increase in NRM intensity upon heating to 200-250°C, not fully developed into a "reversed component" (sample 307-13R1-074).

#### 4.2.1. Energy-Dispersive X-Ray Microanalysis

[21] To estimate Fe/Ti cation ratios and x values, we measured energy-dispersive X-ray spectra from large grains of titanomaghemite using a Leo 982 scanning electron microscope equipped with an Edax Phoenix EDS system at the University of Rochester (Figure 3c). Because the range of X-ray fluorescence is at least several tens times larger than the size of the beam interaction volume [Goldstein et al., 1992], the ED spectra of titanomaghemite were inevitably "contaminated" by characteristic X-ray fluorescence from the surrounding silicate matrix (Si, Al, Mg, Ca, Na, K). Nevertheless, since no Ti was found in the matrix material from qualitative EDS analyses, and because the highest-energy line in the titanomaghemite spectra (Fe AT(3) is below the K absorption edge of Fe (hence does not excite the characteristic K fluorescence from Fe containing in the matrix), it was possible to attribute the Ti and Fe Ka. lines in measured spectra to titanomaghemite only.



**Figure** 3. (a) Backscattering electron image of the titanomaghemite grains from a sample of basalt from Site 307. (b) Summary of magnetic hysteresis parameters on a Day plot [*Day et al.*, 1977; *Dunlop*, 2002]. Abbreviations are  $//_{r/}$ , coercivity of remanence;  $/-/_0$  coercivity;  $M_{,y}$ , saturation remanence;  $M_v$ , saturation magnetization; SD, single domain; PSD, pseudosingle domain; and MD, multidomain. Thin solid lines are theoretical curves for mixtures of SD and MD grains after *Dunlop* [2002], (c) Representative ED spectrum from titanomaghemite (15 kV acceleration voltage; 20 mm working distance;  $43.3^{\circ}$  takeoff angle), (d) X-ray powder diffraction spectrum measured on a magnetic separate from a sample of Site 307 basalt. Samples 307-I3R2-023 (Figures 3a and 3c) and 307-13R1-074 (Figure 3d).

[22] Quantification of the measured X-ray spectra was performed with Edax SEM Quant v.3.2 software. Standardless quantification using the Edax PhiZAF algorithm (an Edax implementation of the d>(p, z) method [e.g., *Goldstein* et al., 1992]) was used to estimate the matrix correction coefficients and to calculate weight and atomic percentages of the elements identified in the measured spectra. In our previous study of titanomaghemites from Detroit Seamount basalts [Doubrovine and Tarduno, 2004], the EDS data were measured with the same instrument and were quantified using the same calculation scheme both with a set of natural and synthetic oxide standards (Fe<sub>3</sub>O<sub>4</sub>, FeTiO<sub>3</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO,  $SiO_2$ ) and through the standardless procedure. The comparison of the compositions calculated with and without standards from the same spectra showed that the standardless quantification always underestimates the absolute oxygen content (and hence overestimates the cation contents) in Fe-Ti oxide samples. However, the relative abundances of cations (e.g., Fe/Ti ratios) calculated using the standardless approach were indistinguishable from those measured with standards. Thus we feel standardless quantitative analysis using the Edax PhiZAF algorithm can be used to yield accurate x value estimates.

[23] Ten to twelve grains of titanomaghemite (>3 u,m in size) were analyzed in each sample. Using a simple relationship, x = 3/[1 + (Fe/Ti)], where (Fe/Ti) is the atomic ratio calculated from EDS data, a 0.66-0.82 range of x values was observed for titanomaghemite from Site 307 basalts (Table 2). Both the variation in composition of initial titanomagnetite and the variation of oxidation state between titanomaghemite grains are probably contributing to the scatter of x values.

#### 4.2.2. Lattice Parameters and Oxidation States

[24] X-ray powder diffraction analyses of magnetic separates (using a Philips Multipurpose Diffractometer at the University of Rochester) revealed prominent diffraction lines characteristic for the face-centered cubic structure of titanomaghemite with lattice parameters (a) from  $8.358 \pm$ 

÷

**Table 2.** Values of x and Lattice Parameters<sup>a</sup>

Sample	x <sub>min</sub>	x <sub>max</sub>	<i>a</i> , Å	Δa, Å
307-13R1-074	0.68	0.79	8.358	0.008
307-13R2-023	0.66	0.77	8.379	0.007
307-13R2-059	0.70	0.82	8.371	0.009

<sup>a</sup>Here  $x_{\min}$  and  $x_{\max}$  are minimum and maximum values of x observed in grains of titanomaghemite from the same sample; *a* and  $\Delta a$  are lattice parameter and its  $2\sigma$  uncertainty, respectively.

0.008 Å to  $8.379 \pm 0.007$  Å ( $2\sigma$  uncertainty quoted) (Figure 3d and Table 2). The x values estimated from the EDS data ( $0.66 \le x \le 0.82$ ) and the comparison of lattice parameters with data from well-characterized synthetic titanomaghemites [*Readman and O'Reilly*, 1972; *Nishitani and Kono*, 1982] restrict the oxidation state of titanomaghemite from Site 307 basalts to  $0.88 \le z \le 0.95$  (Figure 4).

[25] The range of oxidation state given above was estimated assuming that titanomaghemite from Site 307 basalt is a pure Fe-Ti oxide. Titanomaghemites in oceanic basalts, however, often contain small amounts of impurity cations, commonly Al and Mg. Studies of synthetic Al- and Mg-substituted titanomagnetites (Fe<sub>3-x-b</sub>M<sub>b</sub>Ti<sub>x</sub>O<sub>4</sub>, where M stands for Al or Mg) and titanomaghemites (Fe<sub>(3-x-b)R</sub>M<sub>bR-</sub>Ti<sub>xR</sub> $\square_{3(1-R)}O_4$ ) show that as the concentration of impurity cations (especially Al) increases, lattice parameters generally decrease [*Richards et al.*, 1973; *O'Donovan and O'Reilly*, 1977; *Özdemir and O'Reilly*, 1981]. A calculation of z which does not take into account the effect of cation

substitution might therefore slightly overestimate the degree of oxidation. In the ED spectra measured on titanomaghemites from Site 307 basalt (section 4.2.1), a small Al peak was observed for all samples (Figure 3c). It is not clear, however, whether this peak originates from titanomaghemite or it is a "contamination signal" due to X-ray fluorescence from the adjacent silicate minerals (e.g., plagioclase). The latter explanation is consistent with the observation of a comparable peak from Si (Figure 3c); Si is not usually present in significant quantities in natural titanomagnetites [e.g., *Creer and Ibbetson*, 1970; *Zhou et al.*, 1999]. Assuming that the entire Al signal comes from titanomaghemite, we calculated the maximum degree of Al substitution ( $0.10 \le \delta_{max} \le 0.16$ ) using the following formula:

$$\delta_{\text{max}} = \frac{3}{1 + (\text{Fe}/\text{Al}) + (\text{Ti}/\text{Al})}$$

where (Fe/Al) and (Ti/Al) are the atomic ratios estimated from the quantification of EDS data. The comparison of lattice parameters (8.358-8.379 Å) with the data of *Özdemir and O'Reilly* [1981] for the series of synthetic Al-substituted titanomaghemites (ATM60/10, x = 0.6,  $\delta =$ 0.1) suggests a ~0.74-0.83 range of z values. This is clearly an underestimate, because (1) the contribution from characteristic X-ray fluorescence in silicate matrix to the observed Al peak was ignored and (2) the effect of the



**Figure 4.** TiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> ternary diagram. Light gray, stippled area is the self-reversal field proposed by *Verhoogen* [1962]; smaller dark gray area is the self-reversal field of *O'Reilly and Banerjee* [1966]. Contours of constant lattice parameter (8.36 and 8.38 Å) for titanomaghemite are after *Readman and O'Reilly* [1972]. Thick horizontal lines are range of x values observed through energy-dispersive spectrometry (see text). Thin dashed lines are lines of constant oxidation parameter (z). Diagonally hatched region indicates compositions of titanomaghemite from Site 307 basalt. Cross-hatched region indicates compositions of self-reversing titanomaghemite from Detroit Seamount basalt [*Doubrovine and Tarduno*, 2004].



**Figure** 5. Acquisition of partial thermal remanent magnetization for Site 307 basalt samples showing reversed NRM components in thermal demagnetization data. Open symbols are magnetization acquired parallel to the applied field. Solid symbols are magnetization acquired perpendicular to the field. Samples (left) 307-13R2-023 and (right) 307-13R2-059.

higher x values of titanomaghemites from Site 307 basalt (0.66 < x < 0.82, rather than x = 0.6) was not taken into .account. We also would like to note that a rhombohedral phase was detected in highly oxidized (z > 0.7) titanomaghemites of *Ozdemir and O'Reilly* [1981] and there are small, but significant discrepancies between this data set and other data sets on substituted [e.g., *Richards et al.*, 1973] and pure titanomaghemites [*Readman and O'Reilly*, 1972; *Nishitani and Kono*, 1982; *Moskowitz*, 1987].

[2ft] Although it is not possible to separate the potential sources of Al in our EDS data, we allow for the possibility of Al substitution in our estimation of z values. Specifically, we suggest that the z value of titanomaghemite from Site 307 basalt lies between 0.78 and 0.95. The lower limit corresponds to the highest lattice parameter and 5 = -0.7; the higher limit corresponds to the lowest *a* and no Al substitution.

# 4.3. Partial Thermoremanent Magnetization Acquisition Experiments

[27] Small, reversed NRM components seen in the thermal demagnetization data (Figures 2a and 2c) may be a selfreversed CRM carried by highly oxidized titanomaghemite with N-type thermomagnetic behavior and compensation points above room temperature. Alternatively, one can argue that the observed increase in the NRM after heating to 200-275°C may be an artifact of thermally induced alteration of titanomaghemite during laboratory heating in air. It is well known that titanomaghemite becomes unstable at elevated temperatures and undergoes inversion [Ozdemir, 1987]. Creation of a metastable spinel inversion product with saturation magnetization higher than that of original titanomaghemite or magnetostatic interactions between the inversion products [e.g., Creer et al., 1970] may therefore be a viable alternative to explain the increase in the NRM intensity upon heating to 200-275°C in thermal demagnetization data.

[23] Experiments on acquisition of the partial thermoremanent magnetization (pTRM) proved to be successful for the discrimination between these two cases [Doubrovine and Tarduno, 2004] and were performed on samples of Site 307 basalt yielding reversed directional components in thermal demagnetization data. In these experiments, unheated, AF-demagnetized (to 150 mT) samples were sequentially heated and cooled in the presence of a 40 u,T magnetic field oriented parallel to the z sample axis in an ASC TD-48 thermaldemagnetizationdevice. UnlikesamplesfromDetroit Seamount, for which partial and full self-reversals of pTRM were observed in similar experiments [Doubrovine and Tarduno, 2004], samples of Site 307 basalt showed the acquisition of normal pTRM only (i.e., pTRM in the direction of the applied field, Figure 5).

[29] In the 200-275°C range, an increase in the slope of the pTRM acquisition curves was observed, indicating more efficient blocking of normal pTRM, as opposed to blocking of self-reversed pTRM expected if the reversed NRM component were a true self-reversed CRM. Thus the results of pTRM experiments suggest that a partial self-reversal of NRM has not taken place in Site 307 basalts and that an increase of the NRM intensity after thermal demagnetization to 200-275°C is likely to be a result of thermally induced alteration of titanomaghemite rather than unblocking of a true self-reversed CRM.

#### 4.4. Thermomagnetic Data

#### 4.4.1. Magnetic Susceptibility Versus Temperature

[30] Magnetic susceptibility versus temperature curves (ni(7)) were measured on whole rock samples and magnetic separates from Site 307 basalts using an AGICO KLY 4S magnetic susceptibility meter equipped with a high-temperature furnace at the University of Rochester. To study the alteration of titanomaghemite during laboratory heating and to estimate the inversion temperatures, n(7) curves were measured in heating-cooling cycles with sequentially increasing maximum temperatures (Figure 6). Measurements were performed in air and argon on whole rock samples and magnetic separates.

[31] In the first heating-cooling cycle, upon heating to 200°C, all thermomagnetic curves showed irreversible behavior. Upon further heating to 250°C, susceptibility curves measured in air showed irreversibility, while the curves measured in argon were reversible. Increasing degrees of



**Figure 6.** Low-field thermomagnetic curves measured in sequential heating-cooling cycles on (a, b) whole rock samples and (c, d) magnetic separates. In Figures 6a and 6c, curves indicate measured in air; in Figures 6b and 6d, curves indicate measured in argon. Colors denote paired heating-cooling cycles. Sample 307-13R2-023.

irreversibility were observed upon heatings to 300°C, 400°C and 500°C, suggesting the onset of inversion between 250 and 300°C. Upon heating to 700°C, titanomaghemite completely inverts to form an iron-rich spinel inversion product [e.g., *Readman and O'Reilly*, 1970; *Ozdemir*, 1987] with Curie temperature between 550 and 570°C.

[32] In 400°C and 500°C cycles, we notice clear difference between the curves measured in air and in argon. When samples were heated in argon, the Curie temperature increased continuously in sequential heating-cooling steps, which is consistent with the inversion of titanomaghemite. However, when the curves were measured in air, we first observed stabilization of Curie temperature at approximately 400°C followed by inversion at higher temperatures. Because the temperature of titanomaghemite inversion is known to increase with the increasing oxidation state [Ozdemir, 1987], the stabilization of Curie temperature at 400°C observed for samples heated in air may suggest that titanomaghemite undergoes additional single-phase oxidation before the inversion and that the irreversibility of susceptibility curves in first heating-cooling cycles may, in fact, be due to the single-phase oxidation, rather than inversion.

#### 4.4.2. Saturation Magnetization Versus Temperature

[33] AF demagnetization data, pTRM acquisition experiments, and irreversibility of susceptibility curves observed upon heating the samples to the temperatures as low as 200°C suggest that the apparent reversed components of NRM seen in thermal demagnetization data from Site 307 basalts may be an artifact of thermally induced alteration of titanomaghemite during laboratory heating. The oxidation state of titanomaghemite from Site 307 basalt (section 4.2) are slightly but significantly lower than those of self-reversing titanomaghemite from Detroit Seamount [Doubrovine and Tarduno, 2004] (Figure 4). These observations suggest that the CRM carried by titanomaghemite in Site 307 basalts has not undergone self-reversal due to ionic reordering. The mechanism of ionic reordering, however, predicts that, at high oxidation states observed in titanomaghemite from Site 307 basalt, titanomaghemite should exhibit "anomalous" thermomagnetic properties with either N-type behavior below room temperature or P-type behavior [Schult, 1968].

[34] To test this prediction, we measured hysteresis loops versus temperature on bulk samples of Site 307 basalt at the Institute for Rock Magnetism, University of Minnesota. We used a Princeton Measurements Corporation Vibrating B11104

Sample Magnetometer (VSM) with an attached cryostat for measurements from 10 K to 400 K (-263 to 127°C) and a VSM equipped with a furnace for measurements from 370 to 770 K (97 to 497°C). Combining the data from the two instruments, we observed well-expressed P-type thermomagnetic behavior in curves of saturation magnetization corrected for paramagnetic slope (Figure 7).  $M_s(T)$  curves were slightly irreversible for the sample heated to 347°C (Figure 7a) and showed increasing degrees of irreversibility, consistent with the inversion of titanomaghemite, for the samples heated to higher temperatures (Figures 7b and 7c). Sharp increases in  $M_s$  observed below 30 K (-243°C) are probably due to magnetic ordering of Fe-rich clays or ilmenite, which are paramagnetic at room temperature and do not contribute into the NRM.

#### 5. Discussion and Conclusions

[35] The rock magnetic and compositional data presented in section 4 provide strong evidence that the NRM of Site 307 basalts is a chemical remanent magnetization carried by highly oxidized, pseudosingle-domain titanomaghemite, which has not undergone self-reversal due to ionic reordering. We believe that the increase in the NRM intensity seen in thermal demagnetization data upon heating to 250-275°C is an artifact of thermally induced alteration of titanomaghemite rather than unblocking of a true reversed magnetization. However, the actual process is not clear and different mechanisms can be suggested.

[36] First, we notice that despite the fact that the compositions of titanomaghemite from Site 307 basalt show lower oxidation states, they are very close to the compositional field of self-reversing titanomaghemite from Detroit Seamount basalts (Figure 4). It is possible that upon heating in air during thermal demagnetization titanomaghemite undergoes further single-phase oxidation, which drives its composition into the high-z self-reversal field (Figure 4). This process may be responsible for the development of a selfreversed CRM during laboratory heating, which gets unblocked between 200 and 275°C. This mechanism is supported by the low-field thermomagnetic curves measured in air suggesting additional single-phase oxidation of titanomaghemite before the inversion (section 4.4.1).

[37] An alternative explanation of the apparent "reversed magnetization component" invokes the interactions (probably of magnetostatic origin) between titanomaghemite grains or multiphase inversion products. During lowtemperature oxidation of titanomagnetite, the decrease in lattice parameter is accommodated by the development of "shrinkage cracks", which may subdivide small, skeletal grains of titanomaghemite into physically separated subgrains. Because of the close proximity, the subgrains unblocked at or below 200°C may acquire a TRM in a backfield of subgrains which remain blocked at these temperatures. This process may result in a partial self-reversal of remanent magnetization, as was documented recently in samples of continental basalts containing inhomogeneously oxidized titanomaghemite [Krdsa, 2003]. Partial self-reversal of this sort can be observed in continuous thermal demagnetization experiments [Krdsa, 2003] but cannot result in an increase of the NRM intensity upon stepwise thermal demagnetization, unless the titanomaghemite grains acquiring a



**Figure** 7.  $M_{r}(T)$  curves obtained by measuring hysteresis loops versus temperature for three representative samples of DSDP Site 307 basalt. Maximum heating temperatures are (a) 347°C, (b) 397°C, and (c) 497°C. Measurements were done in helium atmosphere. Samples 307-13R2-032 (Figure 7a), 307-13R2-059 (Figure 7b), and 307-13R2-023 (Figure 7c).

reversed TRM due to magnetostatic interactions are preferentially destroyed by the inversion.

[33] Magnetostatic interactions in multiphase products of titanomaghemite inversion have sometimes been invoked as a mechanism of partial self-reversal of remanent magnetization [e.g., *Creer et al.*, 1970]. However, to explain the increase of the NRM intensity upon thermal demagnetization to  $250-275^{\circ}$ C by this mechanism, we have to assume (1) positive magnetostatic coupling in the multiphase product of titanomaghemite inversion and (2) inversion temperatures at or below 200°C. Although we cannot completely rule out this possibility, we notice that the low inversion temperatures (<200°C) are atypical for the observed high z values [e.g., *Ozdemir*, 1987] and seem to be inconsistent with the temperature behavior of magnetic susceptibility curves measured in sequential heating-cooling cycles (section 4.4.1).

[39] While the question about the origin of the apparent "reversed NRM components" in Site 307 basalt remains open and deserves further investigation, there is much less doubt about the normal polarity magnetization isolated in AF demagnetization data at peak fields above ~10 mT and in thermal data above 300°C (Figure 2). This magnetization is a CRM carried by pseudosingle-domain titanomaghemite with P-type thermomagnetic behavior. Pseudosingle-domain CRM is likely to pseudomorph the parental TRM of titanomagnetite [e.g., Marshall and Cox, 1971; Ozdemir and Dunlop, 1985]; hence it can be used as a ChRM for constraining paleomagnetic directions (section 3).

[40] Compositions of titanomaghemite from the Site 307 basalts provide important constraints on the conditions needed for the formation of self-reversed CRM components carried by highly oxidized titanomaghemites in submarine basalts. The range of x values observed from the ED spectrometry of titanomaghemite grains in Site 307 basalt (0.66 <x < 0.82) is essentially the same as that from self-reversing titanomaghemites from the Detroit Seamount basalts (0.65 <x < 0.86) [Doubrovine and Tarduno, 2004]. Both estimates overlap with the range of x values typically seen in mid-ocean ridge basalts (0.5 < x < 0.8) [e.g., Furuta, 1993]. Lattice parameters of titanomaghemite from Site 307 basalt (8.358  $\pm$ 0.008 A to  $8.379 \pm 0.007$  A), however, are significantly higher than those measured on magnetic separates from the samples of Detroit Seamount basalt showing prominent self-reversed CRM components  $(8.344 \pm 0.008 \text{ A to } 8.354 \pm 0.008 \text{ A})$ , and consistent with a 8.358  $\pm$  0.008 A to 8.362  $\pm$  0.008 A range obtained from the Detroit samples, which do not show selfreversed components [Doubrovine and Tarduno, 2004]. These comparisons suggest that very high degrees of oxidation are required to produce a true self-reversed CRM by ionic reordering in titanomaghemite. Assuming that the effect of cation impurities on oxidation state is minor, z > 0.95(corresponding to a < 8.36 A for the range of x values given above [Readman and O'Reilly, 1972]) should result in selfreversing behavior. We suggest that the self-reversal field of pure titanomaghemite is restricted to compositions with x >0.65 and z > 0.95 (Figure 4).

[41] As noted by O'Reilly and Banerjee [1966], high oxidation temperatures that might be envisioned to reach the oxidation states required for self-reversal by ionic reordering are incompatible with stability of the cationdeficient titanomaghemite structure. As we have shown previously [Doubrovine and Tarduno, 2004] and in this study, "higher than usual" x values are also needed for selfreversal. In oceanic environments, the oxidation by iron removal can help to produce the high-z high-r compositions of titanomaghemite at low ambient temperatures. The presence of well-defined self-reversed components, such as these seen in samples from Detroit Seamount, may signify localized, long-lived systems characterized by unusually high water flow, which facilitates very efficient removal of iron, allowing titanomaghemite to reach extremely high oxidation states and high x values required to produce a selfreversal by ionic reordering. As such, the presence of selfreversal in titanomaghemite may have some potential to hirtdcast such processes.

#### Notation

- *a* lattice parameter.
- inclination.

A/95 95% confidence interval for inclination.

- precision parameter for a Fisherian distribution of k paleomagnetic directions.
- K precision parameter for a Fisherian distribution of virtual geomagnetic poles.
- $H_c$ coercive force.
- coercivity of remanence.  $H_{cr}$
- $M_A$ magnetization of tetrahedral sublattice (A) of titanomagnetite or titanomaghemite.
- magnetization of octahedral sublattice (B) of  $M_B$ titanomagnetite or titanomaghemite.
- $M_r$ saturation remanent magnetization.
- spontaneous or saturation magnetization.  $M_{s}$
- number of samples. n
- angular dispersion of paleomagnetic directions. S
- S angular dispersion of virtual geomagnetic poles.
- Т temperature.
- titanium content of titanomagnetite or titanomagheх mite.
- oxidation parameter of titanomaghemite. Z
- 8 degree of cation substitution in impure titanomaghemite.
- K, magnetic susceptibility.

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