Saturation magnetostriction and its low-temperature variation inferred for natural titanomaghemites: implications for internal stress control of coercivity in oceanic basalts

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1 INTRODUCTION

Titanomagnetite Fe$_3$Ti$_{1-x}$O$_4$ with $x \approx 0.6$ is the most abundant primary magnetic mineral of oceanic basalts and oxidizes gradually to titanomaghemites (Prévote et al. 1968; Irving 1970; Johnson & Hall 1978; Petersen et al. 1979). The degree of this low-temperature oxidation is given by the oxidation parameter $z$, which is defined as the ratio of oxidized Fe$^{2+}$ to originally present Fe$^{2+}$ (O’Reilly & Banerjee 1966) and ranges from 0 (non-oxidized) to 1 (fully oxidized).

Titanomagnetite ($x \approx 0.6$, $z \approx 0$) is an important carrier of remanent magnetization in young basalts near oceanic ridges. Its saturation magnetization $J_S$, magnetocrystalline anisotropy constant $K_1$ and saturation magnetostriction $\lambda_S$ have long been known and have been measured as a function of low temperature (Syono 1965; Klerk et al. 1977; Kakol et al. 1991). It is likely that the stability of whether cooling to 120 °K causes $H_CJ_S$ for each oceanic basalt to vary in approximate proportion to $(1 - \frac{T}{T_C})^n$ with $n$ near 1.9 and 2.0 (where $T$ is temperature and $T_C$ is Curie point, both in °K). This implies that $\lambda_S$ of titanomaghemite with $x \approx 0.55$ and $z \approx 0.9$ also varies in approximate proportion to $(1 - \frac{T}{T_C})^n$ with $n$ near 1.9 or 2.0 on cooling to 120 °K (assuming that $\sigma_i$ remains constant on cooling). Our results support the hypothesis that coercivity (magnetic stability) is often magnetostrictively controlled by internal stresses in the highly oxidized titanomaghemite typical of oceanic basalts older than $ca$ 10 Myr. We suggest that this hypothesis can be further tested by more extensive observation of whether cooling to 120 °K often causes $H_CJ_S$ of such basalts to vary in approximate proportion to $(1 - \frac{T}{T_C})^n$ with $n$ near 1.9 or 2.0.

Key words: coercivity, magnetostriction, oceanic basalt, titanomaghemite.

SUMMARY

Highly oxidized titanomaghemite in oceanic basalts often carries remanent magnetization of high coercivity (stability), helping preserve the oceanic magnetic anomaly pattern. We study the source of this high coercivity in four oceanic basalts (from ODP sites 238, 572D, 470A and 556) containing highly oxidized titanomaghemite (titania content parameter $x \approx 0.55$ and oxidation parameter $z \approx 0.9$ on average). Most of the titanomaghemite is likely in single-domain grains with uniaxial anisotropy because the ratio of saturation remanence $J_{RS}$ to saturation magnetization $J_S$ approaches 0.50 ($J_{RS}/J_S = 0.46$ on average). We show that the uniaxial anisotropy is very likely magnetostrictively controlled through internal stresses $\sigma_i$ in the titanomaghemite grains. This allows us to use a novel indirect method to estimate the saturation magnetostriction $\lambda_S$ of the titanomaghemite. A saturation remanence $J_{RS}$ is given along the axis of a cylindrical sample of each basalt. Then a small compression $\sigma$ is applied repeatedly along this axis and the reversible change $\Delta J_{RS}$ in $J_{RS}$ is measured. Combining equations from single-domain theory for this piezomagnetic effect and for the sample’s coercive force $H_C$ gives $\lambda_S = 1.39H_CJ_S\frac{1}{2}\frac{\Delta J_{RS}}{J_{RS}}$ (using cgs units, or with $H_C$ in mT, $J_S$ in $kA/m$ and $\sigma$ in Pa). This yields four $\lambda_S$ estimates (with $ca$ 50 per cent expected error) ranging from $3 \times 10^{-6}$ to $10 \times 10^{-6}$ and averaging $6 \times 10^{-6}$. Theory for the piezomagnetic effect yields four $\sigma_i$ estimates averaging $2 \times 10^6$ Pa. This is similar to the internal stress magnitude thought to be responsible for the high coercivity of ball-milled single-domain titanomagnetite ($x \approx 0.6$) and natural single-domain haematite. We also show that cooling to 120 °K causes $H_CJ_S$ for each oceanic basalt to vary in approximate proportion to $(1 - \frac{T}{T_C})^n$ with $n$ between 1.9 and 2.0 (where $T$ is temperature and $T_C$ is Curie point, both in °K). This implies that $\lambda_S$ of titanomaghemite with $x \approx 0.55$ and $z \approx 0.9$ also varies in approximate proportion to $(1 - \frac{T}{T_C})^n$ with $n$ near 1.9 or 2.0 on cooling to 120 °K (assuming that $\sigma_i$ remains constant on cooling). Our results support the hypothesis that coercivity (magnetic stability) is often magnetostrictively controlled by internal stresses in the highly oxidized titanomaghemite typical of oceanic basalts older than $ca$ 10 Myr. We suggest that this hypothesis can be further tested by more extensive observation of whether cooling to 120 °K often causes $H_CJ_S$ of such basalts to vary in approximate proportion to $(1 - \frac{T}{T_C})^n$ with $n$ near 1.9 or 2.0.

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Highly oxidized titanomaghemite dominates in oceanic basalts older than ca 10 Myr and is likely the main carrier of the remanence responsible for most oceanic magnetic anomalies (Bleil & Petersen 1983). It has been suggested that the stability of this remanence is often controlled through internal stresses (Housden & O’Reilly 1990), which are inferred to be high from shrinkage cracks in the titanomaghemite (Petersen & Vali 1987). However, this hypothesis has been difficult to test because neither \( \lambda_S \) nor its thermal variation have been measured for titanomaghemite. This is because titanomaghemite is not available in large enough samples for its \( \lambda_S \) to be measured by the conventional methods used for titanomagnetite.

In this paper, we indirectly estimate the saturation magnetostriction \( \lambda_S \) of highly oxidized titanomaghemite typical of oceanic basalts older than ca 10 Myr. We use four oceanic basalts containing titanomagnetite (\( x \approx 0.55, z \approx 0.90 \) on average) that is likely mostly in single-domain grains with uniaxial anisotropy resulting from internal stresses. We measure the reversible effect of a small uniaxial compression upon saturation remanence \( J_{RS} \) in each basalt. Our measurements are compared with predictions from single-domain theory for this piezomagnetic effect (Bozorth 1951; Hodych 1977) and for \( H_C \) (Stoner & Wohlfarth 1948). This yields estimates of \( \lambda_S \) averaging \( 6 \times 10^{-6} \) for the titanomaghemite, which is an order of magnitude less than \( \lambda_S \) for the corresponding titanomagnetite. It also yields estimates of internal stress magnitude \( \sigma_i \), that average \( 2 \times 10^8 \) Pa, which is similar to \( \sigma_i \) inferred for ball-milled single-domain titanomagnetite with \( x \approx 0.6 \) (Day et al. 1977; O’Reilly 1984 p. 140). Although the effect of uniaxial compression upon magnetization of rocks (including oceanic basalts, Pozzi 1975) has been measured before, we seem to be the first to use the results to estimate \( \lambda_S \) or \( \sigma_i \).

We also indirectly estimate the low-temperature variation of \( \lambda_S \) using our four oceanic basalts with single-domain titanomagnetite and our one oceanic basalt with pseudo-single-domain titanomaghemite. All five basalts show \( H_C J_S \) increasing in approximate proportion to \((1 - \frac{C}{n})^6 \) with \( n \) between 1.9 and 2.0 on cooling to 120 K (where \( T \) is temperature and \( T_C \) is Curie point, both in K). This implies that \( \lambda_S \) for their titanomagnetite (\( x \approx 0.55, z \approx 0.90, T_C \approx 610^\circ \)K on average) also increases on cooling to 120 K in approximate proportion to \((1 - \frac{C}{n})^6 \) with \( n \) near 1.9 or 2.0, which is similar to how \( \lambda_S \) increases on cooling in the corresponding titanomagnetite. This supports the hypothesis that magnetostriiction commonly controls remanence stability through internal stresses in the highly oxidized titanomaghemites typical of older oceanic basalts, helping preserve the oceanic magnetic anomaly pattern.

### 2 EXPERIMENTAL METHODS AND RESULTS

#### 2.1 Properties of the titanomaghemite-bearing oceanic basalts

We studied the five oceanic basalts whose hysteresis properties had been measured in fields of up to 5 T by Matzka et al. (2003). Four of these (238, 572D, 470A and 556) are likely dominated by single-domain titanomagnetite and one (495) by pseudo-single-domain titanomaghemite. All were from different Ocean Drilling Programme (ODP) sites whose sample codes are given in Table 1. The samples

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Oceanic basalts</th>
<th>Dolerites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>238</td>
<td>572D</td>
</tr>
<tr>
<td>ODP code</td>
<td>238-61-4(6)</td>
<td>572D-34-1(99)</td>
</tr>
<tr>
<td>Ocean</td>
<td>Indian</td>
<td>Pacific</td>
</tr>
<tr>
<td>Age (Myr)</td>
<td>34</td>
<td>16</td>
</tr>
<tr>
<td>( a_0 ) (Å)</td>
<td>8.379</td>
<td>8.372</td>
</tr>
<tr>
<td>( T_C ) (°C)</td>
<td>365</td>
<td>360</td>
</tr>
<tr>
<td>( \text{Ti}/\text{Fe} )</td>
<td>0.242</td>
<td>0.214</td>
</tr>
<tr>
<td>( x )</td>
<td>0.51</td>
<td>0.50</td>
</tr>
<tr>
<td>( z )</td>
<td>0.89</td>
<td>0.91</td>
</tr>
<tr>
<td>( J_{RS}/J_S )</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>( J_S (\text{250 m}^3/\text{m}) )</td>
<td>44</td>
<td>90</td>
</tr>
<tr>
<td>( F (\times 10^{-2}) )</td>
<td>0.94</td>
<td>1.05</td>
</tr>
<tr>
<td>( \alpha_{0S} (\times 10^{-2}) )</td>
<td>±0.22</td>
<td>±0.20</td>
</tr>
<tr>
<td>( d (\mu m) )</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>( H_C (\text{mT}) )</td>
<td>25.0</td>
<td>37.6</td>
</tr>
<tr>
<td>( J_S J_{RS} (\times 10^9 \text{ Pa}^{-1}) )</td>
<td>2.76</td>
<td>2.21</td>
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<tr>
<td>( r )</td>
<td>0.32</td>
<td>0.43</td>
</tr>
<tr>
<td>( \lambda_S (\times 10^{-6}) )</td>
<td>4.2</td>
<td>10.4</td>
</tr>
<tr>
<td>( \sigma_i (\times 10^8 \text{ Pa}) )</td>
<td>1.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>
are from three different oceans and range in age from 15.7 to 34 Myr (Table 1). Ages are from Juárez et al. (1998) except for sample 572D whose age is from Mayer & Theyer (1985).

Polished sections of each basalt were examined with reflected light microscopy. The main magnetic mineral was identified as titanomaghemite with samples 470A and 495 also containing isolated grains of hemoilmenite. Shrinkage cracks in titanomaghemite (Petersen & Vali 1987) appear in samples 572D, for grains larger than 10 µm, and 495, for grains larger than 18 µm.

The volume fraction \( F \) of titanomaghemite was measured for each of the five oceanic basalt cylinders used for stress experiments. This was done by polishing both faces of each basalt cylinder and measuring the fraction of titanomaghemite on each face with the aid of a scanning electron microscope (SEM) operated at 4000× magnification in backscatter mode. The fractional area \( f \) occupied by titanomaghemite in the 26×23 µm area image on the SEM screen was measured (as was the size of the titanomaghemite grains). This was repeated for at least 100 positions on each face, evenly spaced to avoid bias. Averaging the resulting >200 measurements of \( f \) gives the average \( F \) for each cylinder, which is listed in Table 1 along with its 95 per cent confidence interval (estimated from the standard deviation of the >200 measurements of \( f \)). The grain-size distribution was used to estimate the volumetrically average grain size (i.e. half the total volume of titanomaghemite is in equal or smaller grains and half in equal or larger grains). Grains less than \( \approx 0.5 \) µm across were not measured, being difficult to image in backscatter mode. Even with the finest-grained sample (572D), this should not have led to more than \( \approx 10 \) per cent underestimation of titanomaghemite content, judging by the grain-size distribution. The approximate Ti/Fe ratio of many grains was checked on the SEM using energy-dispersive X-ray (EDX) analysis, to be sure that the bright-appearing grains being measured were titanomaghemite rather than ilmenite, magnetite or pyrite.

For each basalt, the atomic \( \frac{Ti}{Fe} \) ratio, the Curie point \( T_C \), the lattice constant \( a_0 \) and the Curie point \( T_C \) were measured for the titanomaghemite to estimate its \( x \) and \( z \) values (Table 1). The ratio of Ti to Fe atoms was measured for 40 titanomaghemite grains on the polished ends of each oceanic basalt cylinder using the SEM with EDX analysis. The average of the 40 measurements for each basalt should be accurate to within 0.01 with 95 per cent confidence, judging by the standard deviation and by measurements of an ilmenite standard.

Lattice constants \( a_0 \) (Table 1) were determined on magnetic extracts that were mixed with SiO\(_2\) powder as a standard. For samples 238 and 572D, a Guinier-type camera was used (Co K\(_\alpha\)\(_1\) radiation using an imaging plate in asymmetric back-reflection configuration). For samples 470A, 495, and 556 a diffractometer was used (Mo K\(_\alpha\)\(_1\) radiation in transmission).

Curie points \( T_C \) were determined using thermomagnetic curves and the method of Grommé et al. (1969). The curves were measured for small basalt chips in air in a 400 mT field with a variable field translation balance. For basalts 470A and 556, natural remanence has been thermally demagnetized (fig. 6 of Matzka et al. 2003) and shows dominance by the same \( T_C \) mineral as in the corresponding high-field thermomagnetic curves.

The composition parameters \( x \) and \( z \) of the titanomaghemites were estimated from the lattice constant \( a_0 \) and the Curie point \( T_C \) using the \( a_0 \) and \( T_C \) contour plots of Readman & O’Reilly (1972). They were also estimated from \( a_0 \) and the Ti/Fe atomic ratio assuming oxidation through iron loss and using the \( a_0 \) contour plots of Readman & O’Reilly (1972). The average of the two sets of \( x \) and \( z \) estimates are presented in Table 1. The two sets of \( x \) estimates differed on average by 0.04 and the two sets of \( z \) estimates by 0.01. The measurements of Zhou et al. (1999) of \( a_0 \) versus \( z \) in titanomaghemite in oceanic basalts imply that the \( a_0 \) contour plots of Readman & O’Reilly (1972) are reasonably reliable (more so than those of Xu et al. 1996).

Magnetic hysteresis curves were measured on small basalt chips to a maximum field of 5 T with a Quantum Design Magnetic Properties Measurement System (MPMS, Quantum Design, San Diego, CA, USA). The contribution of paramagnetic minerals to the hysteresis curves was determined using a linear fit between 2 and 5 T and was subtracted from the hysteresis curves before calculating the hysteresis parameters. This yielded the \( J_{RS}/JS \) ratios listed in Table 1 for each of the oceanic basalts. Magnetic hysteresis parameters, including coercive force \( H_c \) and saturation magnetization \( J_S \), were also measured in this way as a function of low temperature. These measurements were used to plot the variation of \( H_c \) and \( H_cJS \) on cooling for each of the basalts (Fig. 1).

Magnetic hysteresis curves were also measured for each of the oceanic basalt cylinders used for the stress experiments (to reduce error resulting from sample inhomogeneity). A maximum field of 0.28 T in a variable field translation balance was used, yielding the values of \( H_c \) listed in Table 1. It also yielded values of \( J_{RS} \) per unit volume of basalt for each cylinder. This \( J_{RS} \) was divided by the \( J_{RS}/JS \) ratio in Table 1 to yield an estimate of the saturation magnetization \( J_S \) per unit volume of titanomaghemite. This \( J_S \) was then divided by \( F \) in Table 1 to yield the saturation magnetization \( J_S \) per unit volume of titanomaghemite in the basalt cylinder (which is the \( J_S \) listed in Table 1). The error in \( J_S \) is estimated as ca 30 per cent, most of it ascribed to error in measurement of \( F \).

### 2.2 Magnetite-bearing continental dolerites

We also studied two magnetite-bearing basaltic samples (9144 and 4305) from two separate dykes in a Mesoproterozoic swarm near Nain, Labrador. Their magnetite is likely dominantly found in single-domain grains (judging by \( J_{RS}/JS \) approaching 0.5) with uniaxial anisotropy provided by grain elongation (judging by \( H_c \) showing little change on cooling). The properties of these samples (Table 1) and how they were measured are described in detail by Hodych (1996) and by Hodych et al. (1998).

### 2.3 Stress experiments

For the stress experiments, cylinders of rock 8.7 mm in diameter and 6 to 7 mm in length were prepared. (The cylinder of 470A was only 3 mm long but was extended by gluing on ceramic end pieces.) The ends of each cylinder were ground flat, parallel to the cylinder axis. The samples were given a saturation remanence \( J_{RS} \) at room temperature in a field of 800 mT either along or perpendicular to the cylinder axis. The stress experiments were conducted inside a magnetic shield with a residual magnetic field of less than 5 nT. A non-magnetic aluminum press (Fig. 2) was used to exert axial compressive stress parallel to the sample’s cylinder axis. It is of similar design but smaller than the press described by Hodych (1973). Its special design allows the piston to tilt and provide uniform axial stress, even if the sample’s flat ends are not quite parallel. A hand-operated pump was used to compress the oil that pushes down on a 12.7 mm diameter tiltable piston via a rubber diaphragm. The pressure on the 8.7 mm diameter sample should be \( \frac{12.7^2 \times 10^5}{\pi} \times \) the oil pressure that was measured with a Bourdon gauge (rated accurate to 0.5 per cent).
respectively. The observational points, varies from 1.9 to 3.1 for basalts 556 and 470A, respectively.

Hc divided by J0, probe oriented parallel to the remanence direction. A relative changes in its magnetic field were measured by a fluxgate magnetometer (MacIntyre Electronic Design Associates, Dulles, VA, USA) with a field neutralization control allowed us to measure field changes as low as 1 nT. In experiments with JRS parallel to the cylinder axis, the probe was mounted in position f1 (second Gaussian position, e.g. Bozorth 1951 p. 839) as indicated in Fig. 2. In experiments with JRS perpendicular to the cylinder axis, the probe was in position f2 (first Gaussian position). Magnetometer drift during each set of experiments was small enough to be ignored (ca 2 nT).

We tested to ensure that compressing a sample did not move it enough to produce magnetic field changes at the probe that could be wrongly interpreted as magnetization changes. An aluminium cylinder of sample size was made and two holes were drilled through its centre, so that one hole was along the cylinder axis and the other hole was perpendicular to the axis. To produce an axial (or a perpendicular) remanence, a magnetized needle was inserted into the axial (or perpendicular) drill hole with plastic modelling material to hold it in place without transmitting stress from the cylinder to the magnetic needle. Compressing this test sample to the maximum stress used with the rock samples resulted in apparent magnetization changes smaller than 0.2 per cent for both axial and perpendicular remanence. Hence, this source of error should be negligible for the rock samples.

For the stress experiments, the samples were subjected to a small base load σB = −1.5 × 10⁶ Pa (compressive stress is of negative sign). From that load, an additional compression σ was applied in steps of −4.4 × 10⁶, −8.8 × 10⁶, −13.2 × 10⁶, and then −17.6 × 10⁶ Pa (−176 × 10⁶ dyn cm⁻²). For each step, the stress was cycled four times between σB and σB + σ and the remanence was measured after each pressure change. Stress-induced irreversible changes of remanence were observed only in the first of the four cycles for every step. Hence, only the last three of the four cycles were used to calculate ΔJRS, the mean reversible part of the remanence change induced by stress σ, which is given by

$$\Delta J_{RS} = J_{RS}(\sigma_B + \sigma) - J_{RS}(\sigma_B).$$  \hfill (1)

Using a small base load σB avoids spurious effects from small sample movements that might occur while the sample seats itself at small loads and has negligible effect on ΔJRS because the reversible stress-induced remanence change is proportional to σ.

The results of the pressure experiments are shown in Fig. 3 for oceanic basalts 572D and 238 and for the continental dolerite 9144. The observed reversible fractional change in saturation remanence $\Delta J_{RS}/J_{RS}$ is plotted versus the uniaxial stress σ that caused it. The error bars represent an error in the fluxgate reading of ±1 in the last digit (±1 nT). For all samples, axial compression applied parallel to the remanence direction causes a reversible remanence decrease that is proportional to σ. The slope of the least-squares fit line (through the origin) gives the value of $\frac{\Delta J_{RS}}{\Delta \sigma}$. The reversible fractional change in JRS per unit stress (listed in Table 1 for each sample). When axial compression is applied perpendicular rather then parallel to the remanence direction, the reversible fractional change in JRS is still proportional to σ but of opposite sign (an increase) and smaller by the factor r (listed in Table 1 for each sample).

An irreversible change in the remanence was observed during the experiments. Unlike the reversible change, the irreversible change was a decrease whether stress was applied parallel or perpendicular to JRS. These irreversible remanence changes were a small percentage of the total remanence (5 per cent at most).
3 DISCUSSION

3.1 Saturation magnetization $J_S$ of the titanomaghemite in our oceanic basalts

It is important to reliably determine saturation magnetization $J_S$ of the titanomaghemite in our oceanic basalts because our $\lambda_S$ estimates for the titanomaghemite are proportional to $J_S$ (as will be shown below). We measured $J_S$ (as outlined above) rather than attempting to estimate it from the composition of the titanomaghemite because $J_S$ may depend strongly upon how the composition was reached. Although the titanomaghemite very likely oxidized through removal of iron rather than addition of oxygen, $J_S$ can depend strongly upon how the removal of iron was partitioned between tetrahedral and octahedral sites (Bleil & Petersen 1983; Matzka et al. 2003). The $J_S$ measurements (Table 1) for the titanomaghemite in our five oceanic basalt samples range from 23 to 90 kA m$^{-1}$. Most of this variation should be real (because the error in $J_S$ is estimated at only ca 30 per cent). The $J_S$ values and their large variation conform to the $J_S$ measurements of Bleil & Petersen (1983) for oceanic basalts of similar $T_C$.

3.2 Evidence for single-domain titanomaghemite with uniaxial anisotropy resulting from internal stresses in four of our oceanic basalts

Four of our five oceanic basalt samples contain titanomaghemite that is likely mostly in randomly-oriented single-domain grains dominated by uniaxial anisotropy because their $J_{RS}/J_S$ ratio approaches 0.5, as expected theoretically for such grains (Stoner & Wohlfarth 1948). In contrast, the titanomaghemite in oceanic basalt 495 is likely mostly in pseudo-single-domain grains because $J_{RS}/J_S$ is 0.35. This is supported by Bitter pattern observations for 495 showing domain walls in titanomaghemite grains larger than ca 5 $\mu$m across. Titanomaghemite grains this large dominate 495 (Table 1) but our other four oceanic basalts are dominated by smaller titanomaghemite grains (ca 2.2 to 2.8 $\mu$m across). The single-domain grains likely dominating these four oceanic basalts possess uniaxial (as a result of the shape or internal stresses) rather than cubic (magnetocrystalline) anisotropy. This is shown by $J_{RS}/J_S$ approaching 0.5 but not the 0.831 (if $K_1 > 0$) or 0.866 (if $K_1 < 0$) expected theoretically (Joffe & Heuberger 1974) for randomly-oriented single-domain titanomaghemite grains dominated by magnetocrystalline anisotropy. (Indeed, none of the 93 oceanic basalt samples studied by Matzka (2001) show $J_{RS}/J_S$ significantly exceeding 0.5 when corrected (Matzka et al. 2003) for overestimation of paramagnetism.)
or for $H$ (Joffe & Heuberger 1974) predicts the following for titanomaghemite in randomly-oriented single-domain grains dominated by uniaxial anisotropy, as will now be shown. Assuming that the rotational hysteresis (as discussed below). Substituting this value of $K_1$ and $J_S = 49 \text{ mT}^2$ (the average $J_S$ for our four single-domain titanomaghemites) into eqs (2) and (3) predicts $H_C = 5.4 \text{ mT}$ if $K_1 < 0$ and $H_C = 9.2 \text{ mT}$ if $K_1 > 0$. The average $H_C$ of 31 mT observed for our four basalts with single-domain titanomaghemite is much greater than either of these predictions, making magnetocrystalline control of their $H_C$ unlikely. (Pseudo-single-domain titanomaghemite with magnetocrystalline control of $H_C$ might fortuitously give $J_{bs}/J_S$ near 0.5, but its $H_C$ should be even smaller than 5.4 or 9.2 mT).

Having shown that four of our basalts are very likely dominated by randomly-oriented single-domain titanomaghemite grains with uniaxial anisotropy, we consider whether the uniaxial anisotropy is the result of grain elongation or internal stresses. Assuming that the uniaxial anisotropy is the result of grain elongation (with $N_x$ and $N_y$ the self-demagnetizing factors across and along the long axis of the

![Figure 4](image-url)
single-domain grain, respectively), single-domain theory (Stoner & Wohlfarth 1948) predicts the following for \( H_c \) (in cgs units with \( \mu_0 = 1 \), or for \( H_c \) in mT, \( J_S \) in \( \mu_B \) m and \( \mu_0 = 4\pi \times 10^{-7} \) Pa):

\[
H_c = 0.479\mu_0(N_b - N_s)J_S.
\]

(4)

Even if the titanomaghemite grains were extremely elongated so that \( N_b - N_s = 0.5 \) (2\( \pi \) in cgs units), eq. (4) with average \( J_S = 49 \mu_B \) m predicts that average \( H_c \) resulting from shape anisotropy should not exceed 15 mT. This is much less than the average \( H_c \) of 31 mT observed in these basalts (Table 1). Furthermore, for all five of our oceanic basalts, we observe that cooling from 300 to 120 °C causes a large increase in \( H_c \) (Fig. 1b) whereas \( J_S \) decreases (\( J_S \) versus \( T \) is not plotted explicitly, but can be derived from Fig. 1). Certainly \( H_c \) does not vary in proportion to \( J_S \) as expected from eq. (4), ruling out control of \( H_c \) by shape anisotropy. Hence, \( \lambda_s \) control of \( H_c \) seems the only viable option and the way \( H_c \) varies on cooling very likely reflects how \( \lambda_s \) varies on cooling as will be discussed in Section 3.5.

3.3 Inferring \( \lambda_s \) for single-domain titanomaghemite in our oceanic basalts

For all five of our titanomaghemite-bearing basalt samples, \( J_{RS} \) decreases reversibly when compressed parallel to \( J_{RS} \) (Fig. 3). This shows that \( \lambda_s \) must be positive for their highly oxidized titanomaghemites, as is the case for titanomagnetite (\( \lambda_s \approx 0.6 \)) and maghemite. This is not a trivial result because \( \lambda_s \) is negative for maghemite (Dunlop & Özdemir 1997, p. 51).

Average magnetostriction \( \lambda_s \) can be indirectly estimated for randomly-oriented single-domain grains with uniaxial anisotropy from measurements of \( \frac{1}{2} \frac{\Delta J_S}{J_{RS}} \) (the reversible fractional change in \( J_{RS} \) per unit of small axial compression \( \sigma \) applied parallel to \( J_{RS} \)) by using the following equation (in cgs units or for \( H_c \) in mT, \( J_S \) in \( \mu_B \) m and \( \sigma \) in Pa):

\[
\lambda_s = 1.39H_cJ_S \frac{1}{\sigma} \frac{\Delta J_S}{J_{RS}}.
\]

(5)

Eq. (5) is valid whether the uniaxial anisotropy is the result of grain elongation or internal stresses, as we shall now show. Assuming the uniaxial anisotropy is the result of grain elongation, eq. (5) can be derived by combining eq. (4) with the following theoretical expression (Hodych 1977) for \( \frac{1}{2} \frac{\Delta J_S}{J_{RS}} \) (in cgs units with \( \mu_0 = 1 \), or for \( J_S \) in \( \mu_B \) m and \( \sigma \) in Pa with \( \mu_0 = 4\pi \times 10^{-7} \) Pa):

\[
\frac{1}{\sigma} \frac{\Delta J_S}{J_{RS}} = \frac{3}{2} \mu_0(N_b - N_s)J_S.
\]

(6)

Assuming the uniaxial anisotropy is the result of internal stresses \( \sigma_s \) in the single-domain grains, eq. (5) can be derived by combining the following theoretical expressions for \( H_c \) (Stoner & Wohlfarth 1948) and \( \frac{1}{2} \frac{\Delta J_S}{J_{RS}} \) (Bozorth 1951, p. 625) valid for cgs units or for \( H_c \) in mT, \( J_S \) in \( \mu_B \) m and \( \sigma \) in Pa:

\[
H_c = 1.437\lambda_s\sigma_s J_S.
\]

(7)

\[
\frac{1}{\sigma} \frac{\Delta J_S}{J_{RS}} = \frac{1}{2\sigma_s}.
\]

(8)

Assuming that the easy axes of the elongated or stressed grains are randomly oriented relative to crystallographic axes, the average saturation magnetostriction estimated by eq. (5) should equal \( \lambda_s = \frac{2}{5} \lambda_{100} + \frac{2}{5} \lambda_{111} \) (Bozorth 1951, p. 652) where \( \lambda_{100} \) and \( \lambda_{111} \) are saturation magnetostriction along the [100] and [111] axis, respectively.

Substituting the observed \( H_c \), \( \frac{1}{2} \frac{\Delta J_S}{J_{RS}} \) and \( J_S \) into eq. (5) yields indirect estimates of \( \lambda_s \) for the single-domain titanomaghemite dominating oceanic basalts 238, 572D, 470A and 556 (Table 1). There could be large errors in these estimates of \( \lambda_s \). Underestimation of \( \lambda_s \) could result from not all of the titanomaghemite being in single-domain grains as suggested by \( J_{RS}/J_S \) being on average 0.46 rather than the 0.50 expected from single-domain theory. It is also suggested by the ratio \( r \) (Table 1) being on average 0.38 rather than the 0.50 expected from single-domain theory (Hodych 1977). On the other hand, overestimation of \( \lambda_s \) could result from our assumption that the average uniaxial compression \( \sigma \) delivered to the titanomaghemite grains is the same as that applied to the basalt sample. The compression could be significantly higher if titanomaghemite (like magnetite) is more rigid than the basalt as a whole (Hamano 1983).

To determine how much error is likely in our \( \lambda_s \) estimate for titanomaghemite, we estimated \( \lambda_s \) in the same way for magnetite. Magnetite is likely to yield higher error in \( \lambda_s \) estimation by our method because its magnetostriction is uncommonly anisotropic (\( \lambda_{100} = -19.5 \times 10^{-6} \), \( \lambda_{111} = 72.6 \times 10^{-6} \)). We used the two basaltic dyke samples (9144 and 4305), which had the highest \( J_{RS}/J_S \) (=0.45 and 0.42, respectively) of a suite of magnetite-bearing Precambrian dykes from Nain, Labrador. Because \( J_{RS}/J_S \) approaches 0.50 and \( H_c \) shows little change on cooling to 77 °K, the magnetite in both 9144 and 4305 is likely mostly in single-domain grains dominated by uniaxial anisotropy provided by grain elongation (Hodych 1996). Because the magnetite is intergrown with ilmenite lamellae exsolved along \{111\} planes, the magnetite grains are likely elongated along \{110\} directions. Magnetic interaction between these elongated grains can likely be ignored in first approximation (Hodych 1996). Substituting \( H_c \), \( \frac{1}{2} \frac{\Delta J_S}{J_{RS}} \) and \( J_S \) from Table 1 into eq. (5) yields indirect estimates of \( \lambda_s \) for 9144 and 4305. Although these are on average 43 per cent less than \( \frac{2}{5} \lambda_{100} + \frac{2}{5} \lambda_{111} \) for magnetite, they are on average only 23 per cent less than \( \frac{2}{5} (\lambda_{111} + \lambda_{100}) \), which is the \( \lambda_s \) expected if the magnetite grains are elongated along \{110\} instead of along random crystallographic directions (Hodych 1977). This suggests that our \( \lambda_s \) estimates for titanomaghemite in samples 572D, 238, 556 and 470A are likely within ca 50 per cent of the true value (taking into account additional error contributed by \( J_S \)).

Our experimental estimate of average \( \lambda_s \) is \( ca 6 \times 10^{-6} \) for titanomaghemite with \( z \approx 0.55 \) and \( z \approx 0.9 \). This is much higher than the ca \( 1 \times 10^{-6} \) expected if \( \lambda_s \) varies in approximate proportion to \( (1 - z)^2 \) as predicted by Housden & O’Reilly (1990). However, they point out that their prediction neglects the contribution of Fe\(^{3+}\) ions to \( \lambda_s \) and shows increasingly underestimate \( \lambda_s \) as \( z \) approaches 1. Moskowitz (1980) used rotational hysteresis data (Manson et al. 1979) to estimate how \( K_1 \) varies with \( z \) in titanomaghemite and then assumed that \( \lambda_s \) varies in proportion to \( K_1 \). However, the rotational hysteresis data of the synthetic single-domain titanomaghemites of Manson et al. (1979) are more likely dominated by \( \lambda_s \) acting through internal stresses rather than by \( K_1 \). This is because the titanomaghemites were prepared by wet grinding in a ball mill for four days. In titanomagnetites (\( z \approx 0.6 \)) this typically produces single-domain grains whose coercive force is too high to be the result of shape or magnetocrystalline anisotropy and is thought to be the result of magnetostriction acting through internal stresses that would have to be ca \( 1 \times 10^{13} \) Pa in magnitude. Assuming that this is also true of the single-domain titanomaghemites of Manson et al. (1979), the rotational hysteresis magnitudes reported would
imply $\lambda_S \approx 4 \times 10^{-6}$ for titanomaghemite with $x = 0.5$, $z = 0.8$ or with $x = 0.6$, $z = 0.84$. This follows from peak rotational hysteresis per unit volume per cycle $W_{ip} = 1.8(\frac{\lambda_S}{\lambda})$ for randomly-oriented single-domain grains with uniaxial anisotropy resulting from stress according to theory by Jacobs & Luborsky (1957), using cgs units or $W_{ip}$ in $\frac{1}{2} \sigma_1$ and $\sigma_1$ in Pa. This estimate is in reasonable agreement with our average $\lambda_S$ estimate, but our estimate has the advantage of not needing to assume that the internal stress magnitude is $\approx 1 \times 10^8$ Pa.

3.4 Inferring internal stress magnitude for single-domain titanomaghemite in our oceanic basalts

We have shown that oceanic basalts 572D, 238, 556 and 470A are very likely dominated by single-domain titanomaghemite with uniaxial anisotropy resulting from internal stresses. Hence, we can use eq. (8) and measurements of $\frac{1}{2} \frac{\lambda}{\lambda_S}$ to infer the internal stress magnitude $\sigma_1$ in their single-domain titanomaghemites. These $\sigma_1$ estimates (Table 1) range from 1.1 to 2.3 $\times 10^8$ Pa with average $\sigma_1 = 1.8 \times 10^8$ Pa. The error in estimating $\sigma_1$ is independent of error in $J_S$ and may be similar to the ca 23 per cent error in estimating $\lambda_S$ of single-domain magnetite in our dolerites from measurements of $\frac{1}{2} \frac{\lambda}{\lambda_S}$.

Internal stress $\sigma_1 \approx 1.8 \times 10^8$ Pa is not unreasonably high because a similar internal stress magnitude is assumed to explain the high coercivity of single-domain haematite (Porath 1968; Dunlop & Özdemir 1997 p. 72) and the high coercivity of ball-milled titanomagnetite with $x = 0.6$ (Day et al. 1977; O’Reilly 1984 p. 140). For large multidomain titanomaghemite grains ($x \approx 0.6$, $z < 0.6$), Appel (1987) estimated the internal stress magnitude to average ca $5 \times 10^7$ Pa. It seems likely that the much higher internal stresses in our titanomaghemites with higher oxidation degree are the result of shrinking of the crystal lattice during low-temperature oxidation. This is thought to produce the severe cracking observed for titanomaghemite particles greater than ca 5 $\mu$m (Petersen & Vali 1987). Housden & O’Reilly (1990) suggested that titanomaghemite grains smaller than the threshold of shrinkage crack formation deformed plastically and that their internal stress is comparable to that of ball-milled titanomagnetics. They assumed internal stresses of ca $2 \times 10^8$ Pa for the small titanomaghemite grains that are important carriers of natural remanence in oceanic basalts. Our estimates of $\sigma_1$ support this assumption.

3.5 Inferring how $\lambda_S$ varies upon cooling for titanomaghemite in our oceanic basalts

Having shown that oceanic basalts 572D, 238, 556 and 470A are very likely dominated by single-domain titanomaghemite whose $H_C$ is magnetostrictively controlled by internal stress, we expect that eq. (7) applies and that $H_C$ should vary in proportion to $\frac{\lambda}{\lambda_S}$ upon cooling from room temperature. Approximately the same is expected theoretically if the titanomaghemite is in pseudo-single-domain grains (as in oceanic basalt 495) or multidomain grains, provided that opposition to domain wall motion is magnetostrictively controlled through internal stresses (Hodych 1982b). Hence, measuring how $H_C J_S$ varies upon cooling in our oceanic basalts should allow us to infer how $\lambda_S$ of their titanomaghemite varies upon cooling. This assumes that internal stresses remain approximately constant upon cooling. This assumption seems justified for magnetite because $H_C J_S$ commonly varies in approximate proportion to $\lambda_S$ for multidomain and pseudo-single-domain magnetite (Hodych 1982a; Hodych et al. 1998).

The assumption that internal stresses remain approximately constant on cooling also seems justified for titanomaghemite ($x \approx 0.55$), as will now be shown. For single-domain titanomagnetite ($x \approx 0.55$, $T_C = 205^\circ$C) in glass ceramic, Worm & Markert (1987) showed that $H_C$ increases on cooling similarly to $\lambda_S$ (and unlike $K_1$). This can be seen in Fig. 4 where these $H_C$ data are plotted along with data for $\lambda_S$ and $K_1$ from Syono (1965) for synthetic titanomagnetite ($x = 0.56$, $T_C = 170^\circ$C). Hence, it is very likely that $H_C$ is magnetostrictively controlled through internal stresses. The variation of $H_C J_S$ is also shown (using $J_S$ data for $x = 0.55$ titanomagnetite from Kakol et al. 1991) and is similar to that of $H_C$ because $J_S$ shows relatively little variation on cooling. Both $H_C J_S$ and $\lambda_S$ vary on cooling in approximate proportion to $(1 - \frac{T}{T_C})^n$ where $n = 2.2$ for $H_C J_S$ and $n = 1.9$ for $\lambda_S$ (where $T$ is temperature and $T_C$ is Curie point, both in $^\circ$K). The difference in $n$ of ca 0.3 gives an estimate of the error expected if one assumes that $\sigma_1$ remains constant on cooling and infers the low-temperature variation of $\lambda_S$ from that of $H_C J_S$ in single-domain titanomaghemite with $x \approx 0.55$. Note that the power-law exponent $n$ is sensitive to error in $T_C$. We used the $\lambda_S$ data of Syono (1965) rather than that of Klerk et al. (1977) because the latter implied unusually low $T_C$ values. Above room temperature, $\lambda_S$ obeys the same power law but the exponent $n = 1.3$ for titanomagnetite with $x = 0.6$ or 0.4, as shown by Moskowitz (1993).

For all five of our oceanic basalts, cooling from room temperature to 120 $^\circ$K causes $H_C J_S$ to increase in approximate proportion to $(1 - \frac{T}{T_C})^n$ with $n$ between 1.9 and 2.0. This is shown in Fig. 1(a), whose curves were drawn by assuming that $H_C J_S$ for a given basalt would increase upon cooling from room temperature in approximate proportion to $(1 - \frac{T}{T_C})^n$ where $T_C$ is the Curie point measured for that basalt (Table 1). Various values of $n$ were tried (in increments of 0.1) and for each basalt the best fit to the observational data points was obtained with $n = 1.9$ or 2.0.

For the four oceanic basalts dominated by single-domain titanomaghemite, this observed increase of $H_C J_S$ on cooling implies (eq. 7) that $\lambda_S$ also increases in proportion to $(1 - \frac{T}{T_C})^n$ with $n$ near 1.9 or 2.0 on cooling from room temperature to 120 $^\circ$K. This assumes that internal stresses $\sigma_1$ remain constant, which may cause an error of ca 0.3 in the power-law exponent, judging by the behaviour of single-domain titanomaghemite with $x \approx 0.55$. The fifth oceanic basalt (495) is dominated by pseudo-single-domain titanomaghemite whose $H_C J_S$ behaves similarly, suggesting that its $\lambda_S$ varies in approximate proportion to $(1 - \frac{T}{T_C})^{1.9}$ on cooling from room temperature to 120 $^\circ$K.

Housden & O’Reilly (1990) suggested that $H_C$ would vary with temperature in approximate proportion to $(1 - \frac{T}{T_C})^{2.4}$ for single-domain and perhaps multidomain titanomaghemites with $x \approx 0.6$ in oceanic basalts. As shown in Fig. 1(b) for our oceanic basalts, $H_C$ varies in approximate proportion to $(1 - \frac{T}{T_C})^n$ on cooling to 120 $^\circ$K. However, the observed $H_C$ data points do not fit this power law as well as $H_C J_S$ does. Also, $n$ is not as constant as with $H_C J_S$, but varies from 1.9 to 3.1, because of variation in the way $J_S$ decreases on cooling from basalt to basalt. This varied behaviour of $J_S$ is consistent with evidence (Matzka et al. 2003) that the titanomaghemite is a ferrimagnet of P-type (Néel 1948) in basalts 238, 556 and 572D and of N-type in basalts 470A and 495.

Our observations suggest that $H_C J_S$ commonly varies in approximate proportion to $(1 - \frac{T}{T_C})^n$ on cooling with $n$ showing little variation from 1.9 or 2.0 for single-domain (and perhaps pseudo-single-domain) natural titanomaghemites with $x \approx 0.55$ and $z \approx 0.9$. As shown above, this variation of $H_C J_S$ on cooling is very likely the
result of $H_C$ being magnetostrictively controlled by internal stresses in the titanomaghemites. Our results support the hypothesis (Housden & O’Reilly 1990) that internal stresses in titanomaghemites are an important source of magnetic stability in oceanic basalts, helping preserve the oceanic magnetic anomaly pattern. We suggest testing this hypothesis further by extensive observation of whether it is common for $H_C$, $J_S$ of such basalts to vary on cooling in approximate proportion to $(1 - \frac{1}{T})^\gamma$ with $n$ near 1.9 or 2.0.

One could similarly test the proposal of Gee & Kent (1995) that magnetocrystalline anisotropy rather than internal stresses may commonly dominate coercivity in the relatively unoxidized titanomaghemites of basalts on mid-ocean ridges. They proposed this to explain why their $J_{BS}/J_S$ estimates often significantly exceeded 0.5 in their mid-ocean-ridge basalts samples. However, this may be an artefact of their using a maximum field of only 1 T, causing serious overestimation of $J_{BS}/J_S$, as was demonstrated for our titanomaghemite-bearing oceanic basalts by Matzka et al. (2003).

The importance of internal stress control of coercivity in mid-ocean-ridge basalts would be supported if $H_C$, $J_S$ of the basalts was found to commonly vary in approximate proportion to $x$ rather than $K_I$ on cooling. This variation with $x$ has been observed in the two oceanic basalts bearing multidomain titanomagneteite studied by Hodych (1982a). However, corresponding data for oceanic basalts bearing single-domain or pseudo-single-domain titanomagneteite are lacking.

4 CONCLUSIONS

(i) For a sample of coercive force $H_C$ dominated magnetically by randomly-oriented single-domain grains with uniaxial anisotropy and saturation magnetization $J_S$, theory predicts that the reversible change $\Delta J_{BS}$ in saturation remanence caused by applying a small axial stress $\sigma$ parallel to $J_S$ should yield an estimate of saturation magnetostriction $\lambda_S$ given by eq. (5): $\lambda_S = 1.39 H_C J_S^2 \sigma / J_{BS}^2$.

(ii) We describe a small non-magnetic press and how it was used with a fluxgate magnetometer in field-free space to measure $1 J_{BS} / J_S$, the reversible fractional change in saturation remanence per unit of compression applied parallel to the remanence direction of our rock samples.

(iii) The estimate of $\lambda_S$ given by eq. (5) was tested by measuring $\Delta J_{BS}$ for two basaltic samples containing single-domain magnetite grains (with uniaxial anisotropy) intergrown with ilmenite lamellae. Eq. (5) yielded $\lambda_S$ estimates of 19 and $22 \times 10^{-6}$. This is in satisfactory agreement with directly measured $J_{BS}$ and $\lambda_{100}$, because it is on average only ca 23 per cent lower than the $\lambda_S = \frac{1}{2} (\lambda_{111} + \lambda_{100})$ expected for single-domain magnetite elongated along [110] directions by ilmenite exsolution lamellae.

(iv) In the same way, $\lambda_S$ was estimated for titanomagneteite (with titanium content parameter $x \approx 0.55$ and oxidation parameter $z \approx 0.90$) by measuring $\Delta J_{BS}$ for four oceanic-ridge basalts samples dominated by single-domain titanomagneteite grains with uniaxial anisotropy. Eq. (5) gives estimates of $\lambda_S$ that should be within 50 per cent of the true values, where $\lambda_S = \frac{1}{2} (\lambda_{110} + \lambda_{111})$ (assuming the easy axes of the grains are along random crystallographic directions). The estimates of $\lambda_S$ range from $3 \times 10^{-6}$ to $10 \times 10^{-6}$ and their average is $6 \times 10^{-6}$.

(v) We show that the uniaxial anisotropy in the single-domain titanomagneteite grains dominating four of our oceanic basalts is very likely the result of internal stresses $\sigma$. The magnitude of $\sigma$ was estimated using eq. (8): $\frac{1}{2} \lambda_{111} \rho = \sigma^0$. This yields $\sigma \approx 2 \times 10^6$ Pa on average, which is similar in magnitude to the $\sigma$ thought to be responsible for the high coercivity of natural single-domain haematite and ball-milled single-domain titanomagneteite ($x = 0.6$).

(vi) For each of our four oceanic basalts dominated by single-domain titanomagneteite, $H_C J_S$ varies on cooling to 120 K in approximate proportion to $(1 - \frac{1}{T})^\gamma$ with $n$ between 1.9 and 2.0. This implies that $\lambda_S$ of the titanomagneteite ($x = 0.55, z \approx 0.90$) also varies on cooling in approximate proportion to $(1 - \frac{1}{T})^\gamma$ with $n \approx 1.9$ or 2.0 (assuming that internal stresses remain constant on cooling, which may cause an error of ca 0.3 in the power-law exponent). This is similar to the variation of $\lambda_S$ on cooling in the corresponding titanomagneteite.

(vii) Our results support the hypothesis that it is common for coercivity to be magnetostrictively controlled by internal stresses in the highly oxidized titanomaghemites typical of oceanic basalts older than ca 10 Myr, helping preserve the oceanic magnetic anomaly pattern. To test this hypothesis further, we suggest more extensive observation of whether $H_C J_S$ of such basalts does commonly vary in approximate proportion to $(1 - \frac{1}{T})^\gamma$ with $n$ near 1.9 or 2.0, on cooling to 120 K.

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