Geomagnetic Paleointensities by the Thellier's Method From Submarine Pillow Basalts: Effects of Seafloor Weathering

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Measurements of geomagnetic paleointensity using the Thellier's double-heating method in vacuum have been made on 10 specimens of submarine pillow basalt obtained from 75 fragments dredged from localities 700,000 years old or younger. In the magnetic minerals, the titanium/iron ratio parameter x and the cation deficiency (oxidation) parameter z were determined by X-ray diffraction and Curie temperature measurement. Fresh material (z = 0) provided excellent results: most of the natural remnant magnetization (NRM) could be thermally demagnetized before the magnetic minerals became altered, and the NRM-TRM lines were straight and well constrained, and geologically reasonable paleointensities were obtained. Somewhat oxidized material (z = 0.2) also provided apparently valid paleointensities: values were similar to those from fresh specimens cut from the same fragments, although only half or less of the NRM could be thermally demagnetized before alteration of the magnetic minerals. More highly oxidized material (z = 0.6) gave a result seriously in error: the paleointensity value is much too low, because of continuous disproportionation of titanomagnetite during the heating experiments and because seafloor weathering had decreased the NRM intensity. From limited published data, the extent of oxidation of titanomagnetite to cation deficient titanomagnetite in pillow basalt exposed on the seafloor appears to be approximately z = 0.3 at 0.2-0.5 m.y., z = 0.6 at 1 m.y., and z = 0.8-1.0 at 10-100 m.y. This implies that valid paleointensities can be obtained from exposed submarine basalt, but only if the basalt is younger than a few hundred thousand years. Equally good paleointensities were obtained from strongly magnetized (H-type) basalt and moderately magnetized (L-type) basalt. The degree of low-temperature oxidation of cubic iron-titanium oxides in submarine basalts correlates very well with the diminution of amplitude of linear magnetic anomalies when both are compared as a function of crustal age. Systematic radial variation of Curie temperature is a primary feature of submarine basalt pillows, so that estimation of the oxidation parameter z from the Curie temperature alone by assuming a value for x can be in error. Reasonably precise and self-consistent values of both x and z can be obtained if both the cubic cell dimension and the Curie temperature of the cubic oxide are measured.

INTRODUCTION

This paper presents and discusses the results of geomagnetic paleointensity measurements made by the Thellier's double heating method [Thellier and Thellier, 1959] using dredged fragments of submarine pillow basalt. We determined paleointensities from 10 specimens cut from 75 pillow fragments; the fragments were obtained from the Juan de Fuca Ridge, the East Pacific Rise, the Costa Rica and Galapagos Riffs, and the central Indian Ocean. All the samples had been dredged from very near the centers of the central magnetic anomalies over the respective spreading centers and hence are probably less than 100,000 years old, except for the Juan de Fuca sample which was obtained from the edge of the central anomaly and may be as old as 600,000-700,000 years. Our objectives were to find whether accurate paleointensities could be obtained from relatively fresh submarine pillow basalt and to assess the effect of low-temperature oxidation of titanomagnetite in the basalts on the paleointensity determinations.

Kono [1971] has summarized published paleointensity deter-
intensity of magnetization of the seafloor [Klitgord et al., 1975].

It is well known that the amplitudes of linear marine magnetic anomalies diminish with increasing distance from the actively spreading ridge, i.e., with increasing age of the magnetized rocks. In general, the amplitudes measured at the sea surface diminish to about one-third of that of the central anomaly over distances corresponding to a few million years [for example, see Klitgord et al., 1975]. Prérot and Grommé [1975] have shown that the geomagnetic field has maintained a nearly constant average intensity during that time, so that the broad change in anomaly amplitude cannot be due to very long period variation in geomagnetic intensity. Intensities of natural remanent magnetization (NRM) of dredged basalt samples have been found to decrease with increasing age [Carmichael, 1970; Irving et al., 1970a]. Prérot and Grommé [1975] have found that when all available data are averaged, the NRM decrease in dredged basalts parallels the decrease in anomaly amplitude; the ultimate NRM amounts to about one-third of the initial average value. Irving et al. [1970a] attributed this decrease in NRM intensity to low-temperature oxidation of titanomagnetite in the basalts by a combination of contact with seawater and exposure to somewhat elevated temperature in the volcanic zone at the spreading center. In a detailed study of one dredged pillow fragment, Marshall and Cox [1972] showed that sea-floor weathering oxidizes titanomagnetite to the cation-deficient spinel titanomaghemite, and that although the NRM direction was unaffected, the intensity of NRM diminished by 40%. The results of Marshall and Cox tend to confirm the mechanism suggested by Irving et al. [1970a], though without requiring elevated temperatures.

In an extensive investigation, Klitgord et al. [1975] have calculated the apparent crustal magnetizations, assuming a 0.5-km layer thickness, by inverting near-bottom (deep-tow) magnetic profiles taken across or near six different spreading ridges in the eastern Pacific. They find a rapid initial decrease of magnetization outward from the spreading center, amounting to roughly 50% in 0.5 m.y., and a more gradual decrease from there out to 6 m.y. Magnetizations at the spreading centers are from four to six times greater than magnetizations in 4-m.y.-old crust. Klitgord et al. [1975] attribute this decrease entirely to sea-floor weathering of pillow basalt, and explain the initially rapid rate by oxidation of the outer (variolitic) zones of the lava pillows, which were shown by Marshall and Cox [1971a] to be the most strongly magnetized before weathering, if the diameters of the pillows are sufficiently large. The most recent of these kinds of data have come from the Mid-Atlantic Ridge at about 37°N latitude (including the Famous area). Measuring NRM in basalt samples recovered by dredge and submersible, Johnson and Atwater [1977] showed that the intensity decreased by 50% at a crustal age of approximately 0.2 m.y., and that the total decrease was a factor of about 6 and had occurred when the crust aged to 1.5 m.y. In analyzing near-bottom magnetic profiles in the same area, Macdonald [1977] found similar total decreases in magnetization. Comparing these results, there seems to be some indication that the rate of decrease of NRM intensity is greater for the Mid-Atlantic Ridge than for spreading ridges in the eastern Pacific, though this could result from comparing magnetic anomaly analyses with direct measurements in sea-bottom basalts.

A similar, but quantitatively twice as great, decrease in NRM intensity has been observed in the large number of basalt samples that have been obtained from the Mid-Atlantic Ridge at 45°N. Here the intensity of NRM decreases by a factor of 10 within 10 km of the ridge axis and maintains a roughly constant value from there outward [Irving et al., 1970b; Carmichael, 1970]. The abruptness of this decrease was discussed by Irving [1970], who contrasted it with the smaller decrease in anomaly amplitude away from fast-spreading ridges such as the East Pacific Rise, and suggested that at slow-spreading ridges such as the Mid-Atlantic the basalts remain at somewhat elevated temperatures near the eruptive centers for relatively longer times, thus accelerating the rate of oxidation of titanomagnetite. Marshall and Cox [1972] concluded that oxidation due to sea-floor weathering could not account for all of the tenfold decrease in NRM away from the Mid-Atlantic Ridge.

All other factors remaining equal, the intensity of NRM in basalt depends on the spontaneous magnetization (measured as the induced magnetization in a saturating field) of the ferrimagnetic minerals [Marshall and Cox, 1972]. The variation of spontaneous magnetization with oxidation depends critically on the cation distribution and detailed mechanism of oxidation of titanomagnetite. An experimental study of the formation of titanomaghemite by low-temperature oxidation has been reported by Readman and O'Reilly [1972] who show that for compositions of titanomagnetite typical of basalts, the spontaneous magnetization decreases with oxidation. The amount of decrease depends strongly on the proportion of ulvospinel in the titanomagnetite, however, and it appears that the oxidation must be more than 80% complete to produce the fivefold decrease in spontaneous magnetization.

Oxidation of titanomagnetite may be roughly indicated by decreases in the FeO/Fe₂O₃ ratios in the bulk-rock analyses, and may be estimated from the Curie temperatures of the rocks because the Curie temperature rises with progressive low-temperature oxidation [Readman and O'Reilly, 1972]. In the case of the Mid-Atlantic Ridge samples, decrease in the FeO/Fe₂O₃ ratio [Irving et al., 1970b] and increase in Curie temperature [Carmichael, 1970] both occur with increasing distance from the ridge axis, but these changes are somewhat more gradual than the decrease in NRM intensity. This suggests that some other factor in addition to oxidation may be responsible for the tenfold NRM decrease observed at the Mid-Atlantic Ridge at 45°N latitude.

This possibility was anticipated by Carmichael [1970], who sought an explanation by considering variations in the intensity of the earth's magnetic field. Carmichael performed paleointensity experiments on the dredged samples, and found that the two samples from the ridge axis, which also had the highest NRM intensities, acquired their TRM in a field approximately 2.4 times stronger than the present field at the sample site. These results were subsequently confirmed by Ade-Hall et al. [1973], who, using a drill operating on the seafloor, obtained six cores of pillow basalt from the median valley of the Mid-Atlantic Ridge in the same area from which the dredged samples were obtained. Ade-Hall and his coworkers obtained paleointensities from 1.3 to 2.9 times the present field at the site. The paleointensities for median valley samples determined by Carmichael [1970] and Ade-Hall et al. [1973] are remarkably high, but not unprecedented. The highest published value obtained by the Thellier's method reported in the summary by Kono [1971] is 3.1 times the present field, and of the remaining 33 determinations, the highest is 2.3 times the present field.

All paleointensity methods depend on reproducing faithfully in the laboratory, in a known magnetic field, the process by which the rock became magnetized in nature. The most
common method is to heat and cool igneous rocks in a known field, giving them a TRM, which is then compared to the intensity of NRM to obtain the ancient field strength. For the comparison to be meaningful, the NRM must be natural TRM, unaltered by later geological processes, and TRM of the rock must be proportional to the field strength in which it cools. Several attributes of submarine pillow basalt make it potentially useful for this purpose. The pillow form indicates rapid cooling from melt temperature to seafloor temperature, and if the fragments are dredged from very young seafloor there is little likelihood of their having been buried and reheated. The low observed Curie temperatures (150°–350°C in general) mean that the TRM was acquired at temperatures lower than those at which deuteric subsolids oxidation of titanomagnetite is likely to have occurred [Grommé et al., 1969]. The size of titanomagnetite grains in submarine pillow basalt is very small, ranging from a few hundred angstroms to about 10 μm [Carmichael, 1970; S. E. Haggerty in Brooke et al., 1970; Marshall and Cox, 1971a; Evans and Wayman, 1972; Ryall and Ade-Hall, 1975a; Wayman and Evans, 1977]. The smallest visible grains are equant, but larger grains are usually skeletal or dendritic. The magnetic domain structure in simply shaped titanomagnetite grains and its dependence on grain size and elongation have recently been estimated on theoretical grounds by Butler and Banerjee [1975]. For equant grains of titanomagnetite containing 60 mol % of ulvöspinel in solid solution (typical of submarine basalts), Butler and Banerjee estimate the grain diameter for the transition from superparamagnetic behavior to single-domain structure to be about 0.08 μm, and the diameter for the transition from single-domain to two-domain structure to be about 0.2 μm. These critical diameters are not greatly dependent on titanium content, and the superparamagnetic-single-domain transition diameter is only slightly dependent on grain shape, but Butler and Banerjee show that elongate grains have markedly higher critical diameters for the single-domain to two-domain transition; specifically, for an elongation of 2.5 this critical diameter is about 1 μm. Thus a large proportion of the NRM carrier in submarine pillow basalts appears to have single-domain or pseudo-single-domain magnetic structure, as predicted by Marshall and Cox [1971a] and Evans and Wayman [1972]. Hence on general grounds it seems that fresh submarine pillow basalt would obey the additivity rule of partial TRM's and that the TRM would be closely proportional to the field present during cooling [Stacey and Banerjee, 1974; Levi, 1975].

The serious problem with determining paleointensities from submarine basalts, which is the main point of this paper, is the fact that low-temperature oxidation of titanomagnetite to titanomaghemite causes the NRM no longer to be natural TRM [Hall, 1977]. As indicated above, the intensity is diminished, and furthermore the blocking temperature distribution may increase and change in shape. An example of this problem occurs in the work of Carmichael [1970] on the Mid-Atlantic Rift rocks. In addition to the results mentioned above, Carmichael determined paleointensities from samples dredged up to 135 km from the ridge axis, having probable ages up to 14 m.y. The older samples nearly all gave paleointensities less than half the present field. It seems certain that this is due to titanomaghemitization rather than to a long-term change in geomagnetic field intensity.

The paleointensity determinations by Carmichael [1970] and Ade-Hall et al. [1973] were done using modifications of the method of van Zijl et al. [1962] in which a.f. demagnetization curves of NRM and total artificial TRM are compared. Ade-Hall et al. [1973] tested the method using a historically erupted Icelandic basalt, and Carmichael [1970] compared the results of this method for one specimen with the results of the Thellier's double-heating method; in both cases the comparisons were satisfactory. Ozima et al. [1968] have performed paleointensity determinations using the Thellier's method on five dredged fragments of basalt from the Pacific Ocean, and obtained values of 0.2–1.7 times the present field. The ages of these rocks ranged from 40 to 90 m.y., and Ade-Hall et al. [1973] pointed out that all of the samples but one contained titanomaghemite and that the reliability of the results cannot be judged from the published data.

Three commonly used methods of determining paleointensities, including the two mentioned above, were compared using the same rocks by Coe and Grommé [1973], who concluded that despite the additional labor entailed, the Thellier's method offers a significant advantage because NRM/TRM ratios can be obtained before the rocks are heated sufficiently to cause alteration of the magnetic minerals. Although submarine basalts generally have low Curie temperatures, fresh titanomagnetite is extremely vulnerable to oxidation [Verhoogen, 1962], and titanomaghemite is metastable and inverts promptly to a mixture of magnetite and other oxides on moderate heating [Ozima and Ozima, 1971], so that the advantage of the Thellier's method is likely to be important for these rocks.

The most recent attempt to determine paleointensities from submarine lavas using the Thellier's method is that of Dunlop and Hale [1976], who used DSDP samples from holes 332B and 335 of leg 37, west of the Mid-Atlantic Ridge. The ages of the rocks are about 3.5 and 10–17 m.y., respectively, and of the five samples used by Dunlop and Hale, four gave low apparent paleointensities, between 0.35 and 0.10 oe, while the fifth gave a more normal value of 0.45 oe. Because of the generally low quality of the NRM-TRM data they obtained, Dunlop and Hale [1976] did not interpret their results as representing true values of the geomagnetic intensity, but emphasized the difficulty of working with basalts that have such low Curie temperatures, many of which show irreversible alteration of magnetic properties on heating above 200°C. Although Dunlop and Hale did not discuss the possibility of the existence of titanomaghemite in their samples, it may be inferred to have been present from their description of the irreversibility of many of the thermomagnetic curves. Carmichael [1977] also investigated samples of basalt from DSDP leg 37, and concluded that titanomaghemite was present in nearly all of them and that as a result, reliable paleointensities could not be obtained. We will show in this paper that basalt containing titanomaghemite, formed by low temperature oxidation of originally stoichiometric titanomagnetite, will give spuriously low paleointensities even when the Thellier's method is used, but that unaltered basalts give excellent results.

**Samples and Experimental Methods**

The samples used in this study were cored from small pillow basalt fragments dredged from oceanic rises; the locations of the dredge sites are given in Table 1. The specimen numbering convention is illustrated by the following hypothetical example: 93B-2:11 AE, where 93 is the number of the dredge haul, B indicates a second fragment from the haul, -2 indicates a second core cut from the fragment, 11 is the distance of the specimen from the outer surface of the pillow in cm., and AE means the specimen was cut from the altered or weathered edge of the fragment (corresponding to a primary
TABLE 1. Locations of Dredged Pillow Basalt Fragments

<table>
<thead>
<tr>
<th>Site</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth, m</th>
<th>( F_s )</th>
<th>( F_{o} )</th>
<th>( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 Juan de Fuca Rise</td>
<td>46.1°N</td>
<td>130.0°W</td>
<td>2400–2700</td>
<td>0.542</td>
<td>0.551</td>
<td>9</td>
</tr>
<tr>
<td>26 East Pacific Rise (Orozco Fracture Zone)</td>
<td>15.3°N</td>
<td>104.6°W</td>
<td>2900–3300</td>
<td>0.407</td>
<td>0.379</td>
<td>12</td>
</tr>
<tr>
<td>7 Costa Rica Rift</td>
<td>3.2°N</td>
<td>83.0°W</td>
<td>2542</td>
<td>0.350</td>
<td>0.346</td>
<td>10</td>
</tr>
<tr>
<td>17 Galapagos Rift</td>
<td>0.8°N</td>
<td>86.1°W</td>
<td>2412</td>
<td>0.340</td>
<td>0.344</td>
<td>9</td>
</tr>
<tr>
<td>93 Central Indian Ocean</td>
<td>12.4°S</td>
<td>65.8°E</td>
<td>3500–3900</td>
<td>0.388</td>
<td>0.367</td>
<td>8(93), 14(93B)</td>
</tr>
<tr>
<td>104 Central Indian Ocean</td>
<td>19.8°S</td>
<td>66.1°E</td>
<td>2800</td>
<td>0.396</td>
<td>0.399</td>
<td>17</td>
</tr>
</tbody>
</table>

Symbols: \( F_s \), present total field strength at site (oe); \( F_{o} \), total field at site corresponding to geocentric axial dipole with moment = \( 8.9 \times 10^{25} \) G cm³; \( r \), estimated origin radius of pillow (cm).

fracture). For most of the pillow fragments, on which at least some of the glassy crust remained, the outer surface is very nearly the same as the original cooling surface. An example of how the pillow fragments were sampled is shown in Figure 1 of Marshall and Cox [1972].

Two of the dredge hauls (93 and 104) were obtained from the central rift zone of the central Indian Ocean Ridge [Engel and Fisher, 1969; Marshall and Cox, 1971a]. Dredge sites 7 and 17 were near the middle of the central magnetic anomaly on the Costa Rica and Galapagos rift zones, respectively [Anderson et al., 1975]. Site 26 was located at the intersection of the East Pacific Rise and the Orozco Fracture Zone, well within the central magnetic anomaly (R. N. Anderson, personal communication, 1973). Site 12 was located 20 km west of the axis of the Juan de Fuca Ridge near the edge of the central magnetic anomaly [Marshall and Cox, 1971a]. No direct age determinations have been made on these rocks, but the ages may be estimated from their locations: fragment 12 is probably 600,000–700,000 years old, and all the other fragments are probably of the order of 50,000 years old or less.

The fragments vary in their degree of seafloor weathering. The two fragments from dredge haul 93 show no visible sign of weathering except a very thin (~0.1 mm) coating of yellow-gray to red-brown clay on most of their surfaces. Although fragment 104B appears almost as fresh, thin section examination shows that clay fills the vesicles and occurs as a patchy alteration of the groundmass within several mm of the surface of the fragment. Fragment 17D is slightly more weathered and has, in addition to a 1 to 2-mm thick weathered rim, 0.5-mm thick patches of manganese oxide and 0.1-mm thick patches of palagonite in its glassy crust. The fragments from the remaining three dredge hauls (7, 12, and 26) are considerably more weathered: 0.1–2 mm of manganese oxide and palagonite encrust the glass, and the weathered rims are 1 to 2 cm thick.

Detailed studies of the magnetic properties of these pillow fragments have been made, and most of the results have been published. Experiments on the artificial production of chemical remanent magnetization (CRM) in fragment 12 and the Indian Ocean samples were described by Marshall and Cox [1971b]. The petrography and Curie temperatures, and the variations in NRM intensity, susceptibility, and saturation magnetization have been reported by Marshall and Cox [1971a] for fragments 12, 93, and 104. The changes in the magnetic properties resulting from weathering of fragments 12 and 26 were investigated by Marshall and Cox [1972]. For fragments 7 and 17, the NRM intensities, susceptibilities, Curie temperatures, saturation magnetization, and preliminary values of the paleointensities have been reported in Anderson et al. [1975].

Submarine basalt pillows were classified by Marshall and Cox [1971a] into two types, H and L, primarily by their intensity of NRM. When fresh, H-type pillows have NRM intensities in their interiors around 0.03 emu/cm³ or more, while L-type pillows have interior NRM's around 0.01 emu/cm³. A better intrinsic way of making this distinction is to use the saturation magnetization (\( J_s \)), and Anderson et al. [1975] have shown that NRM intensity, susceptibility, and \( J_s \) are all proportional to the volume proportion of titanomagnetite in pillow fragments from the localities described above. H-type pillows have \( J_s \) between 0.6 and 1.0 emu/g, and L-type pillows have \( J_s \) between 0.1 and 0.5 emu/g, but from the data summarized in Anderson et al. [1975], \( J_s \) appears to be gradational and the distinction at \( J_s = 0.5 \) or 0.6 emu/g may be arbitrary. Nevertheless, on and around the Galapagos spreading center this difference in titanomagnetite content appears to be at least partly responsible for large regional differences in linear magnetic anomaly amplitudes. Anderson et al. [1975] have shown that these differences are well correlated with iron and titanium content of the basalts, that is, the H-type pillows have just twice the TiO₂ content of L-type pillows, and about 1.5 times the iron content calculated as FeO. Anderson et al. [1975] account for these and other geochemical differences as resulting from the crustal melting anomaly represented by the Galapagos Islands [see also Vogt and Boer, 1976], and it appears likely that many of the other reported occurrences of such strongly magnetized submarine basalt may have a similar cause, as has recently been shown for the Juan de Fuca Ridge by Vogt and Byerly [1976]. In fact, as we will show below, when the crustal magnetizations along deep-sea magnetic profiles reported by Kligord et al. [1975] are converted to a common geomagnetic latitude, rock generated at the Galapagos spreading center and the Juan de Fuca Ridge is seen to be twice as strongly magnetized as rock generated at the East Pacific Rise, the Pacific-Antarctic Ridge, the Costa Rica Rift, and the Gorda Rise, and the difference persists out to a crustal age of at least 5 m.y. This longevity of relative magnetization intensities is strong evidence supporting the conclusion of Anderson et al. [1975] that strong magnetization can be the result of initially high titanium and iron content in the basaltic rocks, and suggests to us that this geochemical difference characterizes the entire part of crustal layer 2 that generates the marine magnetic anomalies [Blakely, 1976; Butler et al., 1976] rather than just the pillow basalt.

We have discussed H and L types of pillows at length because H types have very large NRM intensities, up to 0.09 emu/cm³. Stacey and Banerjee [1974] have estimated that in the case of an infinite planar body of rock cooling in an external field \( H = 0.5 \) oe oblique to the plane (say 45°) the self-demagnetizing field of the bulk rock will cause the direction of TRM to be appreciably deflected from the direction of \( H \) if the intensity of TRM exceeds about 0.002 emu/cm³. It can be shown that if the TRM blocking temperature distribution is as broad as the temperature range through which \( J_s \) and the susceptibility increase below the Curie temperature, partial
TRM's for lower blocking temperatures should show greater deflections. Hence if this effect is important, progressive change in partial NRM direction should be observed as specimens are progressively thermally demagnetized in paleointensity determinations. We looked for but did not observe this effect in the experiments to be described below, but the effect depends on the shape of the body of basalt as it cools in nature, and it is as reasonable to suppose that equant basalt pillows cool individually as that they cool simultaneously in large numbers arranged in an extensive sheet.

For the paleointensity experiments the samples were ring-shaped wafers, 2.5 cm in diameter and 1 cm thick, with a 0.6-cm diameter axial hole. The small cores obtained from the centers of the wafers were used for initial Curie temperature measurements. After completion of the paleointensity experiments additional small cores were cut from the wafers for a second set of Curie temperature measurements. Ten such samples were taken from seven pillow fragments dredged at the six sites. Six were taken in pairs from each of three fragments, one of each pair from the altered (weathered) margin of a fragment adjacent to a primary radial fracture and the other from the fresher interior. The remaining four samples were taken from the fresh interiors of four pillow fragments that were only slightly weathered.

The paleointensity measurements were done according to the Thellier's original method, with an applied field of 0.4 oe directed along the wafer axes and in opposite directions during each of the paired heatings; the specimens were heated in a vacuum of approximately $10^{-6}$ torr. The reason for using the Thellier's original method, rather than the modification due to R. S. Coe [Coe and Grommé, 1973] in which the specimens are heated and cooled alternately in zero field and a known field, was to avoid the necessity of measuring very small magnetic moments. A slight disadvantage of the Thellier's original method may be that the change of NRM, rather than being observed directly after the first of each of the paired heatings, is obtained by calculation after both heatings of a pair are completed.

Saturation magnetizations and Curie temperatures were measured using an automatic recording balance in which the specimens were heated and cooled at 10°C per minute in a vacuum of less than $10^{-4}$ torr. Saturation magnetizations were obtained from magnetization curves in fields from 0 to 8000 oe, and were calculated so as to eliminate the contribution made by paramagnetic silicates to the induced magnetization. Curie temperatures were measured using the graphical convention of Grommé et al. [1969] and Readman and O'Reilly [1972]. In order to compare the thermal decay of NRM with the temperature dependence of saturation magnetization, intensities of NRM in some samples were measured between room temperature and the Curie point by heating the samples in air in a nonmagnetic furnace beneath an astatic magnetometer; the method and apparatus have been described by Marshall and Cox [1971]. Weak-field susceptibilities were measured at 1000 Hz with a commercial bridge at room temperature.

Magnetic concentrates were obtained by hand crushing and grinding under acetone, and using a hand magnet for separation. These specimens were cut separately from the pillow fragments at locations adjacent to the specimens used for the paleointensity experiments. Cubic cell dimensions were obtained by X-ray diffraction from the magnetic concentrates, using the (311), (400), (333), and (440) reflections from CuKa radiation and a spinel internal standard. Cell dimensions for the two specimens from fragment 12 were reported by Marshall and Cox [1972]. Fragment 93 was too fine grained for a clean magnetic separate to be made, but from the others it was possible to calculate cell dimensions with standard deviations ranging from 0.2 to 0.01%.

In this paper the compositions of titanomagnetites and titanomaghemites will be described in the usual way with the parameters $x$ and $z$. The Ti/Fe ratio is indicated by $x$, which is defined as the mole fraction of ulvöspinel in stoichiometric titanomagnetite, $Fe_{x}Ti_{1-x}O_{4}$, with $0 \leq x \leq 1$. The degree of oxidation to cation-deficient or nonstoichiometric titanomaghemite is indicated by $z$, the mole fraction of Fe$^{+}$ oxidized to Fe$^{+++}$ as defined by the reaction

$$Fe^{++} + \frac{1}{2}zO \rightarrow zFe^{+++} + (1 - z)Fe^{++} + \frac{1}{2}zO$$

where $0 \leq z \leq 1$ [O'Reilly and Banerjee, 1967].

For the calculation of $x$ for stoichiometric titanomagnetites we have used only the Curie temperature and cubic cell dimension data obtained from synthetic materials by Akimoto et al. [1957] and Osima and Larson [1970]. Although other similar data have been published by other authors, these are the only cases where Curie temperatures and cell dimensions were determined from the same samples. Between $x = 0.35$ and $x = 0.70$ both quantities vary nearly linearly, and we have computed least-squares linear regressions for this interval as follows:

$$x = 0.744 - 0.00119T_c$$

$$x = 6.477a - 54.30$$

where $T_c$ is the Curie temperature in degrees Celsius and $a$ is the cubic cell edge in angstroms.

**Curie Temperature Variation Within and Among Single Pillows**

The variations of Curie temperature ($T_c$) with distance inward from the original cooling surfaces are illustrated in Figure 1 for three pillow fragments. The interiors of two of these (93B and 104B) are fresh and have undergone no low-temperature oxidation (M. Marshall, unpublished data, 1971), so that the variation in $T_c$ is considered to be a primary feature. The uniform values of $T_c$ between 180° and 200°C in the interiors of these pillows appear to be fairly typical of fresh submarine pillow basalt [Carmichael, 1970; Ade-Hall et al., 1973; Ryall and Ade-Hall, 1975a]. Evidence of high-temperature deuteric oxidation is seen at 11 and 12 cm in fragment 93B, where $T_c$ apparently has values distributed between 250° and 550°C [Grommé et al., 1969] and red hematitic staining is seen on the primary fracture surfaces. Of considerable interest are the higher values of $T_c$ at distances between 1 and 5 cm from the

![Fig. 1. Curie temperature variation in three basalt pillow fragments as a function of radial depth below original outer surface of pillow. Fragments 93B and 104B are fresh; fragment 12 is weathered.](image-url)
original surface. Maximum values (250°-300°C) occur in particular petrographic zones described by Marshall and Cox [1971a]: zone 2, the variolitic layer at 1–1.5 cm and zone 3, fans and sheaves of silicate minerals at 1.5–3 cm. As the crystal sizes increase toward the uniform centers of the pillow fragments, the Curie temperatures decrease to uniform values. There is an indication in Figure 1 that \( T_c \) also decreases outward toward zone 1 (glassy crust, 0–1 cm) from the maximum seen in zones 2 and 3. Similar data have been published by Ryall and Ade-Hall [1975a] from four pillow samples dredged from within and just outside the median valley of the Mid-Atlantic Ridge at 45°N. The variation of \( T_c \) illustrated by Ryall and Ade-Hall is qualitatively similar to that shown in Figure 1; maximum values occur at around 1 cm inward from the margins and minimum values occur at depths between 5 and 8 cm, the variation is of the same magnitude, but the outermost decrease toward zone 1 was not observed.

In fragment 12 (Figure 1) the effect of low-temperature oxidation has enhanced the initial variation of \( T_c \): specimens between 0 and 3 cm and at 9 cm are from the weathered rim, and most of the remainder are from the much less altered interior. At a depth of 9 cm, oxidation has raised \( T_c \) from 170° to 240°C in a sample from the altered edge adjacent to a radial fracture [Marshall and Cox, 1972]. We note, however, that the outward decrease in \( T_c \) toward or in the glassy crust has apparently been preserved in this fragment despite the weathering.

Three possible explanations exist for the higher Curie temperatures of the oxides in the outer parts of these pillow fragments: (1) cation deficiency due to weathering, (2) cation deficiency preserved from magmatic temperatures due to quenching by seawater, and (3) primary variation in Ti/Fe ratio. The first explanation was adopted by Ryall and Ade-Hall [1975a], who assumed that the lowest \( T_c \) they measured (150°C) represented the only stoichiometric titanomagnetite, having \( x = 0.6 \), and that all other higher Curie temperatures indicated titanomaghemite. For the two younger pillow fragments they studied, both probably less than 30,000 years old, \( z \) values were estimated from the Curie temperatures alone to range from 0 to 0.55. A similar assumption was made by Grommé and Mankinen [1976] in a study of Oligocene to Mioocene basalt cored by the DSDP on the Nazca plate. Values of \( z \) ranging from 0.10 to 0.95 were estimated from the Curie temperatures assuming \( x = 0.65 \) for all of the 24 specimens studied, using the experimental data of Readman and O'Reilly [1972]. Cell dimension measurements of the titanomaghemite in five of the specimens confirmed these estimates closely, but we are still doubtful about the validity of assuming constant \( x \) for a large suite of specimens.

The second explanation arises from the experimental work of Hauptman [1974], who performed controlled oxygen-fugacity experiments at high temperature on artificial samples of titanomagnetite with \( x = 0.60 \). The samples were quenched from 1275°C after equilibration with various gas mixtures. Hauptman sought to test the degree of nonstoichiometry attainable at high temperature and to determine its effect on the Curie temperature. A different oxidation parameter \( \gamma \) was used by Hauptman, where \( z = 2y/(1 - x) \), and from his experiments he found that the variation of Curie temperature with oxidation, for \( x = 0.60 \), was \( T_c(\gamma) = 149 + 89\gamma \), in degrees Celsius, for \( 0 \leq \gamma \leq 0.06 \), or \( T_c(z) = 149 + 71z \), for \( 0 \leq z \leq 0.08 \). Hauptman noted that this dependence of \( T_c \) on oxidation was almost 10 times greater than had been observed in the low-temperature experiments of Readman and O'Reilly [1972], and ruling out cation distribution and lattice shrinkage as inadequate, he concluded that special but unspecified imperfections must be the cause. He predicted that this phenomenon of high Curie temperatures might be observed in "geologically recent rapidly cooled submarine basalt" [Hauptman, 1974]. If cation deficiency is the cause of the higher Curie temperatures at the margins of submarine basalt pillows, then Hauptman's high-temperature oxidation mechanism is more attractive. For the two unaltered samples illustrated in Figure 1, if low-temperature oxidation were operative, the maximum \( z \) value at the margins would be of the order of 0.6 for fragment 104B and 0.45 for fragment 93B [Readman and O'Reilly, 1972]; these degrees of titanomaghemitization would cause irreversibility in the \( J_s - (T) \) curves obtained in vacuum [Ozima and Ozima, 1971; Grommé and Mankinen, 1976] but such irreversibility was not observed. Moreover, samples taken from these fragments adjacent to primary radial fractures, but at depths beneath the outer surface greater than 5 cm, have low Curie temperatures (less than 200°C) like those in the interiors, and it is improbable that weathering should have penetrated the outer parts of the pillows to depths of 4 or 5 cm while having no effect along these primary fractures. On the other hand, values of \( z = 0.16 \) for fragment 104B and 0.10 for fragment 93B are obtained if, to account for different initial compositions, initial values of 193°C and 195°C, respectively (interior values in Figure 1) are substituted for the constant 149°C in Hauptman's equation given above. These values of \( z \) would not cause irreversibility in \( J_s - (T) \) curves [Grommé and Mankinen, 1976]. We note that for fragment 104B a twofold extrapolation of Hauptman's data is required. The oxygen partial pressures in the experiments cited ranged from \( 10^{-8} \) to \( 10^{-6} \) atm [Hauptman, 1974], and the calculation for fragment 104B requires an oxygen partial pressure at the sea floor probably greater than \( 10^{-4} \) atm, but this is apparently reasonable considering the observations of Garner and Ford [1969] in the median valley of the Mid-Atlantic Ridge.

If the third mechanism, primary variation in the Ti/Fe ratio of the titanomagnetites with distance inward from the pillow margins, were responsible for the \( T_c \) variations, \( x \) in fragment 104B would increase from a minimum of 0.42 in zone 2 to a uniform value of 0.54 in the center, and the corresponding change in fragment 93B would be from \( x = 0.46 \) to \( x = 0.54 \). Because of the small size of the titanomagnetite grains, we have not attempted to measure the \( x \) values directly with a microprobe. The only evidence we have is from specimen 26:3 which contains stoichiometric titanomagnetite (\( x = 0.52 \), \( z = 0 \)) and presumably represents zone 3 of fragment 26. The variation of \( T_c \) with depth in fragment 26 is unknown, however. Hence the present evidence does not allow us to decide between primary Ti/Fe variation and quenched cation deficiency as the cause of the radial variation of Curie temperature, but weathering seems to be a doubtful cause.

This discussion raises the question of to what extent the Ti/Fe ratio in submarine basalt titanomagnetites may vary with time and place of eruption. It will be shown below that \( x \) at the time of crystallization seems to vary between 0.50 and 0.65 in general, but if oxidation is to be estimated from \( T_c \) alone, as has been done [Ryall and Ade-Hall, 1975a; Grommé and Mankinen, 1976] and will be done later in this paper, narrower limits on \( x \) are desirable. If the magnetic differences between H and L types of pillows are due to differences in Fe and Ti content of the rocks, then the fact that the proportional Ti increase in H-type pillows is greater than the Fe increase and also is the same as the \( J_s \) increase [Anderson et al., 1975] might
lead us to expect that Curie temperatures in the interiors of fresh H-type pillows would be lower than in L-type pillows. This is the case for the Galapagos spreading center samples: $T_c = 150°-165°C$ for H-type pillows and $T_c = 200°-215°C$ for L-type pillows, corresponding to $x = 0.59$ and 0.53, respectively. Conversely, for the H and L samples from the Indian Ocean (104B and 93B, respectively), Figure 1 shows that the interior Curie temperatures are the same for both, corresponding to $x = 0.54$. For the youngest Mid-Atlantic Ridge samples from within the median valley discussed by Ryall and Ade-Hall [1975a], the minimum $T_c$ of the H-type fragment (197, at 75 cm depth) is 150°C to give $x = 0.60$, but the minimum $T_c$ of the L-type fragment (56, at 5.5 cm depth) is 200°C to give $x = 0.54$, if both values represent stoichiometric magnetite. These values are the same as those for the Galapagos spreading center samples, suggesting that the $z$ values estimated by Ryall and Ade-Hall [1975a] may be too high for all their samples save sample 197. From this discussion and the data of Grommé and Mankinen [1976], it appears that primary Curie temperatures in submarine basaltic pillows can vary between 125° and 200° or even 300°C, depending on the source of the basalt and on the depth within the individual pillows. Corresponding $x$ values range from 0.63 to 0.42. Clearly, to estimate $z$ for basalt in any one submarine province, Curie temperature determinations must be augmented by at least some cell dimension measurements, and some vestige of the original glassy outer surface of the pillow fragment should be preserved so that distance from the pillow surface can be estimated.

**Graphical Determination of Iron-Titanium Ratio and Degree of Oxidation in Titanomagnetite**

A convenient way of representing the compositions of naturally occurring titanomagnetite and titanomaghemite is by plotting them on the ulvöspinel-magnetite-hematite-pseudobrookite quadrilateral of the FeO-TiO$_2$-Fe$_2$O$_3$ compositional triangle [Verhoogen, 1962]. This can be done if any two of the following are known: Ti/Fe ratio, cell dimension, and Curie temperature, provided that other elements such as Mg and Al are not present in the oxides. Because of the very small grain size, the Ti/Fe ratio in titanomagnetite in submarine basalt is difficult to measure, so that cell dimensions and Curie temperatures have generally been used [Carmichael, 1970; Ryall and Ade-Hall, 1975a; Grommé and Mankinen, 1976]. The basis for doing this is the experimental work of Readman and O'Reilly [1970, 1972], who produced titanomagnhemite with various values of $x$ and $z$ by oxidizing wet-ground synthetic titanomagnetite at temperatures between 200° and 300°C for times up to several hours. Readman and O'Reilly [1972] determined Curie temperatures and cell dimensions for the synthetic titanomaghemites, the compositions of which were well distributed over the quadrilateral, and illustrated contour diagrams for both parameters. We have recontoured the quadrilateral, using the data in Figures 1 and 3 of Readman and O'Reilly [1972] and also incorporating the data for stoichiometric titanomagnetite of Akimoto et al. [1957] and Ozima and Larson [1970]; these contours are shown in Figure 2a.
The utility of using the Readman and O'Reilly data for determining $x$ and $z$ of natural titanomagnetite can be illustrated by several examples. A diverse collection of six dredged or drilled submarine basalts, including the 'experimental Mo-tane' basalt EM-7, was studied by Ozima et al. [1974]. The samples ranged in age from <0.5 to 126 m.y. Ozima et al. determined $x$ and $z$ by wet-chemical analyses of magnetic concentrates from the samples, and also measured Curie temperatures and cell dimensions of the concentrates. In Figure 2b we have plotted the $x$ and $z$ values calculated by Ozima et al. [1974] from the chemical analyses, and also the $x$ and $z$ values for the same samples using the contours of Figure 2a. The result of using Curie temperatures and cell dimensions is to diminish the scatter in values of $x$ and to increase all the values of $z$ considerably. This may be attributed to the presence of silicate impurities in the magnetic concentrates, which would cause errors in the chemical analyses but would not affect measured cubic cell dimensions or Curie temperatures. Possibly fortuitously, five of the six compositions determined by cell dimension and Curie temperature fall on a straight line nearly parallel to a redox line (a line of constant $x$) and passing through the point $x = 0.60$ for $z = 0$.

Two more examples are illustrated in Figure 3a, both from basaltic rocks recovered in DSDP cores. Cell dimensions of magnetic separates and Curie temperatures of whole samples were obtained by Grommé and Mankinen [1976] from sites 319 (early Miocene) and 321 (late Eocene) of DSDP leg 34. The compositions of these samples, from the Nazca plate, surprisingly lie along the same near redox trend line that is shown in Figure 2b and the $z$ values are also similar to the replotted data of Ozima et al. [1974].

Microprobe analyses and cell dimension measurements were made by Ridley et al. [1974] for cubic iron-titanium oxides in three DSDP leg 6 basalts: two from site 54 (early Miocene, Paracel Vela Basin) and one from site 57 (late Oligocene, Caroline Ridge). The Curie temperatures are unknown, so the Ti/Fe ratio and the cell dimensions were used to plot the compositions in Figure 3a. The site 57 sample is apparently stoichiometric, and the site 54 samples are oxidized, which is in good agreement with the results of Ridley et al. [1974], who concluded that the site 54 samples were highly oxidized. The difference results because we have neglected the effect on the cell dimensions of the Al, Mg, and Mn that Ridley et al. reported in their microprobe analyses.

Two potential problems exist if cell dimension and Curie temperature data are used to estimate $x$ and $z$ in this way. The first is the presence of Mg and Al in solid solution in the titanomagnetite. Following Richards et al. [1973], we denote $\delta$ as the number of substituted ions per formula unit of titanomagnetite, that is, $\delta/3$ is the fraction of substituted cations per cation. From 31 microprobe analyses of optically homogeneous titanomagnetite in continental basaltic rocks published by Creer and Ibbetson [1970], we calculate $\delta_{Al} = 0.16 \pm 0.08$ (s.d.) and $\delta_{Mg} = 0.15 \pm 0.04$ (s.d.). From the three analyses of DSDP leg 6 basalt given by Ridley et al. [1974], the average values are $\delta_{Al} = 0.091$ and $\delta_{Mg} = 0.015$. Bence et al. [1975] have published microprobe analyses of titanomagnetite in seven submarine basalts from DSDP leg 15 (central Carribbean); average values calculated from their data are $\delta_{Al} = 0.130 \pm 0.037$ (s.d.) and $\delta_{Mg} = 0.037 \pm 0.020$ (s.d.). Thus from the limited data available, Al and Mg appear to be significant constituents of basaltic titanomagnetite, though less so in submarine basalts.

A study of synthetic titanomagnetite ($x = 0.6$) doped with Al and Mg has been made by Richards et al. [1973]. These authors used values of $\delta$ ranging from 0 to 0.25 for Al and Mg.
separately, and measured the variations of cell dimension, Curie temperature, and saturation magnetization with $\delta_{\text{Al}}$ and $\delta_{\text{Mg}}$. Both cell dimension and Curie temperature decrease with increasing $\delta$, and the effects due to $\delta_{\text{Al}}$ are much greater. For example, using $x = 0.6$ and the average values of $\delta$ calculated from the data of Creer and Ibbsen [1970], the effect of Al is to reduce $T_c$ from 205$^\circ$ to 150$^\circ$C, and $a$ from 8.485 to 8.459 $\AA$, and the effect of Mg is to reduce $T_c$ from 205$^\circ$ to 195$^\circ$C and $a$ from 8.485 to 8.477 $\AA$. A difficulty, however, in interpreting the experimental data of Richards et al. [1973] is that the values of $T_c$ and $a$ given by them for $\delta = 0$ correspond $x = 0.53$ and 0.70, respectively, according to the deterministic equations given above. Ignoring this discrepancy, another way to look at the problem is to assume that the effects on both cell dimensions and Curie temperatures due to Al and Mg are additive and to use the equations given by Richards et al. [1973] that describe their experimental results. Starting with $x = 0.6$, and using the average values of $\delta_{\text{Al}}$ and $\delta_{\text{Mg}}$ given above for submarine basalts in the equations of Richards et al., one calculates predicted values of $T_c$ and $a$ that, when plotted on the contours of Figure 2a (that is, falsely assuming $\delta = 0$), would give apparent values of $0.8 < x < 0.9$ and $0.5 < z < 0.6$.

As was shown above, such combinations of $T_c$ and $a$ are not seen in natural examples. Furthermore, as will be shown below, four of the eight specimens used in the present study have cell dimensions and Curie temperatures that place them on or very near the stoichiometric titanomagnetite-ulvöspinel join using the data of Figure 2a, which would be impossible if their titanomagnetite contained appreciable Al or Mg in solid solution. Richards et al. have argued in the opposite direction, using the microprobe analyses and Curie temperatures of titanomagnetics published by Creer and Ibbsen [1970]. Assuming that these data represent oxidized (cation-deficient) compositions, Richards et al. used their experimentally derived deterministic equation to calculate what the original (preoxidation) Curie temperatures would have been, and found for 20 examples an average value of $21^\circ$C. Seven of the 20 calculated Curie temperatures are never observed in natural basalt, no matter how fresh. From these discrepancies between the properties of synthetic and natural materials, it appears to us that the Al and Mg that is always seen in microprobe analyses of basaltic titanomagnetite must reside in submicroscopic spinellid intergrowths, rather than being in true solid solution. If this is so, then errors in determining $x$ and $z$ using $a$ and $T_c$ will not occur if the possible effects of Al and Mg are ignored. We note that Haggerty [1976, figure Hg-33] has published photomicrographs of exsolution lamellae of pleonaste in titanomagnetite (pleonaste is a solid solution between Mg Al$_2$O$_4$ and Fe Al$_2$O$_4$), although such features are absent in the electron micrographs of Evans and Wayman [1972] and Wayman and Evans [1977].

The second potential problem in estimating $x$ and $z$ arises because there are two sets of experimental data for the titanomagnete-titanomagnetite system, and they do not agree. An excellent illustration is shown in Figure 12 of Butler et al. [1976], where titanomagnetite with $x = 0.7$ determined by microprobe and Curie temperature $= 380^\circ$C would have $z = 0.4$ using the experimental data of Ozima and Sakamoto [1971] and $z = 0.9$ using the data of Readman and O'Reilly [1970, 1972]. In these experiments, both groups of workers produced artificial titanomagnetite by wet-grinding synthetic titanomagnete with various $x$ values to sizes below 1 $\mu$m and then oxidizing this material at temperatures below 300$^\circ$C. While Readman and O'Reilly were able to produce single-phase titanomagnete throughout most of the possible compositional field, Ozima and Sakamoto found that oxidation beyond $z = 0.3$ caused formation of more than one oxide phase. Readman and O'Reilly determined $z$ values from weight changes using a thermobalance, while Ozima and Sakamoto calculated $z$ from wet-chemical analyses. The evidence from differential thermogravimetry presented by Readman and O'Reilly [1970] seems persuasive that they did not produce multiple phases during their oxidation experiments. The single-phase data of Ozima and Sakamoto [1971] cover only a small fraction of the whole compositional field, but in this area their results differ from those of Readman and O'Reilly [1972] by a factor of two. Furthermore, of a set of 13 combined cell dimension and Curie temperature measurements of magnetic separates from submarine basalts (data from this paper and Grommé and Mankinen [1976]), seven lie outside the compositional field covered by Ozima and Sakamoto's single-phase experimental data, and of the remaining six, four cannot be reconciled with their data. Hence on grounds of experimental evidence and compatibility between Curie temperatures and cell dimensions of artificial and natural titanomagnetite, we consider that the results of Readman and O'Reilly [1972]

### TABLE 2. Magnetic Properties of Samples and Paleointensity Results

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$a$ ± s.e.</th>
<th>$x$</th>
<th>$z$</th>
<th>NRM $\times 10^3$</th>
<th>$X$</th>
<th>Type</th>
<th>$J_a/J_s$</th>
<th>$J_s$</th>
<th>$T_c$</th>
<th>$J_s'$</th>
<th>$T_s'$</th>
<th>$N$</th>
<th>$T_s$</th>
<th>$f$</th>
<th>$q$</th>
<th>$F_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:4</td>
<td>8.460 ± 0.001*</td>
<td>0.60</td>
<td>0.30</td>
<td>29.8</td>
<td>8.4</td>
<td>66</td>
<td>H</td>
<td>n.d.</td>
<td>0.78</td>
<td>187†</td>
<td>0.07</td>
<td>130</td>
<td>12</td>
<td>137</td>
<td>265</td>
<td>0.42</td>
</tr>
<tr>
<td>12:4–6 (AE)</td>
<td>8.434 ± 0.005*</td>
<td>0.71</td>
<td>0.62</td>
<td>22.1</td>
<td>4.3</td>
<td>95</td>
<td>L</td>
<td>n.d.</td>
<td>0.60</td>
<td>218†</td>
<td>0.90</td>
<td>340†</td>
<td>10</td>
<td>155</td>
<td>266</td>
<td>0.14</td>
</tr>
<tr>
<td>26:3</td>
<td>8.465 ± 0.007</td>
<td>0.52</td>
<td>0.02</td>
<td>8.6</td>
<td>2.2</td>
<td>95</td>
<td>L</td>
<td>0.48</td>
<td>0.21</td>
<td>219†</td>
<td>0.26</td>
<td>323</td>
<td>17</td>
<td>20</td>
<td>250</td>
<td>0.81</td>
</tr>
<tr>
<td>26:5–7 (AE)</td>
<td>8.449 ± 0.010</td>
<td>0.56</td>
<td>0.35</td>
<td>6.7</td>
<td>1.3</td>
<td>126</td>
<td>L</td>
<td>0.43</td>
<td>0.20</td>
<td>240†</td>
<td>0.26</td>
<td>312†</td>
<td>13</td>
<td>72</td>
<td>220</td>
<td>0.53</td>
</tr>
<tr>
<td>7D–2:3</td>
<td>8.466 ± 0.006</td>
<td>0.53</td>
<td>0.05</td>
<td>13.2</td>
<td>5.3</td>
<td>71</td>
<td>L</td>
<td>0.36</td>
<td>0.51</td>
<td>203</td>
<td>0.61</td>
<td>268</td>
<td>11</td>
<td>139</td>
<td>243</td>
<td>0.70</td>
</tr>
<tr>
<td>7D–2:8 (AE)</td>
<td>8.452 ± 0.014</td>
<td>0.54</td>
<td>0.28</td>
<td>10.5</td>
<td>3.8</td>
<td>80</td>
<td>L</td>
<td>0.37</td>
<td>0.43</td>
<td>238†</td>
<td>0.58</td>
<td>355†</td>
<td>11</td>
<td>142</td>
<td>250</td>
<td>0.33</td>
</tr>
<tr>
<td>17D–2:5</td>
<td>8.476 ± 0.005</td>
<td>0.59</td>
<td>0.00</td>
<td>76.2</td>
<td>12.0</td>
<td>187</td>
<td>H</td>
<td>0.40</td>
<td>1.00</td>
<td>156</td>
<td>1.23</td>
<td>200</td>
<td>18</td>
<td>83</td>
<td>279</td>
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<tr>
<td>93:3</td>
<td>n.d.</td>
<td>0.07</td>
<td>1.5</td>
<td>123</td>
<td>L</td>
<td>0.47</td>
<td>0.12</td>
<td>253</td>
<td>0.14</td>
<td>282</td>
<td>10</td>
<td>20</td>
<td>176</td>
<td>0.55</td>
<td>26.1</td>
<td>0.49</td>
</tr>
<tr>
<td>93B:5</td>
<td>n.d.</td>
<td>0.07</td>
<td>2.0</td>
<td>156</td>
<td>L</td>
<td>0.55</td>
<td>0.16</td>
<td>180</td>
<td>0.17</td>
<td>210</td>
<td>17</td>
<td>71</td>
<td>263</td>
<td>0.91</td>
<td>48.6</td>
<td>0.44</td>
</tr>
<tr>
<td>104B–2:11</td>
<td>8.463 ± 0.003</td>
<td>0.54</td>
<td>0.00</td>
<td>25.2</td>
<td>9.8</td>
<td>68</td>
<td>H</td>
<td>0.23</td>
<td>0.72</td>
<td>194</td>
<td>0.60</td>
<td>210</td>
<td>15</td>
<td>111</td>
<td>266</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Symbols: $a$, cubic cell edge (angstroms); $x$, mol percent of ulvöspinel; $z$, oxidation parameter; NRM, intensity ($10^{-3}$ emu/cm$^3$); $X$, volume susceptibility ($10^{-2}$); $Q$, NRM/$_{X}F$ (values from Table 1); Type, $H$ = high magnetization; and $L$ = low magnetization; $J_a/J_s$, ratio of IRM produced by 8000 oe to $J_s$; Saturation magnetization (emu/gm); $T_c$, Curie temperature (degrees Celsius); $J_s'$ and $T_s'$, values after completion of Thellier experiments; $N$, number of NRM-TRM points used to determine $F_a$; $T_a$ and $T_s$, temperature range of NRM-TRM points used to determine $F_a$ (degrees Celsius); $f$, fraction of total NRM used to determine $F_a$; $q$, quality factor [Coe et al., 1978]; $F_a$, calculated paleointensity (oersteds).

*Data from Marshall and Cox [1972].
†Disproportionates completely on heating above 350$^\circ$C.
‡Disproportionates slightly on heating above 350$^\circ$C.
shown in Figure 2a reasonably accurately represent naturally oxidized titanomagnetite.

Effects of Oxidation

Compositions of titanomagnetite and titanomaghemite in the pillow fragments used in this study are shown in Figure 3b; the measured cell dimensions and Curie temperatures as well as other magnetic properties are given in Table 2. Compositional data for fragments 93 and 93B are missing because the fine grain size and paucity of oxide grains in these samples made it impossible to obtain clean magnetic separates. For reference, the compositional trend during oxidation from Figures 2b and 3a is also shown in Figure 3b. As discussed above, the H-type fragments, with the exception of 104B, have lower Curie temperatures and hence higher values of \( \chi \) than the L-type fragments (see Table 2). The significance of this is hard to assess, because on one hand it seems unlikely that all but one of the six samples investigated by Ozima et al. [1974] are of H type. On the other hand all of the Nazca plate samples studied by Grommé and Mankin [1976] that have \( \chi \) less than 0.4 also have saturation magnetizations greater than 0.8 emu/g and hence are of H type; all these specimens originated at about the same latitude on the now-extinct Galapagos Rise. For the moment it appears that our supposition stated above may be correct: higher Ti (and Fe) content of the lava causes Ti/Fe ratios in primary titanomagnetite to be higher, and Curie temperatures thus to be lower, as well as causing a greater amount of titanomagnetite to crystallize [Anderson et al., 1975]. This only emphasizes the approximation underlying the estimation of \( z \) from Curie temperature alone.

In keeping with their young age, the pillow fragments used in this study have lower \( z \) values than most of the other examples cited above: four of the eight specimens contain titanomagnetite that is stoichiometric or nearly so. The effect of seafloor weathering is clearly seen in Figure 3b; in the three fragments from which paired samples were taken, \( z \) is about 0.3 greater in the less fresh parts. The higher \( z \) values for fragment 12 are consistent with its probable greater age relative to the other fragments, and in general the \( z \) values in qualitative agreement with the visually apparent relative extent of weathering of all the pillow fragments.

In the diagrams of Figures 2 and 3, there are two limiting paths for the course of the low-temperature oxidation reaction: a line parallel to the base of the triangle, and a line radiating from near the FeO apex and passing through the original stoichiometric composition. The first limit represents no change in cation ratio, so that oxidation proceeds by diffusion of divalent Fe out of the original oxide lattice and topotactic combination with oxygen at the crystal surfaces [Colombo et al., 1965]; this is presumably accompanied by sufficient diffusion of Ti to maintain compositional uniformity. The second limit represents maximum loss of divalent Fe from the oxide grains. The slight upward slopes of the compositional trend lines in Figures 2b and 3a indicate that a small but real decrease in Fe/Ti ratio occurs during oxidation [Creer and Ibbetson, 1970; Marshall and Cox, 1972; Grommé and Mankin, 1976; Marshall, 1978]. This trend is confirmed by the three pairs of specimens illustrated in Figure 3b. The reality of Fe loss during oxidation means that when highly oxidized titanomaghemite is analyzed with an electron microprobe, the observed values of \( z \) may be as much as 0.1 higher than the original preoxidation composition.

It has been generally observed that among the effects of low-temperature oxidation on magnetic properties are reduction of the NRM and increase of \( T_c \) and intrinsic coercivity of NRM. These effects are somewhat masked in the data of Table 2, partly because for the three fragments for which comparisons are possible (12, 26, and 7D) the less-oxidized specimens were taken from within 3 or 4 cm of the original pillow cooling surface while the more-oxidized specimens were mostly taken from the original (prefracturing) interiors of the pillows, and also because the maximum difference in \( z \) for any pair is only about 0.3. In small basalt pillows such as these, \( J_c \) in fresh material increases inward from a low value at the cooling surface, and reaches a maximum only at a depth of about 5 cm [Marshall and Cox, 1971a; M. Marshall, unpublished data, 1971]. Hence the fact that \( J_c \) in the weathered and unweathered specimens from fragments 26 and 7D are now the same may be because \( J_c \) in the deeper (now weathered) parts was originally higher than \( J_c \) at 3 cm depth in unweathered material. For the L-type fragments (26 and 7D), in which the weak-field susceptibility \( \chi \) is largely independent of depth within the pillow [Marshall and Cox, 1971a], oxidation reduces \( \chi \) more than it does NRM, resulting in a net increase in the Koenigsberger ratio \( Q \). This phenomenon may result from the general increase in coercivity, as manifested by the increase in median destructive field (MDF) that results from low-temperature oxidation [Marshall, 1978; Johnson and Atwater, 1977; Johnson and Hall, 1978]. Increase in \( Q \) with oxidation is also observed in the H-type fragment (12), but we note that increase of \( Q \) with oxidation is not observed in H-type basalt from the Nazca plate [Grommé and Mankin, 1976] nor in the basalt at DSDP site 61 on the Pacific plate [Marshall, 1978]. Butler [1973] has pointed out that an increase in coercivity with oxidation is not necessarily expected on theoretical grounds, but Ryall et al. [1977] and Johnson and Hall [1978] have illustrated the physical changes in natural titanomagnetite that accompany low-temperature oxidation. Well-developed shrinkage cracks are visible at values of \( z \) around 0.3–0.6, and alteration and granulation of titanomaghemite become visible at values of \( z \) above about 0.6. Johnson and Hall cite this reduction in effective grain size as a possible cause of the increase in MDF.

Because of lack of sufficient material, MDF values were not determined for the specimens used in this study. We did, however, measure the ratios \( J_c/J_c \), where \( J_c \) is the isothermal remanent magnetization produced by a saturating direct field (in this case, 8000 oe). For single-domain grains whose coercivity is dominated by uniaxial shape anisotropy, the theoretical value of this ratio is 0.5 [Stacey and Banerjee, 1974], with higher values up to 0.8 indicating dominance of magnetocrystalline anisotropy in single-domain grains if \([111]\) are the axes of 'easy' magnetization, and values below about 0.1 indicate multi-domain magnetic structure. The observed ratios (Table 2) range from 0.23 to 0.55 with an average of 0.41, suggesting the predominance in these samples of uniaxial (elongate) single-domain titanomagnetite or titanomaghemite.

Thermal Dependence of NRM and Spontaneous Magnetization

A common difficulty in rock magnetism is to correlate properties of NRM with bulk magnetic properties measured in a strong field (such as \( J_c \) and \( T_c \)) and with the characteristics of the oxide minerals that are observable with an optical microscope. The reason for this is that if a wide distribution of ferrimagnetic grain sizes, say from 0.1 to 50 \( \mu \)m, exists in a specimen, then the major proportion of NRM (the primary
TRM in fresh basalt) will be carried by the finest grains because they have single-domain or pseudo-single-domain magnetic structure, while the volumetrically more important (and optically visible) larger grains will dominate the induced magnetization and X-ray diffraction data. Because of this problem, we have compared the thermal dependence of strong-field magnetization \( J_s(T) \) with the thermal demagnetization of NRM as measured at high temperature, which we will term \( J_a(T) \).

The results of these experiments are shown in Figure 4. In these diagrams, the estimated contribution of paramagnetic silicates has been subtracted from the \( J_a(T) \) curves to facilitate direct comparison. All four \( J_a(T) \) curves in Figure 4 are reversible or nearly so, indicating that \( z \) is low or zero. For specimen 12:5, \( z \) is probably 0.3 by analogy with specimen 12:4 (Table 2). The Curie temperatures for fragments 93A and 104 are between 200° and 250°C, but comparison with the data in Figure 1 and Table 2 for other fragments from the same dredge hauls suggests that these are not oxidized. In all four sets of \( J_a(T) \) curves there is an indication of a trace amount of nearly pure magnetite; this is most evident for specimen 104:2. As will be shown later, the same slight inflection at 570°C is seen in the \( J_a(T) \) curves for some other low- \( z \) specimens, and probably results from slight oxidation or disproportionation during the \( J_a(T) \) measurements.

For all specimens, the demagnetization curves of \( J_a \) are from 30° to 60°C below the corresponding \( J_a(T) \) curves, but the two kinds of curves are always roughly parallel. This might seem to indicate that the Curie temperatures, cell dimensions, and \( x \) and \( z \) parameters derived from them represent moderately well the minerals that carry the NRM. In all four examples, however, a small fraction of \( J_a \) persists above the main Curie temperatures that are obtained from the \( J_a(T) \) curves using our method. This could result either from the existence in the rock (before heating) of a small amount of NRM-carrying material with higher Curie temperatures, or from the production of such material during the \( J_a(T) \) decay experiments. If the latter occurs, a 'memory' of the NRM may exist in the new material [Marshall and Cox, 1971b]. Both of these possibilities will be discussed below.

**PALEOMAGNETIC DETERMINATIONS**

The results of the paleomagnetic experiments are given in Figure 5 and Table 2. For all 10 specimens, at least 10 and often more of the NRM-TRM points obtained from the paired heatings fall on a line sufficiently straight to calculate an apparent paleomagnetism. The points used for these estimates were selected subjectively. Deviant low-temperature points presumably represent thermal demagnetization of viscous remanent magnetization (VRM), and deviant high-temperature points represent alteration of the magnetic minerals, as is confirmed by the partial thermoremanent magnetization (PTRM) checks illustrated in Figure 5. (For a discussion of the use of PTRM checks, see Coe [1967].) No points were discarded within the temperature interval used to calculate the straight line for each specimen. The fraction \( f \) of the total NRM that corresponds to the straight-line portion of the data extrapolated to TRM = 0 is given in Table 2 for each specimen.

In fitting straight lines to the NRM-TRM points we assumed that errors in both quantities were proportional to their magnitudes, so that the line of adjustment in the least-squares solution is the negative of the slope of the best-fitting line [York, 1967]. A quality factor has been devised by Coe et al. [1978] that takes into account the NRM fraction \( f \), the uncertainty in slope of the least-squares line, and the uniformity of spacing of NRM-TRM points along the line. Values of this quality factor \( q \) are given in Table 2. In our experience, usable paleomagnetic determinations have \( q \) factors greater than about 10. In Table 2, values of \( f \) closer to unity mean that VRM was minimal and that alteration of the magnetic minerals did not occur until most of the NRM was thermally demagnetized. We see from Table 2 that two of the three noticeably altered ('AE') specimens gave quality factors less than 10 and that there is a distinct inverse correlation between quality factor and degree of low-temperature oxidation.
Fig. 5. NRM-TRM diagrams representing results of Thellier paleointensity experiments, done in vacuum in a field of 0.4 oe. Circles are NRM-TRM points. Triangles are PTRM checks; dashed lines connect these points to NRM-TRM point representing maximum temperature to which specimen was heated before doing the check. NRM values for PTRM checks are estimated by linear interpolation between NRM-TRM points at next lower and higher temperatures. Temperatures for NRM-TRM points and PTRM checks are designated in degrees Celsius. Solid lines are least-squares straight lines used to estimate indicated paleointensity. Note that horizontal and vertical scales are not the same; the ratios vary in different diagrams for convenience in drawing.

For the most part, the best paleointensity determinations were made using the specimens for which z = 0. These are 26:3 (Figure 5b), 17D-2:5, and 104B-2:11 (Figure 5e) and judging by its low Curie temperature, 93B:5 (Figure 5d). In these examples, VRM is either absent or is removed by about 110°C, alteration of the magnetic minerals does not occur until nearly all of the NRM is removed at temperatures above 250°C, and the PTRM checks are good up to these temperatures. f is about 80% or more and q is 40 or more. Geologi-
cally reasonable values of paleointensity are obtained, and both H and L types of basalt give equally good results.

Specimen 93:3, for which z could not be directly determined, has a Curie temperature of 253°C which, because it was obtained at 3 cm from the pillow surface, indicates that it is not oxidized according to our conclusion in an earlier section (Figure 1). Its NRM-TRM diagram has a peculiar feature (Figure 5d): above about 180°C the NRM-TRM line is offset toward the right but the slope remains about the same as for the lower temperature part, resulting in a quality factor of 26. This same effect, although in the opposite direction, was observed by Coe and Grommé [1973] in one specimen with a rather different magnetic mineralogy and is apparently due to alteration of the TRM capacity of the minerals, but the details remain unexplained.

Of most interest are the results from the paired specimens taken from the same pillow fragments. For fragment 26 (Figure 5b) similar values of paleointensity were obtained from the unweathered (z = 0) and weathered (z = 0.35) specimens. In the weathered specimen less of the NRM (53%) could be used before alteration began at 220°C, while in the unweathered specimen alteration did not begin until 250°C and 81% of the NRM could be used. Little or no secondary magnetization (VRM) appears to have been present in these specimens. Fragment 7D provided similar results (Figure 5c), although VRM seems to have persisted in both specimens to about 140°C. Alteration of the magnetic minerals starts at about 240°-250°C for both specimens. Surprisingly, the apparent paleointensity obtained from the weathered specimen (z = 0.28) is 15% higher than from the unweathered specimen (z = 0.05), which is experimentally significant but is within the variation found in single subaerial lava flows [Coe et al., 1978]. As in the previous example, much more of the NRM in the unweathered sample (70%) was usable than in the weathered sample (33%).

The most weathered fragment, 12, gave rather different results (Figure 5a). The less oxidized specimen (z = 0.30) gave a low but not unreasonable paleointensity of 0.19 oe, which by analogy with the z values of the examples just described may be a correct value. For this specimen the values of f and q are similar to the other two specimens having z = 0.3. The more oxidized specimen (z = 0.62) gave a much lower paleointensity (0.09 oe), only 14% of the NRM could be used for the best-fit straight line, and the quality factor is only 1.7. Obvious alteration began at about the same temperature, 265°C, for both specimens.

These results from the double-weathering experiments may be summarized at this point as follows: for fresh basalt having z ≥ 0.05, very high quality paleointensities may be determined from both H and L type pillow basalts. These samples have NRM intensities ranging from 7 × 10⁻⁴ to 76 × 10⁻⁴ emu/cm³ and over 90% of the NRM in the strongest specimen could be used to define the paleointensity. Formation of titanomagnemitie by seafloor weathering does not seem to affect the paleointensities up to z = 0.3, but the fraction of NRM usable for the paleointensity determination is halved. Alteration of magnetic minerals begins at about the same temperature in all cases, and the lower values of f in the weathered samples results from the higher temperatures at which much of their NRM is demagnetized. Oxidation to a z value greater than about 0.3, however, results in a spuriously low paleointensity value as well as markedly reducing f even further.

The fact that reasonably reliable paleointensities may be obtained from material oxidized up to z about 0.3 is surprising and requires some explanation. We have suggested above that much or most of the magnetic material in these samples has single-domain structure and has coercivity controlled by uniaxial shape anisotropy. Johnson and Merrill [1974] have performed low-temperature oxidation experiments on uniaxial single-domain particles of cation-deficient magnetite wherein z was increased from an initial value of about 0.4 to a final value of 1.0. They found that an initial anhysteretic magnetization (ARM) was decreased by 12% during oxidation and that no CRM was produced, in contrast to the observation that CRM is produced during similar experiments using multidomain material. Assuming that they have adequately simulated NRM with the initial ARM, Johnson and Merrill conclude that NRM in single-domain magnetite will be preserved during low-temperature oxidation to maghemite in nature, and ascribe this either to the high value of shape anisotropy or to positive exchange coupling between the unoxidized and oxidized phases. It seems possible that the argument of Johnson and Merrill can be extended to our samples. The decrease in NRM intensity as z increases from 0 to 0.3 would be due only to the concomitant decrease in spontaneous magnetization. If no change in grain configuration occurs during this moderate oxidation (that is, the single-domain grains are so small that they do not develop shrinkage cracks), then the TRM capacity would be diminished only by the reduction in spontaneous magnetization and to a first approximation the NRM-TRM ratios would be unchanged. This interpretation is supported by the petrographic observations of oxidized multidomain titanomagnetite published by Ryall et al. [1977] and Johnson and Hall [1978], in which neither shrinkage cracking nor formation of other minerals is seen until z has exceeded 0.3. At z = 0.3 a useful NRM-TRM line segment can still be obtained because most of the NRM can be thermally demagnetized before significant disproportionation occurs at 220°-250°C. Obviously, as stated by Johnson and Merrill [1974], this accurate preservation of NRM during oxidation would not occur in multidomain material.

The reason for the flattening of NRM-TRM slope seen for specimen 12:4-6(AE) may be found in the work of Marshall and Cox [1971b]. Their experiments showed that when a titanomaghemite-bearing submarine basalt is heated, titanium-poor magnetite forms from the disproportionation of titanomaghemite. This breakdown commences at about 250°C, and if z and hence Tc are high enough, some NRM may still exist in the specimen. If the heating is done in a weak field (0.5 oe), the newly formed magnetite acquires two components of high-temperature chemical remanent magnetization (TCRM): one parallel to the ambient field and one parallel to the NRM. It appears to us that in specimen 12:4-6(AE), the disproportionation probably began at about 150°C (Figure 5a) and the 'transfer' of NRM from titanomaghemite to magnetite occurred gradually up to 260°C. Because magnetite has a much greater spontaneous magnetization, the production of TCRM in new magnetite almost counteracts the thermal destruction of NRM in the original titanomaghemite. This means that the fact that 10 of the NRM-TRM points for this specimen lie on a straight line is entirely accidental. The same effect may be seen for specimen 26:5-7(AE) (Figure 5b), where above 220°C the NRM appears not to be decaying as rapidly as at lower temperatures and the capacity for acquisition of TRM appears to be increasing, though in this instance alteration commenced at a high temperature.

This 'stretching-out' of the NRM-TRM diagram may also be seen in the results of Dunlop and Hale [1976], who performed paleointensity experiments using the Thellier's method on DSDP leg 37 basalts, as mentioned above. Dunlop and Hale remarked that all of the determinations were of low
Fig. 6. Comparisons of \( J_z(T) \) variations and thermal unblocking of NRM, in specimens used in paleointensity experiments. \( J_z(T) \) curves are numbered as follows: 1, 2 (solid lines) heating and cooling curves before paleointensity experiments; 3, 4 (long dashes), heating and cooling curves after paleointensity experiments. (The contribution of paramagnetic silicates was not removed from these \( J_z(T) \) curves.) Heating and cooling curves are indicated by arrows. Curves labeled 5 (short dashes) are estimated contribution to \( J_z \) from paramagnetic silicates. Circles are NRM values at room temperature obtained from Thellier experiments (NRM(\( T_R \))); lines connect points used in least-squares evaluation of paleointensity, which presumably represent only natural TRM, at least in specimens for which \( z \approx 0 \). Triangles are NRM values recalculated to simulate those that would be measured at the temperatures indicated on the diagrams (\( J_z(T) \)) (see text and Figure 4). \( H_f \) = fields used in \( J_z(T) \) experiments. \( z \) values are from Table 2; those in parentheses are inferred only.
quality, all of the apparent paleointensities from 10.5- to 16.5- 
m.y.-old rocks were low, and only some of the specimens from 
3.5-m.y.-old basalt gave near-normal paleointensities. Dunlop 
and Hale's NRM-TRM diagrams look very much like our 
Figures 5a and 5b though with fewer points, and it appears 
that in their experiments disproportionation of titanomagnetite may have begun as low as 125°C. The hydrothermal 
experiments of Ryall and Ade-Hall [1975b] indicate that if z 
exceeds 0.7, disproportionation may occur at a temperature as 
low as 150°C.

In all of the specimens except those from fragment 26, the 
onset or further development of alteration of magnetic minerals 
resulting from heating has the opposite aspect from that 
described above: instead of the stretching out effect, both 
NRM and TRM are abruptly diminished, resulting in a 'hook' 
shape in the NRM-TRM diagram (see especially Figures 5c, e, 
and h). The highest-temperature PTRM checks confirm that 
these specimens have lost part of their TRM capacity. Now, in 
all these experiments the heating was stopped when the 
points clearly began to deviate from the straight line, even 
though appreciable NRM might still remain in the specimen. 
Had the experiments been continued, we would predict from 
the preceding discussion, from the results for fragment 26, 
and from similar results from subaerial basalts [Coe et al., 1978] 
that the hooked trend of the NRM-TRM points would again 
reverse toward the direction of increasing TRM capacity.

Many authors have described experiments in which partial 
or occasionally complete self-reversal of NRM can be pro-
duced by carefully controlled heating of basalt in which at 
least part of the magnetic minerals have low Curie tem-
peratures [Petherbridge, 1977, and references therein; Ryall and 
Ade-Hall, 1975b]. The following are common to most of these 
experiments: (1) the magnetic phase carrying the reversed 
magnetization has a higher Curie temperature, above 500°C, 
(2) this phase forms either by oxidation of part of the original 
titanomagnetite or by disproportionation of part of the origi-
nal titanomaghemite, and (3) the tendency for partial self-
reversal disappears on further heating. The cause may be 
either magnetostatic or atomic exchange interaction between 
the natural and artificial phases. These results may explain the 
high-temperature hooks in our NRM-TRM data. Alterna-
tively, these hooks may simply result from abrupt increase of 
blocking temperatures accompanying alteration of the mag-
netic minerals, if the new blocking temperatures are higher 
than the temperatures reached in the heating experiments at 
which the alteration occurred.

In summary, we can construct a generalized and qualitative 
explanation for the features of our NRM-TRM diagrams, in 
order of increasing temperature: (1) the first change in slope 
(<150°C) represents complete removal of VRM. (2) The sec-
ond change in slope (between 220° and 280°C) represents the 
commencement of rapid alteration of the magnetic minerals. 
This alteration varies in nature from specimen to specimen, 
but apparently includes the production of varying amounts of 
nearly pure magnetite. If at point (2) the change in slope is 
toward decreasing NRM and decreasing TRM capacity, it can 
probably be explained by magnetization of new magnetite in 
antiparallel to original grains carrying NRM or laboratory
TRM, as in the self-reversal experiments mentioned in the preceding paragraph. If at point (2) the change is predominantly toward increasing TRM capacity, it almost certainly results from magnetization of the new magnetite in the external applied field, without any magnetic interaction between the parent and daughter phases.

Between points (1) and (2) the NRM-TRM values always lie on or near a straight line. If $z = 0$, this straight line represents thermal demagnetization of natural TRM and hence provides a reliable paleointensity. If $z \approx 0.3$, the NRM that is demagnetized in the straight-line interval is diminished with respect to the original TRM, but the slope still represents a moderately accurate paleointensity because the TRM capacity is proportionately diminished. This would be very unlikely to be true in multidomain material, however. If $z > 0.3$, this straight line does not represent a paleointensity at all. In this case, disproportionation of titanomagnetite apparently begins gradually at around $150^\circ$C, and the resulting magnetite is apparently positively coupled to the NRM-carrying parent grains [Marshall and Cox, 1971b], probably by exchange interaction, so that an artificial progressive increase in unblocking temperature of NRM occurs. This process is followed by abrupt and complete breakdown of titanomagnetite at about $280^\circ$C; the temperature of maximum breakdown rate would depend on the value of $z$ and the experimental heating and cooling rates.

**J(T) and NRM(T) Comparisons**

One important feature of our paleointensity experiments remains to be discussed. In Table 2 it can be seen that the temperatures of the terminations of the straight-line segments of the NRM-TRM diagrams are nearly always higher than the initial Curie temperatures obtained from the $J_i(T)$ curves. Excepting specimen 93:3, which behaved peculiarly, this difference averages $52^\circ$C with s.d. $= \pm 43^\circ$C. Also listed in Table 2 are the Curie temperatures of all specimens after completion of the Thellier experiments ($T'_{C}$), again obtained from $J_i(T)$ curves. These final Curie temperatures are from $25^\circ$C to $105^\circ$C higher than the terminations of the straight NRM-TRM segments (i.e., higher than the onsets of mineralogical alteration) in all but three specimens, and these three exceptions all have $z = 0$. All of the final Curie temperatures ($T'_{C}$) and most of the final values of saturation magnetization ($J'_i$) are greater than the initial values before the Thellier experiments (Table 2). These observations suggest that some degree of mineralogical alteration has occurred during the last stages of all the Thellier experiments and also that a fraction of NRM might reside in material with somewhat higher unblocking temperatures than the predominant Curie temperatures obtained from the $J_i(T)$ curves.

It seems desirable to compare directly in some way the thermal variation of $J_i$ and NRM, and this is attempted in Figures 6b–6f. In these diagrams, heating and cooling curves of $J_i$ both before and after the Thellier experiments are shown without subtracting the contributions of paramagnetic silicates (curves labeled (1)–(4)). The room-temperature NRM remaining after each step in the Thellier experiments is also shown. Because these two quantities cannot be strictly compared, we have attempted to simulate the data of Figure 4 in the following way. The contribution of induced magnetization in paramagnetic iron-bearing silicates ($H_{x_s}$ where $x_s$ is the paramagnetic susceptibility and $H$ is the strong magnetizing field) is estimated as being a large fraction of $J_i$ above $600^\circ$C, and its temperature variation is shown as the curves labeled (5) in Figure 6. Then denoting as before the intensity of NRM measured at temperature $T$ as $J_i(T)$, we estimate it by the relation

$$J_i(T) = \frac{\text{NRM}(T)[J_i(T) - H_{x_s}(T)]}{J_i(20) - H_{x_s}(20)}$$

where NRM($T$) is the NRM measured after heating to temperature $T$ and cooling, and $J_i(T)$ is taken from the measured curves, and $J_i(20)$ and $H_{x_s}(20)$ are the room temperature values. (Note that in Figure 6 the appropriate baselines for $J_i(T)$ are the curves of $H_{x_s}$, while the appropriate baselines for NRM and $J_i$ are the abscissae, and also that the NRM and $J_i$ scales are normalized to $J_i(20)$ of curves (1).) In Figure 6 all the curves of $J_i(T)$ are either coincident with or somewhat below the initial curves of $J_i(T)$, as in Figure 4, and there is little variation in the $J_i(T)$ curves for different specimens except that due to differences in $T_c$. This is to be expected because $J_i$ is such a strongly varying function of $T$ within about $200^\circ$C of $T_c$, as in these examples. Hence it appears necessary to compare NRM($T$) with $J_i(T)$.

When this is done, the differences are significant. For all specimens in which $z$ is very low or zero (Figures 6c, 6e, 6g, 6h, 6i, and 6j) the curves of NRM($T$) are nearly congruent with the initial $J_i(T)$ curves but are displaced to somewhat higher temperatures. For specimens in which $z$ is about 0.3 (Figures 6a, 6d, and 6f) the curves of NRM($T$) have somewhat flatter slopes and are displaced to relatively higher temperatures than the $z = 0$ examples. For the specimen in which $z = 0.62$ (Figure 6b), this displacement of NRM($T$) to higher temperatures is much greater and the slope of the NRM($T$) curve is very flat. Hence we see that, although strictly speaking NRM($T$) and $J_i(T)$ are different kinds of functions because NRM($T$) is measured at room temperature, nonetheless comparing them is a sensitive test of the presence of titanomaghemite.

Of the four titanomaghemite-bearing specimens, three have initial (and final) $J_i(T)$ curves which exhibit the 'hump' around $450^\circ$C that results from disproportionation of metastable titanomaghemite to a Ti-poor titanomagnetite and nonmagnetic phases [Ozima and Ozima, 1971], as shown in Figures 6b, 6d, and 6f. Surprisingly, specimen 124, for which $z = 0.3$, does not show this hump (Figure 6a). Grommé and Mankinen [1976] found that in DSDP leg 34 basalts from the Nazca plate, the disproportionation resulting from heating was only evident for specimens having $z$ greater than about 0.4. Hence it appears that a thermomorphic curve that is reversible in vacuum does not necessarily indicate that the titanomaghemite is not oxidized up to $z = 0.3$. Also, very slight disproportionation is seen in specimen 26:3, for which $z = 0$ (Figure 6e), which could be due either to a small amount of titanomaghemite or to the presence in the specimen of water bound in alteration minerals which was released on heating and oxidized some of the stoichiometric titanomagnetite. The latter explanation probably also applies to specimen 104B-2:11 (Figure 6j) in which a minor amount of magnetite was formed above about $550^\circ$C. The remaining four specimens have essentially reproducible initial $J_i(T)$ curves (Figures 6e, 6g, 6h, and 6i).

In all 10 specimens the NRM-TRM experiments increased the Curie temperatures (Table 2 and Figure 6), and in 9 of the 10 specimens $J_i$ increased also, as mentioned above. This alteration tends to be greater for specimens with higher $z$, though the correlation is only approximate, partly because the specimens were heated to somewhat different maximum temperatures in the NRM-TRM experiments. A better correlation is seen between changes in $T_c$ and $J_i$; the greater the increase in
Fig. 7. Curie temperature (circles) and NRM intensities (triangles) of basalt samples dredged from median valley and flanks of Mid-Atlantic Ridge at 45°N, from Carmichael [1970]. Distance is measured from center of median valley, both east and west. Solid bar and squares represent minimum and maximum half-widths, respectively, of median valley in this area.

$T_c$, the greater the percentage increase in $J_s$. This seems to indicate that the alteration that occurred at the ends of the NRM-TRM experiments, at least for the low-$z$ specimens, was slight oxidation and disproportionation in which the composition of the magnetic phase moved along the stoichiometric ulvospinel-magnetite join toward more Fe-rich titanomagnetite. For the higher-$z$ specimens the nature of the alteration is harder to specify because from Figure 6 it is evident that the Curie temperatures increased uniformly for each entire specimen, but very little pure magnetite was produced by disproportionation. The alteration in these specimens is apparently a combination of further oxidation, as seen in the low-$z$ samples, combined with partial disproportionation of the titanomagnetite to a slightly more Fe-rich titanomagnetite and a nonmagnetic oxide. The main evidence that the alteration resulting from the NRM-TRM experiments was probably slight oxidation in all specimens comes from the cooling parts of the second sets of $J_s(T)$ curves (curves marked (4) in Figure 6). For the specimens that did not disproportionate markedly during the $J_s(T)$ runs, these last cooling curves are much closer to the initial $J_s(T)$ than the final heating curves. In other words heating to 600°C in the $J_s(T)$ apparatus reversed the alteration produced by the NRM-TRM experiments. Marshall and Cox [1972] showed that this lowering of Curie temperature is due to the presence of vapor in the $J_s(T)$ apparatus which is derived from vacuum diffusion pump oil and results in a strongly reducing environment at high temperature. The oxygen fugacity at temperatures around 600°C is apparently sufficiently low that very finely unmixed Fe-rich titanomagnetite and ilmenohematite are reduced and mix to form titanomagnetite with a composition similar to that before the NRM-TRM experiments. A similar phenomenon has been reported by Shive and Diehl [1977].

**Paleointensities From the Mid-Atlantic Ridge**

Most of the published paleointensities obtained from submarine basalt were determined using dredged samples from the median valley and flanks of the Mid-Atlantic Ridge in the vicinity of latitude 45°N, as mentioned earlier in the introduction. The broadest coverage was that of Carmichael [1970], who studied samples from between 135 km west to 60 km east of the spreading center. NRM intensities and Curie temperatures of Carmichael's samples are shown in Figure 7, in which the data are plotted as a function of distance from the spreading center without distinguishing the east and west flanks of the ridge. The diminution of NRM intensity with distance from the spreading center is essentially the same as was found by Irving et al. [1970b], and Carmichael concluded from his experiments that about half of this was due to variation in geomagnetic field strength. Not noted by Carmichael was the increase in Curie temperature with distance away from the spreading center, which is only a little less abrupt than the decrease in NRM. If, as was indicated by Carmichael [1970], the ages of the samples are proportional to their distances from the spreading center, then we can surmise that, neglecting initial variations of $x$, the increase in Curie temperature is due to progressive titanomaghemitization of the original titanomagnetite. This might be expected to affect the experimental values of paleointensity.

In Figure 8 we have plotted the paleointensities determined by Carmichael [1970] for the Mid-Atlantic Ridge samples against their Curie temperatures. The distances from the spreading center are indicated for all the samples, and the corresponding ages range from zero at the center to roughly 10-14 m.y. In the median valley samples, with the lowest Curie temperatures, the measured paleointensities are about twice the predicted average value (0.55 oe) calculated from the summary by Kono [1971], while outside the median valley the paleointensities are lower. There is an unmistakable tendency...
for the older samples, with higher Curie temperatures, to give paleointensities significantly lower than the predicted mean; in particular the average for all eight samples having Curie temperatures greater than 300°C is 0.20 oe, or 37% of the average value for that latitude predicted for an axial dipole field. The six samples with Curie temperatures between 175° and 300°C gave an average paleointensity of 0.53 oe, essentially the same as the predicted average.

We have shown in a preceding section that paleointensity determinations by the Thellier's method will give answers that are too low if the basalt contains titanomagnetite with z > 0.35. If the carriers of NRM have single-domain magnetic structure, the cause is the formation of Ti-poor titanomagnetite or even pure magnetite from titanomagnetite by disproportionation during the laboratory heating experiments, resulting in a marked increase in TRM capacity. (Note that if a fresh unoxidized subaerial basalt is heated in air, the resulting oxidation and disproportionation of titanomagnetite will also cause an increase in TRM capacity, although somewhat less.) The paleointensity method used by Carmichael [1970] and by Ade-Hall et al. [1973] requires heat the samples above their Curie temperatures before any NRM/TRM ratios can be determined, and hence the same source of error may be expected to occur. For this reason, the paleointensities found by Carmichael [1970] using samples with Curie temperatures above 300°C are likely to be too low.

Also shown in Figure 8 are the paleointensities published by Ade-Hall et al. [1973]; their samples were obtained using an ocean-floor core drill within 2 km of the center of the median valley of the Mid-Atlantic Ridge at the same latitude as the dredge-haul samples of Carmichael [1970]. The results of Ade-Hall et al. show more scatter, both in paleointensity and in Curie temperature, than those of Carmichael from the same locality. Part of the scatter in paleointensities may be the result of less-than-ideal behavior of the samples for unknown reasons. Of the six pairs of paleointensities from the same drill cores, three are discrepant outside the error limits quoted by Ade-Hall et al. [1973]. The important point is that all of the paleointensity determinations made on basalt from within the median valley of the Mid-Atlantic Ridge at 45° N are higher than the predicted mean value for that latitude. Because nothing in our experimental results would predict an error in this sense, we agree with the previous authors' conclusions that the geomagnetic field was exceptionally strong when their samples acquired NRM.

Because the samples described by Ade-Hall et al. were obtained within 2 km of the center of the median valley, they are probably too young to have been appreciably oxidized. It follows that the range of Curie temperatures reported by Carmichael and by Ade-Hall et al. probably reflects initial variation of iron/titanium ratio in titanomagnetite, possibly complicated by varying depth of the specimens within the original pillows. Neglecting the latter, the maximum range of initial magnetite/ulvöspinel ratio indicated by the Curie temperatures alone is 0.46 < x < 0.60. The lower limit of x would be somewhat higher if the samples with higher Curie temperatures happened to have been obtained from near original pillow cooling surfaces.

**Rate of Formation of Titanomagnetite**

The maximum age of oceanic basalt from which reliable paleointensities can be obtained obviously depends on the rate of oxidation of titanomagnetite to titanomagnetite in the basalt on the ocean floor. This rate must be affected by many factors that are difficult to evaluate, such as hydrothermal activity at the spreading center, differences in permeability due to variable degree of fracturing of the basalts, and depth of burial by sediment. Nevertheless we have attempted a rough estimate based on the data of Carmichael [1970] and Ozima et al. [1974], and the results are illustrated in Figure 9.

From Carmichael's [1970] Curie temperature data we have estimated z using the contours of Figure 2a; the plotted points represent an Fe/Ti ratio corresponding to z = 0.59, which is the value for Carmichael's accurately analyzed unoxidized sample, and the vertical error bars in Figure 9 represent the range of z for 0.55 < z < 0.65. The horizontal error bars in Figure 9 represent the differences between the radiometric ages (fission-track or potassium-argon) of the samples published by Carmichael [1970] and by Aumento [1969] and the ages corresponding to seafloor spreading rates on the Mid-Atlantic Ridge at 45°N we have calculated from the poles and rates of spreading derived by Pitman and Talwani [1972] from analyses of magnetic anomalies. Outside the median valley, the radiometric ages are younger than the seafloor spreading ages up to...
about 3 m.y., but are greater for older ages, the differences range from −60 to +67% of the seafloor spreading ages. The plotted points are the averages of the ages found by the two methods, except for the median valley samples, for which the radiometric ages are used. The points in Figure 9 due to Ozima et al. [1974] are the z values estimated by us (Figure 2b) and the potassium-argon ages published by them. Data from DSDP basalt (Figure 3a) are omitted from Figure 9 because oxidation rates may be much lower and more variable in subsurface basalt [Ryall et al., 1977; Marshall, 1978].

We see from Figure 9 that oxidation at the seafloor surface proceeds to z about 0.5 in a time of the order of 1 m.y. and is nearly complete (z = 1.0) sometime between τ = 10 and 100 m.y. [see also Johnson and Atwater, 1977]. It turns out that a first-order rate equation of the form log (1 − z) = t/τ, as proposed by Ozima et al. [1974], cannot be used to represent the formation of titanomaghemite. If, as we concluded above, reliable paleointensities cannot be determined if z exceeds 0.3 or 0.4, then Figure 9 demonstrates that basalt dredged from the seafloor used in such experiments must be younger than 1 m.y., and for best results it should be younger than 0.1 m.y.

In Figure 10 we have plotted the portion of the data of Figure 9 between 0 and 6 m.y. on a linear age scale, for comparison with the oceanic crust magnetizations calculated by Klitgord et al. [1975] by inversion of near-bottom magnetic anomaly data. In p forming their inversions, Klitgord et al.

![Diagram](image_url)

**Fig. 10.** Circles and triangle are z values of dredged basalts as in Figure 9. Squares are crustal magnetizations (J_c) for 0.5-km thick magnetized layer calculated from deep-tow magnetometer data by Klitgord et al. [1975], and recalculated to equivalent magnetizations at the pole (see text). Magnetizations of crust generated at the Galapagos spreading center (GSC) and Juan de Fuca Ridge (JDF) are shown separately because they arise from more strongly magnetic rocks (H-type). Magnetizations of crust generated at the Pacific-Antarctic Ridge, East Pacific Rise, Costa Rica Rift, and Gorda Rift are averaged and the error bars represent one standard deviation; these values correspond to ordinary (L-type) magnetic rocks.

reduced the anomaly profiles to the pole in the sense that the remanent magnetizations and present ambient field were made vertical, but the crustal magnetizations given by them correspond to the present latitudes of the various spreading ridges. We have calculated the equivalent magnetizations (J_c) at the pole, assuming an axial geocentric dipole field of unvarying dipole moment, by the relation \( F = 2F/(1 + 3 \cos^2 \phi) \) where \( F \) is the magnetizing field at the pole, \( F \) is the magnetizing field at the site, and \( \phi \) is the geographic colatitude of the point of origin of the magnetized ocean crust. The values of \( J_c \) corresponding to \( F \) for 'ordinary' or L-type crust were averaged for each point along the four profiles shown by Klitgord et al., and the error bars in Figure 10 are the standard deviations of the four (or fewer) data points for each geomagnetic reversal age at which Klitgord et al. calculated magnetizations. (The two profiles over H-type crust are shown without any averaging.)

When Figure 10 is compared with Figure 13 of Klitgord et al. [1975] it can be seen that the differences in calculated magnetizations for the four profiles over L-type crust are greatly reduced when the magnetizations are converted to equivalent magnetizations at the pole in this way. This is evidence that the magnetizations calculated by Klitgord et al. are an appropriate representation, although they assumed a magnetized layer thickness of 0.5 km which is probably only true for crust younger than a few hundred thousand years [Blakey, 1976]. Figure 10 also demonstrates the point we made earlier, that the difference in strongly magnetized (H-type) and less strongly magnetized (L-type) oceanic crust persists at least up to crustal ages close to 5 m.y., and hence must be due to a geochemical difference in the entire part of crustal layers 2 and 3 that is permanently magnetized at or near the spreading center at which it formed.

The main point of Figure 10 is to show that the diminution of integrated magnetization intensity with increasing age of oceanic crust is, to a first approximation, consistent with the increase of the titanomaghemite oxidation number z in the topmost pillow basalts of the magnetized layer. This concordance is all the more remarkable when we note that these z data nearly all come from the slow-spreading Mid-Atlantic Ridge while the crustal magnetizations were all estimated from medium and fast-spreading ridges in the eastern Pacific, that the exact relationship between decrease of T/R intensity and increase in z in pillow basalts is only poorly known, and that as crustal age increases, the topmost pillow basalt layer becomes progressively less important a contributor to the linear magnetic anomalies. Nonetheless there can be hardly any remaining doubt that, as first proposed by Irving [1970] and Irving et al. [1979a], formation of titanomaghemite from titanomagnetite in pillow basalt on the sea floor is the main cause of the decrease in linear magnetic anomaly amplitude away from actively spreading ridges.

**Summary and Conclusions**

*Estimation of composition and degree of cation-deficiency in titanomagnetite and titanomaghemite.* Combining bulk Curie temperatures with cubic cell dimensions calculated using X-ray diffraction patterns obtained from magnetic separates provides an internally consistent method of estimating the Ti/Fe parameter \( x \) and the oxidation parameter \( z \). To do this we have combined the experimental data of Akimoto et al. [1975] and Ozima and Larson [1970] for stoichiometric compositions with that of Readman and O'Reilly [1972] for cation-deficient oxidized compositions. For submarine basalts, all available published data and the new data of this study provide values of \( z \)
between 0 and 1 (with one exception) which is the maximum possible range of \( z \), and the projected values of \( x \) fall in the restricted range from 0.52 to 0.70. On the compositional diagram, all points plot near a family of oxidation-reduction paths, but a systematic deviation is seen which indicates that a small proportion of iron is lost from the oxide grains during low-temperature oxidation. For stoichiometric compositions \((z = 0)\) the range of \( x \) is from 0.52 to 0.60 in submarine basalts, but the consistency of these values with direct microprobe measurements remains to be established. The experimental work of Richards et al. [1973] predicts that the presence of minor amounts of Mg and Al in solid solution in the cubic ferrimagnetic oxides would cause large errors in this method of estimating \( x \) and \( z \), but the internal consistency of the results suggests to us that the Mg and Al reported in published microprobe analyses occurs in submicroscopic spinel intergrowths in the ferrimagnetic oxides, rather than in solid solution.

**Radial variation of Curie temperature in submarine basalt pillows.** The pillow fragments used in this study are all small: the estimated original pillow diameters range from 16 to 34 cm. In these small fragments, a significant variation of bulk Curie temperature along the pillow radius is observed and is almost certainly a primary feature. In the well-crystallized interiors (beyond about 5 cm inward from the original cooling surface) the Curie temperatures are mostly uniform in single fragments and are between 150°C and 200°C in unoxidized basalt. In the outer, less well crystallized zones, the Curie temperatures are higher, between 250°C and 300°C. In the outermost glassy shell, however, the Curie temperatures are somewhat lower than the maximum values but still are significantly higher than those in the interior. The most probable explanation of this variation is cation-deficiency quenched from high temperature during the initial cooling of the pillows, following the experimental work of Hauptman [1974], although primary radial variation of Ti/Fe ratio in the oxide minerals may also be a partial or complete explanation. Formation of titanomagnetite due to submarine weathering cannot, however, account for the observed variation. There is some indication that interior Curie temperatures are lower (150°C–165°C) in more strongly magnetic (H-type) basalt pillows than in less magnetic pillows (L-type), most of which give values of 200°C. This difference, if real, is what would be qualitatively predicted from the observations by Anderson et al. [1975], Vogt and de Boer [1976], and Vogt and Byerly [1976], that H-type basalt has higher Ti and total Fe and a higher Ti/Fe ratio in its bulk chemical composition than does L-type basalt. All these factors indicate that errors may result if the Curie temperature alone is used to estimate the oxidation parameter \( z \). To assume a single value or restricted range of the Ti/Fe parameter \( x \) is probably invalid, even within single pillow fragments, if samples are obtained only from the outermost parts of pillow fragments originating from widely separated localities.

**Magnetic properties of basalt used in this study.** Both H and L types of basalts were used, and for fresh (unoxidized) material the most convenient distinction is that H-type basalt has a saturation magnetization \((J_s)\) greater than 0.55 emu/gm. This difference is also reflected in the NRM intensities: the range for fresh H-type specimens is from 25 to 76 × 10^-8 emu/cm³ and for fresh L-type specimens it is from 7 to 13 × 10^-8 emu/cm³. The average value of the ratio (saturation isothermal remanence)/(saturation magnetization) is 0.41 with a range from 0.23 to 0.55. This high ratio indicates that the ferrimagnetic oxides are predominantly single-domain in magnetic structure and that their coercivities are predominantly determined by uniaxial shape anisotropy. In these samples the values of \( x \) range from 0.54 to 0.71 and the values of \( z \) range from 0 to 0.62. From three pillow fragments that had weathered zones parallelly primary cooling fractures, paired weathered and unweathered samples were used, with the weathered samples having \( z \) about 0.3 greater than the unweathered (or less weathered) samples. Because of limitations in the sampling arrangement, however, detailed comparisons of the effects of weathering on magnetic properties could not be made. Of the 10 specimens used, 6 were oxidized (weathered) only slightly or not at all. From comparisons (using other similar specimens) of the thermal decay of NRM as measured at room temperature with the thermal variation of strong-field induced magnetization, we have concluded that the mineral responsible for the bulk Curie temperature (and also that is obtained as a magnetic separate) is the carrier of much but not all of the NRM in each specimen.

**Paleointensities determined using the Thellier’s method.** The four specimens which were completely fresh \((z = 0)\) gave the best results, as expected: secondary magnetization (assumed to be of viscous origin) was either absent or was removed by 110°C; 80% or more of the NRM could be thermally erased before alteration of the magnetic minerals commenced at about 250°C; both H-type and L-type specimens gave equally good results; and geologically reasonable paleointensities were obtained. Using this kind of material, and if the experiments are done in vacuum, at least 10 NRM-TRM points can be used to define the best-fit straight line if the temperatures of the paired heatings are chosen at intervals of about 10°C.

Partly because of the increase in blocking temperature distribution with increasing \( z \), and also because of the increasing degree of metastability of more highly cation-deficient titanomagnetite, progressively less of the NRM in more oxidized samples could be thermally demagnetized before alteration commenced. The specimens having \( z \) around 0.3, while apparently yielding approximately correct paleointensities, could only be thermally demagnetized to about 70 to 50% of their initial NRM intensity, that is, only 30 to 50% of the NRM could be used to define the paleointensity.

The three comparisons of two specimens, more and less oxidized, cut from the same fragments turned out as follows: for fragment 26, specimens with \( z = 0 \) and 0.35 yielded paleointensities of 0.44 and 0.41 oe, respectively. For fragment 7D, specimens with \( z = 0.05 \) and 0.28 yielded 0.29 and 0.34 oe, respectively. This agreement is as good as is commonly observed in Holocene subaerial basalt flows, although in the case of fragment 7D the fact that the more oxidized specimen gave a 15% higher paleointensity is surprising. From these two comparisons, we conclude that low-temperature oxidation up to \( z = 0.35 \) does not render submarine basalt useless for determining paleointensities, although the values obtained will be less certain than if perfectly fresh basalt were used.

The third comparison, fragment 12, the most weathered, gave different results: the specimen with \( z = 0.30 \) had a paleointensity of 0.19 oe and the specimen with \( z = 0.62 \) had a paleointensity of 0.09 oe. The former value may be approximately correct, but the latter value, while geologically possible, is obviously incorrect. Although a straight line with a slope of 0.09 oe could be drawn through a set of 10 successive NRM-TRM points, only 12% of the NRM was encompassed by it. In this case the linearity of the 10 points is apparently fortuitous, and we interpret the excessively shallow slope of the NRM-
TRM line as resulting from disproportionation of titanomaghemite to Ti-poor titanomagnetite plus nonmagnetic phases, commencing at about 150°C. An explanation of the persistence of NRM during heating of this specimen probably lies in the experimental results of Marshall and Cox [1971b]. They found that if titanomaghemite-bearing basalt (with high $z$) is heated to close to (but not above) its Curie temperature, as disproportionation proceeds the NRM will be transferred in part to the newly formed magnetite, apparently as a result of positive exchange interaction between the natural and artificial phases. In brief, we conclude that apparent paleointensities determined using the Thellier’s method from basalts with $z$ greater than about 0.35 will be too low. There are apparently at least two reasons for this. First, progressive gradual disproportionation of high-$z$ titanomaghemite during the heating experiments is accompanied by transfer of NRM to artificially formed Ti-poor titanomagnetite having higher blocking temperatures and higher spontaneous magnetization than the parent mineral. Second, the petrographic observations of Ryall et al. [1977] and Johnson and Hall [1978] have shown that severe chemical and physical alteration of titanomaghemite grains commences at about $z = 0.3$. Although these petrographic observations necessarily were made on multidomain grains, one would expect such alteration to be even more severe in the single-domain and pseudo-single-domain grains because of their smaller size. In other words, low-temperature oxidation above $z = 0.3$ means that not only will the Thellier double-heating method cause serious alteration in the laboratory, but also the grains carrying remanent magnetization are very different from what they were when the basalt acquired its natural TRM.

These conclusions apparently are only valid for basalt in which nearly all the NRM is carried by single-domain grains. In basalt in which the NRM resides in multidomain grains, we would expect severe errors in paleointensity determinations using specimens with $z$ even lower than 0.3. The reason is that if the stability of TRM in multidomain grains depends on pinning of domain walls by imperfections within the grains, the cation diffusion accompanying oxidation would be expected to change the number and locations of these imperfections and hence would change the capacity of the grains to acquire TRM. Similarly, the exact domain structure of pseudo-single-domain grains depends strongly on the intrinsic magnetic parameters such as spontaneous magnetization [Butler, 1973], and any changes in these resulting from even slight oxidation would probably result in marked changes in the capacity of the grains to acquire TRM in the laboratory.

The fact that we were able to obtain approximately correct paleointensities up to $z = 0.3$ must mean that, although NRM was decreased by oxidation, capacity to acquire TRM decreased proportionately. This is only likely if the single-domain nature of the grains was unchanged by oxidation, so that the decrease in NRM and TRM due to oxidation resulted only from decrease in spontaneous magnetization and no other factors.

Rate of formation of titanomaghemite in submarine basalt. Knowledge of the rate at which titanomagnetite is oxidized to titanomaghemite in basalt pillows exposed on the seafloor would provide some idea of the maximum age of the submarine basalt that could be expected to yield reliable paleointensities. From the limited published data, mainly that of Carmichael [1970] for basalt generated at the Mid-Atlantic Ridge, and making the crude assumption that $z$ can be estimated from measured Curie temperature alone, we find that $z$ is roughly 0.6 in 1-m.y.-old basalt and is roughly 0.8 in 10-m.y.-old basalt; $z$ approaches 1.0 in still older basalt. A value of $z$ of 0.3 is reached by about 0.2–0.5 m.y.; hence we conclude that a few hundred thousand years is the maximum age of dredged samples of submarine basalt from which reliable paleointensities can be obtained.

Two factors could affect this age limit, which is derived from data only from dredged (and hence exposed) basalt pillow fragments: (1) increased temperatures, perhaps up to 100°C, that would result from hydrothermal activity at spreading ridges could accelerate the formation of titanomaghemite. (2) Because low-temperature oxidation depends on more or less intimate access of seawater to the basalt, formation of titanomaghemite could be expected to be retarded in massive unfractured basalt flows or shallow sills [Ryall et al., 1977; Marshall, 1978; Johnson and Hall, 1978].

From these considerations it appears that the uniformly low paleointensities that Carmichael [1970] obtained from basalt fragments dredged in the Atlantic at distances greater than 10 km from the Mid-Atlantic Ridge are too low because of progressive submarine weathering of the basalt. Although Carmichael used a different experimental method, the behavior of titanomagnetite on heating can be shown to cause errors similar to those we found using the Thellier’s method [Coe and Grommé, 1973]. The same explanation probably accounts for the low values of paleointensity found by Dunlop and Haele [1976], who used the Thellier’s method with DSDP core samples obtained several kilometers from the Mid-Atlantic Ridge.

On the other hand, our experimental results provide no reason to discount the unusually high paleointensities that Carmichael [1970] and Ade-Hall et al. [1973] reported for basalt observed from the median valley of the Mid-Atlantic Ridge at 45°N.

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