University of Portland
Pilot Scholars

Environmental Studies Faculty Publications and Presentations

Environmental Studies

10-10-1973

Stable Single-Domain to Superparamagnetic Transition During Low-Temperature Oxidation of Oceanic Basalts

Robert F. Butler
University of Portland, butler@up.edu

Follow this and additional works at: http://pilotscholars.up.edu/env_facpubs

Part of the Environmental Sciences Commons, Geology Commons, and the Geophysics and Seismology Commons

Citation: Pilot Scholars Version (Modified MLA Style)

Butler, Robert F., "Stable Single-Domain to Superparamagnetic Transition During Low-Temperature Oxidation of Oceanic Basalts" (1973). *Environmental Studies Faculty Publications and Presentations*. 20.
http://pilotscholars.up.edu/env_facpubs/20

This Journal Article is brought to you for free and open access by the Environmental Studies at Pilot Scholars. It has been accepted for inclusion in Environmental Studies Faculty Publications and Presentations by an authorized administrator of Pilot Scholars. For more information, please contact library@up.edu.

Stable Single-Domain to Superparamagnetic Transition during Low-Temperature Oxidation of Oceanic Basalts

ROBERT F. BUTLER

Department of Geology and Geophysics, University of Minnesota
Minneapolis, Minnesota 55455

Recent experimental data on synthetic titanomaghemites indicate that oxidation is accompanied by a decrease in magnetocrystalline anisotropy K_1 as well as a decrease in the saturation magnetization σ_s. Theory of relaxation times predicts that the decrease of σ_s and K_1 with oxidation will cause single-domain titanomagnetite grains with initially low blocking temperatures to become superparamagnetic as they are oxidized to titanomaghemite. For titanomagnetites ($Fe_{3-x}Ti_xO_4$) of composition $x = 0.4$ and $x = 0.5$ the affected blocking temperature range is approximately 200° and 125°K below the Curie point, respectively. However, for $x = 0.6$ titanomagnetites the blocking temperature range affected is within 80°K of the Curie point and spans a temperature interval from 325° to as high as 380°K, depending on the degree of oxidation. The rapid quenching of oceanic pillow lavas (average composition $x \cong 0.6$) produces efficient thermoremanence carriers but will also result in a significant grain size and blocking temperature distribution. Thus low-temperature oxidation of oceanic basalts could cause a significant portion of the originally stable carriers of natural remanence to become superparamagnetic. This mechanism could aid in explaining the large natural remanent magnetization intensity decrease of dredged basalts with distance from the mid-Atlantic ridge.

In a series of articles concerning dredged basalts from the mid-Atlantic ridge at 45°N by *Irving et al.* [1970], *Schaeffer and Schwarz* [1970], *Carmichael* [1970], *Park and Irving* [1970], and *Irving* [1970] a 90% decrease in natural remanent magnetization (NRM) intensity was found as the sample localities moved from the median valley to the ridge flanks. *Irving et al.* [1970] found that most of this large decrease occurred over a distance of only 6 km from the median valley. At a half-spreading rate of 2 cm/yr this would represent only 0.3 m.y. Total iron content ($FeO + Fe_2O_3$) was found to be constant, but the ferrous/ferric ratio (FeO/Fe_2O_3) decreases sharply with distance from the ridge. Blocking temperature T_B and median destructive field (af field at which 50% of the NRM has been destroyed) were found to increase with distance from the ridge.

Curie point (T_c), cell edge, and microprobe studies by *Schaeffer and Schwarz* [1970] indicate that the titanomagnetite phase of the dredged basalts has an Fe/Ti ratio of approximately 4.6. This ratio corresponds to a titanomagnetite composition ($Fe_{3-x}Ti_xO_4$) of $x = 0.55$. Curie point and cell edge data of *Carmichael* [1970] indicate an average composition of $x \cong 0.6$. Scanning electron microscopy has revealed the existence of abundant very-fine-particle ($<1\ \mu$) titanomagnetites in the dredged basalts [*Evans and Wayman,* 1972]. Such fine-particle titanomagnetites would be expected to act as single-domain or pseudo-single-domain carriers of remanent magnetization.

Park and Irving [1970] discovered that the ratio of NRM of the median valley rocks to NRM of samples from the ridge flanks could be decreased by comparing intensities after af demagnetization. However, the ratio never dropped below 3:1. This finding would suggest that viscous demagnetization of low-coercivity particles cannot entirely account for the NRM decrease with age. Park and Irving suggested that the variation in magnetic properties might be due to some type of oxidation process. *Carmichael* [1970] has attributed some of the NRM decrease to paleofield variations.

In a review and discussion of the series of articles on the mid-Atlantic ridge at 45°N *Irving* [1970] pointed out that the rapid quenching of basalt in the axial zone along

Copyright © 1973 by the American Geophysical Union.

with the sulfide content of the basalts would produce very-fine-grained titanomagnetite grains with little or no high-temperature deuteric oxidation. These fine-grained titanomagnetites would be very efficient thermoremanent magnetization (TRM) carriers but would also be susceptible to low-temperature oxidation. The constant $FeO + Fe_2O_3$ and decreasing FeO/Fe_2O_3 ratio along with increasing H_2O content with distance from the median valley led Irving to suggest that the changes in magnetic properties of the dredged basalts could be due to oxidation of the original titanomagnetite to a cation-deficient titanomaghemite. The NRM decrease would then be caused partly by viscous demagnetization of low-coercivity grains and partly by oxidation of titanomagnetite to titanomaghemite.

On theoretical grounds *Marshall and Cox* [1972] excluded viscous demagnetization as a cause for the NRM intensity decrease. In a single pillow basalt fragment with varying degrees of oxidation, a 40% decrease in NRM intensity and saturation magnetization was found in the weathered zone, compared with the fresh interior. An increase in Curie point and median destructive field along with a decrease in cell edge was found with increasing degree of oxidation. Marshall and Cox thus proposed that the changes in magnetic properties with distance from the median valley found in the study reviewed by *Irving* [1970] are analogous to the changes observed with increasing degree of weathering within their single pillow basalt fragment. They further suggest that the NRM decrease with distance from the ridge is entirely due to maghemitization.

By spectral analysis of marine magnetic anomalies *Cox et al.* [1972] have shown that the source of the linear magnetic anomalies can best be modeled with a two-layer oceanic crust. The thin upper layer becomes less magnetic as it moves away from the ridge, whereas the thicker, initially less magnetic lower layer keeps its initial intensity of magnetization. Maghemitization of the upper layer is proposed as a mechanism for the decrease in intensity of magnetization.

Banerjee [1971, 1972] has suggested that an intrinsic decay mechanism due to ionic diffusion of Fe^{2+} ions in quenched titanomagnetites may lead to a decrease in remanence coercivity with increasing age. This decrease could produce a decrease in NRM intensity that would add to the decrease due to oxidation.

Readman and O'Reilly [1972] have studied the magnetic properties of synthesized titanomaghemites with increasing degree of oxidation. Degree of oxidation z is defined as the fraction of total Fe^{2+} ions initially in the sample that have been converted to Fe^{3+}. Readman and O'Reilly oxidized very-fine-grained titanomagnetites ($Fe_{3-x}Ti_xO_4$) with $x = 0.0$, 0.4, 0.7, and 1.0 to cation-deficient titanomaghemites by heating in air to 200°–300°C. Magnetic properties and weight changes of the samples were carefully monitored as oxidation proceeded. Curie temperature was found to increase with increasing z, whereas cell edge and saturation magnetization σ_s decreased. Rotational hysteresis experiments on the $x = 0.4$ sample suggest a strong decrease in the magnetocrystalline anisotropy constant K_1 with increasing oxidation. Similar rotational hysteresis data on $x = 0.5$ and $x = 0.6$ also indicate a decrease in magnetocrystalline anisotropy with increasing z [*Manson,* 1972].

Marshall and Cox [1972] have pointed out that the decrease in σ_s accompanying oxidation will decrease NRM intensity by diminishing the saturation magnetization of the stable single-domain grains in sea floor basalts. We propose that the decrease in σ_s and K_1 observed by Readman and O'Reilly will lead to an additional decrease in NRM intensity by causing a significant portion of titanomagnetite grains that, when they are unoxidized, are stable single-domain grains to become superparamagnetic as they are oxidized to titanomaghemite. Thus not only will the intensity of NRM due to the stable single-domain grains decrease by oxidation, but the number of such grains will be diminished by oxidation.

THEORY OF RELAXATION TIMES

According to *Neel* [1955] the relaxation time of a single-domain grain is given by

$$1/\tau_0 = C \exp(-vH_c\sigma_s/2kT) \qquad (1)$$

where τ_0 is relaxation time in seconds, C is frequency factor of 10^9 sec^{-1}, v is grain volume in cubic centimeters, H_c is coercive force of the grain in oersteds, σ_s is saturation magnetization in electromagnetic units per cubic centimeter, k

is the Boltzmann constant, and T is absolute temperature. For cubic grains whose coercive force is determined by magnetocrystalline anisotropy [*Chikazumi*, 1964]

$$H_c = \tfrac{4}{3}K_1/\sigma_s \tag{2}$$

where K_1 is the magnetocrystalline anisotropy constant. If magnetocrystalline anisotropy is dominant, (1) will become

$$1/\tau_0 = C \exp(-2vK_1/3kT) \tag{3}$$

However, if shape anisotropy is dominant,

$$H_c = \Delta N_D \sigma_s \tag{4}$$

where ΔN_D is the difference in self-demagnetizing factor between the polar and equatorial axes of ellipsoidal particles. For shape anisotropy, (1) will become

$$1/\tau_0 = C \exp(-v\Delta N_D \sigma_s^2/2kT) \tag{5}$$

Although σ_s decreases with increasing x and the absolute value of coercivity arising from shape anisotropy (for a given ΔN_D) decreases with increasing Ti content, the relative importance of shape anisotropy and magnetocrystalline anisotropy is not easy to predict. *Syono* [1965] reports that the room temperature magnetocrystalline anisotropy constant K_1 also decreases with increasing x in the composition range of the dredged oceanic basalts ($0.4 \leq x \leq 0.6$). In fact, K_1 changes from negative to positive at $x \cong 0.65$. Thus calculations of coercivities for titanomagnetites in the range $0.4 \leq x \leq 0.6$ should consider both shape anisotropy and magnetocrystalline anisotropy. The possibility that coercive force could be controlled by magnetostriction will be discussed later.

At the blocking temperature T_B the relaxation time $[\tau_0(T_B)]$ is given by

$$1/\tau_0(T_B) = C \exp[-2vK_1(T_B)/3kT_B] \tag{6}$$

for magnetocrystalline-controlled coercive force, where $K_1(T_B)$ is the magnetocrystalline anisotropy constant at T_B. For shape-controlled coercivity the blocking temperature relaxation time will be

$$1/\tau_0(T_B) = C \exp\{-v\Delta N_D[\sigma_s(T_B)]^2/2kT_B\} \tag{7}$$

If the blocking temperature is known from thermal demagnetization experiments and a value can be assigned to $\tau_0(T_B)$ by setting it approximately equal to the time spent at the blocking temperature during the experiment (e.g., 10^3 sec), the volume of the grains with a given T_B can be calculated (when single-domain behavior is assumed) by

$$v = [\ln C\tau_0(T_B)][3kT_B/2K_1(T_B)] \tag{8}$$

for magnetocrystalline anisotropy and by

$$v = \{\ln C\tau_0(T_B)\}\{2kT_B/\Delta N_D[\sigma_s(T_B)]^2\} \tag{9}$$

for shape anisotropy.

Given the activation volume v corresponding to various blocking temperatures, the relaxation time at room temperature (290°K) as a function of oxidation state z can be calculated by

$$1/\tau_0(290°\mathrm{K}, z) = C \exp[-vH_c(290°\mathrm{K}, z) \cdot \sigma_s(290°\mathrm{K}, z)/2k \cdot 290°\mathrm{K}] \tag{10}$$

where $H_c(290°\mathrm{K}, z)$ is the coercive force at 290°K and oxidation state z and $\sigma_s(290°\mathrm{K}, z)$ is the saturation magnetization at 290°K and z; $H_c(290°\mathrm{K}, z)$ is

$$H_c(290°\mathrm{K}, z) = \tfrac{4}{3}K_1(290°\mathrm{K}, z)/\sigma_s(290°\mathrm{K}, z) \tag{11}$$

or

$$H_c(290°\mathrm{K}, z) = \Delta N_D \sigma_s(290°\mathrm{K}, z)$$

for magnetocrystalline and shape anisotropy, respectively, where $K_1(290°\mathrm{K}, z)$ is the magnetocrystalline anisotropy constant at 290°K and oxidation state z. Substituting v from (8) and (9) and $H_c(290°\mathrm{K}, z)$ from (11) into (10) yields

$$1/\tau_0(290°\mathrm{K}, z) = C \exp\{-[\ln C\tau_0(T_B)] \cdot [T_B K_1(290°\mathrm{K}, z)/K_1(T_B) \cdot 290°\mathrm{K}]\} \tag{12}$$

for magnetocrystalline anisotropy and

$$1/\tau_0(290°\mathrm{K}, z) = C \exp\{-[\ln C\tau_0(T_B)] \cdot [T_B(\sigma_s(290°\mathrm{K}, z))^2/(\sigma_s(T_B))^2 \cdot 290°\mathrm{K}]\} \tag{13}$$

for shape anisotropy. Thus we should be able to calculate room temperature relaxation times as a function of blocking temperature of the unoxidized titanomagnetite and oxidation state

of the titanomaghemite resulting from low-temperature oxidation.

If $\tau_0(290°K, z)$ falls below a value that is less than the time span of interest to paleomagnetism, the grain can be considered to have become thermally unstable or superparamagnetic. Therefore knowledge of composition and blocking temperature of titanomagnetite in fresh oceanic lavas along with knowledge of the dependence of coercive force on oxidation state should allow us to determine what blocking temperature range will become superparamagnetic as a result of low-temperature oxidation to titanomaghemite. If a significant proportion of the NRM is contained in grains that are stable single domains when they are stoichiometric but that become superparamagnetic when they are oxidized to cation-deficient spinels, this mechanism could help to explain the large observed decrease in NRM intensity with distance from the median valley.

RELAXATION TIME CALCULATIONS

Unfortunately, not all the data required for calculation of $\tau_0(290°K, z)$ are presently available or easy to measure. Specifically, K_1-T and σ_s-T data are required. *Syono* [1965] gives K_1-T/T_c for $x = 0.31$ in the temperature range $0.1 \leq T/T_c \leq 0.5$ and K_1-T/T_c for $x = 0.56$ in the range $0.5 \leq T/T_c \leq 0.7$. To determine K_1-T for $x = 0.4$, 0.5, and 0.6 titanomagnetites, several extrapolations of the available data are required. First, we must extrapolate Syono's K_1-T/T_c data for $x = 0.31$ and 0.56 to the Curie temperature in some 'reasonable' fashion. Such an extrapolation along with the original data is shown in Figure 1*a*. Second, we must interpolate the temperature dependence of K_1 for $x = 0.4$, 0.5, and 0.6 from the dependence of K_1 on T/T_c for $x = 0.31$ and 0.56. This interpolation can be accomplished by making the reasonable assumption that the form of K_1-T/T_c will be similar for $x = 0.4$ and 0.31 and that similarity of form will exist between $x = 0.5$, 0.56, and 0.6. Thus K_1-T/T_c for $x = 0.4$ can be estimated by

$$K_1(x = 0.4, T/T_c) = [K_1(0.4, 290°K) \cdot K_1(0.31, T/T_c)/K_1(0.31, 290°K)]$$

where $K_1(0.4, 290°K)$ and $K_1(0.31, 290°K)$ are the room temperature magnetocrystalline anisotropy constants taken from *Syono* [1965]. The resulting K_1-T curves for $x = 0.4$, 0.5, and 0.6 are shown in Figure 1*b*. Room temperature relaxation time calculations for titanomagnetite grains whose coercivity is controlled by magnetocrystalline anisotropy can now be made.

Similar relaxation time calculations for grains whose coercive force is dominated by shape anisotropy can be made only if we know the temperature dependence of σ_s. *Stephenson* [1972*a*] theoretically derived normalized σ_s-T/T_c curves for $0 \leq x \leq 0.95$. The solid line plots of σ_s-T in Figure 2 were calculated by using the normalized σ_s-T/T_c calculations of Stephenson along with σ_s-x data from *O'Reilly and Banerjee* [1965].

However, comparison of *Stephenson's* [1972*b*] predicted σ_s-T/T_c behavior for pure magnetite

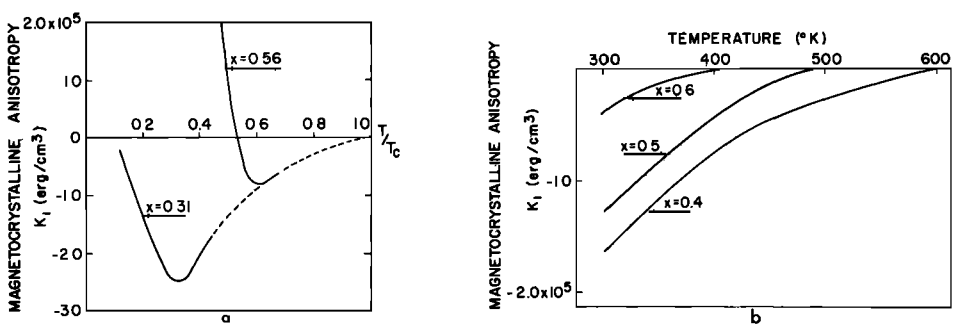

Fig. 1. Magnetocrystalline anisotropy constant K_1 (*a*) as a function of T/T_c (the solid lines are from *Syono* [1965], whereas the dashed lines are extrapolations; the extrapolated curves overlap for $T/T_c > 0.7$) and (*b*) as a function of temperature for titanomagnetites of composition $x = 0.4$, 0.5, and 0.6 (the curves were derived from assumed similarity of the form of K_1-T/T_c for $x = 0.31$ and $x = 0.4$ and similarity of K_1-T/T_c for 0.5, 0.56, and 0.6).

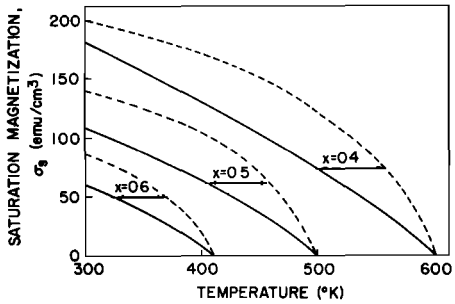

Fig. 2. Saturation magnetization σ_s versus temperature for titanomagnetite of $x = 0.4$, 0.5, and 0.6. Normalized magnetization versus T/T_c plots of *Stephenson* [1972*a*] and σ_s-x data from *O'Reilly and Banerjee* [1965] were used to calculate the solid curves. The experimental σ_s-T/T_c curve of *Weiss* [1907] was used to derive the dashed curves.

does not agree with the experimental curve of *Weiss* [1907]. Stephenson suggests that the discrepancy is due to positive $Fe^{3+}Fe^{2+}$ BB interactions that have been neglected in his theoretical treatment. Since B site Fe^{3+} concentration decreases with increasing x, theory and experiment should be in better agreement as x increases.

Because the accuracy of Stephenson's theoretical model for titanomagnetites is unconfirmed, σ_s-T curves for $x = 0.4$, 0.5, and 0.6 were also calculated by using the experimental σ_s-T/T_c data of *Weiss* [1907] for magnetite on the assumption that the normalized σ_s-T/T_c behavior will not change with increasing x. The resulting plots are shown by dashed lines in Figure 2. The actual σ_s-T behavior will likely fall between these curves. Thus results obtained by using either the *Stephenson* [1972*a*] theoretical σ_s-T curve or the *Weiss* [1907] experimental curve should be considered extrema, the actual behavior falling between the two.

Room temperature relaxation times as a function of oxidation state can be calculated by (12) and (13) if the dependence of K_1 and σ_s on oxidation state is known. These dependences can be estimated from the data of *Readman and O'Reilly* [1972] and *Manson* [1972].

Saturation magnetization (4.2°K) as a function of oxidation state is given in terms of Bohr magnetons μ_B per molecule for $x = 0.4$ and $x = 0.7$ in Figure 2 of *Readman and O'Reilly* [1972]. If we assume that the form of σ_s-z for $x = 0.5$ will follow that of σ_s-z for $x = 0.4$ and that σ_s-z for $x = 0.6$ will be similar in form to the data given for $x = 0.7$, the oxidation state dependences of saturation magnetization shown in Figure 3*a* can be derived. Since the saturation magnetization versus z data of *Readman and O'Reilly* [1972] were determined at 4.2°K, they must be adjusted to room temperature. As was true with the σ_s-T curves of Figure 2, both the *Stephenson* [1972*a*] and *Weiss* [1907] σ_s-T/T_c curves were used for this adjustment from 4.2° to 290°K. The increase in Curie temperature with increasing z has also been taken into account in deriving the room temperature σ_s-z curves of Figure 3*a*.

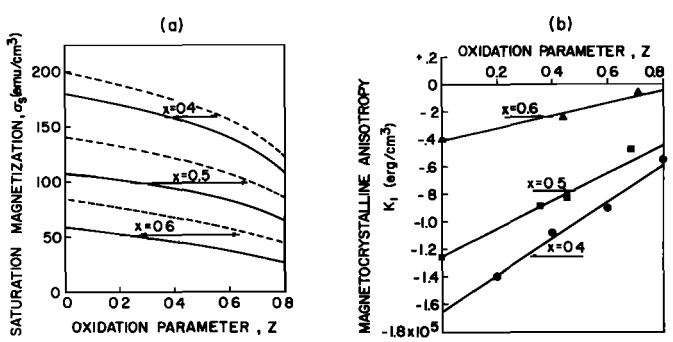

Fig. 3. Oxidation state dependences. (*a*) Saturation magnetization σ_s as a function of oxidation state z. The plots were derived from the μ_B/molecule-z data of *Readman and O'Reilly* [1972] for $x = 0.4$ and 0.7. The dashed curves indicate data adjusted to 290°K by using the *Weiss* [1907] σ_s-T/T_c dependence, whereas the solid curves indicate data adjusted by using the σ_s-T/T_c plots of *Stephenson* [1972*a*]. (*b*) Magnetocrystalline anisotropy constant K_1 versus oxidation parameter z. Data points were calculated from rotational hysteresis data of *Readman and O'Reilly* [1972] and *Manson* [1972] by using $K_1 \propto H_p(z)\sigma_s(z)$.

Rotational hysteresis data from *Readman and O'Reilly* [1972] allow an estimate of the dependence of magnetocrystalline anisotropy on oxidation state for titanomagnetite of $x = 0.4$. The maximum realizable shape anisotropy field for $x = 0.4$ would be $2\pi\sigma_s = 1.5$ koe for needle-shaped grains. The magnetocrystalline anisotropy field is of the order of $(4/3)K_1/\sigma_s = 1.1$ koe. However, for the synthetic ball-milled samples, ΔN_D should be substantially less than 2π. Thus magnetocrystalline anisotropy should dominate for the synthetic $x = 0.4$ samples. Since H_p (peak hysteresis loss field) is proportional to K_1/σ_s, K_1 can be calculated as a function of z by using $K_1(z) \propto H_p(z)\sigma_s(z)$. The resulting K_1-z ($x = 0.4$) curve is shown in Figure 3*b*. The rotational hysteresis data of *Manson* [1972] on $x = 0.5$ and $x = 0.6$ titanomagnetites allow calculation of H_p-z plots from which K_1-z can be obtained. The resulting K_1-z curves are also shown in Figure 3*b*.

By means of the newly derived dependence of K_1 and σ_s on oxidation state, room temperature relaxation times $\tau_0(290°\text{K}, z)$ can be determined by the use of (12) and (13). The results of these calculations are shown in Figures 4 and 5, which show the oxidation state at which $\tau_0(290°\text{K}, z)$ falls below 10^4 years as a function of the blocking temperature of the unoxidized grain (10^4 years is small compared to the times of interest in studying the decay of marine magnetic anomalies). For example, an unoxidized titanomagnetite grain of composition $x = 0.6$ whose coercive force is controlled by magnetocrystalline anisotropy and whose blocking temperature is initially 350°K will become superparamagnetic ($\tau_0(290°\text{K}, z) < 10^4$ years) when it is oxidized to titanomaghemite of $z \hat{=} 0.5$. The corresponding transition curves for shape-controlled anisotropy are shown in Figure 5(*a*, *b*).

Because the true σ_s-T behavior will likely fall between the two dependences used in the relaxation calculations for grains with shape-controlled coercivity, the transition curves of Figure 5(*a*, *b*) represent limits within which the true shape anisotropy transition curves will fall. The necessary extrapolation of available K_1-T data used in obtaining the transition curves of Figure 4 introduces some uncertainty into the calculations. An error in the estimated K_1-T behavior would shift the transition curves up or down the blocking temperature axis. However, since the blocking temperatures affected are within 125°K of the available experimental magnetocrystalline anisotropy data, no extensive extrapolation of K_1-T is required, and the calculated transition curves of Figure 4 are thought to be accurate to within 10°–20°K.

DISCUSSION

It appears that oxidation to titanomaghemite and the resulting transition of some grains from stable remanence carriers to superparamagnetic ones will be most important for $x = 0.6$ titanomagnetites. For $x = 0.4$ and $x = 0.5$ the range of blocking temperatures affected is far below the Curie temperature. Conditions under which a significant portion of the NRM would be blocked at temperatures 150°–250°K below the Curie temperature are difficult to imagine. However, for $x = 0.6$ (the composition of interest for oceanic basalts) the range of blocking temperatures affected is within 100°K of the Curie temperature. Blocking temperature distributions extending to 100°K below the Curie temperature are not at all uncommon.

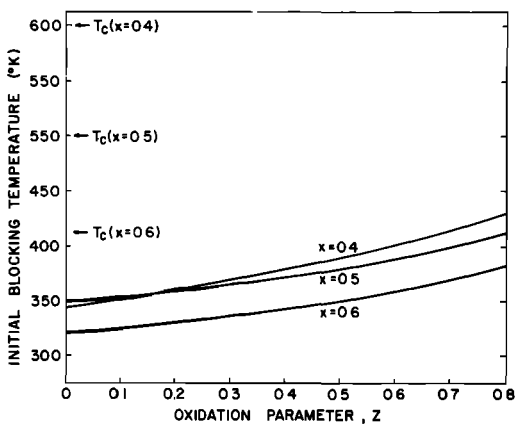

Fig. 4. Stable single-domain to superparamagnetic transition curves of $x = 0.4$, 0.5, and 0.6 titanomagnetites for grains in which coercivity is dominated by magnetocrystalline anisotropy. The lines show the degree of oxidation at which a titanomagnetite grain with initial blocking temperature given on the y axis will become superparamagnetic ($\tau_0(290°\text{K}, z) < 10^4$ years). For example, a titanomagnetite grain with $x = 0.4$ and a blocking temperature of 375°K will be a stable single domain in the unoxidized state but will become superparamagnetic at room temperature if it is oxidized to titanomaghemite with $z = 0.35$.

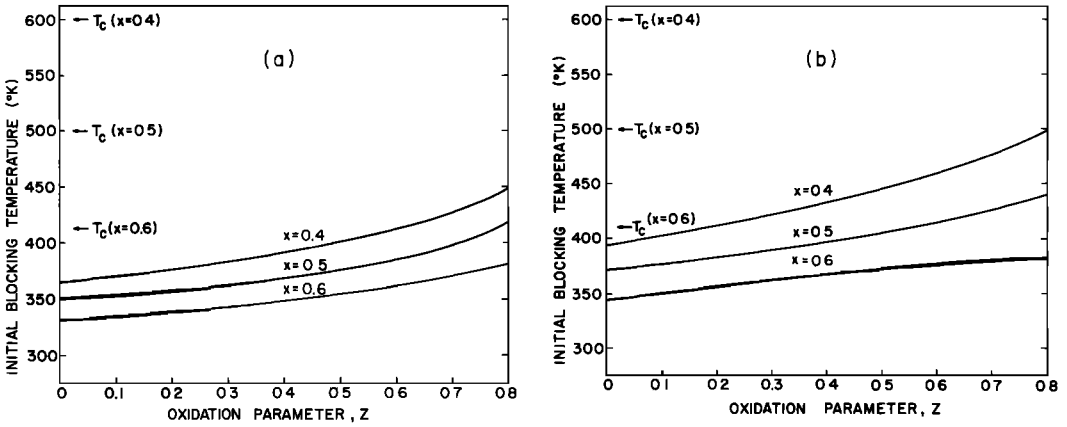

Fig. 5. Stable single-domain to superparamagnetic transition curves of $x = 0.4$, 0.5, and 0.6 titanomagnetites for grains with dominant shape anisotropy for the σ_s-T behavior predicted by (*a*) *Stephenson* [1972*a*] and (*b*) *Weiss* [1907]. The curves illustrate the oxidation state at which a titanomagnetite grain of initial blocking temperature given on the y axis will become superparamagnetic (τ_0(290°K, z) $< 10^4$ years). For example, in Figure 5*a* a titanomagnetite grain of $x = 0.6$ and initial blocking temperature of 350°K will be stable single domain for $z < 0.5$ but will become superparamagnetic if it is oxidized to a cation-deficient spinel of $z \geq 0.5$.

The range of blocking temperatures that will be affected obviously depends on the degree of oxidation. For titanomagnetite of $x = 0.6$ and dominant magnetocrystalline anisotropy, grains with initial blocking temperatures of 320°–380°K will become superparamagnetic (and therefore will not contribute to NRM intensity) when oxidation proceeds to $z = 0.8$. However, if titanomaghemitization proceeds only to $z = 0.5$, only grains with initial blocking temperatures of 320°–350°K will become superparamagnetic. It should be noted that the bulk effect of oxidation will be to cancel the contribution of low blocking temperature grains to the NRM while only reducing the contribution of grains with higher T_B by the amount of the σ_s decrease. This effect could help to explain the increase in mean blocking temperature with distance from the median valley noted by *Irving* [1970].

It is interesting to note that the evolution of thermomagnetic curves with degree of oxidation shown in Figure 5 of *Readman and O'Reilly* [1972] along with the attendant Curie point increase can nicely explain the increased blocking temperature of grains whose initial T_B is close to the Curie temperature. For example, an $x = 0.6$ grain with shape-controlled coercivity and blocking temperature within 10°–20°C of the Curie point will be very strongly blocked at room temperature and will not become superparamagnetic during low-temperature oxidation. Although the room temperature saturation magnetization σ_s of this grain will decrease during oxidation, the increasing Curie point will change the σ_s-T curve so as to produce an increase in blocking temperature. Similar changes in K_1-T with increased Curie point will also produce an increase in T_B for grains with magnetocrystalline-dominated coercivity and initial blocking temperature close to the Curie temperature. Thus the oxidation-induced stable single-domain to superparamagnetic transition of grains with low blocking temperatures along with the increasing blocking temperature of the remaining stable single-domain grains will yield the increase in mean blocking temperature with distance from the median valley that was observed by *Irving* [1970].

Unfortunately, the quantitative importance of the calculations above in accounting for the large NRM intensity decrease of dredged basalts with age is difficult to ascertain. First, the degree of oxidation of the dredge samples is not accurately known because the determinations of cell edge, Curie temperature, and saturation magnetization required to place these samples within the cation-deficient field are very difficult to perform on natural samples.

Second, the blocking temperature distribution of the natural samples is not accurately known. However, for the decrease in saturation magnetization alone to account for the 90% decrease in natural remanent intensity observed by *Irving et al.* [1970], low-temperature oxidation to greater than $z = 0.8$ would be required. An additional NRM decrease resulting from the stable single-domain to superparamagnetic transition of low blocking temperature grains would allow the observed NRM decrease to be accounted for by a much lower (and more reasonable) degree of oxidation.

Inspection of Figures 4 and 5 indicates that, if the blocking temperature distribution in the fresh basalts of interest ($x \simeq 0.6$) extends to only 60°K below the Curie temperature, little oxidation is required before a significant portion of the previously stable remanence carriers will become superparamagnetic. For $x = 0.6$ grains with dominant magnetocrystalline anisotropy, oxidation to $0.5 \leq z \leq 0.8$ will cause grains in the initial blocking temperature range 350°–380°K to become superparamagnetic. For $x = 0.6$ grains with dominant shape anisotropy, oxidation into the range $0.2 \leq z \leq 0.8$ would progressively initiate the stable single-domain to superparamagnetic transition for the blocking temperature range 340°–380°K. Thus, given a distribution of blocking temperatures appreciably below the Curie point, oxidation to titanomaghemite will cause a significant portion of the originally stable carriers of NRM to become superparamagnetic.

The rapid quenching of oceanic pillow basalts produces small titanomagnetite grains that are efficient TRM carriers (in the fresh material) and are susceptible to low-temperature oxidation. Rapid quenching will also assure a wide grain size distribution. This grain size distribution will result in a spread of blocking temperatures appreciably below the Curie temperature. Therefore the quenching process assures that a significant portion of the NRM carriers in fresh pillow lavas will fall prey to the transition to superparamagnetism outlined above as low-temperature oxidation proceeds.

As was mentioned previously, the increase in the mean blocking temperature with distance from the median valley reported by *Irving et al.* [1970] and *Irving* [1970] could result from the oxidation-induced stable single-domain to superparamagnetic transition of the low blocking temperature grains along with the increased blocking temperature of the remaining stable grains. However, the parallel increase in resistance to af demagnetization reported by *Irving et al.* [1970] for the dredged basalts and similar increase in af demagnetization resistance of the weathered region in the single pillow basalt studied by *Marshall and Cox* [1972] is more difficult to explain. If coercive force is due to shape anisotropy, af demagnetization resistance should decrease as σ_s decreases with oxidation. However, if coercivity is dominated by magnetocrystalline anisotropy and K_1 decreases more slowly than σ_s, K_1/σ_s would increase with oxidation, and af demagnetization resistance would increase. Although peak rotational hysteresis loss field H_p decreases with oxidation for $x \leq 0.55$, H_p increases during oxidation for $x \geq 0.6$ [*Manson*, 1972]. This increase in H_p indicates a corresponding increase in microscopic coercivity with oxidation for $x \geq 0.6$. *Marshall and Cox* [1972] have suggested that inhomogeneous oxidation could produce internal strains that would produce higher coercivity through magnetostrictive effects.

The effects of internal stress on the coercivity of stoichiometric titanomagnetites in the composition range $x = 0.5$–0.6 may be significant. Because the magnetostrictive constant λ_{100} is increasing in the range $0.4 \leq x \leq 0.6$ [*Syono*, 1965], whereas σ_s is decreasing, and magnetostrictive $H_c = 3\lambda\sigma/\sigma_s$, where σ is stress, internal stress may become an important contributor to coercivity in the $x = 0.6$ composition region. The dependence of λ on temperature (above room temperature) and oxidation state is unknown. Both magnetocrystalline anisotropy and magnetostriction arise from the energy dependence of the electron probability distributions on the direction of the orbital angular momentum vector **L** and the interatomic spacing. These energy dependences are manifested in macroscopic direction and stress dependences of the magnetic moment via spin-orbit coupling. Given the similarity in origin of magnetostrictive and magnetocrystalline anisotropy, it would be not only reasonable but even imperative to predict a similarity in the dependences of λ and K_1 on oxidation state. Thus the possibility that the initial coercivity of $x = 0.6$ titanomagnetites could be due to magnetostriction will not affect

the qualitative aspects of the theory outlined above. A decrease in λ with oxidation would produce the same stable single-domain to superparamagnetic transition in the lower blocking temperature grains as is predicted by the decrease of K_1 with z.

CONCLUSION

Although several extrapolations and interpolations of available data are required in the calculations of activation volumes and room temperature relaxation times, it seems clear that the outlined theory of stable single-domain to superparamagnetic transition during low-temperature oxidation can help explain the large NRM intensity decrease with increasing age observed in dredged oceanic basalts. The resulting diminished contribution of low blocking temperature grains along with increased T_B of the remaining stable single-domain grains could also help to explain the increased mean blocking temperature with increasing distance from the median valley. The decreasing contribution to marine magnetic anomalies of the upper layer in the two-layer model of oceanic crust proposed by *Cox et al.* [1972] could also be aided by the mechanism above of NRM intensity decrease.

Thus the decrease in natural remanence intensity observed in oceanic basalts may be due not only to the decrease in saturation magnetization by oxidation of the stable single-domain grains as proposed by *Marshall and Cox* [1972]. Oxidation to a cation-deficient spinel will also decrease the number of stable NRM carriers by causing a significant portion of the titanomagnetite grains to become superparamagnetic as they are oxidized.

Acknowledgments. I am indebted to Subir Banerjee for many helpful discussions of this project and for critically reviewing the manuscript. I also thank Peter Shive for reading the manuscript in preliminary form.

This work was supported by NSF grant GA 35249.

REFERENCES

Banerjee, S. K., Decay of marine magnetic anomalies by ferrous ion diffusion, *Nature Phys. Sci.*, *229*, 181, 1971.

Banerjee, S. K., Rock magnetic aspects of marine magnetic anomalies, *Comments Earth Sci. Geophys.*, *2*, 169, 1972.

Carmichael, C. M., The mid-Atlantic ridge near 45°N, 7, Magnetic properties and opaque mineralogy of dredged samples, *Can. J. Earth Sci.*, *7*, 239, 1970.

Chikazumi, S., *Physics of Magnetism*, pp. 136–138, John Wiley, New York, 1964.

Cox, A., R. J. Blakely, and J. D. Phillips, A two-layer model for marine magnetic anomalies (abstract), *Eos Trans. AGU*, *53*, 974, 1972.

Evans, M. E., and M. L. Wayman, The mid-Atlantic ridge near 45°N, 19, An electron microscope investigation of the magnetic minerals in basalt samples, *Can. J. Earth Sci.*, *9*, 671, 1972.

Irving, E., The mid-Atlantic ridge near 45°N, 14, Oxidation and magnetic properties of basalt; Review and discussion, *Can. J. Earth Sci.*, *7*, 1528, 1970.

Irving, E., W. A. Robertson, and F. Aumento, The mid-Atlantic ridge near 45°N, 6, Remanent intensity, susceptibility, and iron content of dredged samples, *Can. J. Earth Sci.*, *7*, 226, 1970.

Manson, A., Rotational hysteresis measurements on oxidized synthetic and natural titanomagnetites, Ph.D. thesis, Univ. of Newcastle upon Tyne, Newcastle, England, 1972.

Marshall, M., and A. Cox, Magnetic changes in pillow basalt due to sea floor weathering, *J. Geophys. Res.*, *77*, 6459, 1972.

Neel, L., Some theoretical aspects of rock magnetism, *Advan. Phys.*, *4*, 191, 1955.

O'Reilly, W., and S. K. Banerjee, Cation distribution in titanomagnetites $(1 - x)Fe_3O_4$-xFe_2TiO_4, *Phys. Lett.*, *17*, 237, 1965.

Park, J. K., and E. Irving, The mid-Atlantic ridge near 45°N, 12, Coercivity, secondary magnetization, polarity, and thermal stability of dredged samples, *Can. J. Earth Sci.*, *7*, 1499, 1970.

Readman, P. W., and W. O'Reilly, Magnetic properties of oxidized (cation deficient) titanomagnetites (Fe, Ti, $\square)_3O_4$, *J. Geomagn. Geoelec.*, *24*, 69, 1972.

Schaeffer, R. M., and E. J. Schwarz, The mid-Atlantic ridge near 45°N, 9, Thermomagnetics of dredged samples of igneous rocks, *Can. J. Earth Sci.*, *7*, 268, 1970.

Stephenson, A., Spontaneous magnetization curves and Curie points of cation deficient titanomagnetites, *Geophys. J.*, *29*, 91, 1972*a*.

Stephenson, A., Spontaneous magnetization curves and Curie points of spinels containing two types of magnetic ion, *Phil. Mag.*, *25*, 1213, 1972*b*.

Syono, Y., Magnetocrystalline anisotropy and magnetostriction of Fe_3O_4-Fe_2TiO_4 series—With special application to rock magnetism, *Jap. J. Geophys.*, *4*, 71, 1965.

Weiss, P., Hypothesis of the molecular field and ferromagnetic properties, *J. Phys. Radium*, *6*, 661, 1907.

(Received February 9, 1973;
revised June 28, 1973.)