Reports

Magnetite: Behavior near the Single-Domain Threshold

Abstract. *Maximum values for the single-domain threshold* d_0 *and superparamagnetic threshold* d_s *in pure magnetite are found to be* 570 ± 50 *and* 350 ± 50 *angstroms, respectively. Particles larger than* d_0 *but smaller than about 0.25 micron have size-dependent saturation remanences and coercive forces like those of multidomain particles, but intense and stable thermoremanent magnetization like that of single-domain particles. The presence of magnetite grains in this size range could account for the essentially single-domain character of stable natural remanence in many volcanic and intrusive rocks.*

Controversy over the domain state of titanomagnetite grains carrying stable natural remanent magnetization (NRM) in igneous rocks has continued for more than a decade. Part of the NRM is evidently carried by low-coercivity multidomain (MD) grains, but rocks that are reliable in a paleomagnetic sense also possess a stable NRM component, apparently carried by single-domain (SD) grains with coercivities greater than a few hundred oersteds. Yet it has generally been believed that the bulk of the grains, even in fine-grained volcanic rocks, are larger than 1 μm, and magnetite of this size is known to exhibit MD hysteresis (*1*) and domain structure (*2*).

In an effort to reconcile these conflicting facts, it has been supposed either that MD particles contain SD regions (*3, 4*) or else that small MD grains possess a net moment in the "demagnetized" state, due to Barkhausen discreteness in wall positions, which imparts a pseudosingle-domain (PSD) behavior (*5–7*). Larson *et al.* (*4*), on the basis of observed abundances of grains near the limit of optical resolution in size, have pointed out a third and simpler possibility, namely, that true SD particles are in fact rather common in many volcanic rocks and account for much of the stable NRM. This idea has recently gained support with the demonstration (*8, 9*) that certain intrusive rocks also possess a component of NRM with SD-like stability carried by submicroscopic (< 0.5 μm) magnetite particles exsolved in silicate minerals.

My general aim in the study presented here was to stimulate the TRM (thermoremanent magnetization) and hysteresis of these submicroscopic particles, using synthetic magnetite powders of controlled composition and grain size. The electron microscope studies of Evans and Wayman (*8*) suggest 0.05 to 0.5 μm as an appropriate range of grain size. Since most theoretical calculations of the threshold d_0 for SD behavior in equidimensional magnetite particles are also associated with this size range [actual calculated values (*4, 5, 10*) range from 0.03 to 0.1 μm], a particular aim was to determine an experimental value for d_0.

Four samples containing synthetic magnetite particles precipitated from solution were used in the study. X-ray diffraction and thermomagnetic analysis confirmed that the powders contained only pure Fe_3O_4 with a Curie point of $583° \pm 5°C$. Electron micrographs and x-ray line broadening indicated that each particle was a single-crystal cube.

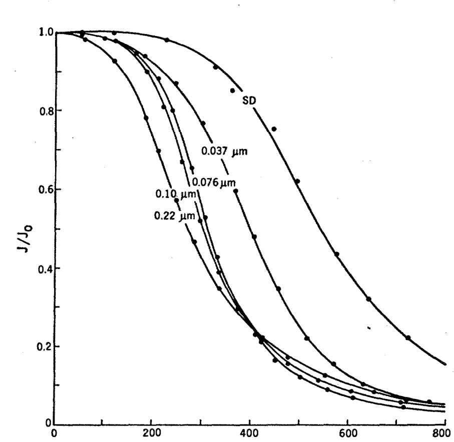

Fig. 1. Normalized AF demagnetization curves of 1-oersted TRM's; *J*, magnetization; J_0, initial value of the magnetization.

In order to obtain magnetic properties referring to a single grain size, either for comparison with theory (*5, 11, 12*) or as a step in determining d_0, the spread of grain sizes in a particular sample must be as small as possible. Grain size spectra from electron micrographs gave the mean grain sizes $\bar{d}$ listed in Table 1 and the following spreads: sample 1, 0.16 to 0.30 μm; sample 2, 0.07 to 0.14 μm; sample 3, 0.04 to 0.12 μm; and sample 4, 0.01 to 0.06 μm. The overlap between sample spectra is not serious except for samples 2 and 3. The standard deviation about $\bar{d}$ ranged from 20 to 40 percent. Measurements of surface area from nitrogen adsorption were also used to find $\bar{d}$, based on the fact that the particles are cubic. The agreement between the two estimates of $\bar{d}$ was within 5 percent.

Each sample contained 1 percent Fe_3O_4 (by volume). The magnetite was dispersed as uniformly as possible in kaolin by prolonged mixing, but some particle clumping doubtless persisted. After vacuum annealing for 24 hours at 750°C, the samples were sealed in quartz tubes under vacuum. Annealing produced virtually no decrease in the saturation magnetization J_s and a change of only a few percent in the saturation remanence J_{rs} and coercive force H_c. Nevertheless, all TRM's were produced below 600°C to avoid magnetizing any hematite that might have been generated. Hysteresis was measured in a maximum field of 1500 oersteds and magnetizations were measured ballistically, with apparatus similar to that of West and Dunlop (*13*).

Table 1 summarizes the grain size dependence of the initial volume susceptibility χ_0, the reduced saturation remanence (applied field $H = 1500$ oersteds) J_{rs}/J_s, the coercive force H_c, TRM (in $H = 1$ oersted) J_{tr}, and the Koenigsberger ratio $Q_t = J_{tr}/\chi_0$. The reference sample, labeled SD, contained elongated Fe_3O_4 particles 0.03 by 0.2 μm. Such particles are known to exhibit SD behavior (*1*), although equidimensional particles of the same volume may well be MD, and the SD properties of this particular sample have been well documented (*14*). Most tabulated properties of the SD sample

Table 1. Some hysteretic and thermoremanent properties of the experimental samples; χ_0 and J_{tr} values refer to a unit volume of magnetite. Symbols are defined in the text; e.m.u., electromagnetic unit.

Sample	$\bar{d}$ (μm)	χ_0 (e.m.u.)	J_{rs}/J_s	H_c (oersteds)	J_{tr} (1 oersted) (e.m.u.)	Q_t
1	0.22	0.292	0.113	92	8.0	27
2	.10	.280	.199	137	12.5	45
3	.076	.268	.242	155	11.8	44
4	.037	.236	.289	205	6.0	26
SD		.186	.464	325	15.5	83

are influenced by shape anisotropy and can only be compared in a general way with those of samples 1 through 4; a specific exception is J_{rs}/J_s, which is independent of anisotropy.

Samples 1 through 4 display a coercive force dependent on grain size, characteristic of both MD and incoherently reversing SD grains. The former domain structure is more likely: the lowest-energy incoherent reversal mode in equant particles is magnetization curling (*15*) with a nucleating field varying as d^{-2}, whereas $H_c \propto d^{-0.4}$ in samples 1 through 4, in exact agreement with Parry's (*6*) observations on magnetite grains between 1.5 and 120 μm in size.

A MD structure is likewise favored by the χ_0 and J_{rs}/J_s data. The χ_0 values for samples 1 through 4 are all close to 0.25, the appropriate value (*5*) if χ_0 is controlled by self-demagnetizing effects, whereas χ_0 is significantly lower than 0.25 for the SD sample. The J_{rs}/J_s data are definitive. A SD grain, whether it reverses coherently or incoherently, cannot have J_{rs}/J_s less than 0.5 (J_{rs}/J_s may even be higher than this for equidimensional grains, where crystalline and shape anisotropies are of comparable magnitude). Table 1 shows that J_{rs}/J_s is close to 0.5 for the sample containing elongated SD particles, but is only 0.12 to 0.29 for the samples with equant particles. This result cannot be explained in terms of a mixture of SD and MD particles, for sample 4 contains no particles larger than about 0.06 μm whereas samples 1 through 3 contain practically no particles below this size. Since sample 4 contains some MD particles (which are necessarily < 0.06 μm), the other samples must contain exclusively MD particles.

Thermal demagnetization of the TRM's listed in Table 1 revealed a superparamagnetic (SPM) fraction in sample 4: samples 1 through 3 had no blocking temperatures below 550°C, but sample 4 had blocking temperatures distributed down to room temperature and presumably below. The value of J_{rs}/J_s (from 6000-oersted hysteresis curves) was temperature independent in samples 1 through 3, as expected, but increased by 18 percent between room temperature and -196°C in sample 4. If we assume that all SPM moments are stabilized by cooling to -196°C and neglect any grain size dependence of remanence in MD particles, the SPM volume fraction of sample 4 should be about 18 percent. The known size distribution of sample 4 then yields (*16*) 0.035 μm for the SPM threshold d_s of equant magnetite. The uncertainty in this figure is probably ± 0.005 μm. Agreement with theoretical estimates for d_s of approximately 0.03 μm (*5, 11*) is good.

I next obtained an upper bound for d_0 from the grain size distribution of sample 4, on the assumption of 18 percent SPM grains ($J_{rs}/J_s = 0$), 58 percent SD grains ($J_{rs}/J_s = 0.5$), and 24 percent MD grains ($J_{rs}/J_s = 0$, an extreme value!), giving $J_{rs}/J_s = 0.29$ overall, as observed. This calculation yielded $d_0 = 0.057 \pm 0.005$ μm. (However, d_0 could well be substantially less than this; my data are even consistent with d_0 being less than d_s, that is, with there being no stable SD range in equidimensional magnetite particles.)

Table 2. A comparison of experimental TRM intensities with values predicted on the basis of Stacey's (*5*) pseudosingle-domain theory. Units are electromagnetic units per cubic centimeter of magnetite.

Sample	$\bar{d}$ (μm)	TRM in 1 oersted		TRM in 100 oersteds	
		Theor.	Exp.	Theor.	Exp.
1	0.22	13.1	8.0	28.4	38.4
2	.10	3.9	12.5	46.4	70.0
3	.076	2.1	11.8	48.5	85.4
4	.037	0.3	6.0	26.8	87.3

In contrast to the essentially MD character of the hysteretic properties of samples 1 through 4, the thermoremanent properties J_{tr} and Q_t (Table 1) are much higher than usual MD values (*6*). The Q_t values in fact are similar to those of the most stable rocks used in paleomagnetism. The J_{tr} values show a maximum near $d = 0.1$ μm. Although this result at first appears curious, it is not actually inconsistent with theory. Néel's (*11*) SD theory of TRM predicts

$$J_{tr}(H) = J_{rs} \tanh (\alpha d^3 H) \quad (1)$$

whereas Stacey's (*5*) theory for small MD grains with PSD behavior gives

$$J_{tr}(H) = A d^{-1} \tanh (\beta d^2 H) \quad (2)$$

apart from a small correction factor. In these equations, A is a constant, and α and β are functions of the blocking temperature. For constant H (here, 1 oersted), the J_{tr} of SD grains increases with d according to Eq. 1, but, if an SD-MD transition is assumed near $d = 0.1$ μm, J_{tr} will decrease above this size. (This interpretation is of course inconsistent with the hysteresis data.) Stacey's theory (Eq. 2) leads directly to a maximum in the J_{tr}-d characteristic.

Neither theory is quantitatively sufficient over the entire size range covered by samples 1 through 4. Equation 1 predicts approximately the correct 1-oersted TRM for sample 4, but for larger grain sizes the tanh factor is near saturation and the predicted TRM's are much too high. On the other hand, Table 2 demonstrates that Stacey's (*5*) theory (a more detailed analog of Eq. 2 was used for calculations) predicts reasonable TRM values only for sample 1. For smaller grain sizes, the predicted values are much too low, even for $H = 100$ oersteds.

Neither theory can explain the shape of the measured J_{tr}-H characteristics, none of which even approximately resembles a tanh function. In fact, they come closer to obeying Néel's (*12*) MD theory of TRM, in which TRM varies as H in low fields and as $H^{1/2}$ in higher fields. Experimentally, the TRM of samples 1 through 4 varies as H to a power between 0.5 and 0.75 initially, with a sharp change to a power between 0.3 and 0.4 above 10 to 15 oersteds.

Figure 1 demonstrates that the stability of TRM against alternating field

(AF) demagnetization decreases with increasing grain size in the range from 0.037 to 0.22 μm but not as rapidly as the coercive force H_c (Table 1). Thus particles throughout this size range display SD-type coercivities. The median demagnetizing fields are 300 to 400 oersteds, and about 3 percent of each 1-oersted TRM is unaffected by an AF of 1000 oersteds.

From the results of the present study, it is apparent that the Néel (*11*) SD theory of TRM cannot be applied to magnetite grains as large as 0.076 μm. In fact, 0.057 μm is probably an upper limit (and 0.035 μm a lower limit) for SD behavior at room temperature. Above the SD threshold, low J_{rs}/J_s values (Table 1) clearly reflect a nonuniform remanent state. The TRM data indicate that Stacey's (*5*) theory of PSD behavior in small MD grains does not apply to grains as small as 0.10 μm, although it may describe 0.22-μm particles adequately. Very likely, in grains as small as 0.1 μm, the width of a domain wall is a substantial fraction of the diameter of the grain. Amar (*17*), for example, has calculated wall widths of 120, 160, 190, and 225 Å in iron particles ($d_0 \cong 150$ Å) having diameters of 200, 400, 600, and 1000 Å, respectively. If similar figures apply to magnetite, the particles in samples 2 through 4 probably do not have a domain structure in the normal sense and Stacey's postulated four-domain structure is almost certainly inapplicable. An obvious first step in constructing a satisfying theory of TRM in such particles would be to determine by direct observation the true magnetic structure in the remanent state, but this is of course extremely difficult in submicroscopic particles.

There exists at present no unified picture which can reconcile the MD-like hysteresis and SD-like TRM of magnetite particles just above the SD threshold (sizes between 0.05 and 0.20 μm). These particles exhibit neither true SD nor PSD behavior. From a purely experimental point of view, however, it is sufficient to note that such particles, if present in significant numbers in an igneous rock, will carry a component of NRM having SD-type stability.

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Ratite Eggshells from Lanzarote, Canary Islands

Abstract. *Struthious and aepyornithoid eggshells from Tertiary calcareous sediments on Lanzarote prove the presence, until about 12 million years ago, of large flightless birds. The calcarenite horizon is recognized as an old land surface. Mesozoic sedimentary rocks in the basement of the volcanic islands of Lanzarote and neighboring Fuerteventura indicate that at least part of the Canary Archipelago is underlain by continental crust. Separation of the eastern Canaries from Africa might have been by rifting, and a land connection might still have existed in the lower Pliocene.*

Ratite eggshells from Lanzarote, one of the islands in the northeastern corner of the Canary Archipelago, were recognized by Rothe (*1*) as remains of Miocene to Pliocene ostriches. He found the shells in the calcarenite horizon at the northern tip of the island, in Valle Chico (29°13′08″N, 9°46′40″W) and in Valle Grande (29°12′38″N, 9°46′20″W). The locality is approximately 150 km from the nearest point on the African continent.

A morphological study of the two nearly complete eggshells and 302 shell fragments and an analysis of their pore patterns reveal two kinds of ratite eggshells. They are identified as struthious, that is, belonging to the ostrich genus *Struthio*, and as aepyornithoid, that is, resembling the Malagasy aepyornithid eggs (*2*).

The struthious eggshells from Valle Chico and Valle Grande are on the average 2.0 mm thick. Their pore pattern of irregularly distributed tiny circular pores (Fig. 1) resembles most closely that of the recent *Struthio c. camelus* and the typical Pleistocene "Struthiolithus" eggshells. Also, the size and the shape of the two nearly complete struthious eggshells from Lanzarote (*1*) match those of other fossil and recent ostrich eggs (*3*).

The aepyornithoid eggshells were also found in Valle Chico and Valle Grande. Their pore pattern (Fig. 2) does not resemble that of any of the known struthious eggshells but coincides with those known from extinct *Aepyornis* species of Madagascar (*2*). Since further evidence is needed to prove a possible phylogenetic relationship, the aepyornithoid eggshells from Lanzarote are presently treated as distinct from the family-specific aepyornithid eggshells. The pore pattern of the aepyornithoid shell fragments from Lanzarote is characterized by elongated linear and forked pore grooves, dagger-point pores, and sting pores. They are conspicuously oriented parallel to one another and to the longitudinal axis of the egg. From the material collected so far it is not clear whether the aepyornithoid eggshells belonged to a single species of bird. Their pore pattern varies and covers the same spectrum of interspecific variability typical of the aepyornithid eggshells from Madagascar. Apart from the pieces with a majority of elongated longitudinal pore grooves, the collections also contain fragments in which the short dagger-point and sting pores prevail. Furthermore, the aepyornithoid eggshells are not uniformly thick. Some