Single Domain Oxide Particles as a Source of Thermoremanent Magnetization

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(Received June 2, 1977)

Single domain (SD) particles have long been suggested as a potentially strong and stable source for the paleomagnetic signal, but their actual occurrence in rocks has been much questioned. Two possible modes of occurrence of SD Fe-Ti oxides can be distinguished. These are as magnetite rods bounded by ilmenite lamellae in intergrown grains (analogous to Alnico permanent magnet alloys), and as isolated ultrafine particles, perhaps representing part of a much broader grain-size distribution (analogous to the oxide coatings used in tape recording). The evidence for the presence in rocks of these two types of magnetic particle is reviewed. Where intergrown grains are present the SD 'Alnico model' seems to be valid, and where isolated titanomagnetite grains are involved the SD 'tape-recorder model' is satisfactory. Where pure Fe₃O₄ particles are involved the situation is less clear, and current thinking stresses the role of the so-called pseudo-single domain (PSD) moments.

1. Introduction

The search for an adequate explanation of the origin of the paleomagnetic signal has had a long and interesting history. In terms of igneous rocks, which have played a major role in paleomagnetic research, there is no doubt that some form of thermoremanence (TRM) is dominant. Néel (1949) originally proposed an elegant single domain (SD) theory, but later (Néel, 1955) came to favour multidomain (MD) particles as the dominant TRM carriers on the grounds that the average particle size encountered in rocks is much too large to permit SD behaviour. Nevertheless, the TRM's carried by most rocks persistently exhibit SD-like properties—in particular high coercivities (Dunlop, 1973). Furthermore, pure MD theories proved inadequate (Stacey and Banerjee, 1974, p. 110), and the pendulum returned towards SD theory, aided by observational evidence that sufficiently small magnetic particles may, in fact, occur in rocks. Currently, there is much support for a compromise situation which stresses the role of particles lying in the transition region between true SD and true MD behaviour. These so-called pseudo-single domain (PSD) effects were first invoked by Stacey (1961), and are reviewed by Banerjee (1977) and by Dunlop (1977).

Two problems have persistently hampered progress. Firstly, it has proved difficult to establish a complete understanding of the physics of PSD particles, to the extent that an adequate theory it still lacking (Dunlop, 1977). Secondly, the critical
particle size for true SD behaviour in magnetite is less than the wavelength of light ($\sim 0.5 \mu\text{m}$), which renders SD particles very difficult to locate and identify. This paper reviews and discusses the data pertinent to the second of these problems.

2. Naturally Occurring Ultrafine Particles

Despite Néel's (1955) original doubts, it now appears that particles small enough to be single domains do, in fact, occur in rocks, although only a few cases have been studied in detail. This situation contrasts with that found in technological applications such as tape recording and permanent magnet materials, where a vast literature now exists (e.g., Bate, 1975; Hadfield, 1962). In terms of the materials found in nature it is convenient to distinguish two modes of occurrence for SD particles; individual ultrafine particles, perhaps representing one end of a continuous distribution, and as small regions of larger grains which are subdivided by intergrowth structures of two or more phases. These two modes are discussed separately.

2.1 Intergrowths

Magnetite and ilmenite commonly occur together in large grains (10–100 $\mu\text{m}$) intimately intergrown on a submicron scale. The ilmenite forms an octahedral pattern of lamellae developed on the (111) planes of the magnetite. Such grains have an appearance not unlike the so-called Widmanstätten patterns observed in iron meteorites. This form of subdivision was first put forward as a source of high coercive forces, and thus of stable remanence, by Graham in 1953, and was further supported by Powell (1963) and Larson et al. (1969). It has a close analogue in the development of permanent magnet materials, since Alnico alloys (which account for 50% of the U.S. permanent magnet market, Cullity, 1972), are essentially two-phase materials consisting of a series of magnetic rods embedded in a non-magnetic matrix. The desirable properties of these materials are attributed to the microstructure revealed by electron microscopy (De Vos, 1969) and in particular, the magnetic hardness is caused by 'the shape anisotropy of singledomain particles' (Cullity, 1972, p. 568).

In samples of geophysical interest the control of coercivity by subdivision is now well established (see Table 1 for summary), and the techniques necessary to reveal microstructure are available (e.g., see Hoblitt and Larson, 1975). However, the corresponding domain state has proved more difficult to firmly establish. Strangway et al. (1968) attributed the very high stability found in many volcanic rocks to the presence of elongated volumes of magnetite bounded by ilmenite lamellae. They suggested that some of these will be single domains whose shape anisotropy gives rise to high coercivities. The actual model they used to calculate critical SD sizes is unphysical in that the domain walls they envisaged were not true Bloch walls. Nevertheless an improvement suggested by Murthy et al. (1971) indicated that the actual critical sizes obtained were not much in error. Stacey and Banerjee (1974) considered sheet-like lamellar intergrowths and concluded that 'for all macroscopic prop-
Table 1. Various indicators of magnetic hardness in homogeneous and intergrown grains.*

<table>
<thead>
<tr>
<th>Authors</th>
<th>‘Hardness’ indicator</th>
<th>Sample</th>
<th>Homogeneous</th>
<th>Intergrown</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strangway et al. (1968)</td>
<td>% of 1.2 Oe TRM</td>
<td>WR-3-4-2</td>
<td>4.2%</td>
<td>12.7%</td>
</tr>
<tr>
<td></td>
<td>remaining after 1,000 Oe AF demagnetization</td>
<td>WR-1-2-2</td>
<td>7.2%</td>
<td>22.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PJ-16-3-3</td>
<td>8.9%</td>
<td>13.1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PJ-11-3-3</td>
<td>9.3%</td>
<td>14.5%</td>
</tr>
<tr>
<td>Larson et al. (1969)</td>
<td>Coercive force ($H_c$)</td>
<td>sample 13 (basalt)</td>
<td>45 Oe</td>
<td>180 Oe</td>
</tr>
<tr>
<td></td>
<td>Remanent coercivity ($H_{cr}$)</td>
<td></td>
<td>108 Oe</td>
<td>386 Oe</td>
</tr>
<tr>
<td>Evans and Wayman (1974)</td>
<td>MDF of 1.2 Oe ARM</td>
<td>magnetite-ulvospinel</td>
<td>37 Oe</td>
<td>170 Oe</td>
</tr>
<tr>
<td>Davis and Evans (1976)</td>
<td>MDF of 1.2 Oe ARM</td>
<td>magnetite-ilmenite</td>
<td>60 Oe</td>
<td>315 Oe</td>
</tr>
<tr>
<td>Manson and O’Reilly (1976)</td>
<td>Coercivity spectra peaks derived from IRM induction</td>
<td>sample RK (basalt)</td>
<td>~200 Oe</td>
<td>700 Oe</td>
</tr>
</tbody>
</table>

* This table is intended simply to illustrate the relationship between microstructure and magnetic hardness, and is by no means exhaustive. For fuller discussions and other examples reference should be made to the original papers.

...
resolvable by optical microscopy and the grains therefore remained in Class I of Wilson and Watkins (1967). Moreover, the magnetic changes were well in progress before any observable microstructure could be detected even by electron microscopy. This finding concurs with the results of Creer and Petersen (1969) who appealed to submicroscopic exsolution to explain the magnetic properties of oxidized basalts. One is also reminded of the conclusions reached by Radhakrishnamurthy and Deutsch (1974) who invoke 'some yet unknown mechanism of subdivision' to explain magnetic evidence for the presence of superparamagnetic (SP) particles in basalts. In some cases, magnetic interaction within dense clusters of SP particles causes finite values of coercive force and remanence to reappear (Radhakrishnamurthy et al., 1973; Evdokimov, 1963), thus enabling such material to carry paleomagnetic information.

Another class of intergrowths which have been investigated in some detail are the Widmanstätten patterns found in iron meteorites. Interest in these extraterrestrial objects stems from the possibility that they carry a record of interplanetary magnetic fields which may have played an important role in the early development of the solar system. Compared to terrestrial basalts the Widmanstätten intergrowths are very coarse (≈1 mm) and the magnetism correspondingly soft. However, some areas are subdivided on a finer scale, and the micro-kamacite regions in these so-called plessite areas appear to be singledomain grains capable of carrying a stable remanence (Brecher and Cutrera, 1976). It is important to realize that although micro-kamacite regions appear capable of carrying a stable remanence it is apparently still an open question as to whether they actually do retain a memory of their early magnetic environment (Brecher and Albright, 1977).

2.2 Distribution of isolated particles

Strangway (1961) suggested that the source of stable remanence in certain Canadian diabases might be what he termed a 'powder distribution' of very fine opaque particles occurring in pyroxene and olivine grains. Subsequently Evans and McElhinny (1969) and Evans et al. (1968) suggested that at least some of the stable remanence of the very ancient (2600 my) Modipe Gabbro of southern Africa resides in minute, often elongated, magnetite particles exsolved within pyroxene grains. Similar suggestions involving opaque grains in feldspar crystals have been put forward by Hargraves and Young (1969) and Murthy et al. (1971).

Since the resolving power of optical microscopes is inadequate to penetrate the 'SD barrier' further work has inevitably required the application of electron microscopy. Evans and Wayman (1970) followed up the work on the Modipe Gabbro by applying a two-stage replication technique in an attempt to discover if the particle size distribution continues below the optical limit. It was demonstrated that optically unresolvable particles are plentiful and the authors concluded that SD magnetite particles can, and do, occur naturally in rocks (see Evans and Wayman, 1970, Fig. 6). Four words of warning are appropriate. Firstly, as in all microscopy, a two-dimensional cross section yields no information about the third dimension
of each particle. Secondly, a single demonstration case does not provide sufficient basis for a meaningful assessment of the overall significance of the phenomenon. Thirdly, no claim can be made that the minute part of the sample studied is at all representative of the entire rock. Fourthly, replication techniques can resolve ultrafine textures but yield very little compositional information, being limited to what can be inferred from the action of the etchant employed.

Evidence for SD particles occurring in the interior of silicate grains is also provided by the work of Hoye and O'Reilly (1973) and Hoye and Evans (1975). These investigations concern the growth of iron oxide particles (thought to be Fe$_3$O$_4$) by oxidation of synthetic olivines (Fe, Mg)$_2$SiO$_4$. Acquisition of chemical remanent magnetization (CRM) as the magnetic particles nucleate and grow was monitored and found to pass through a peak after several hundred minutes oxidation time. This observation parallels that found by Kobayashi (1961) who investigated CRM in a Cu-Co alloy and reports a similar, but much sharper, peak. In both cases the shape of the CRM vs oxidation time curve reflects the gradual growth of particles from superparamagnetic (SP) to SD and thence to PSD (or multidomain, MD) configurations. The occurrence of ultrafine iron oxide particles in oxidized olivines is confirmed by the work of Champness (1970), both on mineralogical grounds and by direct observation using high voltage transmission electron microscopy.

3. Discussion

Two modes of occurrence for ultrafine magnetic particles capable of carrying a strong and stable paleomagnetic signal can be distinguished. In terms of technological developments these correspond to Alnico permanent magnets (magnetite/ilmenite intergrowths), and to oxide coatings employed in tape recording (isolated ultrafine particles of magnetite or titanomagnetite).

The 'Alnico model' is very attractive—the microstructural control of magnetic hardness in natural samples is well established (Table 1), and there is good evidence for the presence of rod-like magnetite regions acting as SD particles. This SD model is further strengthened by the observation that the high packing factors found in intergrown grains can be expected to somewhat increase the critical size necessary for SD behaviour (Morris and Watt, 1957). Apparently, even when no subdivision is visible SD properties may appear (Radhakrishnamurthy and Deutsch, 1974; Manson and O'Reilly, 1976). Strong support for these findings is provided by the work of Jensen and Shive (1973) who analysed Mössbauer spectra of synthetic titanomagnetites and demonstrated that the titanium ions tend to cluster together and thereby introduce inhomogeneity which they suggest might be regarded as incipient exsolution.

The 'tape-recorder model' has received support from electron microscopy (Evans and Wayman, 1970) and from Bitter pattern studies (Soffel, 1968, 1969, 1971). Single-domain magnetite and titanomagnetite particles do apparently occur naturally in at least some rock samples. They can also be generated in
synthetic silicate samples by suitable laboratory treatment (Hoye and O'Reilly, 1973). When present they represent a potent source of strong, stable remanence which 'have a disproportionate effect on remanent properties' (Dunlop and West, 1969). For example, Strangway et al. (1968) argue that SD volume fractions as small as a few ppm suffice to account for typical NRM values of strongly magnetized rocks such as basalts. However, Ryall and Ade-Hall (1975) have pointed out that although TRM per unit volume increases dramatically as grain size decreases, when the actual volume of individual particles is taken into account each large particle contributes as much to the total TRM as do many small particles. They show that the grain size distribution of Evans and McElhinny (1969) combined with the experimental TRM vs grain size curve (Dunlop, 1973) indicates that PSD grains a few microns in size dominate the total TRM of certain oceanic basalts. There are several objections to their procedure:

1. The applicability of a particle size distribution determined from a Precambrian gabbro to a Tertiary oceanic basalt is highly questionable.

2. The grain counts reported by Evans and McElhinny (1969) were intended simply to indicate that the size distribution continues below the optical limit. It is inadmissible to use data derived from optical microscopy to represent the quantative significance of sub-microscopic particles. Even the electron microscope results of Evans and Wayman (1970) are inadequate in this respect—they simply confirm the extension of the size distribution below the limit of optical resolution. No claim that these measurements were representative was ever made or implied.

3. The situation discussed by Ryall and Ade-Hall (1975) is much closer to that reported in a very important series of papers by Soffel (1968, 1969, 1971). In the present context two major conclusions emerge from Soffel's work on German Tertiary basalts. Firstly, after a thorough study of the magnetic properties and domain configurations, including direct Bitter pattern observations, Soffel (1971, p. 207) concludes that 'the stable component of the TRM of the two basalts is located entirely in the small particles with less than 1 micron diameter having single domain configuration.' Secondly, the actual critical size for SD behaviour in the titanomagnetites is considerably larger than for pure Fe3O4. Soffel (1971, p. 469) concludes that for titanomagnetites of composition 0.55Fe2TiO4-0.45Fe3O4 'most of the particles with diameters of 1.5 microns or less must be regarded as single domain particles.' Thus the conclusion of Ryall and Ade-Hall that optically visible grains dominate the remanence does not conflict with a SD origin of TRM. This view is strengthened by the extremely re-entrant nature of the surfaces of the typical dendritic opaques found in oceanic basalts. Morphologies of this kind imply that although a grain may have an overall size of several microns it effectively consists of several smaller units.

Despite these objections to the specific treatment given by Ryall and Ade-Hall (1975), their general point concerning the actual magnetic moments of particles merits attention. The point concerns the amount of TRM contributed by SD particles compared to that of PSD and MD grains. Strangway et al. (1968) concluded
that a volume fraction of magnetite on the order of a few ppm suffices to account for typical TRM's encountered in basalts, and Evans and McElhinny (1969) have reiterated this conclusion. This is misleading because it assumes a specific TRM close to the saturation magnetization value of magnetite (480 emu·cm⁻³). The correct approach, using Néel's (1949) theory, indicates that specific TRM's are generally much smaller (Fig. 1). Nevertheless the effectiveness of SD grains as TRM carriers remains—particles just below the SD threshold and having axial ratio 1.5 to 1, claimed by Stacey and Banerjee (1974, p. 109) to occur commonly in igneous rocks, have specific TRM ~ 50 emu·cm⁻³ and thus need only occupy a volume fraction of 20 ppm to account for a typical basalt remanence of 10⁻³ emu·cm⁻³. By comparison 1 μm magnetite grains possess PSD thermoremanence of about 2 emu·cm⁻³ (Dunlop, 1973) and MD particles (> 20 μm) yield TRM's of 0.1 emu·cm⁻³ (Stacey and Banerjee, 1974).

In conclusion it must be stressed that although the natural occurrence of SD
particles has been demonstrated in some test cases, there is still no firm data on the actual size distributions and relative proportions of SP, SD, PSD and MD grains found in rocks. Where intergrown grains are present the SD 'Alnico model' seems appropriate, where isolated titanomagnetite grains are involved the SD 'tape recorder model' is satisfactory. Where pure Fe₃O₄ particles are involved the situation is less clear, and current thinking stresses the role of PSD moments (Stacey and Banerjee, 1974; Dunlop, 1977; Banerjee, 1977). In all cases, including that of 'mixed' remanence, it should be kept in mind that progressive alternating field demagnetization, as undertaken in all modern paleomagnetic work, can be expected to enhance the single domain contribution.

Financial support was provided by the National Research Council of Canada.

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