

The effect of low-temperature oxidation on large multi-domain magnetite

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Abstract. Natural samples of oxidized and unoxidized magnetite have been used to study the effect of low-temperature oxidation on magnetic domain state. All of the magnetites studied were large multi-domain (MD) grains, ranging in size from 53 μm to at least 250 μm . Hysteresis data typical of MD grains are obtained from unoxidized magnetite samples while data from partially oxidized samples are characteristic of pseudo-single domain (PSD) grains. Our results demonstrate that low-temperature oxidation can seriously affect the magnetic properties of magnetite by significantly increasing the PSD-MD threshold size. The presence of a suppressed Verwey transition at 118 K in the oxidized samples indicates that the oxidation may only be surficial and that there may exist a core of magnetite under the maghemitized surface shell. We suggest three possible mechanisms for the observed PSD-like behavior. First, the magnetite core could be reduced sufficiently in volume to make it a PSD grain, independent of the surficial maghemite. Second, internal stress in the composite grain due to lattice mismatches between the magnetite core and maghemite rim will increase the domain wall energy and make it more difficult to add walls for a given grain size. Coupled with a reduced volume of the magnetite core, this could give rise to PSD-like behavior. Third, the composite grain could be a mixture of SD maghemite and MD magnetite which gives rise to bulk PSD-like properties. Our results have potentially important implications for paleomagnetic records because they provide a mechanism whereby a stable chemical remanent magnetization can be acquired by MD grains in sediments and igneous rocks.

Introduction

Magnetite is an important magnetic mineral in paleomagnetic studies and determination of its domain state has always been of interest to paleomagnetists. Single domain (SD) and pseudo-single domain (PSD) grains are usually considered to be the stable remanence carriers in paleomagnetic records, whereas multi-domain (MD) grains are thought to be less important as carriers of stable remanence. The Lowrie-Fuller test [Lowrie and Fuller, 1971], the modified Lowrie-Fuller test [Johnson *et al.*, 1975], the characteristics of alternating field (AF) demagnetization curves [Bailey and Dunlop, 1983; Dunlop, 1983], treatment at cryogenic temperatures [Levi and Merrill, 1978] and measurement of hysteresis parameters [Parry, 1965; Day *et al.*, 1977] have been suggested as means of discriminating between domain states in magnetite.

However, in practice, different methods may produce different results, to some degree, because each method measures different magnetic properties and because a distribution of magnetic grain sizes can give rise to ambiguous results. In this paper, we demonstrate that low-temperature oxidation can further complicate the interpretation of such tests and that it is necessary to employ several measurements in order to understand an assemblage of magnetic minerals.

The effects of low-temperature oxidation on the magnetic properties of titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) have been extensively studied because of their importance to the origin of marine magnetic anomalies [e.g., Marshall and Cox, 1971; Özdemir and Dunlop, 1985; Smith, 1987]. A theoretical model has been developed which shows that the domain boundaries in titanomagnetite ($x = 0.6$) vary as a function of oxidation and that the PSD-MD boundary can be as high as 42 - 150 μm depending on the degree of oxidation [Moskowitz, 1980]. The oxidation of magnetite has also been the subject of considerable research [e.g., Johnson and Merrill, 1973; Özdemir and Dunlop, 1985]. However, little work has been done on large MD magnetite. Here, we report on the effect of low-temperature oxidation on large MD magnetite.

Sample description and methods

Samples were prepared by crushing large natural magnetite crystals (collected from the North Fork of the American River, near Auburn, California), which were then sieved to separate different grain sizes. The original magnetite crystals had undergone surficial low-temperature oxidation, and some of the grains obtained from the crystals were partially oxidized. Discrepancies have been observed between the magnetic properties of crushed grains and those of strain-free crystals grown by modern techniques [e.g., Dunlop, 1986]. Because all of the grains in our study were produced by crushing, such discrepancies should not arise.

Under the microscope, the partially oxidized magnetite grains were dark grey in color, with no fresh surfaces evident. The unoxidized magnetite grains had fresh surfaces and a dark luster. Large oxidized and unoxidized magnetite grains (> 106 μm) were separated with the aid of a microscope. Samples 1 - 5 and 12 - 13 (Table 1) consist of a few large, dispersed grains which were subjected to analysis of magnetic hysteresis properties and behavior at cryogenic temperatures, respectively. Samples 6 - 11 were prepared by dispersing magnetite grains in transoptic powder (methyl methacrylate) under low pressures and moderate temperatures (80-100°C). These samples were then subjected to stepwise AF demagnetization of an anhysteretic remanent magnetization (ARM) and a saturation isothermal remanent magnetization (SIRM). Sample 14 consists of fresh unoxidized magnetite grains. Sample 15 is a mixture of 106 - 250 μm oxidized and unoxidized magnetite grains. Samples 14 and 15 were subject-

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ed to x-ray diffraction analysis. A list of all samples, and the analyses to which they were subjected, is shown in Table 1.

To assess the stability of the samples to AF demagnetization, an ARM was applied to samples 6 - 11 with a peak AF of 100 mT and a bias field of 0.05 mT. The ARM was stepwise demagnetized up to 60 mT, then a second ARM, applied with a bias field of 0.15 mT, was subjected to the same AF demagnetization sequence. This was followed by SIRM acquisition in a maximum field of 430 mT and stepwise AF demagnetization of the SIRM. The four hysteresis parameters (coercive force (B_c), coercivity of remanence (B_{cr}), saturation magnetization (M_s) and saturation remanence (M_r)) were determined using a Princeton Measurements Corporation Micromag Alternating Gradient Magnetometer up to maximum fields of 1T. Behavior at cryogenic temperatures was studied with a Quantum Designs MPMS1 superconducting susceptometer in the UC-Davis Physics Dept. A field of 5.5 T was used for SIRM acquisition at 5 K, and the SIRM was measured in a near-zero field with 5° steps from 5 K to 300 K. X-ray analyses were performed with Cu-K α radiation on a Siemens x-ray diffractometer, also in the UC-Davis Physics Dept.

Results

The x-ray spectrum for sample 14 exactly matches the powder diffraction standard for magnetite (Fig. 1a). The calculated cell edge parameter of 8.39 Å indicates that the unoxidized samples are pure stoichiometric magnetite. For sample 15 (a mixture of oxidized and unoxidized grains; Fig. 1b) the spectral peaks have been split and additional peaks exist with respect to the pure magnetite spectrum of sample 14. The peaks of sample 15 match the spectra expected for magnetite and maghemite with minor hematite, indicating that in this case, the oxidation gave rise to both maghemite and a small amount of hematite.

The behavior at cryogenic temperatures of samples 12 and 13 reveals a major drop in remanence at about 118 K (Fig. 2), which coincides with the Verwey transition for magnetite [Stacey and Banerjee, 1974]. However, in sample 13, which is oxidized, the Verwey transition is suppressed. This result is consistent with those of Özdemir *et al.* [1993] who pointed out

Table 1 Sample description and analyses to which samples were subjected.

Sample	Grain size	Oxidized	Analysis	M_r	χ
1	106-250	yes	Hysteresis		
2	106-250	no	Hysteresis		
3	>250	yes	Hysteresis		
4	>250	no	Hysteresis		
5*	53-106	mixed	Hysteresis		
6	2000	no	AF demag.		
7*	53-106	mixed	AF demag.	4.6	414
8	106-250	yes	AF demag.	2.3	407
9	>250	yes	AF demag.	6.8	316
10	106-250	no	AF demag.	0.8	526
11	>250	no	AF demag.	0.6	542
12	>250	no	Low-T SIRM		
13	>250	yes	Low-T SIRM		
14	powder	no	XRD		
15*	powder	mixed	XRD		

* Oxidized and unoxidized magnetite grains not separated in these samples. XRD is x-ray diffraction, see text for description of analyses. Grain sizes are in μm ; M_r is saturation remanence ($\text{Am}^2\text{kg}^{-1}$); χ is magnetic susceptibility ($10^{-6} \text{m}^3\text{kg}^{-1}$).

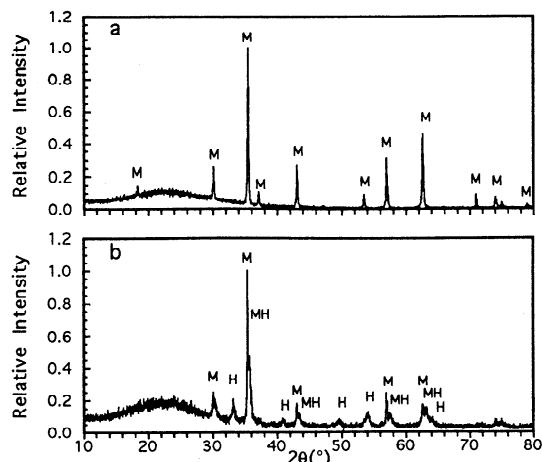


Figure 1. X-ray spectra with expected peaks labelled for spectra of: (a) sample 14: magnetite (M), and (b) sample 15: magnetite (M), maghemite (MH), and hematite (H). Splitting at the top and broadening at the base of the magnetite peaks is indicative of the presence of maghemite.

that the Verwey transition occurs in both SD and MD magnetite and that it can be suppressed by low-temperature oxidation, particularly in SD grains. Because of the presence of the Verwey transition, the cryogenic measurements confirm that our samples all contain some magnetite. The compositions of the grains must be close to stoichiometric magnetite, because even small impurities will lower the transition temperature below 118 K [Stacey and Banerjee, 1974]. The apparent purity of the magnetite is confirmed by temperature dependent susceptibility measurements which indicate a Curie temperature at $\sim 580^\circ\text{C}$. Thus, we conclude that the oxidized grains are only partially oxidized and contain at least a magnetite core.

Hysteresis data are summarized on Figure 3. The grain sizes of these samples are all larger than 53 μm , however, not all of the grains produce results characteristic of MD magnetite [cf. Day *et al.*, 1977]. In particular, the oxidized samples 1, 3, and 5 display PSD-like behavior, despite their size. No constriction of the hysteresis loops is observed, in agreement with XRD data which suggest that hematite is not a significant by-product of oxidation in this study.

AF demagnetization of ARM and SIRM indicates that the magnetic stability is also changed by low-temperature oxidation. The oxidized samples have higher AF stability of SIRM than unoxidized samples (Fig. 4a). Samples 6, 10, and 11,

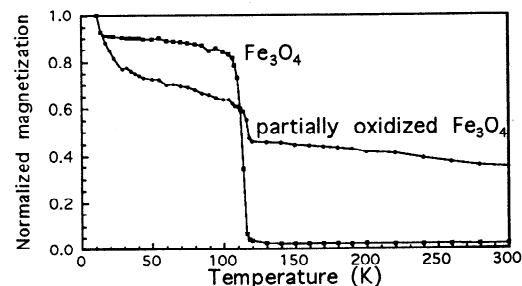


Figure 2. Normalized SIRM of samples 12 (unoxidized) and 13 (oxidized) during warming in zero field from ~ 5 K to 300 K. The suppression of the Verwey transition at 118 K in sample 13 provides evidence that magnetite in this sample has been partially oxidized to maghemite.

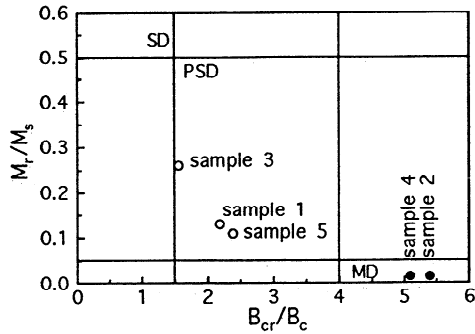


Figure 3. Plot of M_r/M_s vs B_{cr}/B_c , after Day *et al.* [1977]. Open (closed) symbols indicate oxidized (unoxidized) samples. Unoxidized samples display behavior typical of MD grains whereas oxidized samples display PSD-like behavior.

which are not oxidized, have soft, exponential-like AF demagnetization curves for the SIRM, with median destructive fields (MDFs) lower than 5 mT. This type of behavior is typical of MD grains [Dunlop, 1983; Bailey and Dunlop, 1983]. Samples 7, 8, and 9, which are partially oxidized, have more stable AF demagnetization curves, with MDFs higher than 10 mT. For AF demagnetization of the ARM, oxidized samples have curves similar to those of the SIRM demagnetization. The curves are initially convex upward and then convex downward (Fig. 4b), which is not characteristic of MD behavior [Dunlop, 1983]. The curves for unoxidized samples drop very quickly at low fields (5 mT level), before they display fluctuating behavior. The mechanism of these fluctuations is unclear, however, they are reproducible. The amplitude of the fluctuation appears to be related to grain size, and the strength of the bias field in which the ARM is produced. ARMs produced in a larger bias field (0.15 mT) display smaller fluctuations. Despite this problem, clear differences are evident in the AF demagnetization behavior of large oxidized and unoxidized magnetite grains for both SIRM and ARM.

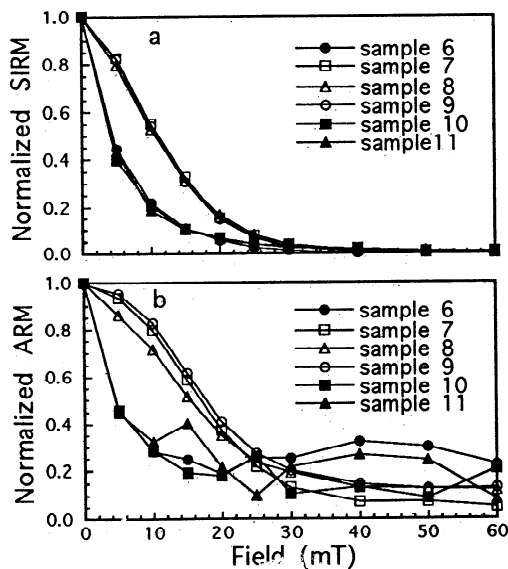


Figure 4. Normalized AF demagnetization curves of: (a) SIRM, and (b) ARM produced in a bias field of 0.15 mT. Open (closed) symbols indicate oxidized (unoxidized) samples. Unoxidized samples display behavior typical of MD grains whereas oxidized samples display harder coercivities and greater resistance to AF demagnetization.

As shown in Table 1 for samples 7-11, the saturation remanence of the oxidized samples is several times that of the unoxidized samples, while the susceptibilities of the oxidized samples are lower than those of the unoxidized samples. These observations are consistent with an effective decrease in grain size from a MD to a PSD state after oxidation because finer grains have higher saturation remanences and lower susceptibilities than coarse grains [cf. Table 4.2 of Thompson and Oldfield, 1986]. Furthermore, this pattern would not be expected if hematite were a major product of the oxidation because hematite has extremely low values of saturation remanence and susceptibility, compared to magnetite.

Discussion and conclusions

As noted above, the presence of a (suppressed) Verwey transition indicates that our large oxidized magnetite samples are only partially oxidized. Most experimental results from natural SD and PSD seafloor titanomagnetites indicate that low-temperature oxidation reduces the magnetic susceptibility, saturation magnetization, saturation remanence and the intensity of natural remanence while increasing the coercive force and coercivity of remanence [Marshall and Cox, 1972; Johnson and Merrill, 1973; Smith, 1987]. One explanation for the magnetic behavior is that the oxidized particles consist of a core of titanomagnetite surrounded by a concentric layer of maghemite [Knowles, 1981]. The maghemitization produces a decrease in cell-edge, which causes the lattice to stretch and crack around the titanomagnetite core [Petersen and Vali, 1987]. Internal stresses develop as a direct result of the oxidation gradient and the variation in lattice parameters within a grain. The mutual stresses between the shells of different stoichiometry both interact with the magnetization to increase the effective anisotropy and coercivity, giving rise to the observed effects [Knowles, 1981; Dunlop, 1986; Petersen and Vali, 1987; Smith, 1987; Özdemir *et al.*, 1993].

For magnetite, the PSD-MD boundary is theoretically located at about 8 μm [Moskowitz and Banerjee, 1979] and most empirical studies produce estimates that lie between 10 and 20 μm [Parry, 1965; Day *et al.*, 1977; Stacey and Banerjee, 1974]. Our experimental results demonstrate that low-temperature oxidation can seriously affect the magnetic properties of magnetite and that oxidized MD grains can produce PSD-like behavior. Moskowitz [1980] has shown that in titanomagnetite the PSD-MD boundary can be as high as 42 - 150 μm , depending on the degree of low-temperature oxidation. However, the model of Moskowitz [1980] does not include a contribution from stress. The exact mechanism for the observed PSD-like behavior in oxidized MD magnetite is therefore uncertain.

The composite nature of the oxidized grains (i.e. maghemite rim and magnetite core) suggests three possible causes for the observed PSD-like behavior [B.M. Moskowitz, pers. comm., 1994]. First, the magnetite core could be reduced sufficiently in volume to make it a PSD grain, independent of the surficial maghemite. Second, internal stress in the composite grain due to lattice mismatches could increase the domain wall energy and make it more difficult to add walls for a given grain size. Coupled with a reduced volume of the magnetite core, this could give rise to conversion to PSD-like behavior. Third, the composite grain could be a mixture of SD maghemite and MD magnetite which gives rise to bulk PSD-like properties. This possibility is supported by the large decrease in remanence below 50 K (Figure 2) which suggests that superparamag-

netic/SD particles are present. All three of these mechanisms appear plausible and could each contribute to the behavior reported here.

The above mechanisms can account for the observed increases in coercivity and MDFs of the ARM and SIRM after oxidation. This suggests that low-temperature oxidation can stabilize the remanence of large MD grains by allowing them to behave like PSD grains. Furthermore, the saturation remanences of the oxidized grains are much higher than those of the unoxidized magnetite grains (Table 1). This suggests that a significant remanence can be acquired during low temperature oxidation. Such behavior has potentially important implications for the interpretation of the magnetic record. For example, it provides a mechanism by which a chemical remanent magnetization can be acquired by MD grains in sediments. If the oxidation occurs shortly after deposition it could give rise to a reliable record of geomagnetic field behavior. However, if the oxidation occurred later, it could give rise to a secondary overprint that is more resistant than would be otherwise expected. MD grains are also common in basaltic rocks. Low-temperature oxidation might allow MD grains to make a significant contribution to the remanence of such rocks. The presence of oxidized MD grains could therefore jeopardize paleointensity determinations from basalts [e.g., Thomas, 1993].

Our results also show that the commonly used tests that are designed to distinguish between MD and SD behavior [e.g., Lowrie and Fuller, 1971; Day et al., 1977; Bailey and Dunlop, 1983] may give misleading results when oxidized grains exist in a sample. This demonstrates the need to characterize mineral magnetic properties using a wide range of magnetic measurements, such as behavior at cryogenic temperatures, high field hysteresis parameters, and AF demagnetization characteristics as well as analytical tools such as x-ray diffraction.

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