Effect of citrate–bicarbonate–dithionite treatment on fine-grained magnetite and maghemite

Christopher P. Hunt [a], Michael J. Singer [b], Gunther Kletetschka [a], Jeff TenPas [b], Kenneth L. Verosub [c]

[a] *Institute for Rock Magnetism, University of Minnesota, Minneapolis, MN 55455, USA*
[b] *Department of Land, Air and Water Resources, University of California, Davis, CA 95616, USA*
[c] *Department of Geology, University of California, Davis, CA 95616, USA*

Abstract

Mineral magnetic properties of soils and parent materials have been interpreted in terms of paleoclimate and rates of soil formation but it is important to understand which minerals contribute to the mineral magnetic signal. Citrate–bicarbonate–dithionite (CBD) treatment has been used to determine the amounts of fine-grained, often pedogenic, ferrimagnetic minerals relative to coarse-grained, often inherited, magnetic minerals. However, questions have been raised about the effect of particle size on the efficacy of CBD in dissolving magnetite and maghemite grains. In this paper we use magnetic susceptibility and its frequency dependence, and the low-temperature behavior of a saturation isothermal remanent magnetization, to track the dissolution of carefully sized magnetite grains. We found that the standard CBD procedure dissolves fine magnetite particles (ca. < 1 μm) but leaves larger particles (ca. > 1 μm) essentially intact. Thin oxidized coatings, presumably maghemite, are also dissolved by the CBD procedure. These results support previous interpretations that the CBD procedure can be used to distinguish between pedogenic and lithogenic magnetic grains, assuming that most pedogenic magnetic grains are sufficiently small (ca. < 1 μm) and most lithogenic magnetic grains are sufficiently large (ca. > 1 μm). These results also show that the standard procedure is too harsh to differentiate between 1 μm grains of magnetite and maghemite. A modified CBD extraction that uses half as much dithionite reduces the magnetic susceptibility of 1 μm magnetite grains by only 10%. This method may be useful in distinguishing between magnetite and maghemite grains in this size range.

1. Introduction

Fine and Singer [1] reported that the citrate–bicarbonate–dithionite (CBD) technique could be used to distinguish between pedogenic and lithogenic (inherited) magnetic particles in soils. In particular, they used data from random powder-mount X-ray analyses to show that magnetite and maghemite could be distinguished by this technique. In subsequent papers [2–4] it was shown that the CBD technique did not dissolve coarse-grained magnetite but did dissolve fine-grained magnetite. In order to be able to use mineral magnetic properties to reconstruct paleoclimates [5] and to determine rates of soil formation [6], it is necessary to have a full understanding of which minerals are dissolved by the CBD technique and how grain size influences the dis-

solution. Here, we report on the mineral magnetic properties of well characterized, sized, magnetite grains, before and after CBD treatment. The mineral magnetic measurements are used to determine the mineralogy and domain state of the dissolved and undissolved material.

2. Methods

2.1. Magnetite samples

Commercial synthetic magnetites, nominally sized at 0.3 μm, 1.4 μm, 7 μm, and 40 μm, were used in this study (Wright Industries pigment numbers 112978, 3006, 041183, and 112982, respectively). Previous analysis of the first two of these magnetites yielded median grain sizes of 0.19 μm and 1.0 μm, respectively [7]. In the present study, the other two magnetites were examined with reflected light microscopy; the 7 μm magnetite was found to be closer to 14 μm, and the 40 μm magnetite was closer to 55 μm. All of the magnetite samples were produced and purchased in 1981 and, although they were kept in closed jars, they had been exposed to the normal atmosphere of the laboratory for 12 years. Özdemir et al. [8] showed that the outer layers of these magnetites had been partially oxidized to form a maghemite skin. They also showed that baking the material in a reducing atmosphere for several hours could restore the saturation magnetization, σ_S, to the pure magnetite value of 90–92 Am^2kg^{-1}. Two of our samples (the 0.19 μm and the 1.0 μm grains) were treated in this way, and the results for reduced and unreduced samples of these grain sizes are included in this paper.

2.2. Citrate–bicarbonate–dithionite procedure

The CBD procedure was developed by Mehra and Jackson [9] to pre-treat clays for X-ray diffraction analysis. Sodium dithionite is a strong reducing agent that reduces and solubilizes secondary iron oxides, including goethite, hematite and maghemite. Once reduced, the Fe^{2+} is chelated by the citrate. The pH of the system is buffered at 7.3 by sodium bicarbonate. Typically,

a 4.0 g sample is ground to pass an 80 mesh sieve and is then suspended in a solution of sodium–citrate–bicarbonate. The solution is heated and, once the temperature reaches 70–75°C, 2.0 g of solid sodium dithionite are added in separate 1.0 g additions. After the second dithionite addition, the suspension is maintained at 75°C for a minimum of 15 min. After dithionite extraction, the soil particles are removed from the suspension by centrifugation, the supernatant is saved for analysis or discarded, and the extraction process is repeated. After the second extraction, the sample is rinsed twice with the sodium citrate solution. In general, little additional iron is removed by additional extractions or washings [10].

In order to monitor the progress of the CBD procedure, we subdivided the extraction procedure used in this study. Initially, 200 mg samples of the sized magnetite grains were dispersed by hand in 4.0 g of acid-washed sand (0.1–0.5 mm grain size). Each sample was heated in citrate–bicarbonate solution, but only 1.0 g of dithionite was added. After 15 min the sample was centrifuged, the supernatant was removed, and the magnetic susceptibility was measured. Three additional 1.0 g extractions and measurements of magnetic susceptibility followed the first measurement. After completion of the CBD treatment, the remaining material was extracted from the sand matrix for additional measurements. In a separate experiment, the low-temperature behavior of the 1.0 μm magnetite was studied after each of seven 1.0 g extractions.

A set of five synthetic maghemite samples, varying in size between 0.1 and 10 μm, each dispersed in $CaCO_3$, was also treated with CBD using two 2.0 g treatments. Magnetic susceptibility was measured prior to and following CBD extraction.

2.3. Magnetic susceptibility

Magnetic susceptibility is a measure of the magnetic response of a material to an external magnetic field. In this study, the low-field magnetic susceptibility was measured on a Bartington Instruments susceptibility bridge using a Model MS-2 sensor. The specific or mass susceptibility

χ, measured in units of $m^3 kg^{-1}$, is defined as the ratio of the material magnetization, σ (per unit mass), to the weak external magnetic field H:

$$\chi = \frac{\sigma}{H}$$

In materials which display hysteresis, the initial slope of the hysteresis loop is taken to be the low-field susceptibility, χ_0.

In ferromagnetic, ferrimagnetic, or canted antiferromagnetic materials, hysteresis behavior and the presence of magnetic domains cause the susceptibility to be dependent on grain size. For example, the magnetic susceptibility of crushed magnetite grains increases by about a factor of 2 between 1 μm and 100 μm, whereas the magnetic susceptibility of grown magnetite grains increases by about a factor of one-third between 0.03 μm and 10 μm. The magnetic susceptibility of grown magnetite grains that are smaller than about 20 nm (thermally unstable superparamagnetic grains) is up to twice that of grains that are greater than about 30 nm (thermally stable single-domain grains) [11]. If a sample has a relatively small range of grain sizes, the magnetic susceptibility is roughly proportional to the quantity of magnetic material in the sample.

2.4. Frequency dependence of magnetic susceptibility

The ability of a magnetic grain to respond to an applied field depends on the frequency of the applied field. This variation is measured by the 'frequency dependence of susceptibility', χ_{fd}, which is usually defined as:

$$\chi_{fd} = \frac{\chi_{low\,frequency} - \chi_{high\,frequency}}{\chi_{low\,frequency}} \times 100\%$$

where $\chi_{low\,frequency}$ and $\chi_{high\,frequency}$ are the in-phase components of the susceptibility, which are typically measured at approximately 470 Hz and 4700 Hz, respectively. In magnetite, grain sizes in a 2 nm wide window near 20 nm will contribute to the magnetic susceptibility at 470 Hz but will not contribute at 4700 Hz; a sample with a significant fraction of grains in this window will have values of χ_{fd} that may be as high as 12% [12].

The parameter χ_{fd} has proven to be useful in detecting the presence of ultrafine-grained magnetic materials, such as magnetite or maghemite, which are often found in soils [1,13].

2.5. Low-temperature behavior

Information about mineral magnetic properties can also be obtained from studies of the behavior of a saturation isothermal remanent magnetization (SIRM) induced at cryogenic temperatures. In this study, samples containing approximately 100 mg of magnetite were placed in gelatin capsules for measurement on a Quantum Design MPMS low-temperature susceptometer. The samples were cooled to 6 K in zero field, and the SIRM was induced by applying a steady magnetic field of 2.5 T for about 1 min. Each sample was then warmed in zero field. The remanence was measured at 6 K, then every 5° from 10 K to 150 K, and finally every 10° from 150 K to 300 K. Dried residues from the CBD treatments were also subjected to this procedure.

At low temperature, magnetite undergoes magnetic and crystallographic transitions that can be used for mineral identification. These transitions can be detected by measuring the thermal demagnetization of the low-temperature SIRM described above. The width of the transition and its precise temperature are sensitive to impurities, grain size and non-stoichiometry [14–16]. In our case, we took advantage of the grain size and impurity dependencies to monitor the progress of the CBD treatment.

Near $T = 118$ K in magnetite, there are a number of changes in physical properties, collectively known as the Verwey transition T_V [17]. The changes which occur here include an abrupt change in magnetocrystalline anisotropy, an anomaly in specific heat, a discontinuity in electrical resistivity (the original 'Verwey transition'), and a fairly large deformation of the lattice [18]. The latter corresponds to the crystal transformation from a cubic system above T_V to a monoclinic or triclinic system below T_V [19]. At a slightly higher temperature is T_K (120–130 K), the magnetic isotropic point, which is the temperature at which the anisotropy constant, K_1, be-

comes zero as it changes sign. Here, the characteristic easy direction of magnetization changes its orientation from the (room temperature) cubic [111] axis to one of the three former cubic [100] axes [16]. Experimental studies [20] have shown that changes in coercivity, magnetic susceptibility and remanence behavior occur near the true Verwey crystallographic transition, and are controlled by the polycrystalline magnetostriction constant, $\overline{\lambda}_S$, rather that at the isotropic point where K_1 goes to zero.

The net effect on the magnetization is an abrupt loss of remanence near the transition. The magnitude of this loss depends on grain size, degree of oxidation, cation substitution and magnetostatic interactions. For example, pure, single-domain and multi-domain magnetite grains show a sharp discontinuity in remanence around 100–120 K, but little loss of remanence below and above the transition. On the other hand, a distribution of superparamagnetic magnetite

Fig. 2. Frequency dependence of susceptibility. The left column of each set is the frequency dependence prior to CBD extraction. The subsequent columns are frequency dependence after 1, 2, 3, or 4 CBD extractions. Samples 1.0 (reduced) and 0.19 (reduced) are 1.0 μm and 0.19 μm magnetite samples that had been reduced prior to CBD extraction and were measured only after the 4th CBD extraction.

grains displays little or no transition; rather, it shows a gradual loss in remanence as the temperature increases and grains of a given threshold size become thermally unstable upon reaching their respective unblocking temperatures. Compared to pure magnetite grains of the same size, grains that have oxidized rims or have surface stresses also show a smaller transition [8]. The low-temperature behavior of SIRM thermal demagnetization has been used in paleoclimate studies to obtain information about the relative importance of superparamagnetic grains versus larger magnetite grains [21–23].
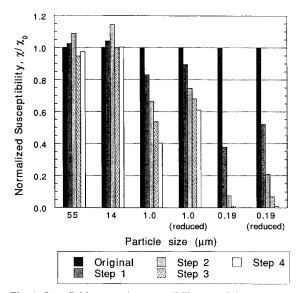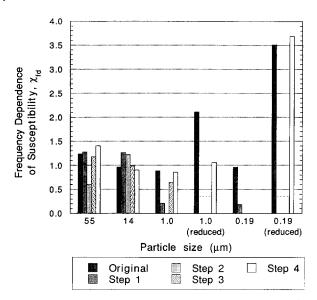

Fig. 1. Low-field magnetic susceptibility remaining as a percentage of initial unnormalized susceptibility for four sized magnetite samples. The left column of each set is the susceptibility prior to CBD extraction. Subsequent columns are the susceptibility remaining after 1, 2, 3, or 4 CBD extractions. Samples 1.0 (reduced) and 0.19 (reduced) are 1.0 μm and 0.19 μm magnetite samples that had been reduced prior to CBD extraction. All values represent the average of three measurements.

3. Results

3.1. Magnetic susceptibility and frequency dependence

Initial mass-normalized susceptibility values were 7.12, 5.12, 3.04, 4.32, 5.10 and 6.11 × 10^{-4}

$m^3 kg^{-1}$ for the 55 μm, 14 μm, 1.0 μm, 1.0 μm (reduced), 0.19 μm and 0.19 μm (reduced) magnetite samples, respectively. These values are in good agreement with previously published size-dependent susceptibility values for magnetite [21]. For the two smaller grain sizes, the susceptibility values of the reduced and unreduced samples decreased after each step of the CBD treatment (Fig. 1). After three steps, the susceptibility of the smallest sample was essentially zero. For the two larger grain sizes, the magnetic susceptibility remained approximately constant throughout the extraction procedure. The five maghemite samples completely dissolved after the first CBD extraction, so that the susceptibility values were

zero. The frequency dependence values were rather lower than those measured for natural soils and showed no clear trend with CBD treatment (Fig. 2).

3.2. Low-temperature behavior of SIRM

The larger grain sizes show only a small difference in low-temperature behavior before and after CBD treatment, whereas the smaller grain sizes show a marked difference. In all cases, the CBD treatment enlarged the remanence drop at the Verwey transition near 118 K, and reduced the fine-grained superparamagnetic component (as determined from the total remanence drop
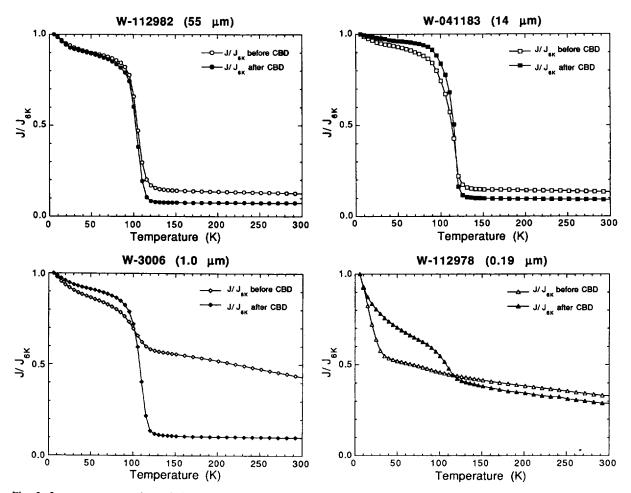

Fig. 3. Low-temperature thermal demagnetization of saturation isothermal remanent magnetization (imparted at 6 K, and normalized to the 6 K value) before and after CBD extraction for four sized magnetite samples.
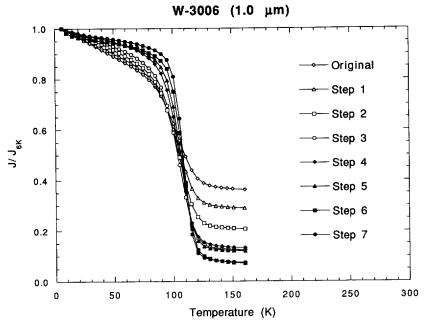
W-3006 (1.0 μm)

Fig. 4. Low-temperature thermal demagnetization of saturation isothermal remanent magnetization (imparted at 6 K and normalized to the 6 K value) before CBD extraction and for 7 CBD extractions of the 1.0 μm magnetite sample. This illustrates that the size and sharpness of the remanence drop at the Verwey transition increased after each CBD extraction step.

between 6 K and 300 K, not including the drop at the Verwey transition) (Fig. 3). For the sample that was subjected to seven CBD steps, the size of the remanence drop at the Verwey transition (i.e., the difference between the values at about 80 K and 150 K) increased after each step, consistent with the loss of a transition-inhibiting oxidized rim. The slope of the unblocking curve also decreased, consistent with the dissolution of ultrafine-grained superparamagnetic particles (Fig. 4).

4. Discussion

Our data show that the CBD treatment progressively dissolves magnetite grains finer than 1 μm while leaving larger grains virtually intact. The step-wise results shown in Fig. 1 indicate that even the smaller magnetite grains can be differentiated from maghemite if fewer grams of dithionite are used in the extraction. In fact, only about 10% of the initial susceptibility is lost by a

1.0 g extraction of the 1.0 μm sample. Unlike the magnetite, the five maghemite samples were fully dissolved by the standard CBD treatment.

It is likely that some of the loss in magnetite susceptibility can be attributed to the removal of oxidized coatings, presumably of maghemite, on the magnetite grains. This conclusion is supported by the observation that the reduced 1.0 μm and 0.19 μm samples (Fig. 1) lost less susceptibility in the CBD extraction than the unreduced samples of the same size.

The CBD treatment did not have a clear effect on the frequency dependence of the magnetic susceptibility. In all cases, the frequency dependence was low and the changes that resulted from successive CBD treatments displayed no obvious pattern. Despite the popularity of this method among environmental magnetists, we find that frequency dependence does not appear to be a very good parameter for measuring changes in the amount of superparamagnetic material, at least for these synthetic samples. In fact, because its window of sensitivity is so small, the frequency

dependence technique was unable to track the changes in the magnetic materials during CBD extraction in our experiments.

5. Conclusions

All of the changes in mineral magnetic parameters induced by CBD treatment are consistent with the complete dissolution of very fine-grained magnetite and with the removal of a Verwey transition-inhibiting outer rim of oxidized material on larger grains. This indicates that the CBD treatment cannot differentiate between very fine-grained magnetite and very fine grained maghemite. In soils, however, both very fine grained magnetite and maghemite of any size are likely to be pedogenic in origin and they will both be removed by the CBD treatment. Thus, earlier interpretations of the pedogenic nature of CBD-soluble magnetic grains were essentially correct.

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