Dissolution behaviour of fine-grained magnetite and maghemite in the citrate–bicarbonate–dithionite extraction method

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Abstract

Mineral magnetic properties of soils and sediments are increasingly used as proxy parameters for environmental and palaeoclimate analysis. To investigate which magnetic minerals contribute to the environmental signal in the samples, chemical techniques such as the citrate–bicarbonate–dithionite (CBD) extraction method have been introduced in environmental magnetism studies. This technique is assumed to distinguish lithogenic (magnetite) from pedogenic (maghemite) mineral content in soils and sediments. Unfortunately, interpretation of the CBD extractions is not straightforward because the procedure is sometimes more suitable for distinction between grain size than for distinction between minerals. The procedure of the CBD extraction technique was investigated to determine the influence of extraction temperature and iron oxide concentration on the dissolution behaviour of the samples. Synthetic samples were extracted at three different temperatures (60º, 70º and 80ºC) at similar iron oxide concentration (5 wt%), and for three different concentrations (0.1 wt%, 1 wt% and 5 wt%) at the same temperature (60ºC). Our results show that a lower extraction temperature reduces the dissolution rate for all samples, while decrease in iron oxide concentration increases the dissolution rate. Thus, the parameters in the CBD procedure have a major influence on the dissolution behaviour of the samples. In practice this means that when natural samples of differing iron oxide concentration are extracted with this technique, the results of the extractions cannot be compared. Therefore, the outcome of this type of extraction experiment can only be accurately interpreted when the effect of the procedure on the dissolution behaviour is taken into account. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Magnetic minerals can record the past geomagnetic field. The physical properties of these minerals vary as a function of mineral type, grain size and shape, crystallinity, and other factors. Palaeomagnetic studies are supported by analysis of these prop- erties. The variations in magnetic properties can also reflect variations in (palaeo)environmental processes and palaeoclimate conditions. In environmental magnetism the mineral–magnetic parameters are applied as proxies for environmental and climate processes. One of the parameters that is often studied in environmental magnetism is the low-field magnetic susceptibility. Le Borgne [1] demonstrated that magnetic enhancement of the topsoil in a soil profile was caused by formation of maghemite in the top-

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soil, which in turn was related to climatic factors like soil humidity. Many others followed his example by studying magnetic susceptibility (e.g. [2–4]), or other magnetic parameters of soils and sediments (e.g. [5–9]).

Unfortunately, the interpretation of environmental magnetism data is not always unambiguous. Therefore, other methods must be incorporated into environmental studies to improve the interpretation of the magnetic data. Chemical extraction techniques are frequently used for this purpose, particularly in soil studies (e.g. [3,10–13]). A popular extraction technique is the citrate–bicarbonate–dithionite (CBD) method of Mehra and Jackson [14]. It is based on reductive iron dissolution with dithionite as reductant and citrate as a chelating agent to bind the dissolved iron. Bicarbonate is used to buffer the H^+ loss during the reaction.

Results of reported CBD extraction studies vary considerably. For example, in some cases the CBD method was reported to dissolve only the pedogenic maghemite [3,12,15], while in other cases the fine-grained magnetite was dissolved as well [11]. However, the results of the different studies are difficult to compare, because the extraction procedure of each study is not always clearly specified. Factors such as amount of sample, type of sample, amount of dithionite and extraction temperature may vary with each study. The reductive dissolution of iron oxides is a kinetic process and factors such as pH, crystallinity and temperature have a major effect on the dissolution rate (e.g. [16–18]). This was already shown by the results of Mehra and Jackson [14] who examined the influence of buffer type, pH and oxidation potential of dithionite on iron dissolution. Therefore, results of extraction studies with differences in extraction procedures will not necessarily reflect the same dissolution behaviour.

In addition to difficulties resulting from the variation of the CBD extraction method, also the sample material itself has proved difficult to control. Preferably, natural samples are used in all experiments because they represent the natural conditions, but the concentration and physical parameters of the magnetic material are not precisely known. In synthetic samples, these conditions can be controlled. Synthetic samples, however, usually contain aggregates of very fine-grained magnetic material formed during sample preparation. Thus, the outcome of extraction experiments using synthetic samples will not necessarily reflect the natural circumstances. This complicates the interpretation of results for either type of samples.

The differences in the results of the various CBD extraction studies could well be related to an incomplete control of the experimental parameters. The purpose of this study is to investigate how the outcome of CBD extractions is affected by changing parameters (extraction temperature and iron oxide concentration) in the extraction method. By having a more complete understanding of the extraction mechanism we hope to devise a procedure which is most effective for chemical maghemite–magnetite distinction. To control the variables in the extraction technique more closely, synthetic samples were used. Samples were prepared to mimic natural samples as best as possible by minimising formation of magnetic aggregates during mixing.

2. Materials and methods

2.1. CBD technique

Many of the adaptations of the CBD technique in environmental magnetism have involved changes in extraction temperature, in concentration of the magnetic minerals in the sample, or in the amount of dithionite used in the extraction step. The present study will therefore focus on two of these variables, to determine to which extent they influence the results of the extraction. Extractions with constant magnetic mineral concentration (5 wt%) were performed at three different temperatures: 60°C, 70°C and 80°C. Further, extractions with a constant temperature of 60°C were performed with varying iron oxide concentrations of 5 wt%, 1 wt% or 0.1 wt%. Table 1 gives an overview of all extraction experiments performed and characteristics of the iron oxides used in the experiments.

2.2. Synthesis of the magnetic minerals

Magnetite and maghemite were prepared according to the procedures described by Schwertmann and Cornell [19]. The magnetite was formed by heat-

Table 1
The experimental parameters of the CBD procedure and characteristics of the magnetic minerals used in the experiments

Experiment	Concentration magnetic mineral (%)	Temperature (°C)	Magnetic mineral used	Curie temperature (°C)	Cell edge (Å)
1	5	80	Magnetite (batch 1)	580	8.37
2	5	80	Maghemite (batch 1)	645	8.35
3	5	70	Magnetite (batch 1)	580	8.37
4	5	70	Maghemite (batch 1)	645	8.35
5	5	60	Magnetite (batch 2)	580	8.37
6	5	60	Maghemite (batch 2)	645	8.33
7	1	60	Magnetite (batch 2)	580	8.37
8	1	60	Maghemite (batch 2)	645	8.33
9	0.1	60	Magnetite (batch 2)	580	8.37
10	0.1	60	Maghemite (batch 2)	645	8.33

ing a de-oxygenated solution of ferrous sulphate and adding an oxygen-free solution of potassium nitrate and potassium hydroxide. The maghemite was formed by heating a batch of magnetite in air at 250°C for 2 h. Approximately 20 g of material is formed.

Two batches of magnetite were prepared; one of these batches was subsequently transformed to maghemite (batch 1 magnetite and batch 1 maghemite). These batches were used to make the samples for the 70°C and 80°C experiments. For the 60°C experiments, which were carried out in a later stage, fresh batches of magnetite and maghemite were prepared (batch 2 magnetite and batch 2 maghemite) in a similar way as the batch 1 minerals.

Minerals of batch 1 were dried in air and stored in a desiccator with silica gel for several weeks prior to the mineralogical and magnetic analyses. Part of the minerals of batch 2 was stored in acetone (propanon) immediately after synthesis (batch 2A) and another part (batch 2B) was dried and stored to determine whether and how the dry storage affected the physical properties of the samples.

2.3. Preparation of synthetic samples

The magnetic material in natural samples is usually distributed homogeneously as separate particles in a paramagnetic matrix. We mimicked natural samples by dispersing the synthesised magnetite and maghemite in calcite powder in concentrations of 0.1 wt%, 1 wt% and 5 wt%. A common method for mixing synthetic samples is manual stirring in a slurry (e.g. [20–23]). When using very fine-grained strongly magnetic particles, this method often results in heterogeneously dispersed samples containing aggregates of closely spaced magnetic particles (e.g. [21,24–26]). The aggregates will exhibit magnetic interaction and may show differences in dissolution behaviour compared to natural samples, caused by a decrease in particle surface. To minimise formation of magnetic aggregates during stirring, the force exerted on the grains during mixing was increased. A combined method of manual and ultrasonic stirring (the 'ultrasonic stirring technique') was developed to prevent formation of aggregates of magnetic material in the matrix as much as possible.

An amount of calcium carbonate (4.00 g $CaCO_3$, analytical grade) was transferred to a mould, placed in an ultrasonic bath (Stopler, Bransonic 12). Approximately 5 ml of acetone was added. After ~30 s of manual stirring of the matrix and the acetone in the ultrasonic bath, a specified amount of magnetic material was added. Subsequently the sample was stirred for at least another minute with the ultrasonic bath still switched on. After mixing, the sample was dried in air in an oven at 40°C overnight. Samples of 4.00 g calcite and 0.20 g (5 wt%) of either magnetite or maghemite were prepared. All samples were weighed in a semi-microbalance (Sartorius, MC1). Samples for the 0.1 wt% and 1 wt% experiments were prepared with respectively 0.004 g and 0.04 g magnetic material instead of 0.20 g. Blank samples (made of 4.00 g calcite only) underwent the same handling as the magnetic samples.

2.4. Magnetic analyses

A modified horizontal Curie balance [27] was used for thermomagnetic analysis. Susceptibility changes with temperature were measured in an argon atmosphere, on a susceptibility bridge equipped with a heating unit (AGICO, KLY-2/CS-3). Isothermal remanent magnetisation (IRM) acquisition and back field demagnetisation fields were induced with a PM4 pulse magnetiser, and measured with a JR5A spinner magnetometer (AGICO) to determine IRM and coercivity of the material. Stationary three-axis alternating field (AF) demagnetisation was performed in a laboratory-built coil (peak field 300 mT), the maximum field used for demagnetisation was 250 mT. All measurements were performed with samples containing 1 wt% or 5 wt% of magnetic mineral. Measurements were performed with samples that were either stirred ultrasonically or mixed manually, to determine whether there were differences in magnetic properties related to the stirring technique. The acquisition and demagnetisation data were used to plot Cisowski and Henkel diagrams [25,28] to study variations in the magnetic interaction in the samples. Magnetic measurements of the samples for the extraction technique were performed after each extraction step.

2.5. CBD extraction procedure

The procedure of Hunt et al. [11], essentially an adapted version of the original method by Mehra and Jackson [14], formed the basis for our extraction procedure, which is detailed in Fig. 1. In each experiment twelve samples and four to six blanks were extracted.

Prior to the start of the extraction experiment the samples were transferred to 100-ml glass centrifuge tubes after which bulk susceptibility and mass of the samples were measured. The samples were kept in the centrifuge tubes during the entire course of the experiment. After each extraction step the samples were dried in air in an oven at 40ºC for ~24 h, and bulk susceptibility and mass of the samples were measured before each new step.

The procedure of the CBD extraction is as follows (Fig. 1). A solution of 40 ml 0.3 M sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, analytical grade) and 5 ml 1 M
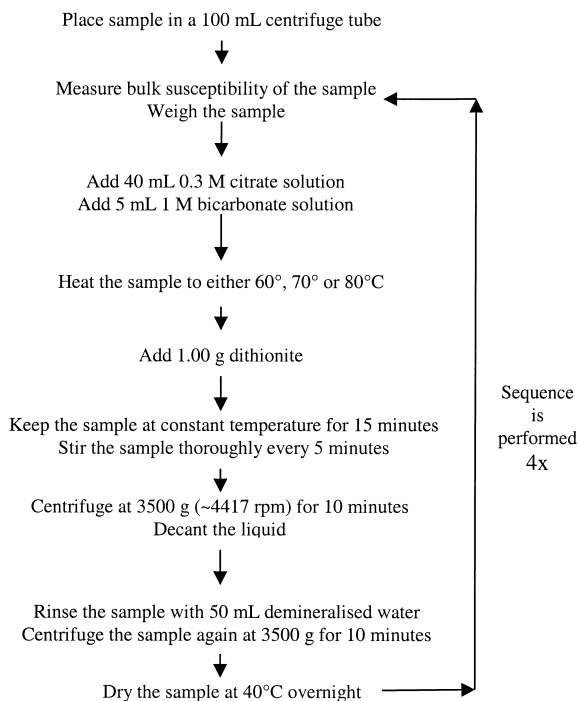

Fig. 1. CBD protocol used in this study.

sodium bicarbonate ($NaHCO_3$, analytical grade) was added to the dry samples. The tubes were placed in a water bath (GFL 1003) at a temperature of either 60º, 70º or 80ºC (temperature variation ±0.1ºC). When the mixture reached the required temperature, 1.00 g sodium dithionite ($Na_2S_2O_4$, analytical grade) was added and the samples were stirred thoroughly for approximately 10–15 s with a glass stirring rod. The samples were kept at constant temperature for another 15 min, and were stirred thoroughly every 5 min.

After 15 min the samples were slightly cooled in air and the liquid was separated from the sample by centrifuging for 10 min at 3500 *g* (~4417 rpm). The liquid was decanted and the samples were rinsed with ~50 ml of demineralised water and centrifuged again at the same settings to separate the solid from the rinsing liquid. The liquid was decanted and the samples were placed in an oven to dry. The bulk susceptibility of the dry samples was measured, mass of the samples was determined and the extraction was repeated three times to give a total of four extraction steps. Of every step one of the samples was kept for magnetic measurements.

3. Results and discussion

3.1. Sample characterisation

3.1.1. Non-magnetic analysis

The magnetite grains are equidimensional, with an average diameter of <0.5 μm (SEM, XL30 lab 6) and a cubic crystal structure (XRD, Philips PW1700, see Fig. 2). The maghemite has a tetragonal crystal superstructure and a morphology equivalent to that of the original magnetite (XRD and SEM observations, see Fig. 2). The diffractograms of the maghemite correspond well with those published by Özdemir [29] and Özdemir and Banerjee [30] for a synthetic maghemite.

SEM studies indicated that the synthetic minerals formed aggregates with a diameter of 5 to 50 μm. The SEM resolution was insufficient to discern separate particles. However, particle size can be estimated at <0.5 μm, because that was the size of the smallest particles detectable by the SEM (see Fig. 3A). This size corresponds well with the results of Schwertmann and Cornell [19] who found grain sizes in the range of 0.02–0.5 μm for minerals prepared in a similar way.

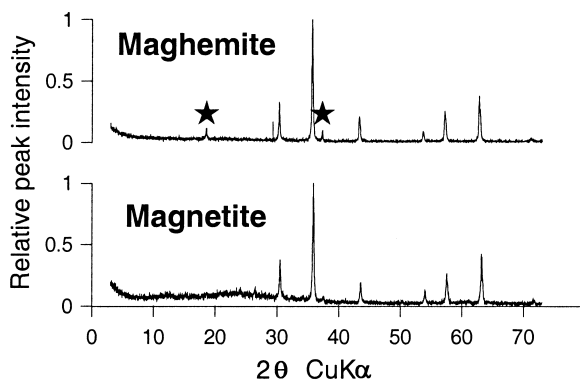Effects of the stirring technique on the dispersion of the magnetic particles in the sample were studied with the SEM. Aggregates were present in all samples regardless of the mixing technique used. However, the average size of the aggregates was ~5–10 μm smaller in the case of ultrasonic stirring of the samples.

3.1.2. Magnetic analysis of magnetite samples

IRM acquisition experiments indicate that the magnetite samples were saturated after application of a field of approximately 100 ± 5 mT. The remanent coercive force (B_{cr}) was 25 ± 2 mT. This compares well with published data [21,31] for randomly oriented single domain magnetite.

Fig. 4 gives thermomagnetic runs for the magnetite of batch 1 and batch 2B. For batch 2, there was no difference in thermomagnetic behaviour related to storage: samples stored in air and those stored in acetone gave similar results. The thermomagnetic behaviour of the magnetite of both batches was very similar except in the 500°–700°C temperature interval. The initial magnetisation varied between 75 and 80 A m^2 kg^{-1}. After heating to 700°C, the remaining magnetisation at room temperature was approximately 1–5 A m^2 kg^{-1} (Fig. 4). In the temperature interval of ~200° to ~300°C there was an increase in decay of the magnetisation. The decrease in magnetisation was irreversible, as becomes apparent from the stepwise run of batch 2 (Fig. 4B). This indicates transformation of magnetite to maghemite. The temperature interval compares reasonably well with published data for conversion temperatures of magnetite to maghemite (e.g. 150°–250°C [32]).

The thermomagnetic behaviour of the magnetite batches differed in the value of the Curie temperature. The magnetite of batch 1 gave a T_C of ~570°C, but shows a tailing of the curve toward 640°C (Fig. 4A), indicating an alteration reaction. The magnetite in batch 2 gave a T_C of 640°C (Fig. 4B), implying complete conversion to maghemite. The maghemite formed from the magnetite during heating in the Curie balance in turn transforms to haematite upon further heating. For batch 1 this transformation starts at ~540°C and for batch 2 at ~630°C. These results are comparable to temperatures published for maghemite–haematite transition (e.g. >350°C [32], most recent: 550°C or 700°C [31]). The final room temperature magnetisation is close to zero, and the conversion is irreversible.

Fig. 2. XRD diagrams of the synthetic iron oxides used in the experiment. XRD analysis was performed with a diffractometer using Cu Kα radiation, 0.02° 2θ steps and a counting time of one second per step. The diagram of the maghemite shows some of the tetragonal superstructure peaks (indicated by stars). The relative peak intensities were calculated by normalising the intensities with the highest value of the peak intensity measured in the sample.
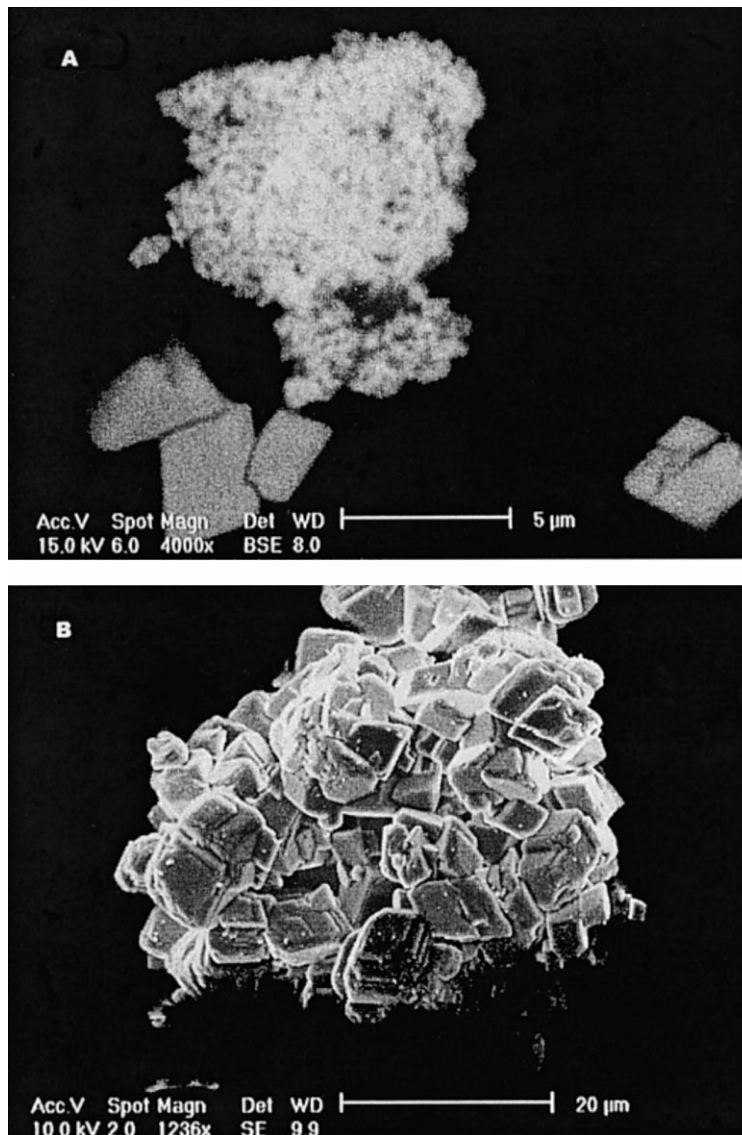
Fig. 3. SEM pictures of the synthetic samples: (A) shows an example of aggregated magnetic minerals (in this case maghemite in an ultrasonically stirred sample) adjacent to separate calcite grains, (B) shows a cluster of calcite grains of various sizes.

Magnetite of batch 1 transformed to maghemite and eventually haematite at lower temperatures than the magnetite of batch 2; therefore batch 2 is more stable upon heating than batch 1. These results indicate that although synthesis of both mineral batches occurred under seemingly identical circumstances, differences in magnetic behaviour can still occur (most likely caused by small differences in mineral structure).

The behaviour of low-field susceptibility (χ_{in}) as a function of temperature was studied as well, and oxidation of magnetite was prevented by measuring in argon atmosphere. Batch 1 samples show irreversible behaviour indicating some structural rearrangement on annealing (Fig. 4C), while batch 2 shows virtually reversible behaviour with a distinct Hopkinson peak (Fig. 4D). Repeated runs on batch 2 magnetite show perfectly reversible behaviour. As
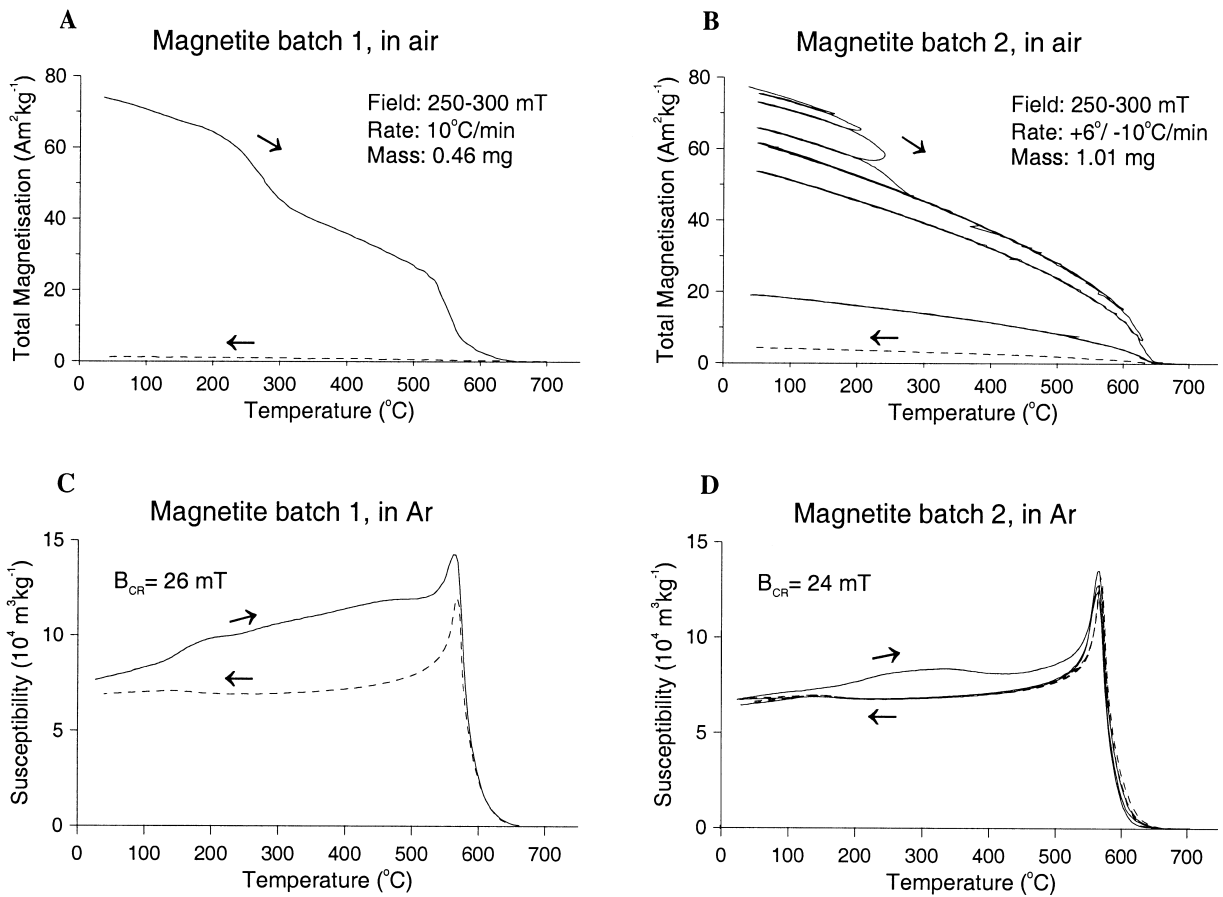
Fig. 4. (A) shows thermomagnetic data (in air) for the synthetic magnetite of the first batch. In (B) the run was divided into several steps to study the loss of magnetisation of the synthetic magnetite of the second batch. The steps were: step 1, 20–60–50°C; step 2, 50–200–50°C; step 3, 50–240–50°C; step 4, 50–280–50°C; step 5, 50–600–50°C; step 6, 50–630–50°C; step 7, 50–660–50°C; step 8, 50–700–30°C. The sample mass as well as heating and cooling rate and field used for analysis are given in the graphs. (C, D) The behaviour of low-field susceptibility versus temperature for the magnetite used in this study. Sample mass ∼0.5 g. Analyses were performed in inert atmosphere.

concluded from the thermomagnetic runs, the second magnetite batch appears to be more thermally stable than the first. Curie temperatures are ∼580°C, typical of magnetite.

3.1.3. Magnetic analysis of maghemite samples

IRM acquisition shows that the maghemite samples were saturated after application of a field of 80 ± 10 mT, lower than the saturation field of the magnetite samples. B_{cr} was 22 ± 1 mT, slightly lower than that of magnetite but comparable to literature values (e.g. natural maghemite ∼23 mT [33]).

The thermomagnetic behaviour of the synthetic

maghemite resembled the behaviour of 'model' ferrimagnetic minerals, and was similar for both batches (Fig. 5). The initial magnetisation was approximately 60 A m^2 kg^{-1}, comparable to values found in literature for a natural maghemite (e.g. 64 A m^2 kg^{-1} [33]). After heating to 700°C, the remaining magnetisation at room temperature was approximately 1–3 A m^2 kg^{-1}.

Batch 2 maghemite (Fig. 5B) indicated a T_C of ∼640°C, typical of maghemite. Similar to the magnetite samples, the storage method did not affect the thermomagnetic behaviour of the maghemite samples. Samples of the first batch started transforming

A

Maghemite batch 1, in air

Field: 250-300 mT
Rate: 10°C/min
Mass: 0.90 mg

B

Maghemite batch 2B, in air

Field: 250-300 mT
Rate: 10°C/min
Mass: 0.68 mg

C

Maghemite batch 1, in Ar

$B_{CR} = 22$ mT

D

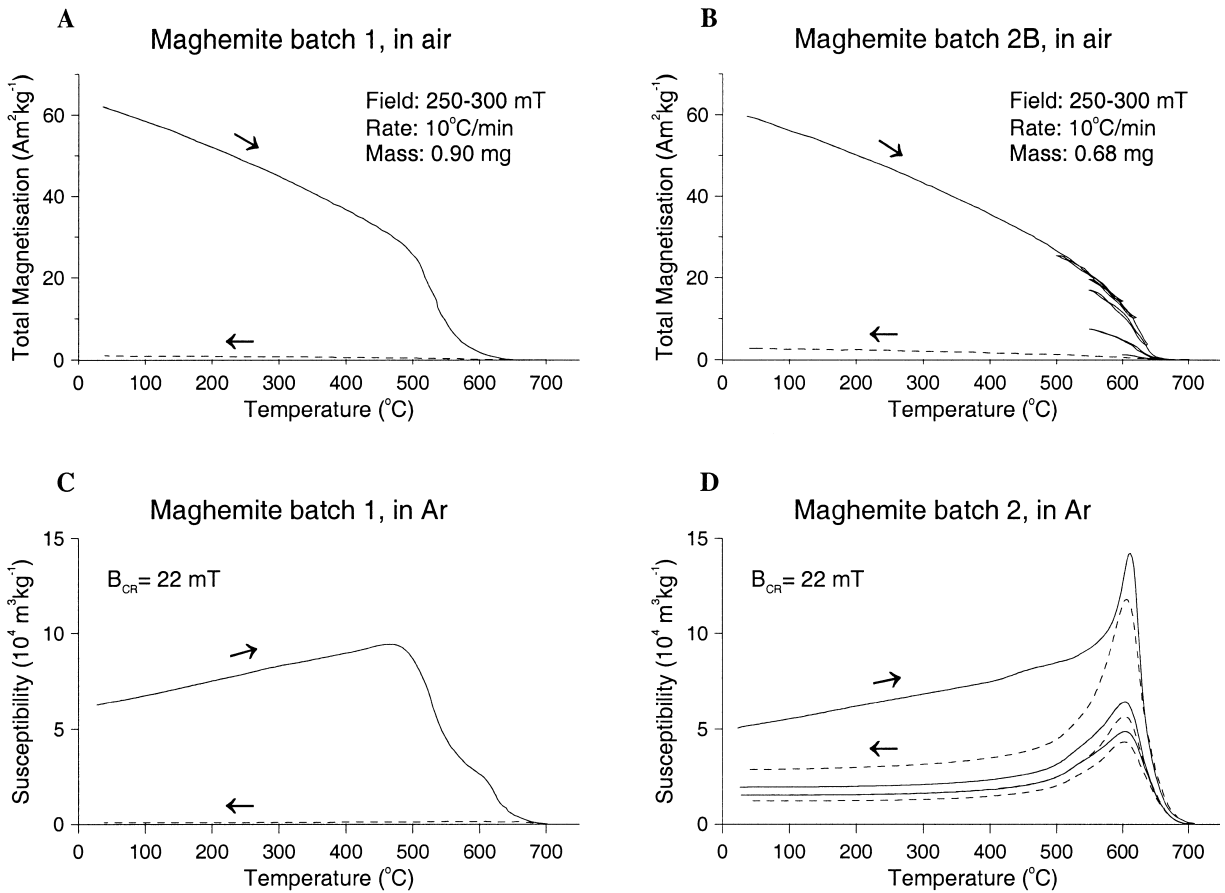### Maghemite batch 2, in Ar

$B_{CR} = 22$ mT

Fig. 5. (A, B) Thermomagnetic data of synthetic maghemite of respectively the first batch and the second batch. The steps of the heating run in (B) were: step 1, 20–600–500°C; step 2, 500–620–550°C; step 3, 550–640–550°C; step 4, 550–660–550°C; step 5, 550–680–600°C; step 6, 600–700–30°C. The sample mass as well as heating and cooling rate and field used for analysis are given in the graphs. (C, D) The behaviour of low-field susceptibility versus temperature for the maghemite used in this study. Sample mass ∼0.5 g. Analyses were performed in inert atmosphere.

to haematite at a temperature lower than the T_C of maghemite. The observed, apparent T_C (∼580°C) represents the rapid loss in magnetisation caused by transformation to haematite, rather than the true Curie point of the sample. The early onset of conversion to haematite indicates that the maghemite of batch 1 was less stable than that of batch 2. For the maghemite of batch two the decrease in magnetisation in the temperature interval of ∼640°–700°C was irreversible (Fig. 5B) and indicates transformation of maghemite to haematite. Comparable temperature ranges have been reported in the literature (e.g. 510°–660°C [30], ∼650°C [33]). The results indicate — like in the case of magnetite — that the seemingly

similar conditions under which the two batches were synthesised do not rule out the possibility of differences in magnetic or structural characteristics of the samples. They show that the maghemite of batch 1 was thermally less stable than that of batch 2. This is consistent with the results of the magnetite batches.

Thermal behaviour of χ_{in} in argon atmosphere for the two maghemite batches is shown in Fig. 5C,D. The results for the two batches differ. Maghemite of batch 1 shows a slow increase in susceptibility during heating. When the temperature rises above 500°C the susceptibility starts to decrease to a value of approximately zero at 700°C. Upon cooling it is evident that the decrease in susceptibility is ir-

reversible and therefore caused by transformation to haematite. The onset of the transformation to haematite has been reported to occur around 300ºC (e.g. 300–450ºC [34]), which is low compared to the 500ºC found for our synthetic samples of batch 1. Thermal conversion of maghemite to haematite, however, is reported to start within a wide temperature range (e.g. 250–900ºC) depending on factors such as method of preparation and morphology of the particles ([29]).

The second batch shows nearly ideal χ_{in} behaviour for maghemite, with a distinct Hopkinson peak at ~600ºC and a T_C of ~645ºC. The cooling path of the previous run is similar to the heating path of the following run during the entire experiment. After heating to 700ºC part of the susceptibility is lost due to conversion of maghemite to haematite. However, susceptibility loss progresses very slowly, and the conversion to haematite is still incomplete after four consecutive runs (Fig. 5D). This indicates that the second maghemite batch is thermally more stable than the first batch, as was concluded from the Curie balance results.

3.2. Results of ultrasonic stirring

The most notable difference between the manually stirred samples and those that were stirred ultrasonically was a more distinctive colour for all

of the latter samples. The manually stirred samples where light in colour and showed visible aggregates of magnetic material, while the ultrasonically stirred samples had a much more homogeneous appearance. Fig. 6 is an example of the difference in colour of samples of similar magnetite concentration, but stirred differently.

SEM observations show that the matrix material, calcite, occurred as aggregates of up to 20 or 30 μm in diameter or as separate grains (Fig. 3). The calcite particles varied in size between 2 and 10 μm. In all samples aggregates of magnetic minerals were ubiquitous. The size of the magnetic aggregates varied from 5 μm to a maximum of approximately 50 μm in the ultrasonically stirred samples and also in the manually stirred samples. The average diameter of the aggregates is approximately 5 to 10 μm smaller in the ultrasonically stirred samples compared to the manually stirred samples.

Henkel plots ([28], not shown) of back field demagnetisation versus IRM acquisition all showed positive interaction between the magnetic particles. Cisowski plots ([25], not shown) of normalised AF demagnetisation and IRM acquisition versus field strength all showed an intersection point (the R-ratio) of less than 0.5 for both ultrasonically and manually stirred samples. The R-ratio of the two curves is $\sim 0.32 \pm 0.02$ for maghemite samples and $\sim 0.34 \pm 0.03$ for the magnetite samples. This value
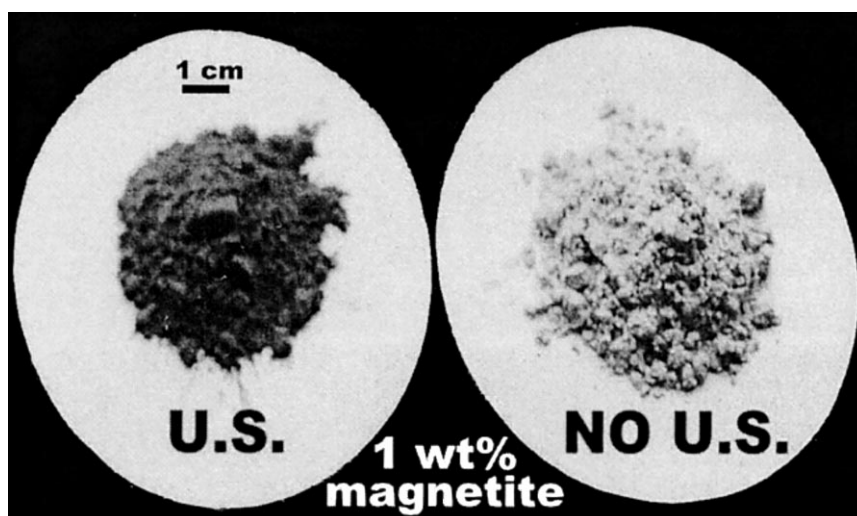

Fig. 6. Photograph of the difference in colour between samples containing 1 wt% magnetite that were stirred ultrasonically (left) or manually (right).

compares well with data for synthetic magnetite samples [21,31]. The results show that, even with ultrasonic stirring, interaction between the magnetic particles is still present. Fabian and von Dobeneck [35] have found that the *R*-ratio is not very specific in differentiating grain sizes and intraparticle forces. Therefore, the ultrasonic method does improve dispersion of very fine-grained magnetic minerals in synthetic samples as was indicated by the change in colour and average magnetic aggregate diameter. The improvement, however, cannot be expressed in magnetic terms because the methods cannot sufficiently distinguish between magnetic interactions caused by varying sizes of aggregates. We have opted to use ultrasonically stirred samples in our extraction experiments.

3.3. Extraction results

In Fig. 7 the results of each extraction experiment are given (averages of twelve samples). CBD extractions at various temperatures and concentrations resulted in the extraction of magnetite as well as maghemite.

3.3.1. Effects of temperature variation

The first three left-hand panels in Fig. 7 show the results of the extractions at different temperatures for samples containing 5 wt% magnetic minerals. The temperatures of 70° and 80°C were used, because these are the most commonly used extraction temperatures in previous studies. The reaction is expected to slow down at lower temperatures, which might make it possible to distinguish between magnetite and maghemite dissolution; therefore a third extraction temperature of 60°C was used.

The bulk low-field susceptibility of all samples decreases more quickly at higher extraction temperatures. The increased dissolution rate at higher temperatures has resulted in an increased susceptibility loss. Magnetite dissolution is most rapid in the first two extraction steps, but when the extraction temperature is lowered the dissolution rate becomes more gradual. For the extraction at 60°C an approximately equal amount of bulk susceptibility (∼22%) is lost in each step. Magnetite does not completely dissolve in four extraction steps at 60°C (∼12% of initial susceptibility left). During the first extraction
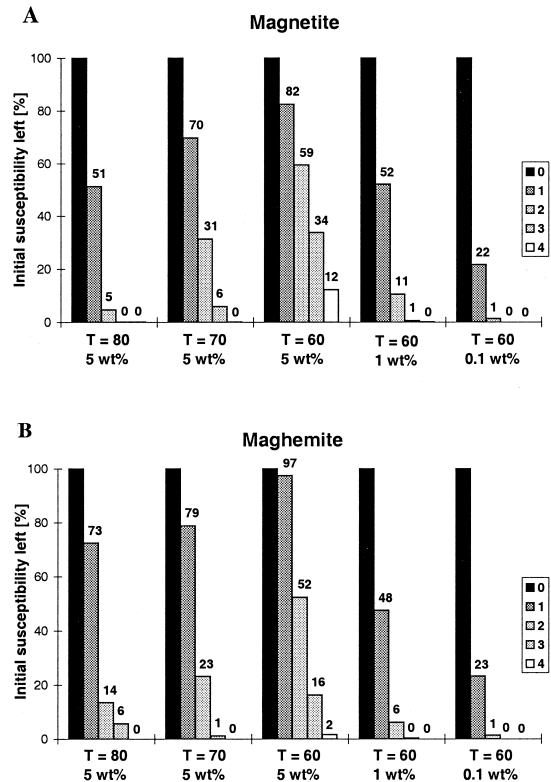

Fig. 7. Average results of the CBD extraction experiments. For each experiment a total of twelve samples and an additional four to six blanks were extracted. Upper chart represents extractions of magnetite, lower chart represents extractions of maghemite. The first three panels from left to right represent extractions at different temperatures, the last panel (right) represents extraction at lower iron oxide concentration.

step, maghemite dissolves distinctly less than in the second step where the highest loss of susceptibility occurs. Maghemite is completely dissolved after four extraction steps at all three temperatures. Therefore, it appears that only at lower temperatures (60°C) the extraction results enable some distinction between samples containing 5 wt% magnetite and those containing 5 wt% maghemite.

3.3.2. Effects of concentration variation

Fig. 7 (the three most right-hand panels) gives the results of the experiments using different concentrations of magnetic minerals at an extraction temperature of 60°C. In the 0.1 wt% as well as the 1 wt% experiment magnetite as well as maghemite

were completely dissolved within the four steps of the experiment. An increase in dissolution rate was noted for both minerals when concentration in the samples was decreased. The dissolution rate in each extraction step was similar for both minerals at similar extraction conditions, indicating that distinction between magnetite and maghemite is impossible at low concentrations of fine-grained magnetic material. The results of both extractions of samples containing 1 wt% magnetite or 1 wt% maghemite at 60ºC were comparable to the results of the 5 wt% magnetite experiment at $T = 80$ºC . This indicates that comparison of different procedures is indeed complicated if not impossible. For samples initially containing 0.1 wt% maghemite, the dissolution rate in the first extraction step was much larger than that of any of the other experiments using maghemite.

The results of the extraction experiments could be influenced by differences in the magnetic minerals of the different batches. The 60ºC extractions were performed with magnetic minerals of batch 2. Results show, however, that the dissolution rate increases consistently with increasing temperature, therefore the changes in dissolution rate do not primarily depend on the batch of magnetic minerals that was used. Apparently, the variations in the procedure have a much greater impact on the dissolution behaviour than differences in mineral structure of the different batches.

Our results confirm that not only temperature but also concentration of magnetic material has a significant influence on the results of the extraction experiments. A low concentration of very fine-grained magnetic minerals — the rule in sediments and soils — can make it virtually impossible to distinguish magnetite from maghemite in samples.

3.3.3. Comparison with previous studies

Our results partly agree with the findings of Hunt et al. [11] in that both fine-grained maghemite and fine-grained magnetite are dissolved with the CBD extraction technique. Furthermore, Hunt et al. found that a reduction in the amount of dithionite used in the extraction, will make it possible to distinguish magnetite from maghemite dissolution because less magnetite will be extracted. A reduction in dithionite can be viewed as similar to an increase in magnetic mineral concentration. We have shown that an in-

crease in concentration will decrease the amount of magnetic mineral extracted, allowing some distinction between the dissolution behaviour of maghemite and magnetite at the lowest extraction temperature used. These concentrations (5 wt%), however, are high as compared to most natural soil and sediment samples.

4. Conclusions

The new ultrasonic stirring method improved dispersion and reduced the average diameter of aggregates of fine-grained magnetic minerals in the sample. However, a perfectly homogeneous dispersion, with non-interacting magnetic particles (as in most natural samples), could not be obtained. Between batches of synthetic minerals, made in a seemingly similar way, the magnetic behaviour may vary. These variations, however, did not noticeably influence dissolution behaviour in our experiments.

Our results show that the outcome of the CBD extraction technique depends not only on the extraction temperature, but also on the concentration of magnetic mineral. Increased temperature will increase the extraction rate of the magnetic minerals. Similarly, decreased concentration of iron oxides (or increased dithionite/ferrimagnetic mineral ratio) increases the extraction rate of the magnetic minerals. At high oxide concentrations (5 wt%) some distinction between fine-grained magnetite and fine-grained maghemite dissolution can be made.

The CBD method dissolves all fine-grained magnetite as well as maghemite. A distinction between these two minerals requires application of more than one extraction procedure. Even when using different procedures on the same set of samples distinction will be difficult, as is illustrated by the similar dissolution behaviour of 5 wt% magnetite at 80ºC and 1 wt% maghemite or magnetite at 60ºC. The CBD extraction treatment is not suitable for distinction between fine-grained magnetic iron oxides.

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