Thermomagnetic measurements of soil iron minerals: the role of organic carbon

M. Hanesch,[1] H. Stanjek[2] and N. Petersen[3]

[1]*Chair of Geophysics, Department of Applied Geosciences and Geophysics, University of Leoben, Peter Tunner Str.* 25-27, 8700 *Leoben, Austria. E-mail: hanesch@unileoben.ac.at*
[2]*Institute of Mining and Economic Geology, Aachen University, Wüllnerstraße* 2, 52062 *Aachen, Germany*
[3]*Ludwig-Maximilians-Universität München, Department of Earth and Environmental Sciences, Geophysics Section, Theresienstrasse* 41, 80333 *München, Germany*

SUMMARY

Thermomagnetic measurements, particularly measurements of the Curie or Néel temperature, are often used to identify magnetic minerals in rocks or sediments. In many samples it is impossible to determine the Curie or Néel temperature as mineral changes occur during heating. Especially in soils or sediments, iron (hydr)oxides may be transformed to ferrimagnetic iron oxides. In this study we analysed the thermomagnetic behaviour of some natural and synthetic iron minerals: goethite, haematite, ferrihydrite, lepidocrocite and siderite. The change of magnetization M with temperature was determined with a magnetic translation balance. The sample was heated in air to a maximum temperature of 700°C and subsequently cooled back to room temperature. By adding organic carbon to synthetic samples and by destroying it in natural samples, the influence of organic substance on the reactions was determined. Goethite, ferrihydrite and haematite transform to a strongly magnetic phase only if organic carbon is present. Lepidocrocite and siderite transform without organic carbon, the reaction of siderite is even weakened if organic matter is added. The transformation starts below 400°C for ferrihydrite and lepidocrocite and around 450°C for goethite. We can conclude that, though these reactions impede the identification of the ferrimagnetic oxides in many soil and sediment samples, they can be used to distinguish between the most common soil iron hydroxides in these environments.

Key words: Curie temperature, iron hydroxides, Néel temperature, soil magnetism.

1 INTRODUCTION

Minerals change their magnetic properties with temperature. Prominent changes occur at the Curie temperature where ferrimagnetic minerals start to behave like paramagnetic minerals, and at the Néel temperature where antiferromagnetic minerals lose their antiferromagnetic characteristics and react like paramagnetic minerals. The Curie and Néel temperatures are characteristic for each mineral and can, therefore, be used for their identification. To determine the Curie or Néel temperature (T_C), the behaviour of either susceptibility or magnetization upon heating is monitored. T_C can then be found by the methods described by Moskowitz (1981).

In environmental magnetism, the high-temperature behaviour of magnetization has, for example, been used to identify the magnetic component in loess-soil sequences (Eyre & Shaw 1994; Evans & Heller 1994) or to characterize soil samples (Özdemir & Banerjee 1982) and magnetic extracts of soils (Maher & Taylor 1988). Some authors use the temperature dependence of susceptibility to determine the magnetic mineralogy of their samples (Zhu *et al.* 2000; Deng *et al.* 2004). Lowrie (1990) proposed the high-temperature

demagnetization of remanences imposed in three orthogonal directions at different field strengths for the identification of minerals in rocks. Thus, for example, the contributions of goethite, haematite and magnetite can be distinguished (e.g. Sangode & Bloemendal 2004). This procedure can be refined by grain size fractionation and using individual samples for each coercivity component (Spassov *et al.* 2003).

For some rock and sediment samples, the measurement of T_C is difficult because chemical or crystallographic transformations of iron oxides take place. This problem occurs above all in soil and sediment samples. Since the laboratory experiments of Van der Marel (1951) and Le Borgne (1960) it is known that soil iron (hydr)oxides transform to ferrimagnetic iron oxides at higher temperatures, for example, during a fire. Schwertmann & Taylor (1989) describe various transformation processes at temperatures between 200° and 400 °C, which partly depend on the presence of organic matter.

On the one hand, these effects prevent the determination of the Curie or Néel temperature in some samples, while on the other hand they can be useful to clarify other questions. Maher (1998)

Table 1. The iron minerals and compounds used for the thermomagnetic measurements. The siderite was kindly provided by the mineralogical institute at Munich university (LMU).

Mineral	Name of the sample	Provenance
goethite	Rustrel jaune	natural, ochre from Rustrel, France
	Rustrel havanne	natural, ochre from Rustrel, France
	Bayferrox 910	synthetic (Bayer inc, Leverkusen, Germany)
haematite	Rustrel rouge	natural, ochre from Rustrel, France
	Bayferrox 120	synthetic (Bayer inc, Leverkusen, Germany)
2-line-ferrihydrite	Col de Galibier	natural, stream bed at Col de Galibier, France
6-line-ferrihydrite	SF2	synthetic, produced by Stanjek & Schwertmann (1992)
lepidocrocite		synthetic, self-produced
siderite		natural

used thermomagnetic measurements to exclude the possibility of fire as an enhancement mechanism in soil. Maher & Thompson (1999) deduced the relative proportion of magnetite and maghemite in loess and soil samples by comparing the amount of magnetization lost during heating.

Another possible use is the interpretation of the transformations in terms of the iron oxides present in the soil. In some studies on soil magnetism, first steps in this direction have been taken (e.g. Kapička *et al.* 2003). Here, we present the thermomagnetic behaviour of some natural and synthetic iron minerals, which can be directly compared to curves measured for soil samples.

2 MATERIALS AND METHOD

2.1 Samples

Table 1 lists the iron minerals which were used for the measurements. The results of X-ray diffraction analyses of the initial and some of the heated samples are compiled in Table 2. Synthetic goethite and haematite were purchased from Bayer Inc., Leverkusen. A product description is given at www.bayferrox.de. Natural goethite and haematite samples are ochres from Rustrel in France. The synthetic 6-line ferrihydrite was produced by Stanjek & Weidler (1992): a 0.06 molar solution of $Fe(NO_3)_3 \cdot 9H_2O$ was hydrolysed by heating to 85°C. The resulting sol was dialysed for 22 days and freeze dried. The natural 2-line ferrihydrite was extracted from a stream bed at the Col de Galibier in France. The sample has various impurities (Table 2).

The synthetic lepidocrocite was produced as described by Schwertmann and Cornell (1991): A solution with 60 mM Fe is prepared from $FeCl_2 \cdot 4H_2O$ and distilled water. Air is supplied while the solution is stirred. Meanwhile the pH is brought to 6.7–6.9 by adding NaOH. This constant pH value is important to prevent other iron minerals from being formed. The end product, an orange-coloured suspension, is centrifuged, washed and dried.

To simulate soil conditions, a part of the samples was mixed 1:1 with calcium carbonate, then 5–10 per cent D-glucose was added. The glucose supplies the organic carbon which is necessary for some of the observed reactions to occur. These mixed samples are named '*iron oxide* + C'. In order to better understand the influence of organic matter, we tried to remove it from some of the natural samples by leaching with 30 per cent H_2O_2.

2.2 Thermomagnetic measurements

The thermal behaviour of the magnetization *M* was determined with a magnetic translation balance. This instrument measures the force

Table 2. Results of X-ray diffraction analyses of the original and some of the heated samples. '+C' means that the sample was mixed with calcium carbonate and glucose before heating (see Section 2.1). MCL: mean coherence length.

Sample	Phases	Content (g/g)	MCL (nm)	Cell lengths (Å)
Bayferrox 910	goethite	1	165	9.9608
				3.0228
				4.6105
Bayferrox 910°C, 700°C	haematite	1	175	5.0359
				13.753
Rustrel jaune	not determined			
Rustrel jaune, 700°C	haematite	1	50	5.0078
				13.677
	quartz			
Rustrel havanne	not determined			
Rustrel havanne, 700°C	haematite	1		5.0078
				13.681
	quartz			
Col de Galibier	ferrihydrite	1		
	quartz			
	mica			
	feldspars			
Col de Galibier, 700°C	maghemite	1	23	8.3490
	quartz			
SF2	ferrihydrite	1		
SF2 + C, 700°C	maghemite	0.271	105	8.3550
	haematite	0.729	16	5.0376
				13.749
lepidocrocite	lepidocrocite	1	41	3.0687
				12.527
				3.8738
lepidocrocite, 700°C	haematite	1	600	5.0385
				13.761
lepidocrocite+C, 700°C	haematite	1	270	5.0352
				13.753
Bayferrox 120	haematite	0.978	430	5.0346
				13.749
	maghemite	0.022	125	8.3604
Rustrel rouge	haematite	1	42	5.0050
				13.677
	quartz			
	kaolinite			
siderite	siderite	1	415	4.6921
				15.372
siderite, 700°C	magnetite	0.776	73	8.4032
	wüstite	0.224	38	4.3117

on a sample in a non-uniform magnetic field. The force on the sample is proportional to the magnetization and to the gradient of the field. The sample is heated to a maximum temperature of 700°C and subsequently cooled back to room temperature. One heating and cooling cycle lasts 30 min. The instrument is described by Soffel (1991). During our experiments the strength of the magnetic field was 5210 Oersted. Therefore, goethite and haematite did not reach saturation. This does not impede the determination of T_C or the monitoring of mineral changes.

The Curie or Néel temperature of the end product was determined by drawing tangents to the curve (Moskowitz 1981). In most cases, only the cooling curve was analysed in this way because the heating curve is usually dominated by mineral changes and, therefore, not suited for the determination of T_C. It should be noted that, if thermal transformations have occurred, the temperatures determined from the cooling curve do not represent the Curie or Néel temperature of the original minerals but those of the secondary phases.

2.3 X-ray diffraction

X-ray diffraction analyses were run on a Guinier image plate system (Huber G670) with samples mixed and ground with Si (pre-ground wafer material) as an internal standard (amount not weighed). After identifying the phases, cell edge lengths, profile parameters and peak intensities were refined with MacClayFit (Stanjek & Häusler 2000). As a profile function the Thompson–Cox–Hastings approach with X as the isotropic size and X_e as the anisotropic size parameter was used (Thompson *et al.* 1987). Mean coherence lengths were estimated from X corrected for the instrumental broadening parameter X_i from the internal standard Si. Semi-quantitative estimates of phase contents were made by recalculating total phase intensities into contents by using calibration simulations with CrystalDiffract.

3 RESULTS AND DISCUSSION

3.1 Iron minerals

Goethite

Goethite is an iron hydroxide occurring in almost every soil type. Fig. 1 shows the thermomagnetic curves of synthetic goethite. The

Néel temperature of pure goethite at about 120°C (Mathé *et al.* 1999) is hardly visible. The drop of magnetization between 250° and 400°C is due to the dehydroxylation of the goethite (Özdemir & Dunlop 1996). It transforms into haematite as shown by the Néel temperature of the cooling curve and by the X-ray diffraction results of the heated sample (Table 2). The dehydroxylation of goethite to haematite between 200° and 400°C was also observed by Ruan *et al.* (2001), using X-ray diffraction of heated samples, and by Przepiera & Przepiera (2003) using thermogravimetric measurements.

If glucose is added, goethite starts to transform into a highly magnetic mineral at 420°C. The Curie temperature of the newly formed mineral in the heating curve is 580°C (Fig. 1b). In the cooling curve, the Curie temperature of the strong magnetic phase was determined as 630°C. Following Schwertmann & Heinemann (1959), we propose the formation of maghemite which, at even higher temperatures, for the most part turns into haematite. The same end product is thus reached with and without the organic carbon, but a different formation path is taken. The transformation of goethite to haematite was also observed in a burnt soil by Stanjek (1987).

The role of organic carbon was yet observed by Hunt *et al.* (1995) when measuring the temperature dependence of susceptibility for a palaeosol. Even if the experiment is carried out in air, the bulk of the sample is under the influence of reducing conditions caused by the presence of organic carbon. These conclusions can also be drawn for the samples used in this study: there is a small red stripe (haematite) at the oxidized side whereas the rest of the sample turns black (magnetite/maghemite) during the experiment.

Dekkers (1990) found intimately intergrown haematite/magnetite aggregates after thermal demagnetization of natural goethites. He explained the presence of magnetite by the reducing capacity of trace amounts of organic matter or the presence of ferrous iron set free by decomposition of clay minerals. The amount of organic matter (and possibly clay minerals), which is present in a sample, might thus control the ratio of haematite to ferrimagnetic minerals (magnetite/maghemite) which is formed.

The reaction of the natural goethite is quite different from the reaction of the synthetic goethite (Fig. 2). The pure samples show a slight reaction above 400°C, probably due to some natural organic carbon content. If additional organic carbon is added, maghemite is formed. Ketterings *et al.* (2000) observed the conversion of goethite to maghemite during slash-and-burn fires on soils in Sumatra and
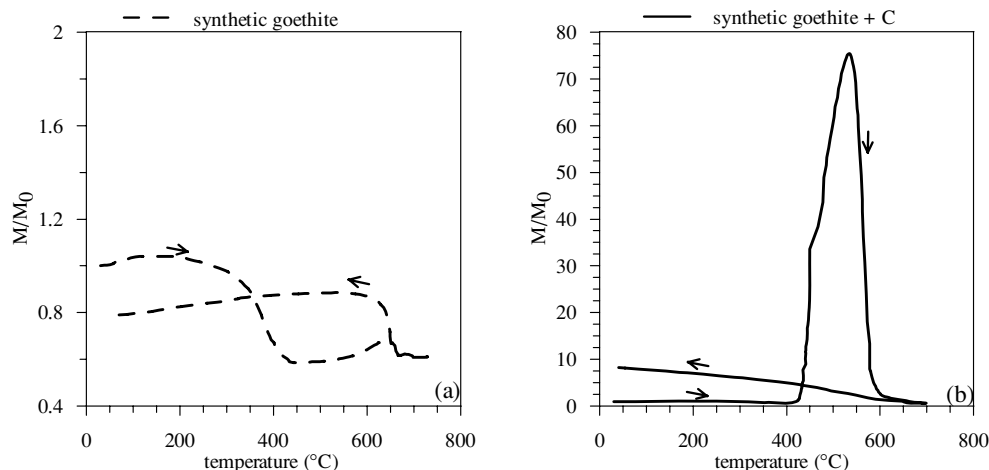

Figure 1. Thermomagnetic measurements of synthetic goethite (Bayferrox 910): (a) pure sample (b) mixed with calcium carbonate and glucose. The pure sample transforms directly to haematite. The mixed sample first forms a highly magnetic mineral, probably maghemite, which is then transformed to haematite.
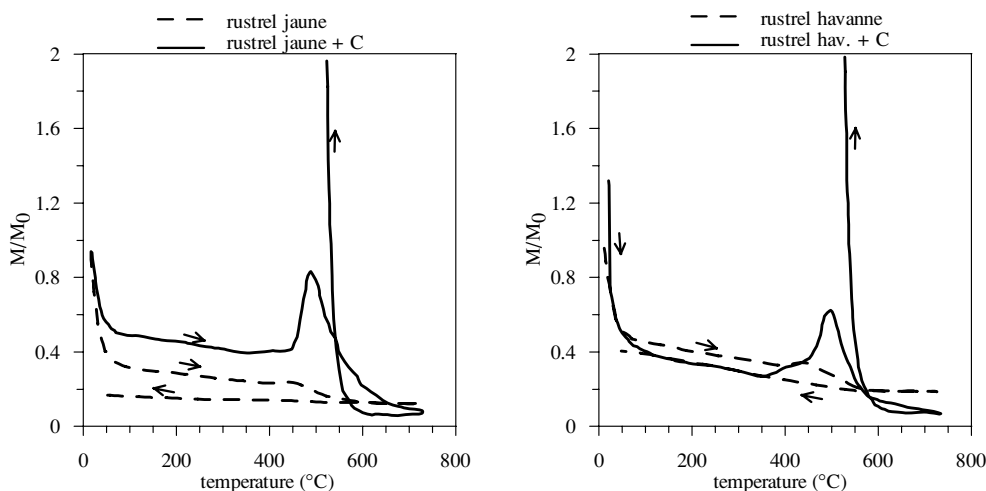
Figure 2. Thermomagnetic measurements of natural goethite. The effect of adding organic carbon is smaller than for the synthetic sample (Fig. 1). The newly formed maghemite does not transform into haematite.
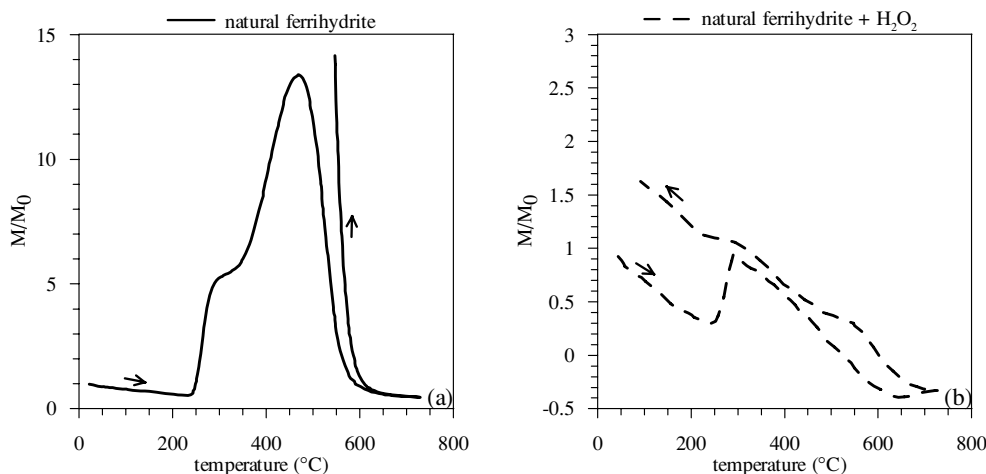

Figure 3. Thermomagnetic measurements of natural ferrihydrite. (a) The pure sample transforms to maghemite (Table 2). (b) Treatment with hydrogen peroxide impairs the reaction as the organic substance is destroyed (note the different scales of the ordinates).

also investigated the role of organic carbon in this process. Adding organic carbon causes a smaller effect in our natural goethite samples than in the synthetic ones. A possible reason might be the smaller grain size of the synthetic goethite. In contrast to the reaction of the synthetic goethite, the newly formed ferrimagnetic mineral did not transform further into haematite when the reaction is started with natural goethites. These minerals often substitute some iron by aluminium, which has a stabilizing effect on the maghemite (Stacey & Banerjee 1974). The low cell constants of the haematites formed by heating of the natural goethite samples (Table 2) indicate aluminium substitution between 12 and 15 per cent (Stanjek & Schwertmann 1992). It is also possible that impurities adsorbed on the surface of the goethite (e.g. silicate or phosphate anions) impede the transformation to haematite.

There is a noticeable difference between the heating and the cooling curve at 600°C. This shows that, due to the fast heating, the transformation is not yet complete during the heating cycle.

Ferrihydrite

The natural 2-line ferrihydrite turns into maghemite upon heating (Fig. 3a, Table 2). The sample contains enough organic material to initiate the reaction. The transformation starts at 240°C and obviously passes through two steps. The reaction could be considerably weakened by treating the sample with hydrogen peroxide, which destroys the organic substance (Fig. 3b).

Synthetic ferrihydrite (Fig. 4) dehydroxylates and dehydrates to haematite (Néel temperature above 650°C). Lewis (1992) also observed this transformation during oven-drying. If glucose is added, maghemite is formed above 300°C. The higher crystallinity of this sample leads to a later starting point of the transformation than for the natural ferrihydrite. The larger part of this maghemite is transformed to haematite at higher temperatures (approximately 73 per cent, see Table 2). Therefore, the cooling curve is lower than the peak of the heating curve but considerably higher than the initial magnetization M_0.
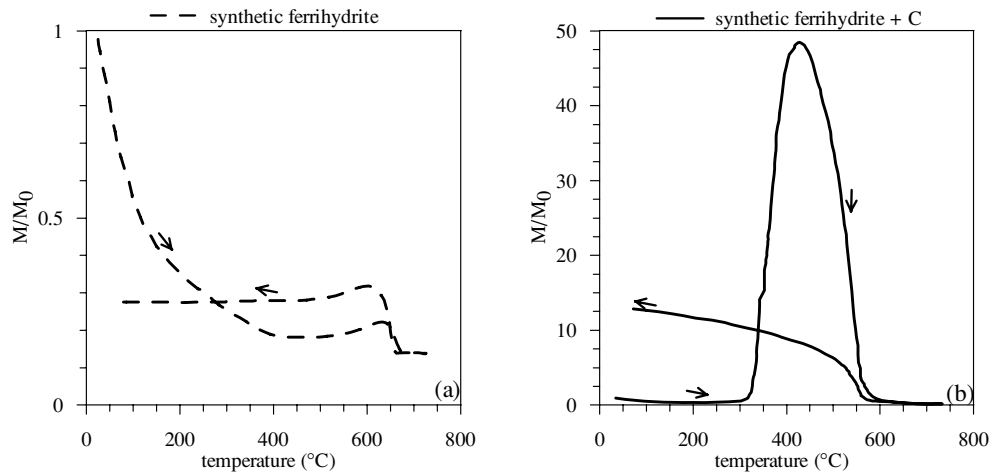
Figure 4. Thermomagnetic measurements of synthetic ferrihydrite (SF2). (a) The pure sample dehydrates to haematite. (b) Mixed with calcium carbonate and glucose, the ferrihydrite transforms to maghemite, which for the most part transforms to haematite.
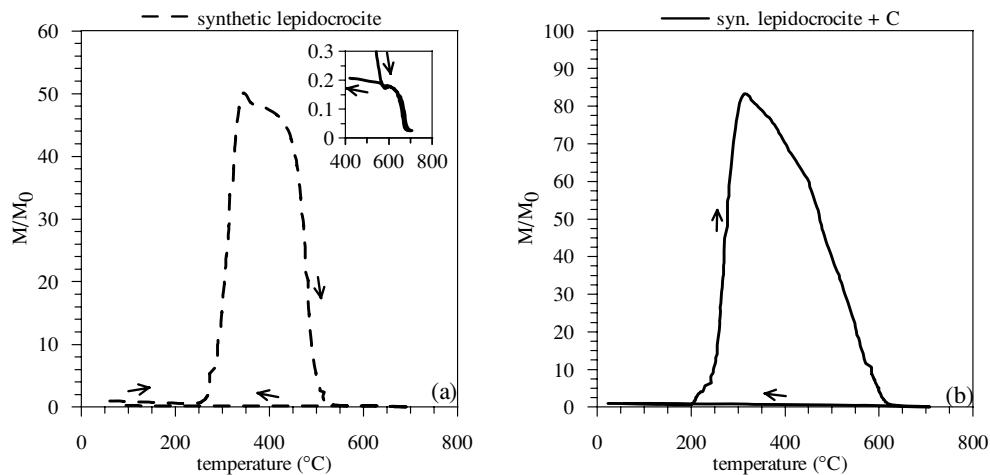

Figure 5. Thermomagnetic curves for synthetic lepidocrocite. It transforms to haematite via maghemite without the presence of organic carbon. Mixed with glucose, the transformation starts earlier and is stronger.

Lepidocrocite

Fig. 5 shows the thermomagnetic curves for synthetic lepidocrocite. This mineral starts to transform to maghemite at 250°C (Hahn & Hertrich 1923; Gehring *et al.* 1990). Gehring & Hofmeister (1994) studied the structural changes of lepidocrocite during the conversion to haematite. They concluded that the conversion to maghemite starts at about 200°C and is completed around 300°C. At higher temperatures, maghemite is converted into haematite (Przepiera & Przepiera 2001; Mitov *et al.* 2002). The presence of organic carbon is not necessary for this reaction. In the magnified display detail of Fig. 5(a), the Néel temperature of haematite is clearly visible. A thorough description of the lepidocrocite–maghemite–haematite reaction chain is given by Gendler *et al.* (2005).

When organic carbon is added to the lepidocrocite sample, the reaction starts at slightly lower temperatures and is slightly stronger, but the end product is the same. The stronger reaction might point to the formation of some magnetite in the mixed sample due to the reducing conditions caused by organic matter.

Haematite

The reactions of synthetic and natural haematite during heating are shown in Fig. 6. The synthetic sample contains 2.2 per cent maghemite which leads to a dominance of the maghemite Curie temperature. In the natural sample, maghemite is also visible magnetically though it was not detected by X-ray diffraction. The cooling curve of the pure samples does not coincide with the heating curve. Probably defects in the haematite lattice are annealed out by the heating (de Boer & Dekkers 1998). We did not observe the Hopkinson-like peaks shown by the synthetic samples of de Boer & Dekkers (2001). The presence of organic substance leads to reducing conditions, which promote the formation of maghemite or magnetite. The stronger reaction of the synthetic sample above 450°C cannot be caused by grain size effects because X-ray analysis showed that the grain size of the synthetic haematite is between 0.5 and 1 μm, whereas the grain size of the natural haematite is between 30 and 35 nm. Possibly, the natural haematite may be surficially protected with adsorbed phosphate and/or silicate. Both anions are known to
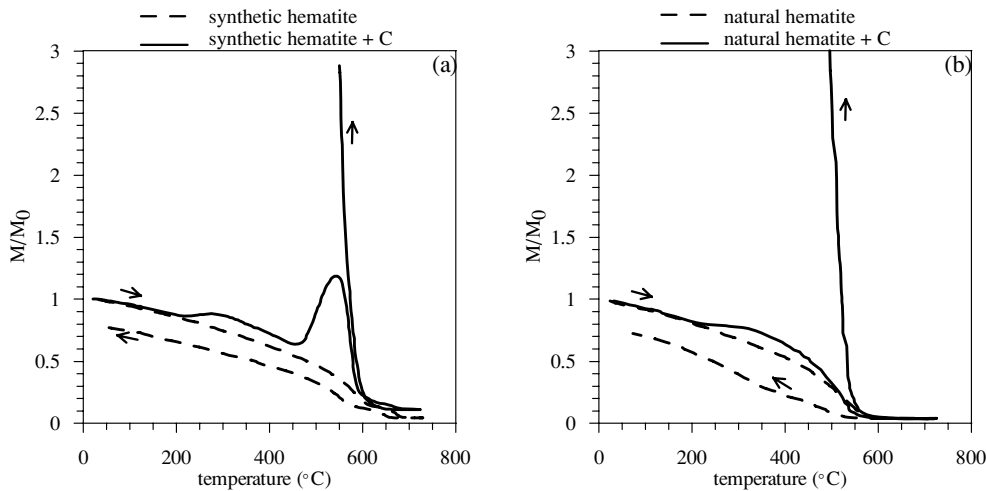
Figure 6. Thermomagnetic curves for synthetic and natural haematite. Addition of organic carbon leads to the transformation into a ferrimagnetic mineral.

retard solid state transformations considerably (e.g. Tronc & Jolivet 1986; Campbell *et al.* 2002).

Siderite

Siderite is not common in soils. It only occurs in small quantities, particularly in humid, iron-rich environments. Nevertheless it was included in this study because its transformation to magnetite, maghemite and haematite upon heating in air was reported by Pan *et al.* (2000). In our experiment, the pure siderite sample is decomposed to magnetite and wüstite (Table 2). Fig. 7 shows the thermomagnetic measurement of siderite and the effect of organic carbon on the reaction: the transformation is considerably weakened. Therefore, it seems unlikely that siderite causes the strong transformations observed in soils.
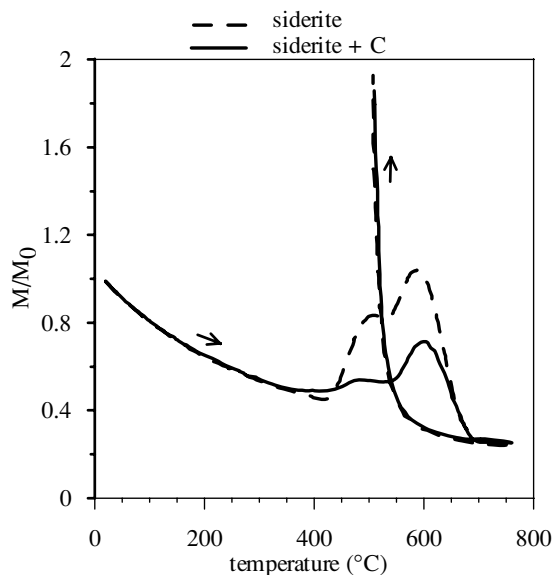

Figure 7. Thermomagnetic curves for natural siderite. The addition of organic carbon weakens the transformation.

3.2 Soil samples

In thermomagnetic curves of soil samples typically two peaks are observed between 200° and 600°C. Fig. 8 shows two examples from Southern Germany: a luvisol and a cambisol. In both cases, the sample from the A-horizon shows two transformations, one starting between 250° and 300°C and one starting at about 450°C. In the B-horizon, only the first transformation takes place. However, this scheme is not generally valid. Fig. 9 shows the measurement from an A-horizon of another luvisol, where only the second transformation is observed.

If we compare these transformations with our measurements of iron oxides, we can say that the formation of a ferrimagnetic phase at 450°C can be attributed to goethite or haematite, whereas the first peak is caused by transformation of ferrihydrite or lepidocrocite, respectively. Goethite is the thermodynamically most stable iron oxide in most soils of the temperate climate. The warmer the climate, the more haematite accompanies the goethite. In tropical soils, haematite is dominating. As our soil samples were all taken in the temperate climate zone, the presence of goethite is to be expected. Goethite and haematite can be distinguished by thermomagnetic measurements only if no other iron oxides are present since the earlier start of the reaction in haematite will be overlain by the much stronger reactions of the less well crystallized iron hydroxides.

Ferrihydrite and lepidocrocite are also common in soils. Ferrihydrite is formed if Fe^{2+}-ions are rapidly oxidized and if the formation of better crystallized iron oxides is impeded by high concentrations of organic anions or soluble silica (Childs 1992). Ferrihydrites in soils are usually young minerals which convert to more stable phases with time. Lepidcrocite is found in reductomorphic soils, that is, soils which temporarily suffer from a lack of oxygen (Brown 1953).

Ferrihydrite and lepidocrocite can be distinguished by thermomagnetic measurements if the organic substance is destroyed. If the transformation is still taking place to about the same extent, lepidocrocite is present in the soil. Fig. 10 shows the thermomagnetic curve measured for a gleysol before and after treatment with hydrogen peroxide. The reaction is considerably weakened when organic material has been destroyed. Therefore, we conclude that this soil does not contain lepidocrocite although the samples were taken from a horizon with temporarily reducing conditions. Before this method
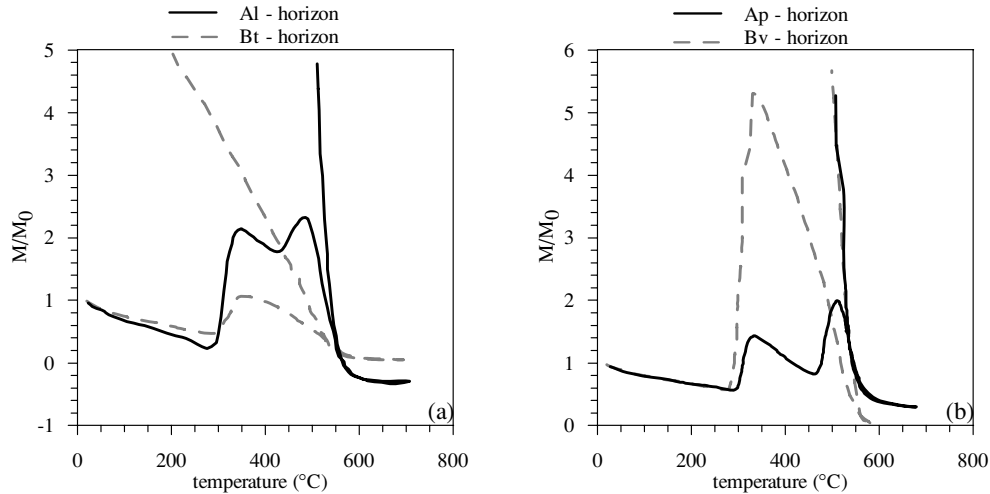
Figure 8. Thermomagnetic curves for the A and B horizons of (a) a luvisol (Degerndorf) and (b) a cambisol from Southern Germany. In the A-horizons, two peaks are observed while in the B-horizon the transformation of iron oxides takes place in a single step.
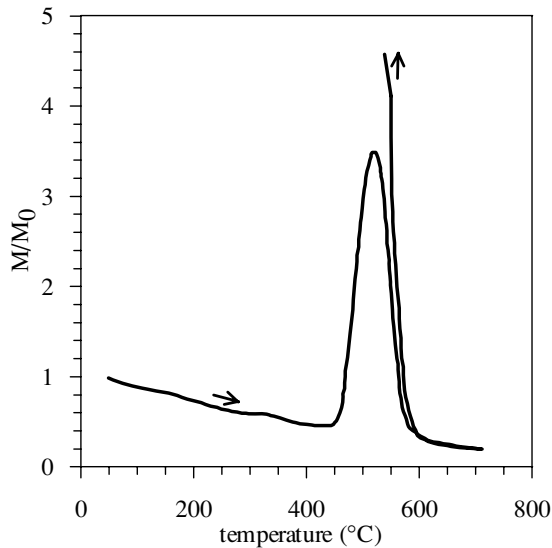

Figure 9. Thermomagnetic curve of the Ap horizon of a luvisol (Niederlippach, Southern Germany). Only the second transformation (*cf.* Fig. 8), which is attributed to goethite, is clearly visible.

Figure 10. Thermomagnetic curves of the MGro-horizon of a gleysol. This horizon has temporarily reducing conditions. Lepidocrocite could, therefore, be present. The considerably smaller peaks after treatment with H_2O_2 show that ferrihydrite is the weakly crystallized iron oxide, which is then transformed to a ferrimagnetic mineral.

of distinguishing between lepidocrocite and ferrihydrite can be applied in further studies it will be necessary to make sure that the treatment does destroy only the organic matter but does not alter the iron oxide minerals. The crystallinity of natural ferrihydrites, for example, seemed to increase slightly after treatment with H_2O_2 (Schwertmann & Murad 1988). Anyway, further investigations of leaching methods and their effects are necessary.

The last example shows that the onset of the transformation depends not only on crystallinity, ion substitution and heating rate, but also on the amount of organic carbon in the sample. An influence of grain size on the transformation temperature was found for the goethite–haematite transformation by Walter *et al.* (2001). Each of these influences would have to be varied independently if we wanted to give exact temperatures for the onset of the transformation. However, generally we can say that the transformation starts
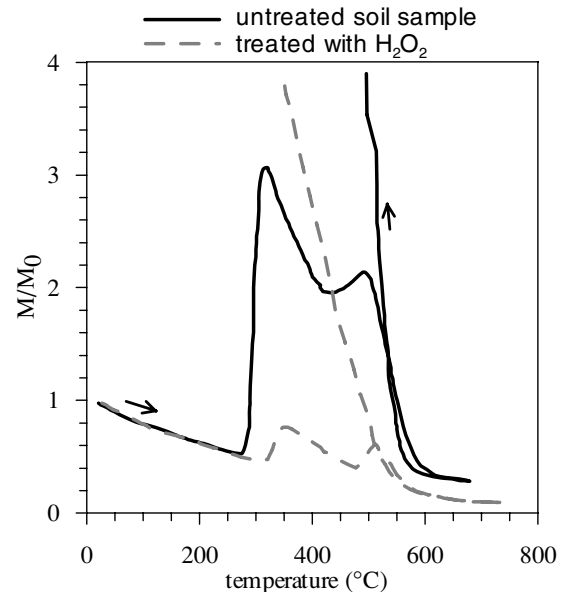
clearly below 400°C for ferrihydrite and lepidocrocite and around 450°C for goethite.

4 CONCLUSIONS

The results of our experiments show that the presence of organic matter causes critical changes in the reaction of iron minerals during heating. Reducing conditions are produced and iron (hydr)oxides transform to ferrimagnetic maghemite or magnetite. The less the minerals are crystallized the earlier these transformations start. Goethite, which starts to react at about 450°C, can easily be distinguished from ferrihydrite and lepidocrocite which begin to

transform between 200° and 350°C, the exact temperature depending on the crystallinity of the sample, the amount of organic carbon in the sample and the heating rate. These reactions can be used to identify the dominating iron hydroxide in soils where organic matter is usually present.

Ferrihydrite and lepidocrocite can be distinguished by the fact that lepidocrocite does not need the presence of organic matter to transform to maghemite. The procedure to destroy the organic matter, however, has still to be tested more thoroughly as it is not clear if the use of hydrogen peroxide affects the iron minerals.

It is improbable that siderite causes the strong reactions we observed in soils upon heating as the transformation of siderite was weakened by the addition of organic matter.

Comparing synthetic and natural samples of goethite and haematite showed that the synthetic samples tend to a stronger reaction than the natural ones. This is probably due to aluminium substitution or surface impurities in these minerals.

ACKNOWLEDGMENTS

REFERENCES

Brown, G., 1953. The occurrence of lepidocrocite in some British soils, *Journal of Soil Science,* **4,** 220–228.

Campbell, A.S., Schwertmann, U., Stanjek, H., Friedl, J., Kyek, J. & Campbell, P.A., 2002. Si incorporation into hematite by heating Si-ferrihydrite, *Langmuir,* **18,** 7804–7809.

Childs, C.W., 1992. Ferrihydrite: A review of structure, properties and occurrence in relation to soils, *Z. Pflanzenernähr. Bodenk.,* **155,** 441–448.

de Boer, C.B. & Dekkers, M.J., 1998. Thermomagnetic behaviour of haematite and goethite as a function of grain size in various non-saturating magnetic fields, *Geophys. J. Int.,* **133,** 541–552.

de Boer, C.B. & Dekkers, M.J., 2001. Unusual thermomagnetic behaviour of haematites: neoformation of a highly magnetic spinel phase on heating in air, *Geophys. J. Int.,* **144,** 481–494.

Dekkers, M.J., 1990. Magnetic properties of natural goethite—III: magnetic behaviour and properties of minerals originating from goethite dehydration during thermal demagnetization, *Geophys. J. Int.,* **103,** 233–250.

Deng, C., Zhu, R., Verosub, K.L., Singer, M.J. & Vidic, N.J., 2004. Mineral magnetic properties of loess/paleosol couplets of the central loess plateau of China over the last 1.2 Myr, *J. geophys. Res.,* **109**(B1), Art. No. B01103, doi:10.1029/2003JB002532.

Evans, M.E. & Heller, F., 1994. Magnetic enhancement and palaeoclimate: study of a loess/palaeosol couplet across the Loess Plateau of China, *Geophys. J. Int.,* **117,** 257–264.

Eyre, J.K. & Shaw, J., 1994. Magnetic enhancement of Chinese loess–the role of γFe_2O_3?, *Geophys. J. Int.,* **117,** 265–271.

Gehring, A.U., Karthein, R. & Reller, A., 1990. Activated state in the lepidocrocite structure during thermal treatment, *Naturwissenschaften,* **77,** 177–179.

Gehring, A.U. & Hofmeister, A.M., 1994. The transformation of lepidocrocite during heating: a magnetic and spectroscopic study, *Clays Clay Minerals,* **42,** 409–415.

Gendler, T.S., Shcherbakov, V.P., Dekkers, M.J., Gapeev, A.K., Gribov, S.K. & McClelland, E., 2005. The lepidocrocite-maghemite-haematite reaction chain—I. Acquisition of chemical remanent magnetization by maghemite, its magnetic properties and thermal stability, *Geophys. J. Int.,* **160,** 815–832.

Hahn, F.L. & Hertrich, M., 1923. Leicht filtrierbares Eisenhydroxid durch Fällung mit Thiosulfat und Jodat. *Berichte der Deutschen Chemischen Gesellschaft,* **26,** 1729–1732.

Hunt, C.P., Banerjee, S.K., Han, J., Solheid, P.A., Oches, E., Sun, W. & Liu, T., 1995. Rock-magnetic proxies of climate change in the loess-palaeosol sequences of the western Loess Plateau of China, *Geophys. J. Int.,* **123,** 232–244.

Kapička, A., Jordanova, N., Petrovský, E. & Podrázský, V., 2003. Magnetic study of weakly contaminated forest soils, *Water, Air, Soil Pollut.,* **148,** 31–44.

Ketterings, Q.M., Bigham, J.M. & Laperche, V., 2000. Changes in soil mineralogy and texture caused by slash-and-burn fires in Sumatra, Indonesia, *Soil Sci. Soc. Am. J.,* **64,** 1108–1117.

Le Borgne, E., 1960. Influence du feu sur les propriétés magnétiques du sol et sur celles du schiste et du granite, *Annales de Géophysique,* **16**(2), 159–195.

Lewis, D.G., 1992. Transformations induced in ferrihydrite by oven-drying, *Z. Pflanzenernähr. Bodenk.,* **155,** 461–466.

Lowrie, W., 1990. Identification of ferrimagnetic minerals in a rock by coercivity and unblocking temperature properties, *Geophys. Res. Lett.,* **17,** 159–162.

Maher, B.A., 1998. Magnetic properties of modern soils and Quaternary loessic paleosols: paleoclimatic implications, *Palaeogeography, Palaeoclimatology, Palaeoecology,* **137,** 25–54.

Maher, B.A. & Taylor, R.M., 1988. Formation of ultrafine-grained magnetite in soils, *Nature,* **336,** 368–370.

Maher, B.A. & Thompson, R., 1999. Palaeomonsoons I: the magnetic record of palaeoclimate in the terrestrial loess and palaeosol sequences, in *Quaternary Climates, Environments and Magnetism*, pp. 81–125, eds Maher, B.A. & Thompson, R., University Press, Cambridge.

Mathé, P.-E., Rochette, P., Vandamme, D. & Fillion, G., 1999. Néel temperature of synthetic substituted goethites and their rapid determination using low-field susceptibility curves, *Geophys. Res. Lett.,* **26**(14), 2125–2128.

Mitov, I., Paneva, D. & Kunev, B., 2002. Comparative study of the thermal decomposition of iron oxyhydroxides, *Thermochim. Acta,* **386,** 179–188.

Moskowitz, B.M., 1981. Methods for estimating Curie temperatures of titanomaghemites from experimental J_s-T data, *Earth planet. Sci. Lett.,* **53,** 84–88.

Özdemir, Ö. & Banerjee, S.K., 1982. A preliminary magnetic study of soil samples from west-central Minnesota, *Earth planet. Sci. Lett.,* **59,** 393–403.

Özdemir, Ö. & Dunlop, D.J., 1996. Thermoremanence and Néel temperature of goethite, *Geophys. Res. Lett.,* **23**(9), 921–924.

Pan, Y., Zhu, R., Banerjee, S., Gill, J. & Williams, Q., 2000. Rock magnetic properties related to thermal treatment of siderite: behavior and interpretation, *J. geophys. Res.,* **105**(B1), 783–794.

Przepiera, K. & Przepiera, A., 2001. Kinetics of thermal transformations of precipitated magnetite and goethite, *J. Therm. Anal. Cal.,* **65,** 497–503.

Przepiera, K. & Przepiera, A., 2003. Thermal transformations of selected transition metals oxyhydroxides, *J. Therm. Anal. Cal.,* **74,** 659–666.

Ruan, H.D., Frost, R.L. & Kloprogge, J.T., 2001. The behavior of hydroxyl units of synthetic goethite and its dehydroxylated product hematite, *Spectrochim. Acta*, A, **57,** 2575–2586.

Sangode, S.J. & Bloemendal, J., 2004. Pedogenic transformation of magnetic minerals in Pliocene–Pleistocene palaeosols of the Siwalik Group, NW Himalaya, India, *Palaeogeography, Palaeoclimatology, Palaeoecology,* **212,** 95–118.

Schwertmann, U. & Heinemann, B., 1959. Über das Vorkommen und die Entstehung von Maghemit in nordwestdeutschen Böden, *Neues Jahrbuch für Mineralogie,* **8,** 174–181.

Schwertmann, U. & Murad, E., 1988. The nature of an iron oxide–organic iron association in a peaty environment, *Clay Minerals* **23,** 291–299.

Schwertmann, U. & Taylor, R.M., 1989. Iron oxides, in *Minerals in Soil Environments*, 2nd edn, SSSA Book Series, no. **1,** 379–438.

Schwertmann, U. & Cornell, R.M., 1991. *Iron Oxides in the Laboratory, Preparation and Characterization*, VCH, Weilheim.

Soffel, H., 1991. *Paläomagnetismums und Archäomagnetismus*, Springer, Berlin, Heidelberg.

Spassov, S., Heller, F., Kretzschmar, R., Evans, M.E., Yue, L.P. & Nourgaliev, D.K., 2003. Detrital and pedogenic magnetic mineral phases in the loess/palaeosol sequence at Lingtai (Central Chinese Loess Plateau), *Phys. Earth planet. Inter.,* **140,** 255–275.

Stacey, F.D. & Banerjee, S.K., 1974. *The physical principles of rock magnetism*, Elsevier, Amsterdam.

Stanjek, H., 1987. The formation of maghemite and hematite from lepidocrocite and goethite in a Cambisol from Corsica, France, *Z. Pflanzenernähr. Bodenkunde,* **150,** 314–318.

Stanjek, H. & Schwertmann, U., 1992. The influence of aluminum on iron oxides: part XVI: hydroxyl and aluminum substitution in synthetic hematites, *Clays Clay Minerals,* **40,** 347–354.

Stanjek, H. & Weidler, P.G., 1992. The effect of dry heating on the chemistry, surface area, and oxalate solubility of synthetic 2-line and 6-line ferrihydrites, *Clay Minerals,* **27,** 397–412.

Stanjek, H. & Häusler, W., 2000. Quantifizierung silikatischer Tonminerale im Textur- und Pulverpräparat mit MacClayFit, *Berichte der DTTG,* **7,** 256–265.

Thompson, P., Cox, D.E. & Hastings, J.B., 1987. Rietveld refinement of Debye-Scherrer synchrotron X-ray data from Al_2O_3, *J. Appl. Cryst.,* **20,** 79.83.

Tronc, E. & Jolivet, J.P., 1986. Surface effects on magnetically coupled iron oxide ('γ-Fe_2O_3'), *Hpyerfine Interactions* **28,** 525–528.

Van der Marel, H.W., 1951. Gamma ferric oxide in sediments, *Journal of Sedimentary Petrology,* **21,** 12–21.

Walter, D., Buxbaum, G. & Laqua, W., 2001. The mechanism of the thermal transformation from goethite to hematite, *J. Therm. Anal. Cal.,* **63,** 733–748.

Zhu, R., Kazansky, A., Galina, M., Guo, B., Zykina, V., Petrovsky, E. & Jordanova, N., 2000. Rock-magnetic investigation of Siberia loess and its implications, *Chin. Sci. Bull.,* **45**(23), 2192–2197.