Doctoral Thesis

Magnetic and spectroscopic investigations of mineral transformations in mixed-valence oxides and magnesium silicates

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Magnetic and spectroscopic investigations of mineral transformations in mixed-valence oxides and magnesium silicates

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Doctor of Sciences

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List of symbols and abbreviations

$A$: hyperfine splitting

$A_{\perp}$: perpendicular hyperfine splitting

$A_{//}$: parallel hyperfine splitting

$B$: external field

$B_{\text{eff}}$: effective field acting on the magnetic moment

$B_c$: coercivity

$B_{cr}$: coercivity of remanence

$B_i$: interaction field

$B_m$: crystalline anisotropy field

$B_s$: shape anisotropy field

$D$: zero field splitting parameter in the z plane

$\delta B$: peak to peak linewidth of the derivative FMR spectrum

$E$: zero field splitting parameter in the x-y plane

$g_e$: free electron $g$-value : 2.0023

$g$: $g$-value matrix

$g_{\perp}$: $g$-value in the x-y plane for an axial $g$ matrix

$g_{//}$: $g$-value in the z plane for an axial $g$ matrix

$g_{\text{eff}}$: effective $g$-value

$g_{xx}$: principal $g$-value along the x axis of the rhombic $g$ matrix

$g_{yy}$: principal $g$-value along the y axis of the rhombic $g$ matrix

$g_{zz}$: principal $g$-value along the z axis of the rhombic $g$ matrix

$h$: Plank’s constant : $6.626068 \times 10^{-34}$ J.s

$K_1$: first magnetocrystalline anisotropy constant

$k_b$: Boltzmann’s constant: $1.38065 \times 10^{-23}$ J K$^{-1}$

$M$: Magnetization

$M_r$: remanent magnetization

$M_s$: saturation magnetization

$m_s$: electron spin magnetic quantum state number

$m_i$: nuclear spin magnetic quantum numbers
SIRM: Saturation isothermal remanent magnetization

$T_c$: Curie temperature

$\gamma$: gyromagnetic ratio of the electron: $1.768 \times 10^{11}$ rad s$^{-1}$ T$^{-1}$

$\mu_b$: Bohr’s magneton: $9.27402 \times 10^{-24}$ J/T

$\mu_0$: magnetic permeability of free space $4\pi \times 10^{-7}$ T$^2$ J$^{-1}$m$^3$

$\nu$: frequency of the microwave radiation

$\chi$: susceptibility

$\chi_m$: mass susceptibility

$\chi'$: in phase susceptibility

$\chi''$: out of phase susceptibility

$\omega$: larmor precession frequency
Abstract

For several decades studies of mineral transformations have attracted broad interest in the earth sciences, in the quest for a better insight into geological processes such as metamorphism or weathering. In this thesis two aspects of mineral transformations are examined which center on the effect of trace elements on thermal stability of Mg-phylosilicate and the relation between magnetization and structural-chemical changes in the mixed valence iron oxide magnetite. The research on these transformations is subdivided into three parts, one focusing on phyllosilicate and the other two on magnetite nanoparticles in bacteria and natural surface-oxidized magnetite particles in Vertisol from Western Africa.

In the study on thermal stability of Mg phyllosilicate, synthetic hectorite was doped with traces of Cu(II) in the range between 0-500 ppm in hydrothermal solutions containing fluorine. The structural properties, the thermal stability, and conversion of treated hectorites were studied by a combined approach using mainly X-ray diffraction (XRD), thermal analyses and electron paramagnetic resonance (EPR) spectroscopy. During hydrothermal treatment the presence of Cu(II) increased the crystallite size and EPR data provided evidence that Cu (II) was both structure-bound and associated with the inner surface of the hectorite particles. Upon heating the formation of free radicals, i.e., defect structures, at 573 K indicated the beginning of the destabilization of the hectorite on a molecular level. Between 873 and 973 K the hectorite converted into enstatite, and in the presence of Cu(II) into enstatite and an amphibole, which was determined as Mg-F richterite by XRD. The formation of richterite as additional conversion product is explained by the creation of structural weakness followed by fragmentation due to structure-bound Cu(II) in fluorine containing hectorite. The above finding indicates that trace elements in concentration in the ppm range can affect the conversion product in high-temperature geochemical system.

The relation of the magnetization and the low-temperature structural transformation of magnetite was investigated by means of static and dynamic magnetic analyses and ferromagnetic resonance spectroscopy on intact magnetosome chains in the strain of
Magnetospirillum gryphiswaldense. The magnetosomes were generally in a stable single-domain state, but magnetosomes smaller than 30 nm characteristic of superparamagnetic magnetite particles were also found. Alternating current (AC) susceptibility revealed that below 150 K all of them were blocked. Ferromagnetic resonance (FMR) spectroscopy indicated that at room temperature the anisotropy of Magnetospirillum gryphiswaldense was dominated by the shape of the magnetosome chains. Low-temperature FMR suggested that this dominant shape anisotropy can affect the detection of the Verwey transition at 100 K. The static and dynamic magnetic analyses showed that the Verwey transition was smeared and that our magnetotactic bacteria failed the Moskowitz test, which is a commonly-used diagnostic tool for detecting magnetotactic bacteria in geological systems. This failure found for Magnetospirillum gryphiswaldense is explained by the biomineralization of non-stoichiometric magnetosomes. This interpretation is based on the increase in high-field susceptibility and the distinct peak in the out-of-phase component of the AC susceptibility below 50 K. These results are attributed to freezing of spins associated with a defect structure in the core and at the surface of nano-sized magnetosomes. The results demonstrate that intrinsic properties of nano-sized magnetosomes are significantly influenced by non-stoichiometry and by the anisotropy excited from their arrangement in the bacteria.

In a further study FMR spectroscopy in combination with dithionite extraction technique was employed to detect maghemitization of magnetite particles in a Vertisol sample. Since maghemitization, i.e., formation of maghemite by partial oxidation of magnetite, suppresses the Verwey transition, this structural-chemical transformation is generally detected by low-temperature magnetic measurements. In the proposed experimental approach the detection of maghemitization is possible at room temperature. This approach is based on two assumptions: first that dithionite as a reductive agent selectively dissolves the ferric oxide and erases the effect of maghemitization on magnetite; and secondly that this effect is reflected by changes in the anisotropy properties detectable by FMR. A comparison of the FMR signal before and after the dithionite treatment revealed significant changes in the linewidths ($\delta B$) and $g$-values ($g_{\text{eff}}$) and their angular dependence. The broadening of $\delta B$ and the shift to higher $g_{\text{eff}}$ and the increase in their angular dependence after dithionite treatment is explained by an increase in magnetocrystalline anisotropy due to the removal of ferric compound, i.e., the maghemitization. Low-temperature FMR measurement of the untreated sample revealed only small changes upon cooling. In contrast, the dithionite-treated sample exhibited an expected spectral change between 100 and 120 K, indicative of the Verwey transition. These results
confirmed the above assumptions and this demonstrates that the FMR in concert with chemical extraction is a tool for detecting maghemitization at room temperature.

In a second study on natural magnetite, the effect of the maghemitization on the grain size distribution of multidomain magnetite is investigated using the Vertisol profile from the savanna woodland in Western Africa. The relatively larger grain sizes in the upper two horizons compared to the lower two horizons of the Vertisol profile are documented by the coercivity ratio ($B_{cr}/B_c$), magnetization ratio ($M_r/M_s$) and the coercivity distribution obtained from hysteresis measurements and first order reversal curves diagrams. The good correlation of the different grain size distribution with the redox-cline in the profile was used to link the magnetic data with climate data, which indicate relatively stable conditions with dry and rainy seasons during the last 10,000 years. Changes in the grain size distributions are schematically explained by the repeated partial oxidation of the magnetite during dry seasons and the reductive dissolution of oxidation product during rainy seasons due to waterlogging. Since the Vertisol is not depleted of magnetite, this redox-induced process of magnetite dissolution in a natural environment is a relatively slow process.
Résumé

Les études sur les transformations minéralogiques ont, depuis des décennies, trouvé un large intérêt dans les sciences de la terre afin de mieux comprendre certains processus géologiques, tels que le métamorphisme ou l’altération météorique. Deux aspects particuliers de ces transformations sont étudiés dans cette thèse, qui on trait d’une part à la stabilité thermique d’un phyllosilicate magnésien en présence d’éléments trace et d’autre part à la relation entre l’aimantation et les changements structuraux et chimiques dans la magnétite. Cette recherche peut être divisée en trois parties. La première se concentre sur le phyllosilicate magnésien ; la deuxième partie se focalise sur la magnétite en tant que nanoparticule d’origine bactérienne alors que dans la troisième partie la magnétite en provenance d’un Vertisol d’Afrique occidentale est étudiée.

Afin d’étudier la stabilité thermique d’un phyllosilicate magnésien renfermant des éléments traces, une hectorite synthétique a été traitée de façon hydrothermale avec des solutions contenant de 0 à 500 ppm de Cu(II). Les propriétés structurales, la stabilité thermique ainsi que les produits de conversion des hectorites traitées ont été analysés principalement par diffractions des rayons X, analyse thermique ainsi que par spectroscopie de résonance paramagnétique électronique (EPR). Il a été observé qu’en présence du Cu(II) la taille des cristallites augmentent lors du traitement hydrothermal. L’analyse par EPR montre que le Cu(II) est localisé dans la couche octaédrique mais aussi à la surface intérieure du minéral. Lorsque l’hectorite est chauffée à 573 K, des radicaux libres sont formés ce qui indique la déstabilisation thermique du minéral à l’échelle moléculaire. Entre 873 et 973 K l’hectorite se transforme en enstatite. En présence de Cu(II) une amphibole, identifiée par rayons X comme étant une richtérite riche en fluor et magnésium, est formée comme phase additionnelle. La formation de richtérite est expliquée par un effet déstabilisant du Cu(II) qui permet la conversion de l’hectorite avant la libération du fluor. Les résultats décrits ci-dessus montrent que les éléments traces peuvent influencer les produits de conversion dans des environnements géochimique de haute température.

La relation entre l’aimantation et le changement structural à basse température de la magnétite (transition de Verwey) a été analysée par des mesures magnétiques statiques, dynamiques ainsi que par spectroscopie de résonance ferromagnétique sur des chaînes intactes de magnétosomes de la bactérie *Magnetospirillum Gryphiswaldense*. Du point de vue
magnétique les magnetosomes étaient généralement des monodomaines stables mais des magnetosomes de moins de 30nm, pouvant être superparamagnétiques ont aussi été observés. Les mesures de susceptibilité dynamiques indiquent que les magnetosomes sont tous bloqués en dessous de 150K. La spectroscopie de résonance ferromagnétique (FMR) montre qu’à température ambiante, l’anisotropie magnétique est dominée par la forme des chaînes résultant de l’alignement des magnetosomes. Les spectres FMR à basse température indiquent que cette anisotropie dominante peut influencer la détection de la transition de Verwey à 100 K. Les mesures magnétiques statiques et dynamiques montrent une transition de Verwey diffuse. La bactérie magnétotactique ne passe pas le test de Moskowitz, alors que c’est un outil largement utilisé pour l’identification de chaînes intactes de magnetosomes dans des systèmes géologiques. L’échec du test par Magnetospirillum gryphiswaldense est expliqué par la biominéralisation de magnétique non stoechiométrique. Cette analyse se base sur les mesures de susceptibilité à fort champ ainsi que par le pic observé dans la susceptibilité hors phase en dessous de 50 K. Ces résultats sont interprétés comme étant dus aux gels des spins associés à des défautsstructuraux liés à la surface ainsi qu’au noyau des magnetosomes nanométriques. Ces résultats montrent que les propriétés intrinsèques des magnetosomes sont influencées de manière significative par la non stoechiométrie ainsi que par l’anisotropie résultant de l’alignement en chaînes.

Une autre application de la spectroscopie de résonance ferromagnétique est présentée dans le chapitre 5, où cet outil analytique a été combiné avec une technique d’extraction chimique (dithionite) pour étudier la maghémitisation de grains de magnétites provenant d’un Vertisol africain. Ce processus d’oxydation de la magnétique est souvent détecté en faisant des mesures magnétiques à basse température, puisque il peut supprimer la transition de Verwey. Nous proposons une approche expérimentale pour identifier à température ambiante la maghémitisation. Cette méthode se base sur deux hypothèses ; d’abord que le traitement à la dithionite dissout les oxydes ferriques et ainsi « efface » les effets de l’oxydation, et deuxièmement que ces changements sont reflétés dans les propriétés d’anisotropie pouvant être détectés par FMR. La comparaison des spectres FMR avant et après le traitement chimique montre un changement significatif de la largeur de raie (δB) de la valeur effective de g (g_{eff}) ainsi que de leur dépendance angulaire. L’augmentation de ces paramètres est expliquée par une augmentation de l’anisotropie magnetocrystalline due à la dissolution de l’oxyde ferrique, c.a.d de la maghémitisation. Les spectres FMR mesurés à basse température sur l’échantillon non traités ne montre pas de changements significatifs. Par contre, ces
mêmes mesures faites sur l’échantillon traité avec la dithionite montre un changement marqué de $\delta B$ entre 100 et 120 K indiquant la transition de Verwey. Ces résultats confirme les hypothèses énoncées plus haut et démontrent que la spectroscopie FMR combinée avec un traitement chimique peut être un outil pour identifier à température ambiante la magnémitisation.

Dans le dernier chapitre, l’effet de la magnémitisation sur la taille des grains de magnétites multidomaines a été analysé dans le profil du Vertisol, situé dans les savannes boisées en Afrique Occidentale. La plus grande taille des grains dans les horizons supérieurs par rapport aux deux horizons inférieurs est documenté par les rapports de coercivité ($B_c/B_s$) et d’aimantation ($M_r/M_s$), obtenues par les mesures d’hystérèse. La bonne corrélation entre la distribution de la taille des grains et la limite redox du profil a été utilisée pour lier les mesures magnétiques avec les données climatologiques. Ces dernières montrent un climat stable avec une alternance entre une saison des pluies et une saison sèche durant depuis environ 10000 ans. Le changement de la taille des grains peut être expliqué par l’oxydation de la magnétite pendant la saison sèche et la dissolution par réduction pendant la saison des pluies, lorsque les deux horizons inférieurs sont saturés en eau. Puisque la magnétite est trouvée dans tout le profil, il peut en être conclu que ce processus de dissolution, gouverné par le changement de conditions redox, est relativement lent.
Chapter 1

Introduction

Mineral transformations have been described in many natural systems, such as weathering environments or metamorphic terrains, and have also been investigated in laboratory studies (e.g., Kretzschmar et al., 1997; Redfern and Carpenter, 2000; Friedrich et al., 2004). The experimental and field data have been used to deduce physical and chemical parameters in geological processes (e.g., Allaz et al., 2005). Mineral transformations can occur through reactions where only the physical properties changes (polymorphic reactions) or through reactions where both physical and chemical properties change.

Polymorphic reactions can be subdivided into reconstructive and displacive processes. Reconstructive transformations involve the breaking of bonds followed by the rearrangements of structural units. Such processes require large amounts of energy and are generally not reversible. Examples are the calcite-aragonite transformation (e.g., Hacker et al., 2005) or the enstatite into protoenstatite conversion (Lee and Heuer, 1987). Displacive reactions are characterised by displacement of atoms and rearrangement of bond angles, i.e., no bonds are broken and therefore such reactions are easily reversible. The low to high quartz transformation (Liebau and Bohm, 1982) belongs to such reactions. A special case of displacive polymorphic reaction is the charge ordering induced transition in mixed valence oxides. The most prominent example of such a reaction is the low temperature change from a cubic to a monoclinic structure in magnetite, known as the Verwey transition. Since magnetite has a broad industrial application and is the major carrier of magnetic information in natural samples, this transformation has attracted interest in mineral physics and rock magnetism for
decades (e.g., Verwey and Haayman, 1941; Özdemir and Dunlop, 1998, Garcia and Subias, 2004).

Transformations which involve both physical and chemical changes are prevalent in geological systems. Examples of such reactions include dehydroxilation processes (release of OH groups) such as the conversion of Mg-phyllosilicates into Mg-pyroxenes and of amphiboles to pyroxenes or olivine (e.g., Bose and Ganguly, 1994; Xu et al., 1996) encountered in metamorphism. Mineral transformations are also found in weathering environments where reactions such as the plagioclase to kaolinite transformation or the magnetite to maghemite conversion have been described (e.g., Papoulis et al., 2004, Chen et al., 2005).

In this thesis, mineral transformations of both groups are presented. The low temperature behaviour of magnetite is used as an example of a polymorphic transformation (Chapter 4). Mineral transformations of the second group are investigated via two examples that occur in different temperature regimes. First, the thermal stability of hectorite (Mg-phyllosilicate) and its conversion products are studied (Chapter 3), and secondly, the conversion of magnetite into maghemite under natural conditions is examined (Chapters 5 and 6).

The different aspects of mineral transformation in this thesis are subdivided into three parts which refer to Chapter 3, Chapter 4, and Chapters 5 + 6. In Chapter 2 the basic principles of the magnetic methods are presented. Special attention is given to electron paramagnetic resonance (EPR) and ferromagnetic resonance (FMR) spectroscopy, since these techniques play a central part in the analysis of the studied mineral transformations.

**Thermal conversion**

Despite the fact that there are a large number of studies on the transformation of minerals (e.g., Fitzgerald et al., 1996; Arlt et al., 2000; Friedrich et al., 2004; Henry et al., 2007) little is known about the effect of trace elements on the reaction path during thermal conversion of minerals. The effect of cation substitution on the thermal conversion was studied extensively for ferric hydroxides and it was found that substitution of Al(III) for Fe(III) increases the mineral stability and was explained by the stronger Al-OH bond (Schulze and Schwertmann, 1987, Wells et al., 2006). In these studies, the amount of cation substitution was generally on the order of a few weight percent (wt%), concentrations that are similar to the abundance in the earth’s crust (Mason and Moore, 1982). In contrast, the
terrestrial abundance of most of the transition metals is less than 0.01 wt% (100 ppm), and their effect on the mineral transformation has not been experimentally studied in detail.

Chapter 3 addresses the question of how trace elements affect the mineral thermal conversion. This problem is examined in a two-step experimental approach, which uses a synthetic hectorite \((Na_x(Mg_{3-x}Li_x)Si_4O_{10}(OH_2))\) as starting material and copper as the trace element. The first step consists of hydrothermal treatment, which loads the hectorite with different concentrations of Cu, varying between 0 and 500 ppm. Such concentrations are similar for a typical terrestrial abundance for Cu of 65 ppm (e.g., Allègre et al., 2001). In the second step the thermal stability of Cu-loaded hectorite is analysed. Apart from the mineral conversion on a long-range scale, the Cu-coordination during the transformation is monitored by EPR spectroscopy. The various effects of trace elements on the mineral transformation are discussed.

Polymorphic transformation

Magnetite undergoes a polymorphic transformation at about 120K, where its structure changes from cubic to monoclinic (Iizumi, 1982; Wright et al. 2000, 2002). This transformation, known as the Verwey transition, is characterised by changes in physical properties such as magnetization and resistivity (Walz, 2002). Although the transformation occurs at a temperature which is below conditions found on the Earth, this intrinsic property is often used as a diagnostic tool for biogenic magnetite in environmental magnetism (e.g., Weiss et al., 2004a, Pan et al., 2005a; Posfai et al., 2006). Biogenic magnetite in geological or environmental systems is mainly formed by magnetotactic bacteria (MTB), which were first described by Blakemore (1975) in marine sediments. Since this discovery, MTB have been reported in soils (Fassbinder et al., 1990) and lacustrine sediments (e.g., Pan et al., 2005b). MTB are characterized by an arrangement of nano-sized magnetite particles in chains. These particles, called magnetosomes, have a narrow shape and size distribution and a homogeneous chemical composition (e.g., Blakemore and Frankel, 1989; Kopp and Kirschvink, 2008). Since the organic cells, which stabilize the magnetosomes, generally decay during diagenesis, the identification of magnetosomes in geological systems is ambiguous. Montgomery et al. (1998) found intact chains of magnetite in Cambrian sediments and interpreted them to be of biogenic origin. Isolated magnetite particles with morphological properties similar to present magnetosomes have been reported in Precambrian sediments (Chang et al., 1989), and have been postulated in the meteorite ALH84001 to be evidence of life on Mars (McKay et al.,
1996). The interpretation of single magnetite crystals as evidence of biogenic origin, however, has been recently questioned by Golden et al. (2004), who synthesized inorganic magnetite with similar morphology as magnetosomes.

In addition to morphological criteria, magnetic methods have been applied to detect magnetotactic bacteria (e.g., Weiss et al., 2004 b; Kopp et al., 2006a). Among these methods, the Moskowitz test, which compares the loss of magnetization on warming through the Verwey transition after field cooling and zero field cooling, is a common empirical tool for detecting chain structure as an indicator of magnetosomes (Moskowitz et al., 1993). Recently FMR spectroscopy at room temperature was used to analyse the magnetic anisotropy resulting from the alignment of magnetosomes in chains. The potential of magnetic methods for detecting magnetotactic bacteria is evident, but the link between low temperature characteristics of magnetosomes and their significance for detecting biogenic origin is still a matter of debate. In Chapter 4 of this thesis the polymorphic transition of magnetosome in cultivated intact magnetotactic bacteria is investigated via an analytical approach which combines low-temperature static and dynamic magnetization experiments with FMR spectroscopy. The purpose of this research is to examine in detail the low temperature characteristics of intact magnetosome chains and to test the robustness of the empirical magnetic tests for detecting magnetosomes.

Maghemitization of natural magnetite

Magnetite is an accessory mineral in many rocks and the most important remanence carrier for paleomagnetism. Its widespread occurrence in depositional or pedogenic environments indicates a relatively high chemical stability under ambient conditions (White et al., 1994). Nevertheless, laboratory and field studies have shown that under oxic conditions magnetite can be transformed into maghemite (Gallagher et al., 1968; Chen et al., 2005). This process is known as maghemitization and has been reported for oceanic basalts (e.g., Horen et al., 1998; Doubrovine and Tarduno, 2004; Wang et al., 2006) and paleosols/loess sequences (e.g., Van Velzen and Dekkers, 1999; Cogoini et al., 2001). Maghemitization can be described schematically as a surface process by which the oxidation of Fe(II) leads to a coating of $\gamma$-Fe$_2$O$_3$. The formation of such a coating can screen the core of magnetite from oxidation (Gallagher et al., 1968; White et al., 1994). This effect may explain the high stability of magnetite under ambient conditions. The potential for direct identification of maghemitization in natural samples by X-ray diffraction is limited because of the low concentration of
magnetite, and also of maghemite, in such samples. Moreover, the similar magnetic properties (coercivity, saturation magnetization) of the two oxides make unambiguous characterization difficult at room temperature. Maghemite is generally unstable at about $T > 400^\circ$C and transforms into hematite (e.g., Gehring and Hofmeister, 1994; Hanesch et al., 2006). Since such a transformation is accompanied by a drastic change in the magnetic properties, i.e., a decrease in susceptibility, it could be used as diagnostic criterion for the detection of maghemitization. Thermal treatment of natural samples, however, can also lead to the decomposition of ferriferous phases and the new formation of magnetic compounds (Hirt et al., 1993). Therefore the thermal transformation of maghemite does not yield an unambiguous identification of maghemitization in multimineral samples. Smirnov and Tarduno (2000) put forward low-temperature measurements to detect maghemitization. Their non-invasive approach is based on the observation that oxidation of magnetite smears out the Verwey transition and increasing maghemitization leads to the suppression of this transition (e.g., Özdemir et al., 1993). The Verwey transition can also be suppressed by increasing Ti content in the magnetite (Kakol et al., 1992), and thus ambiguity remains when interpreting this parameter.

In order to overcome this limitation on the detection of maghemitization in natural samples, a new experimental strategy is presented in Chapter 5. The proposed analytical approach relies on the fact that compared to ferric oxides the mixed valence oxide magnetite is more resistant to chemical reductive dissolution. In this approach it is assumed that reductive dissolution selectively removes the maghemite surface coating so that the magnetite grains exhibit a well-defined, rather than smeared-out, Verwey transition. The above assumption is tested on material from the top layer of a Vertisol, by analysing the Verwey transition using FMR spectroscopy before and after chemical treatment with the reducing agent dithionite.

**Magnetite grain size and redox conditions**

Chapter 6 presents a study on the effect of maghemitization on the grain size distribution of magnetite in the Vertisol profile mentioned above. The soil profile is located in a savannah woodland of southern Mali, which is characterized by a seasonal climate. During the dry season the soil is aerated and oxic conditions prevail, whereas in the wet season waterlogging generates reducing conditions within the profile. Under this assumption the seasonal climate can lead to annual cycles with conditions favourable for the maghemitization of magnetite.
grains and conditions in which maghemite becomes chemically unstable. If changing redox conditions linked to the seasonal climate act over a long time period, it can be supposed that this process will diminish the size of the magnetite grains. This assumption is tested by studying the relationship between the magnetite grain size distribution and the water regime in the Vertisol.

Chapter 7 summarises the four studies presented and discusses their various findings in the context of the chosen experimental strategies. It presents an outlook for further investigations.
Chapter 2

Theoretical background and methods

This chapter summarises the basic principles of rock magnetism and of electron paramagnetic and ferromagnetic spectroscopy, which were used in this study. A more complete description can be found in literature (Dunlop and Özdemir 1997; Roberts et al., 2000; Wertz and Bolton, 1972; Calas, 1988).

2.1 Basic principles of rock magnetism

2.1.1 Susceptibility

Susceptibility ($\chi$) is the ability of a material to become magnetized by an external magnetic field ($H$). The susceptibility is defined as the change of magnetization $M$ per unit of applied field $H$:

$$\chi = \frac{\partial M}{\partial H} \quad (2.1)$$

Based on the response to the applied field, diamagnetic, paramagnetic, and ferromagnetic materials can be distinguished.

2.1.2. Diamagnetism

In diamagnetic materials all electron spins are paired, so that the magnetic moment arising from the electron spin is compensated and the net magnetic moment only results from an
orbital moment. When a field is applied, the electrons precess around the field axis. This movement induces a magnetization opposed to the direction of the applied field, and thus results in a negative susceptibility (Fig. 2.1). Quartz and calcite, but also biological compounds are classical diamagnetic materials in geological environments.

2.1.3 Paramagnetism

Paramagnetic materials possess unpaired electron spins. In the absence of an applied field, the magnetic moments associated with the spins are randomly oriented, i.e., the net magnetization is zero. Applying a field will tend to align the moments parallel to the field. This alignment creates a positive magnetization which increases linearly with the applied field according to

$$\chi H = M$$  \hspace{1cm} (2.2)

The susceptibility of paramagnetic materials is inversely proportional to the temperature. This behavior can be described to a good approximation by the Curie law (e.g., Dunlop and Özdemir, 1997):

$$\chi = \frac{C}{T}$$  \hspace{1cm} (2.3)

where $C$ is the Curie constant, which is material-specific, and $T$ is the temperature in Kelvin. Clay minerals are prominent paramagnetic material in natural environments.

2.1.4 Ferromagnetism

In ferromagnetic materials unpaired electron spins are aligned parallel with respect to each other. The coupling of the electron spins results in a spontaneous magnetization. These materials have relatively high susceptibility and a non-linear response to an applied field, which is characterized by a saturation magnetization, i.e., the maximum magnetization that can be reached in an applied field (Fig. 2.1).

All ferromagnets have an intrinsic temperature above which the magnetic ordering decays and the material becomes paramagnetic due to thermal agitation. This temperature is known as the Curie temperature ($T_c$). Ferromagnetic behaviour is normally observed in metals such as native iron or nickel. Subgroups of ferromagnetism are antiferromagnetism and
ferrimagnetism and they are often found in metal oxides (e.g., hematite $\alpha$-Fe$_2$O$_3$, magnetite Fe$_3$O$_4$), where the spins are ordered in sublattices with opposite alignments.

### 2.1.4.1 Antiferromagnetism

In perfect antiferromagnetic materials, e.g., ilmenite (FeTiO$_3$), the net magnetic moment is theoretically zero because of the compensation of the opposite aligned spins in the sublattices. In oxides where magnetic moments of the sublattices are not perfectly aligned, a weak net magnetization can be generated. This property is referred to as canted antiferromagnetic and is found in hematite ($\alpha$-Fe$_2$O$_3$), one of the major ferric oxides in natural environments. The temperature of the transition from antiferromagnetic ordering to a paramagnetic state is called the Néel temperature ($T_N$). In antiferromagnets this intrinsic property can vary over a wide range, for example from 63 K for ilmenite to 923 K for hematite.

### 2.1.4.2 Ferrimagnetism

In ferrimagnets, the magnitude of the moment in each sublattice varies. The classical example of a ferrimagnet is magnetite (Fe$_3$O$_4$), with its two sublattices A and B. The A sublattice hosts Fe(III) in tetrahedral coordination, whereas the B sublattice consists of both Fe(II) and Fe(III) in octahedral coordination. The A and B sublattices are antiferromagnetically coupled such that the net resultant magnetization stems from the Fe(II) ions in the octahedral site. The Curie temperature of magnetite is 853 K and it reaches its saturation magnetization in relatively low fields, similar to classic ferromagnetic materials.
2.1.5 Magnetic hysteresis

In magnetic hysteresis measurements the effect of an applied field $B$ on the magnetization of the material is examined. It is worth noting that in the following, the applied field is expressed in terms of magnetic induction $B$ in units of Tesla [T] instead of $H$, because in rock magnetism, and in electron paramagnetic spectroscopy, using $B$ is common practice. Both quantities are linked by the relationship:

$$B = \mu_0 H$$

(2.4)

with $\mu_0$ being the permeability of the vacuum.

In hysteresis measurements, the material is first brought to saturation, i.e., to the saturation magnetization, $M_s$. Subsequently $B$ is reduced to zero (Fig. 2.2), and the crossing of the $M$-axis at $B = 0$ is referred to as the remanent magnetization, $M_r$. The field is then progressively increased in the opposite direction until saturation is reached. The crossing of the curve with the $B$-axis, i.e., $M = 0$, is defined as the coercivity ($B_c$). The remanent coercivity ($B_{cr}$) refers to the field which is required to remove the net remanent magnetization.
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Figure 2.2: Hysteresis loop showing the different parameters used when analysing such measurements.

The shape of the loop as well as the magnetization and the coercivity parameters can be used as a diagnostic tool to investigate the magnetic state of a material. For example, ferrimagnetic materials exhibit a narrow loop (i.e., low $B_c$), and $M_s$ is reached at relatively low fields, whereas canted antiferromagnets exhibit the opposite behaviour (i.e., high $B_c$ and $M_s$ at relatively high fields). Hysteresis parameters have also been used for the grain size analysis of magnetite (Day et al., 1977; see also Chapter 6).

2.1.5.1 FORC diagrams

In this thesis first-order reversal curves (FORC) measurements are often used to determine the grain size distribution of magnetite. The basics of this method are outlined in the following.

The FORC method was developed by Pike in 1999 and later applied to earth sciences (e.g., Roberts et al., 2000; Muxworthy and Dunlop 2002; Carvallo et al., 2004). In an early study on natural samples Roberts et al. (2000) demonstrated that FORC is a powerful tool for separating the contribution of high and low coercivity minerals which are superimposed in a standard hysteresis measurement (Fig. 2.2). It is also well-known that the coercivity of magnetite is dependant on grain size. (e.g., Dunlop, 1981). Therefore FORC measurements can be used as a tool for analysing the grain size distribution of magnetite in a natural sample.
The FORC technique is closely related to hysteresis measurements. In this technique the sample is first saturated in a positive field and then the field is decreased to a reversal field $B_r$. The FORC is defined as the magnetization curve obtained when the field is increased from $B_r$ back to saturation (Fig. 2.3a). This procedure is repeated for different values of $B_r$ in order to get a set of FORCs (Fig. 2.3b).

![Illustration of a FORC curve (a) and an example of a set FORC when the measurements are completed (b) (modified from Roberts et al., 2000).](image)

The magnetization at the applied field $B_d$ on the curve with reversal field $B_r$ is written as $M(B_r, B_d)$ with $B_d > B_r$. In a FORC, $B_r$ is constant while $B_d$ varies. The FORC distribution is defined as a mixed second derivative:

$$\rho(B_r, B_d) = -\frac{\partial^2 M(B_r, B_d)}{\partial B_r \partial B_d}$$

To numerically calculate the FORC distribution at a point $P(B_r, B_d)$, a grid containing $(2SF + 1)^2$ points with $P$ at the center is defined, where SF is a smoothing factor generally varying between 2 and 5. The magnetization at these data points is fitted by a polynomial surface of the form $a_1 + a_2 B_r + a_3 B_r^2 + a_4 B_d + a_5 B_d^2 + a_6 B_r B_d$. The value $a_6$ represents $\rho(B_r, B_d)$ at point $P$ (Pike, 1999). This procedure is repeated for each grid point within the diagram limits. The FORC diagram is a contour plot of all these values.

To plot the FORC diagram, two new variables, $B_b$ and $B_c$, are defined. They are related to $B_r$ and $B_d$ as follows:

$$B_b = \frac{B_d + B_r}{2}$$
$B_c = \frac{B_d - B_r}{2}$

where $B_c$ is the coercivity and $B_b$ is the interaction field, as can be seen from a square hysteresis loop. In a FORC diagram, $B_c$ vs $B_b$ is plotted. It is worth noting that $B_c$ obtained from FORC measurement is determined by the peak of the distribution and, in the case of a homogeneous material, corresponds to $B_c$ of the hysteresis loop. In the case of two phases differing by their coercivity, $B_c$ in the hysteresis will be an average value and will not correspond to FORC values.

**Figure 2.4:** Square hysteresis loop with the FORC parameters where no interaction field is present (a); and square hysteresis loop which is shifted relative to the origin due to an interaction field $B_b$ and the subsequent FORC parameters (b) (modified from Roberts et al., 2002).

### 2.1.6 Superparamagnetism

Superparamagnetism refers to materials which exhibit a non-linear response of the magnetization to an applied field and a decay of the magnetization when the applied field is removed, i.e., in an $M$ vs $B$ plot the loop is closed ($B_c=0$). Small ferromagnetic single domain particles are considered as superparamagnetic (SP) entities when their uniform magnetization fluctuates (i.e., the magnetization relaxes). This mainly depends on the relation of the anisotropy energy ($E_a$) to the thermal energy ($E_{th}$) in the particle. The energies are defined as:

$$E_a \approx KV$$

$$E_{th} = k_bT$$
where $K$ is the anisotropy energy constant, $V$ is the particle volume, $k_b$ is the Boltzmann constant and $T$ is the temperature.

If $KV > k_bT$ the particle has a stable spontaneous magnetization. Superparamagnetism can occur if $KV \approx k_bT$, i.e., the particle volume is so small that $E_a$ becomes comparable to the thermal energy. The temperature where the anisotropy energy overcomes the thermal energy of a specific volume is defined as blocking temperature, $T_b$. An alternative definition of $T_b$ relies on the fact that the relaxation time $\tau$ is temperature-dependant, according to the Néel – Arrhenius relation:

$$\tau = \tau_0 \exp \left( \frac{KV}{k_bT} \right)$$  \hspace{1cm} (2.10)

where $\tau_0$ is the characteristic time of a system which is on the order of $10^{-9}$ to $10^{-11}$ s. Due to the inverse temperature dependency of the exponent, at high temperature the relaxation time is short whereas at low temperature it is long. The blocking temperature is the temperature below which the relaxation time is longer than the measuring time ($t_m$). Varying $t_m$ will therefore generate different $T_b$, with $T_b$ increasing as the measuring time decreases.

The relaxation of SP particles is often studied by measuring the low field susceptibility in an alternating field using varying frequencies. In such analyses the response of a sample will be delayed relative to the driving field. The measurement yields two quantities, the in-phase ($\chi'$) and the out-of-phase ($\chi''$) susceptibility. The in-phase is the component which instantaneously responds to the changing field and is related to magnetic anisotropies. The out-of-phase is a delayed response and is linked to dissipation phenomenon such as SP relaxation. $\chi''$ will peak at the blocking temperature. Therefore the measurement of $\chi''$ over a wide temperature range at different frequencies (e.g., 1 to 1000 Hz) permits the determination of the blocking behaviour.
2.2 EPR and FMR spectroscopy

Electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR) spectroscopy, is a method in which electromagnetic radiation is absorbed by molecules, ions and atoms possessing electrons with unpaired spins. This technique has been extensively used in chemistry and physics for more than 60 years to analyse transition metals and rare earth species with unpaired electrons (e.g., Fe(III); Mn(II), Cu(II), Gd(III)), and radicals in solids and liquids (e.g., Abragam and Bleaney, 1970; Misik et al., 1994; Mohanty et al., 2003; Dunbar et al., 2004). In contrast, EPR spectroscopy has received little attention in earth sciences.

A special form of EPR is ferromagnetic resonance (FMR), which detects absorption of electromagnetic radiation by magnetically-ordered materials. The FMR method can provide information on magnetic parameters (susceptibility or magnetocrystalline anisotropy), particle shape and particle arrangement. Recently FMR spectroscopy has attracted interest in rock and environmental magnetism (e.g., Hirt and Gehring, 1991; Kopp and Kirschvink, 2008). In the following, the basic principles of EPR and FMR, used in Chapters 3, 4 and 6, are presented. A more complete discussion of EPR and FMR principles can be found in Wertz and Bolton (1972) and Vonsovskii (1966).

2.2.1 Classical description of the resonance phenomenon

The magnetic moment arising from an electron in an orbit around the nucleus precesses around the direction of an external magnetic field $B$. This is known as the Lamor precession. The angular velocity of the precession, referred to as the Larmor frequency ($\omega$), associated with an electron spin transition can be written as

$$\omega = \gamma B$$

(2.11)

where $\gamma$ is the gyromagnetic ratio.

If an electromagnetic radiation with frequency $\nu$ equal to $\omega$ is applied perpendicular to $B$, energy is absorbed from this radiation due to spin transitions. Such a system is in resonance. This classical description of the resonance experiment is valid for EPR and the uniform mode (i.e., the coupled spins precess with the same frequency and same phase) of FMR. In order to
describe the EPR spectral parameters (e.g., hyperfine splitting) this explanation must be extended using quantum mechanical considerations.

2.2.2 EPR parameters
In a quantum mechanical approach, it is the energy difference between states and transitions induced by the electromagnetic radiation rather than the precession frequency that is considered. To describe the various parameters used for analysing the EPR spectra, first the simplest case with one unpaired electron is presented. Then the more complex case of two or more unpaired electrons is briefly discussed.

2.2.2.1 One unpaired electron in the magnetic field

Resonance conditions.
In the absence of a magnetic field, the magnetic moment associated with an unpaired electron with spin $S = 1/2$ has two degenerate energy levels. The application of an external field $B$ will split the energy levels into a low and a high energy state according to the electron Zeeman interaction. The low energy level corresponds to a moment oriented parallel to $B$, whereas the high energy state occurs for a moment antiparallel to $B$. The energy of the two spin states is given by

$$E = g_e \mu_B B m_s$$

(2.12)

where $g_e = 2.0023$ is the $g$-value of the free electron, $\mu_B$ is the Bohr magneton, and $m_s$ is the spin quantum number which equals -1/2 for the low energy state and +1/2 for the high energy level. The energy difference between the two states is therefore given by:

$$\Delta E = g_e \mu_B B$$

(2.13)

Considering the Bohr frequency condition

$$h\nu = \Delta E$$

(2.14)

where $h$ is Planck’s constant and $\nu$ is the resonance frequency in the microwave window of the electromagnetic spectrum, the resonance condition can be written as:
\[ h\nu = g_e \mu_B B \]  

(2.15)

**Figure 2.5:** Schematic illustration of the Zeeman effect with the splitting of the energy levels as a function of \( B \).

**Crystal field splitting**

Next, the case where the paramagnetic center interacts with its local surroundings is considered. Magnetic perturbations arise from the spin orbit coupling (SOC: see next section) and electrical perturbation excited by the crystal field. These effects lead to a deviation of the \( g \)-value from that of a free electron.

The crystal field is an electric field created by the ligands (i.e., anions) coordinated with transition metals. In the following this effect is discussed using paramagnetic Cu(II), a 3d transition metal with five electronic orbitals, as an example. In an octahedral crystal field, the five orbitals are split into a group of three degenerate (i.e., with the same energy) orbitals denoted as \( T_{2g} \), and a group of two degenerate orbitals labelled as \( E_g \) with higher energy (Fig. 2.6). Since Cu(II) has nine valence electrons, the unpaired one can be located in either \( E_g \) orbital, and therefore no defined ground state occurs. To modify this situation the degeneracy of the \( E_g \) orbitals will be removed by the change of geometry of the crystal field. For Cu(II) this is generally induced by the changed ligand field due to elongation along the fourfold axis of the octahedron. As result the energy of the two \( E_g \) orbitals is split and the unpaired electron is located in the \( d_{x^2-y^2} \) orbital. The lifting of the orbital degeneracy by a change in the geometry of the crystal field is known as the Jahn-Teller effect.
Spin orbit coupling and $g$ anisotropy

The spin orbit coupling (SOC) describes the coupling of the spin of an electron and its orbital motion around the atomic nucleus. This motion is characterized by its orbital angular moment $L$. The spin orbit coupling leads to a departure of the $g$-values from the value of the free electron. The $L$ parameter is affected by the orbital configuration, e.g., the crystal field of the transition metal ion. The crystal field can be anisotropic as in the case of Cu(II) with the Jahn-Teller effect in solids. Here spin-orbit coupling generates an anisotropy which is reflected by an anisotropy of the $g$-values. Taking the anisotropy of the $g$-values into account, equation 2.9 has to be adapted:

$$E = \mu_B \mathbf{g} \cdot \mathbf{B} m_s \quad (2.16)$$

where $\mathbf{g}$ now becomes a matrix of the following form expressed in its principal axis system:
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\[ g = \begin{bmatrix} g_{xx} & \ & \ \\ & g_{yy} & \ \\ & & g_{zz} \end{bmatrix} \]  

(2.17)

with \( g_{xx} \), \( g_{yy} \), and \( g_{zz} \) as the principal values of \( g \).

In crystal fields with low symmetry (triclinic, monoclinic or orthorhombic), the three principal \( g \)-values will be different (\( g_{xx} \neq g_{yy} \neq g_{zz} \)). In EPR spectroscopy such coordination sites are referred to as rhombic (Wetz and Bolton, 1972).

In crystal fields with axial symmetry (tetragonal or trigonal) \( g_{xx} = g_{yy} \neq g_{zz} \); \( g_{xx} \) and \( g_{yy} \) are called the perpendicular \( g \)-value (\( g_{\perp} \)) and \( g_{zz} \) is the parallel \( g \)-value (\( g_{\parallel} \)). In the case of \( g_{\parallel} > g_{\perp} \), the \( g \) matrix can be represented by a rotational ellipsoid, with its long axis parallel to the \( z \) direction (Fig 2.7a). In a powder spectrum, which represents the superposition of a large number of single crystal spectra, all orientations of the ellipsoid relative to \( B \) occur with the same probability. There is only one possible configuration if the long axis is to be parallel to \( B \), whereas there are many possibilities to have the long axis perpendicular to \( B \). In consequence, ellipsoids with the long axis perpendicular to \( B \) will contribute more strongly to the absorption spectrum. This will result in an asymmetric lineshape of the absorption spectrum (Fig 2.7b).

\[ \begin{array}{c}
\text{Absorption} \\
B( g_{\parallel} ) \quad B( g_{\perp} )
\end{array} \]

Figure 2.7: Schematic drawings of the axial \( g \)-ellipsoid (a) and the corresponding EPR absorption spectrum (b). The powder line shape results from the contributions of a large number of individual ellipsoids with different resonance positions (modified from Schosseler, 1998).
Hence, the anisotropy of the $g$-value provides information about the coordination of the paramagnetic center.

### 2.2.2.2 Hyperfine interaction

Hyperfine coupling refers to the interaction of an electron with the atomic nucleus having a spin of $I \neq 0$. The nuclear spin creates a local magnetic field which will be felt by the electron spin. The nuclear spin will interact with an applied field that will split it into $(2I + 1)$ energy levels characterised by the nuclear magnetic spin quantum number $m_i$. The local magnetic field created by the nuclear spin will then split the electronic energy levels into $(2I+1)$ sublevels. For Cu(II) with $I = 3/2$, the two electronic energy levels will both be split into four sublevels. Consequently four transitions corresponding to the selection rules $\Delta m_s = 1$ and $\Delta m_i = 0$ will be observed (Fig. 2.8a). These transitions will be detected as an equally-spaced four-line signal centered at $g$ in the EPR spectrum (Fig. 2.8b). The spacing is defined as hyperfine splitting (HFS) $A$.

In solids, the hyperfine interaction will be anisotropic because one of the two mechanisms which couple the nuclear and the electron spin is the dipole-dipole interaction, and this interaction is anisotropic. An example of the anisotropy of the hyperfine interaction is shown in Fig. 2.9, which exhibits the absorption spectrum in its first derivative form (see paragraph 2.2.6), characteristic of Cu(II) with $I = 3/2$ with four parallel and four perpendicular spectral features.
2.2.2.3 Zero-feld splitting (ZFS)

In systems with more than one unpaired electron, the electron spins interact with each other and their energy levels are split even in the absence of an external field. The Fe(III), which contains five 3d electrons, is a classical example of such a system. In minerals where Fe(III) is coordinated to oxygen atoms, Fe(III) is in a high-spin state, i.e., all five electrons are unpaired (e.g., Goodmann and Hall, 1994). Since EPR spectra of Fe(III) are a by-product of the investigation of mineral transformation in this thesis, the zero-field splitting parameters $D$ and $E$ are only qualitatively considered.

The values of $D$ and $E$ depend on the symmetry of Fe(III) coordination sites. The ZFS along the $z$-axis is represented by $D$, whereas $E$ accounts for the ZFS in the $x$-$y$ plane. For cubic coordination, $D$ and $E$ are 0. In axially distorted sites, $E = 0$ and $D \neq 0$, whereas for rhombic sites, $D$ and $E$ are $>0$. Sites with maximum rhombic distortion correspond to a ratio of $E/D = 1/3$ (e.g., Goodman and Hall 1994). The ZFS has a strong influence on the resonance
conditions of Fe(III) species in distorted ligand fields, which is often discussed using variable apparent g-values ($g_{\text{app}}$) (Fig. 2.10).

![Figure 2.10: Variation of the g-value for Fe(III) in high spin state as a function of the zero field splitting parameters $E$ and $D$ at X-band. The height of the black boxes indicates the relative intensity of the resonance lines (slightly modified from Goodmann and Hall, 1994).]

At X-band (8-10 Ghz), cubic coordination Fe(III) sites yield $g_{\text{app}} \approx 2$. In axially distorted sites, the spectrum will exhibit two lines at $g_{\text{app}} = 6$ and $g_{\text{app}} = 2$. In sites with maximum rhombic distortion, the main signal will be observed at $g_{\text{app}} = 4.3$ whereas a weaker signal at around $g_{\text{app}} = 9$ will also be found. A slight departure from the maximum rhombic geometry generates additional signals in the vicinity of 4.3. Considering these examples, the zero-field splitting can provide specific information on the Fe(III) coordination. It is worth noting that this ZFS-generated effect can also produce complex spectral features at a set of $g_{\text{app}}$-values, which makes detailed description of the Fe(III) geometry of the ligand field very complex.

### 2.2.3 Ferromagnetic resonance

In solids with a net magnetization, FMR spectra can be measured and are characterized by relatively broad signals (Fig. 2.11). In FMR spectroscopy, the magnetic field of the material,
considered as the internal field, will add to the external field and will change the resonance condition. The internal field is produced by different magnetic anisotropies, and therefore Equation 2.1 must be rewritten as

\[ \omega = \gamma B_{\text{eff}} \]  

(2.18)

with \( B_{\text{eff}} \) being the sum of the external and internal fields. For magnetite, which is investigated in this thesis, the most important anisotropies are magnetocrystalline and shape anisotropy.

### 2.2.3.1 Magnetocrystalline anisotropy

The magnetocrystalline anisotropy is related to the mineral crystallographic structure (e.g. Dunlop and Özdemir, 1997). It results mainly from the interaction of the paramagnetic cation with the crystal field. In magnetite, this anisotropy results from Fe(II) ions, since Fe(II) has an orbital angular momentum \( L = 1 \), whereas Fe(III) has \( L = 0 \). Hence, Fe(II) will interact with the crystal field and the spin-orbit coupling will give rise to the preferred magnetization directions in the lattice. The anisotropy energy due to magnetocrystalline anisotropy can be written as:

\[ E_{k} = K_{1} V (\alpha_{1}^{2} \alpha_{2}^{2} + \alpha_{2}^{2} \alpha_{3}^{2} + \alpha_{1}^{2} \alpha_{3}^{2}) + K_{2} V \alpha_{1}^{2} \alpha_{2}^{2} \alpha_{3}^{2} \]  

(2.19)

where \( K_{1} \) and \( K_{2} \) are the first and second order anisotropy constants, \( V \) is the volume of a uniform single crystal and \( \alpha_{i} \) are direction cosines of \( M \) with respect to the unit cell axes.

At room temperature, both \( K_{1} \) and \( K_{2} \) are negative and the easy direction is [111]. For magnetite, \( K_{1} = -13500 \ J/\ m^{3} \) and \( K_{2} = -4400 \ J/\ m^{3} \) at room temperature. Using these values in equation (2.18) with \( \alpha_{i} = \frac{1}{\sqrt{3}} \), it can be seen that \( K_{2} \) makes only a minor contribution to the anisotropy energy at room temperature. The magnetocrystalline anisotropy is temperature-dependant. At about 130 K, \( K_{1} \) is zero and at lower temperature it becomes positive and the easy direction of magnetization changes to [100] (Bickford, 1957; Syono, 1963). The strength of the magnetocrystalline anisotropy can be expressed by the anisotropy field \( B_{m} \). For magnetite at room temperature this internal field is equal to (e.g., Dunlop and Özdemir, 1997):
with $M_s$ the saturation magnetization of magnetite. This anisotropy field is oriented along the [111] direction.

### 2.2.3.2 Shape anisotropy

When exposed to an external magnetic field, ferromagnetic materials are subject to a demagnetizing field which is directionally opposite to the external field. The demagnetization field is the product of demagnetization tensor ($N$) and the magnetization ($M$), where $N$ is shape-dependent (Osborn, 1945). An ellipsoid of revolution, $N$, is characterised by the two factors $N_b$ and $N_a$, which are the demagnetization factors along the short and the long axes respectively. Since $N_a < N_b$, it will be easier to magnetize the material along the long axis. This effect can also be regarded as being caused by an internal field in the direction of the long axis which keeps the moments aligned. The strength of the shape anisotropy field can be defined as

$$B_s = \mu_0 [(N_b - N_a)M_s]$$

(2.21)

This is the field that has to be overcome in order to reverse the direction of the magnetic moments, when $B$ is applied along an easy axis. If $B$ is not parallel to the axis, $B_s$ will be diminished.

The effect of shape anisotropy is clearly demonstrated by FMR spectra recorded on a thin film with its plane oriented perpendicular and parallel to $B$ (Fig. 2.11). In the perpendicular configuration, resonance is reached at a much higher external field than in the parallel configuration, due to the strong demagnetizing field which occurs in the former arrangement.
2.2.3.3 Anisotropy and linewidth of FMR spectra

Taking into account the above anisotropies, the total anisotropy field $B_a$ can be written as

$$B_a = B_m + B_s \quad (2.22)$$

When the easy axis, i.e., the direction of $B_a$, is parallel to the applied field, the total field experienced by the particle will be highest. Thus for experiments carried out at a constant frequency the applied field necessary to reach resonance will be minimum in such a configuration. By contrast, the highest resonance field will be obtained in cases where the hard axis is parallel to $B$.

In a powder spectrum, these two configurations will yield the extremes of the absorption spectrum. Hence, for samples with a strong anisotropy the linewidth of the spectrum will be broad. One has to be aware that line broadening also occurs if the particles in a sample vary in size, shape and chemical composition, i.e., in their anisotropy fields. This variability is often the main reason for line broadening in natural samples, and this can mask the signature of the particles’ intrinsic anisotropy.
2.2.5 Differences between EPR and FMR signals
Due to their higher susceptibility the spectra arising from ferromagnetic materials have a
greater intensity than those from paramagnetic signals. In powder samples with random
orientation of the anisotropy axes, FMR spectra tend to be broad, with a linewidth often
exceeding 100 mT. In contrast, EPR signals are generally much narrower, and additional
features such as hyperfine splittings provide information on the chemical properties of the
paramagnetic species. Another important difference between EPR and FMR is their
temperature dependence. Spectral parameters such as the g-value or the hyperfine splittings of
a paramagnetic species do not change drastically with temperature if the ligand field remains
stable and signal intensity increases with decreasing temperature according to the Curie law.
Since magnetocrystalline anisotropy and shape anisotropy are temperature-dependant the
FMR spectra also change with temperature. In samples where both resonance phenomena are
present, the different temperature behavior can be used to differentiate the FMR and the EPR
contributions to the signal (see Chapter 5).

2.2.6 Measurement of EPR and FMR spectra
The FMR spectra can be measured with the same instrument as used for measuring the EPR
spectra, therefore, the following instrumental description is the one of a classical EPR
spectrometer.

The EPR spectrum can be recorded at various fields and microwave frequencies. X-band
EPR spectroscopy with microwave frequency between 8 and 10 GHz is the most common
instrumentation. Other frequency bands such as S-band (2-4 GHz), Q-band (33-35 GHz) and
W-band (95 GHz) are also frequently used. In this study the measurements were performed at
X-band frequencies and additional measurement of Cu(II) were recorded at Q-band.

In an EPR experiment, the microwave frequency is kept constant and the magnetic field is
swept. The EPR spectrometer consists of three main parts, the microwave (mw) bridge, a
magnet generating the static magnetic field, and the probe head.
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Figure 2.12: Schematic representation of an EPR spectrometer. The reflected microwave radiation is demodulated by the bridge and recorded by the signal channel.

The microwave field is built up in the resonator (typically a rectangular cavity) into which the sample is inserted. The radiation, provided by the microwave bridge, is transferred to the cavity via waveguides. The resonator is critically coupled, i.e., the energy of the microwave radiation is fully absorbed by the cavity. At resonance, absorption by the sample causes a loss of this coupling and some of the mw radiation is reflected. The detection of this reflected signal as a function of the magnetic field yields the EPR spectrum. To increase the signal-to-noise ratio, the signal is modulated by an additional small magnetic field with a typical frequency of 100 kHz. As a result, the EPR spectrum is recorded as the first derivative of the absorption spectrum. The zero crossing of the derivative curve is the peak of the absorption and indicates the g-value (Fig 2.13).
Figure 2.13: Absorption spectrum (a) and its first derivative (b) of the spectra in (a) with the g-value indicated. This value corresponds to the maximum in the absorption spectrum.
Chapter 3

The transformation of synthetic hectorite in the presence of Cu(II)

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Submitted to Clays and Clay Minerals

Abstract
A synthetic hectorite was hydrothermally treated in solutions containing fluorine and different Cu(II) concentrations. The structural properties and the thermal stability and conversion of treated hectorites were studied by a combined approach using mainly X-ray diffraction, thermal analyses and electron paramagnetic resonance spectroscopy. The presence of Cu(II) increased the crystallite size during hydrothermal treatment. Copper (II) was both structure-bound and associated with the inner surfaces of the particles. Upon heating, structural destabilization of the hectorite began at about 300 °C as indicated by formation of free radicals. Between 600 and 700 °C the hectorite converted into enstatite, and in the presence of Cu(II) into enstatite and richterite. The formation of richterite as an additional conversion product is explained by the creation of structural weakness followed by fragmentation due to structure-bound Cu(II) in fluorine containing hectorite. Our results suggest, that traces of Cu(II) characteristic for natural environments, can determine the conversion products in high-temperature geochemical systems.
3.1 Introduction
Little is known on the effect of trace impurities at average concentrations in geological systems on the formation and transformation of layer silicates. Of particular interest in this respect is Cu(II), firstly because of its potentially strong structural effects due to preferred axially-distorted octahedral coordination and secondly because it can be detected spectroscopically at low concentrations.

Hectorite is a Mg-rich trioctahedral smectite. It can be synthesized easily under hydrothermal conditions (Decarreau, 1980). Its thermal conversion into enstatite and cristobalite has been described in detail (McKenzie and Meinhold, 1994). Few studies investigated the effect of metal cations on the crystal growth of hectorite. Decarreau (1981) showed that during synthesis Mg(II) can be substituted by Cu(II) to a certain extent. This was confirmed for the co-precipitation of hectorite in presence of Cu(II) during hydrothermal synthesis, while this was not the case, if synthesized hectorite was reacted with a Cu(II) solution at room temperature (Spagnuolo et al., 2004). On the other hand, Mosser et al. (1997) postulated based on electron paramagnetic resonance (EPR) spectra that heating of Cu(II) exchanged hectorite to about 200 - 300 °C led to migration of Cu(II) into the structure. They explained this behavior by the Hofmann-Klemen effect. Mandair et al., (1990) reported that Cu(II) exchanged hectorite thermally converts to enstatite and an amorphous Si phase. The newly formed enstatite contained Cu(II) in its structure. So far, there are no investigations about the effects of Cu(II) traces on the crystallinity and on the thermal conversion of hectorite.

The aim of this research was to demonstrate the effect of trace concentrations of Cu(II) on the crystallinity of hectorite under hydrothermal conditions, its thermal stability and its conversion products, and to localize Cu(II) in the hectorite and its conversion products.

3.2 Samples and methods
An industrially-produced hectorite (Optigel SH Southern Clay Products, Inc, Gonzales, Texas) was used for the experiments. This synthetic hectorite is characterized by a very fine grain size and a high degree of purity (www.scprod.com).

For the hydrothermal treatment 0.2 g LiF and a variable amount of Cu(NO₃)₂ or CuCl₂, corresponding to Cu(II) concentrations of 0, 50, 150 and 500 mg kg⁻¹, were dissolved in 400 ml deionised water. After adding 20 g hectorite to the solution the mixture was homogenised.
to a gel with a Turrax shear mixer. This gel was put into Teflon lined digestion bombs and incubated for 72 hours at 180 °C. The treated gels were converted into powder form by drying at 65 °C, and in the following the samples are named Cu_0, Cu_50, Cu_150 and Cu_500.

The thermal evolution of untreated and hydrothermally-treated hectorite powders between RT and 850 °C was analysed by differential scanning calorimetry (DSC) and thermal gravimetry (TG) using a Netzsch STA 449 apparatus. For these analyses, 100 mg of sample were heated under a continuous gas stream (20 ml/min N₂ protective gas and 50 ml/min of air as purging gas) at a rate of 10°/min.

The thermal conversion of the sample Cu_150 was studied by stepwise heating from 200° to 1000° C in steps of 100°, remaining 1 hour at each step. A more detailed investigation was performed between 600 and 700°C where the sample was heated in steps of 25°, again remaining 1 hour at each step. Heating, cooling, and storage of the samples took place under ambient atmosphere.

The structural properties of the samples were determined by X-ray diffractometry (XRD, Siemens D5000, with CuKα radiation). The samples were dispersed in ethanol and pipetted on a silicon single crystal plate. X-ray scans were run in step scan mode from 2° to 65° 2θ with a step width of 0.03° 2θ and a counting time of 8 seconds at each step. Single line fitting was performed with the Bruker Topas V2.1 software package. The crystallite size of the samples was evaluated by the full width at half maximum (FWHM) of the (001) and the (060, 330) peaks according to the Scherrer equation followed by the method described by Klug and Alexander (1975).

Fourier-transformed Infrared (FTIR) and EPR spectroscopy were conducted on the starting material, the hydrothermally-treated and stepwise-heated samples. The FTIR spectra were obtained either with a Bruker IFS 66/S or a Perkin Elmer 2000 from pellets prepared by mixing about 2 mg of the sample with 200 mg of KBr. The local structural environments of Cu(II) and Fe(III) were investigated by EPR spectroscopy. The principles of this method can be found elsewhere (e.g., Wertz and Bolton, 1972). The X-band (9.8 GHz) EPR spectra were recorded at room temperature on a Bruker EMX spectrometer, with a power of 6mW, a modulation amplitude of 0.1 mT and a modulation frequency of 100 kHz. A Hall probe was used to control the field strength. Low-temperature measurements at -258 °C were carried out on a Bruker ELESYS at 9.48 GHz with a power of 0.2 mW, and a modulation amplitude of 0.1 mT. In addition, Q–band (33.418 GHz) measurements at room temperature were performed on the sample heated to 1000 °C on a Bruker Elexsys E580. By employing higher
frequency, better resolution is obtained for samples with anisotropic g-values or for samples in which different paramagnetic species with different g-values coexist. The simulation of the spectra was carried out using the Easyspin routine, a Matlab code developed in the EPR group at ETH Zürich (Stoll and Schweiger, 2006).

The EPR spectroscopy was completed by measuring samples Cu_150 and Cu_500 after EDTA treatment. For this treatment, 2 to 4 grams of sample were suspended in 400 ml of 0.2 M Na$_4$-EDTA (pH 11) and mixed with an end-over-end shaker for 24 hours. After mixing, the suspension was centrifuged and the supernatant discarded. The whole procedure was repeated once. Afterwards, the sample was washed in ethanol until the pH in the supernatant was stable. All treated samples were dried at 65 °C.

For transmission electron microscopy (TEM; Philips CM200 operated at 200 kV), the sample Cu_150 after heating to 650 °C was selected. For the preparation, the powder was suspended in acetone and deposited on carbon coated copper grids. Selected electron diffraction (SAED) patterns were indexed using the software package EMS (Stadelmann, 1987).

3.3 Results

3.3.1 Hydrothermal treatment
The XRD pattern of the starting material showed characteristic peaks for hectorite (Fig. 3.1). Hydrothermal treatment led to a narrowing of the peaks. The narrowing was best observed for the (001) and (060, 330) peaks. The crystallite sizes deduced from the FWHM of these two Bragg peaks and expressed as mean coherence length, increased upon hydrothermal treatment (Fig. 3.1, inset). This increase was more pronounced for (060, 330). The presence of Cu(II) in the hydrothermal solution enhanced this effect (Fig. 3.1).
The FTIR spectra of the starting material revealed in the near infrared region a band at 3680 cm\(^{-1}\) typical for O-H stretching vibrations in hectorite (data not shown). According to Farmer (1974), the broad bands at 1014 and 455 cm\(^{-1}\) can be attributed to Si-O stretching, the bands at 660 cm\(^{-1}\) and the weak shoulder at 538 cm\(^{-1}\) to O-H bending and Mg-O vibrations, respectively (Fig. 3.2). After hydrothermal treatment the bands became sharper and an additional shoulder occurred at 1072 cm\(^{-1}\) (Fig. 3.2). The addition of Cu(II) did not lead to significant changes in the position of the bands.
Figure 3.2: Room-temperature mid-FTIR spectra of the starting material (a), and the hydrothermally-treated samples Cu_0 (b), Cu_150 (c), and Cu_150 stepwise heated at 600 °C (d), 650 °C (e), and 1000 °C (f).

Wide-range EPR spectra of the starting material revealed a broad feature centered at $g \approx 2$ and a resonance at $g = 4.3$ (Fig. 3.3a). These features could be attributed to traces of ferric oxides/hydroxides, and to Fe(III) in octahedral sites with rhombic distortion, respectively (e.g.
Meads and Malden, 1975; Gehring and Hofmeister, 1994). No significant spectral changes were observed upon hydrothermal treatment (Fig. 3.3b). Adding Cu(II) nitrate or chloride to the hydrothermal solution led to an additional hyperfine split signal (Fig. 3.3c).

![EPR spectra](image)

**Figure 3.3**: Wide-range EPR spectra of the starting material (a), and the hydrothermally-treated samples Cu_0 (b) and Cu_150 (c).

The four features are typical for parallel components of Cu(II) with a nuclear spin of 3/2 (e.g., Wertz and Bolton, 1972). The perpendicular component consisted of a doublet with perpendicular \( g \)-values (\( g_\perp \)) of 2.05 and 2.04. The relative intensity of the two peaks varied with Cu(II) concentration (Fig. 3.4).

Low temperature measurements at -258 °C of sample Cu_150 exhibited higher resolution of the parallel component whereas the perpendicular component revealed only one feature with \( g_\perp = 2.05 \) (Fig. 3.5). Spectral parameters for two parallel components with slightly different \( g_\parallel \)-values of 2.40 and 2.39 and \( A_\parallel = 10.0 \text{ mT} \) could be deduced from the low-temperature spectrum. Treatment with EDTA led to a pronounced decrease in the Cu(II) signal intensity (Fig. 3.4). The remaining signal revealed no significant changes in the position of the parallel component, and the perpendicular component broadened and exhibited no doublet.
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Figure 3.4: Narrow-range EPR spectra of the hydrothermally-treated samples Cu_50 (a), Cu_150 (b), Cu_500 (c) and Cu_500 after EDTA treatment (d).

Figure 3.5: Low temperature EPR spectrum at -258 °C of the hydrothermally-treated sample Cu_150 (a) and enlarged view of the parallel component (b).
3.3.1 Thermal treatment
The DSC curve of the starting material revealed a first endothermic peak at 149 °C associated with a weight loss of 17 %. A second weak endothermic peak was found at 734 °C followed by a sharp exothermic peak at 748 °C. The latter occurred simultaneously with the step in the TG curve between 747 and 753 °C (Fig. 3.6a).

All hydrothermally-treated samples exhibited an endothermic peak at about 145 °C. The Cu-free sample showed two additional endothermic peaks, a broader one at 714 °C and a sharper one at 739 °C (Fig. 3.6b). The first peak occurred before whereas the second one within the step in the TG curves between 722 and 744 °C. The DSC curve of the Cu-treated samples steadily decreased between 300 and 600 °C. At higher temperature a pronounced endothermic feature with a peak at 702 °C was found (Fig. 3.6c). This endothermic feature occurred concomitantly with a major weight loss between 690 and 725 °C.
X-ray diffractometry of the products after DSC analysis revealed enstatite (MgSiO$_3$) in all samples (Fig. 3.7). In addition, Mg-F richterite (Na$_2$Mg$_6$Si$_8$O$_{22}$F$_2$) (Gibbs et al., 1962) and a distinct diffraction peak of cristobalite (SiO$_2$) were detected for the Cu-treated samples.
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Figure 3.7: XRD of the starting material (a), and the hydrothermally-treated samples Cu_0 (b) and Cu_150 after calorimetric analysis; E = enstatite, C = cristobalite, R = richterite.

The XRD analysis of the conversion via stepwise heating of the sample Cu_150 revealed an intact hectorite with \(d_{(001)}\) spacing of 9.77 Å at 600 °C (Fig. 3.8). Additional peaks occurred after heating to 625 °C, which could be assigned to the (310), (110), and (040) reflections of F-rich Mg-richterite (Gibbs et al., 1962) and to major reflections of enstatite. After heating to 650 °C the hectorite peaks vanished and at 700 °C cristobalite was detected. At 1000 °C richterite disappeared and the peaks of enstatite and cristobalite became sharper, and additional peaks attributed to proto-enstatite occurred. Stepwise heating of Cu-free samples showed no richterite. The formation of richterite in the presence of Cu(II) was confirmed by TEM analysis of the sample Cu_150 heated at 650 °C. This phase exhibited a needle-like morphology and its selected area electron diffraction patterns could be indexed for a monoclinic amphibole C2/m (Fig. 3.9).
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Figure 3.8: XRD of the hydrothermally-treated sample Cu_150 after stepwise heating at 600 °C (a), 625 °C (b), 650 °C (c), 700 °C (d) and 1000 °C (e); H = hectorite E = enstatite, PE = protoenstatite, C = cristobalite, R = richterite.

Figure 3.9: Bright field image of the hydrothermally-treated sample Cu_150 heated at 650°C showing the needle-shaped amphibole (a); (b) shows the (-202) SAED pattern for monoclinic amphibole in the area marked in (a). The pattern was taken with the aperture placed over the two lath-like crystals on top of the aggregate.
The FTIR spectrum of the Cu_150 heated at 600 °C exhibited lower resolution compared to the RT spectrum and only the major bands were visible (Fig. 3.2d). After heating at 650 °C the band at 3680 cm\(^{-1}\) vanished indicating the loss of hydroxyl-groups. Furthermore, in the range characteristic for Si-O stretching (1100 to 800 cm\(^{-1}\)), several bands were generated due to the formation of enstatite and richterite. Considering these two phases, the bands at 762, 729, 680 and 650 cm\(^{-1}\) could be assigned to vibrations of tetrahedral chains whereas the bands at lower wave numbers (545, 507, 430 cm\(^{-1}\)) could arise from lattice modes (e.g., Tarantino et al., 2002) or from Mg-O vibrations (480 cm\(^{-1}\)) (Strens, 1974). At 1000°, the FTIR spectrum became better resolved and all bands were attributed to enstatite (Bilton, 1972). The distinct shoulder at 796 cm\(^{-1}\) is indicative of cristobalite (Gadsen, 1975). Compared to the spectrum at 650 °C, the band at 762 cm\(^{-1}\) was missing in the sample heated at 1000 °C.

Room-temperature EPR spectroscopy of the sample Cu_150 heated at 300°C showed the generation of a sharp signal at \(g = 2\). This signal reached a maximum for the sample annealed at 600°C and vanished above 700°C (Fig. 3.10). Such a signal can be assigned to free radicals (e.g., Wertz and Bolton, 1972). The formation of radicals was also observed for Cu-free samples. The Fe(III) signal at \(g = 4.3\) remained stable for treatments up to 600 °C. For samples annealed at higher temperatures new absorption features in the \(g\)-value range of 3.3 to 9 were generated (Fig. 3.11). The better resolved signals indicated distinct Fe(III) sites in the conversion products with different rhombic distortions (Jones et al., 1974). The Cu(II) signal showed only little changes for samples heated up to 600 °C, (Fig. 3.4 and 3.10), but a new signal with a strong feature at \(g = 2.36\) and smaller components at \(g < 2\) appeared for the sample annealed at 625°C (Fig. 3.10). The signal at \(g = 2.36\) increased at the expense of the signal at \(g = 2.05\) for annealing temperatures between 625° and 650°C. No further increase is observed for the higher annealing temperatures. At 1000 °C the signal was better resolved.
Figure 3.10: EPR spectra of the hydrothermally-treated sample Cu_150 after stepwise heating at 600 °C (a), 625 °C (b), 650 °C (c), 700 °C (d) and 1000 °C (e)
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The Q-band EPR spectrum of the sample Cu_150 heated to 1000 °C exhibited two signals, characteristic for Cu(II) in sites with rhombic and axial distortions, respectively (Fig. 3.12). The spectral parameters for the rhombic site were $g_{xx} = 2.33$, $g_{yy} = 2.29$, $g_{zz} = 1.99$, $A_{zz} = 15 \text{ mT}$, and $A_{xx} = 7 \text{ mT}$; no splitting was found for the y component. For the axial site $g_{\perp} = 2.05$ was measured, while the parallel component was unresolved. The best simulation of the spectrum was obtained with $g_{\parallel} = 2.400$ and $g_{\perp} = 2.055$ for the axial sites (Fig. 3.12). In addition a ratio of 8 between Cu(II) in rhombic and axially distorted sites was estimated from the spectral simulation.
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3.4 Discussion

3.4.1 Cu in the modified starting material
The XRD and FTIR data (Klopprogge et al. 1998) clearly show that the crystallinity, i.e., the size of the crystallites increases preferentially within the basal plane of the hectorite during hydrothermal treatment. The less pronounced narrowing of the basal reflections in the diffractograms may also be due to the presence of stacking faults, which limit the coherence length. Since no Mg and Si were added to the solutions, the increase in crystallite size can be explained by coalescence, or by dissolution-precipitation (recrystallisation). The fact that Cu(II) enhanced the crystallinity suggest that the metal cation is rather substituted into the hectorite structure than forming a separate phase. This interpretation is supported by the hyperfine splitting of the EPR signals which indicates isolated Cu(II) binding sites associated with hectorite. The well-resolved signal can be assigned to Cu(II) in axially distorted sites in the structure or the inner surface, i.e., interlayers and hexagonal cavities of the hectorite.

Figure 3.12: Experimental (a) and simulated (b) Q-band EPR spectra of the hydrothermally-treated sample Cu_150 heated at 1000 °C.
The EPR parameters for the parallel components obtained from low-temperature measurements, point to two Cu(II) sites with slightly different axially distorted symmetry (Fig. 3.5). Taking this into account, the doublet near $g = 2$ recorded at RT (Fig. 3.4) can also be explained by the two Cu(II) sites. Different distributions are possible: (1) both sites are in octahedral sheets, (2) both sites are at the inner surfaces, or (3) the sites are distributed in the structure as well as at the inner surfaces. The EPR signal does not allow distinguishing between these configurations, but the latter possibility is most likely. Changes in the relative intensity of the two signals with increasing Cu(II) concentration can be interpreted as changes in the relative occupation of the different Cu(II) sites. The fact, that EDTA treatment does not separate the two sites indicates that both sites can occur in protected and non-protected locations. Copper(II) bound in octahedral layers is generally protected from EDTA attack except for locations exposed at edges. Similarly, Cu(II) bound in interlayers is easily removed by EDTA only if it is located near the edge of the interlayer. Moreover, all of this gives clues that our hydrothermal treatment can lead to the incorporation of Cu(II) in the hectorite structure most likely in Mg(II) sites.

### 3.4.2 Thermal conversion

The thermal analysis demonstrates that Cu(II) affects the calorimetric behavior of hectorite and its conversion products. The difference in the thermal behavior of the samples with and without Cu(II) becomes visible above 600 °C. In this temperature range, the starting material is characterized by simultaneous dehydroxylation and the conversion into enstatite. The sharp exothermic peak for the untreated starting material indicates that the conversion of hectorite goes along with an increase in crystallinity. The absence of such a dominant exothermic peak for the hydrothermally-treated samples suggests that the hydrothermally-treated samples are better crystallised, which agrees well with the XRD data.

Chipera and Bish (2002) showed for hectorite that defluorination takes place at higher temperatures than dehydroxilation. With this in mind the two endothermic features in the hydrothermally-treated Cu(II)-free sample can be interpreted as two-step structural breakdown, the first feature related to dehydroxilation and the second one to defluorination of the thermally more stable fluorine-enriched areas in the hectorite. The occurrence of only one endothermic feature at lower temperature for the Cu(II) treated samples suggests no
significant defluorination. Moreover, in such a case, the presence of Cu(II) triggers the formation of Mg-F richterite. Since this phase can also be a conversion product of hectorite in the absence of Cu(II) but at a more than five times higher concentration of fluorine than in our experiment (Granquist and Pollack, 1959), it is likely that Cu(II) influences either the distribution or the thermal stability of fluorine in the sample. In the first case the simultaneous enrichment of Cu(II) and fluorine would lead to broadening of the Cu(II) EPR signal due to dipole-dipole interactions, which was not observed. Furthermore, richterite formation is not affected by the Cu/F ratio in the hydrothermal solution. All of this argues in favour of the second explanation, in which the conversion of hectorite occurs while still containing fluorine. As a consequence, the conversion product contains a mineral phase such as Mg-F richterite, which can stabilise fluorine. Considering the mechanism of such a conversion, it is conceivable that the Cu(II) substitution of Mg (II) in octahedral layers of hectorite induces local instabilities due the Jahn-Teller effect. At these sites the breakdown of the octahedral layers preferentially occurs and initiates the conversion. X-ray diffraction shows that richterite is only an intermediate product and converts upon further heating to 1000 °C into enstatite. At this temperature, both Cu(II) and Fe(III) occur in better crystallized structures as indicated by XRD and EPR spectroscopy. Schematically the conversion can be illustrated as follows (Fig. 3.13). In the absence of Cu(II), the randomized breaking apart of the hectorite structure occurs simultaneously with the dehydroxylation and the release of fluorine. As a consequence, no amphibole can be formed. In the presence of Cu(II), the breaking apart of the hectorite structure begins at lower temperature at sites with Cu(II) substitution. Fragmentary hectorite which contains fluorine then adopts a stable amphibole structure, while fragments without fluorine convert directly to enstatite (Fig 3.13). Further increasing temperature converts the amphibole into an enstatite.
Figure 3.13: Schematic model of the thermal conversion of fluorine-enriched hectorite with (right) and without (left) structure-bound Cu(II); open circles symbolise F\textsuperscript{−} anions, and black circles octahedral sites with Cu(II) replacing Mg(II) or Li(I); (a) represents hectorite after hydrothermal treatment (b) an intermediate stage with hectorite fragmentation; (c) formation of enstatite and richterite, respectively and (d) the breakdown of richterite.

3.4.3 Spectroscopic evidence for the conversion of hectorite

On a molecular level, first indications for a thermally induced destabilisation of the hectorite structure is indicated by the appearance of a sharp EPR signal at $g = 2$ at about 300 °C. Such a signal, which can be assigned to a free radical has been observed in different natural and synthetic clay minerals (e.g., Meads and Malden, 1975; Gehring et al., 1993). Often, the radical disappears upon heating to about 400 °C, i.e., structural defects heal. Schosseler and Gehring (1996) reported that upon heating such radicals were generated in vermiculite prior to its thermal breakdown. This was explained as first sign of structural destabilisation. The occurrence of thermally generated radicals in our hectorite agrees well with the findings of Mandair et al. (1990). In their study on synthetic hectorite, they observed a change in the $^{29}\text{Si}$
NMR signal at about 400 °C and explained it by an increase in oxygen anions which are not bridging SiO$_4$ tetrahedra. This structural change leads to Si dangling bonds (E’ centers) and non-bridging oxygen hole centers which give rise to free radical signals (Mohanty et al., 2003). The maximum of the $g = 2$ signal in the Cu$_{150}$ sample at 600 °C points to the highest concentration of defects close to the breakdown of the hectorite structure. At this temperature interlayers are collapsed as indicated by $d_{(001)} < 10$ Å. These XRD and EPR data indicate that the fragmentation of hectorite starts at 600 °C. The similarity of the axial Cu(II) spectra yielded at this temperature and at RT provides evidence that the Cu(II) coordination is only little affected by the early fragmentation stage. At $T > 600$ °C, where the hectorite structure breaks down, the spectra suggest that a minor part of Cu(II) remains in near regular octahedral sites whereas the major part of Cu(II) is forced into distorted sites with rhombic characteristics. These spectral changes suggest that Cu(II) is structure-bound in richterite and/or enstatite.

The orthopyroxene structure has two sites: M1 has rhombic characteristics, whereas M2 is strongly distorted with 6 unequal M-O bond lengths. The Mg-amphiboles (e.g., antophyllite, cummingtonite, richterite) have at least one axially deformed octahedral site (Hawthorne and Oberti, 2007, American Mineralogist Structure Database). Among these amphiboles richterite has a structure where three out of four octahedral sites have axial distortion. Such sites exhibit an ideal geometry for Cu(II) as Jahn-Teller cation (Rao et al., 1992). This suggests that Cu(II) associated with hectorite can easily be transformed into axial sites of richterite. The fact that Cu(II) triggers the formation of Mg-F richterite at a low fluoride content supports this assumption. However, this cannot be verified unambiguously by the EPR data, since also enstatite contains distorted octahedral sites which generate Cu(II) spectra (Mandair et al., 1990) similar to those found for our samples. The stability of the Cu(II) signal at 1000 °C, where no richterite was found by XRD, proves Cu(II) in enstatite. This Cu(II) could be inherited from hectorite as well as richterite which converts into the pyroxene above 900 °C.

The electronic state of Cu(II) in the dominant rhombic sites of enstatite at 1000 °C can be evaluated by using the R factor proposed by Billing et al. (1971). This factor is defined as

$$R = \frac{(g_{yy} - g_{zz})}{(g_{xx} - g_{yy})}$$ (3.1)
for $g_{xx} > g_{yy} > g_{zz}$. The ground state for $R > 1$ is predominantly $d_{z^2}$, whereas for $R$-values $< 1$ the characteristic ground state is $d_{x^2-y^2}$. An $R = 7.5$ for the rhombic sites in sample Cu$_{150}$ treated at 1000°C thus indicate a $d_{z^2}$ ground state of Cu(II) in the enstatite. Such a configuration is unusual since Cu(II) in rhombic distorted sites has generally a $d_{x^2-y^2}$ ground state (Poonguzhali et al., 2002). The $d_{z^2}$ ground state may probably originate from local compression of rhombic sites in the enstatite structure.

### 3.5 Conclusions

1) The presence of Cu(II) during the hydrothermal treatment of the synthetic hectorite increases the crystallize size.

2) During hydrothermal treatment, a fraction of Cu(II) is structure-bound in octahedral layers. The substitution of Mg(II) by Cu(II) creates domains of structural weakness which, upon heating, cause structural fragmentation at rather low temperature. In the presence of fluorine, the thermally induced structural fragments can convert into Mg-F-richterite.

3) The structural destabilisation of the hectorite begins at about 300 °C, and the conversion into enstatite and/or richterite occurs between 600 and 650 °C. After this conversion Cu(II) can be structure-bound both in richterite or enstatite. At 1000°, after conversion of the intermediate richterite into enstatite, Cu(II) is bound in compressed rhombic sites of the enstatite with a $d_{z^2}$ groundstate and in axial sites.

4) Our results suggest, that traces of Cu(II) characteristic for natural environments, can determine the conversion products in high-temperature geochemical systems.
Chapter 4

Ferromagnetic resonance and magnetic characteristics of intact magnetosome chains in *Magnetospirillum gryphiswaldense*

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Abstract

The magnetic characteristics of intact magnetosome chains in *Magnetospirillum gryphiswaldense* bacteria were investigated by means of static and dynamic magnetic analyses and ferromagnetic resonance spectroscopy. The nano-sized magnetosomes are generally in a stable single-domain state, but magnetosomes smaller than 30 nm characteristic of superparamagnetic magnetite particles were also found. Alternating current (AC) susceptibility indicates that all magnetosomes are blocked below 150 K. At room temperature the anisotropy of *Magnetospirillum gryphiswaldense* is dominated by the shape of the magnetosome chains. Low-temperature ferromagnetic resonance (FMR) spectroscopy indicates that this dominant shape anisotropy can affect the detection of the Verwey transition at 100 K. The static and dynamic magnetic analyses show that the Verwey transition is smeared and that our magnetotactic bacteria fail the Moskowitz test. This failure is explained by the biomineralization of non-stoichiometric magnetosomes. This interpretation is based on the increase in high-field susceptibility and the distinct peak in the out-of-phase component of the AC susceptibility below 50 K. These results are attributed to freezing of spins associated with defect structures in the core and at the surface of nano-sized magnetosomes. The results obtained from *Magnetospirillum gryphiswaldense* demonstrate that intrinsic properties of nano-sized magnetosomes are significantly influenced by non-stoichiometry and by the anisotropy excited from their arrangement in the bacteria.
4.1. Introduction
Magnetotactic bacteria were first discovered about 30 years ago (Blakemore, 1975). Since then various species from lacustrine, terrestrial and marine environments have been described (e.g., Paasche et al., 2004; Fassbinder et al., 1990; Petersen et al., 1986). Only a few wild-type bacteria have been cultured in the laboratory (Flies et al., 2005). Prominent among these is *Magnetospirillum gryphiswaldense*, which was first found in the river Ryck near Greifswald, Germany (Schüler, 2002).

Magnetotactic bacteria possess the ability to form intercellular stable single-domain (SSD) magnetite with a narrow range of grain sizes and shape distributions (Blakemore and Frankel, 1989). Smaller particles in the superparamagnetic range (< 30 nm) have also been observed in association with magnetotactic bacteria (Pan et al., 2005a).

Magnetite particles enclosed in membranes are specified as magnetosomes; they are usually arranged in chains along their easy axes, i.e., the [111] direction (Simpson et al., 2005). The development of a genetic system for *M. gryphiswaldense* opened the door for microbiological investigation of the biomineralization of magnetosomes (Schultheiss and Schüler, 2003). Scheffel et al. (2006) pointed out that the alignment of the magnetosomes is a genetically-controlled process. It is generally assumed that the close alignment of magnetosomes in chains, which maximises the magnetic moment felt by these motile bacteria, helps them to orient along the Earth’s magnetic field while seeking optimal oxygen conditions (Blakemore and Frankel, 1981). It has also been suggested that intercellular iron could be used as energy storage for redox-cycling or iron homeostasis (Mann et al., 1990).

Magnetotactic bacteria can be easily identified under the transmission electron microscope (TEM) because of the alignment of uniformly-sized magnetosomes in chains. Transmission electron microscopy is a powerful tool for studying morphological and structural properties of selected numbers of magnetosomes, but it delivers only limited information about magnetotactic bacteria in bulk samples. In recent years several approaches have been developed to detect these organisms in bulk samples using specific magnetic properties of magnetite. An intrinsic property is known as the Verwey transition. On cooling through this transition, magnetite undergoes a structural change from cubic to monoclinic and magnetocrystalline anisotropy energy increases by one order of magnitude. In stoichiometric magnetite this transition occurs at about 120 K, and it is characterized by distinctive changes in magnetization and coercivity (e.g., Özdemir et al., 2002; Muxworthy and McClelland, 2000). The Verwey transition associated with magnetotactic bacteria often occurs at a lower
temperature ($T_v$) around 100 K, and it has been suggested that the lower $T_v$ is an intrinsic property (Pan et al., 2005a; Prozorov et al., 2007). Significant lowering of $T_v$ to about 20 K has been reported for 50 nm nanoparticles (Goya et al., 2003), a size often found in magnetotactic bacteria (e.g., Pan et al., 2005a). Recent reviews of the Verwey transition have shown that the physical details of this transition are still not fully understood (Walz, 2002; Garcia and Subias, 2004). Nevertheless, the empirical Moskowitz test (Moskowitz et al., 1993), which compares saturation isothermal remanent magnetization (SIRM) of magnetosomes above and below $T_v$, has been successfully applied as a magnetic proxy to detect magnetotactic bacteria cultured in the laboratory (Posfai et al., 2006) and collected from recent sediments (Pan et al., 2005b). This test is based on two facts: that in the monoclinic magnetite phase magnetocrystalline anisotropy is much greater than in the cubic phase, and that the magnetosomes aligned in chains generate shape anisotropy. The Moskowitz test proposes that the relative magnitude of demagnetization upon warming across the Verwey transition after field and zero-field cooling conditions is indicative of magnetotactic bacteria. The failure of the test due to smearing or even absence of the Verwey transition has been generally explained by stoichiometric changes due to oxidation after the biomineralization of the magnetite (Moskowitz et al., 1993). The possibility that the Moskowitz test may fail as a result of intrinsic non-stoichiometry of the magnetosomes or because of other physical properties has not yet been clearly resolved.

Recently several authors have proposed ferromagnetic resonance (FMR) spectroscopy, which is sensitive to magnetic anisotropy, as a means of detecting magnetotactic bacteria (Weiss et al., 2004b; Kopp et al., 2006a). They report that the FMR spectra of intact magnetotactic bacteria recorded at room temperature are dominated by shape anisotropy due to the alignment of magnetosomes in chains. The comparison of FMR spectra recorded at room temperature and 77 K shows that the anisotropy properties change significantly above and below $T_v$. These FMR data, however, provide no information on the effect of the anisotropy properties on the Verwey transition.

This study, which combines magnetic analysis and FMR spectroscopy, addresses the anisotropy properties and the effect of non-stoichiometry on the magnetization of magnetotactic bacteria in a temperature range between room temperature and 5 K. We used intact bacteria of the strain *M. gryphiswaldense* because their microbiological properties have been extensively studied (Schüler, 2002, 2004), they can be easily cultured in the laboratory, and they form equidimensional magnetosomes for which the cubic magnetocrystalline
anisotropy is dominant. The magnetic and spectroscopic data reveal for the investigated magnetotactic bacteria a smeared Verwey transition with a temperature of about 100 K.

### 4.2. Samples and methods

The magnetotactic bacteria *M. gryphiswaldense* strain MSR-1, DSM 6361 obtained from the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ), were grown in a medium described by Heyen & Schüler (2003) under micro-aerophilic conditions in 2.5 L batch cultures. For transmission electron microscopy (TEM) the bacteria were fixed in 3% glutaraldehyde/PBS for 2 hours, washed and mixed into a compound with 2% agar. Pieces were cut, dehydrated in a graded series of ethanol and penetrated gradually with Epon 812 resin. After polymerization at 60°C the blocks were trimmed and 60 nm sections were cut and transferred onto formvar/carbon-coated copper grids. The ultra-thin sections were analysed in a Philips CM200 FEG transmission electron microscope.

For the mineralogical, magnetic, and spectroscopic analyses the bacteria were freeze-dried. The mineralogical properties of the magnetosomes were determined by X-ray diffraction (XRD) on a PANalytical X’Pert Pro apparatus, with Cu-K$_\alpha$$_1$ radiation over a 2 $\theta$ range of 15° to 65° with 80 sec per 0.02° step. The sample was fixed on a flat silicon plate with zero background. Using the Bragg equation for cubic systems, the lattice cell parameter $a_0$ was determined by extrapolation of $a$ parameters calculated from each $hkl$ reflections and cot($\theta$)/sin($\theta$) against $\theta = 90^\circ$. The details of this procedure are described elsewhere (Klug and Alexander, 1975). The cation deficiency $\Delta$ for the magnetosomes (Fe$_{3(1-\Delta)}$O$_4$) was deduced by applying Vegard’s rule using the lattice cell parameters for maghemite (Fe$_{2.66}$O$_4$) with $\Delta = 0.11$ and magnetite with $\Delta = 0$ as end-members.

A vibrating sample magnetometer (VSM, Princeton Instruments) was used to measure the magnetic moment ($V \times M$, where $M$ is the magnetization and $V$ the unknown volume) in an applied field ($B$) of the sample between 60 K and 293 K during stepwise warming. The hysteresis loops were recorded while sweeping the external field (sweeping mode) starting in a 1 T field. The coercivity ($B_c$), the remanent magnetic moment ($V \times M_r$, where $M_r$ is the remanent magnetization) and the saturation magnetic moment ($V \times M_s$, where $M_s$ is the saturation magnetization) were determined. In addition, the coercivity of remanence ($B_{cr}$) was determined at room temperature (RT), 130 K, 100 K and 77 K. The saturating field was 500 mT and the measurements were made with a 5 mT increment.
In addition, hysteresis loops in fields up to 5 T and high-field magnetization curves up to 9 T while stepping the external field (persistent mode) were conducted between 150 K and 10 K using a Quantum Design PPMS 9 magnetometer. Hysteresis loops at 20 K in zero-field-cooled (ZFC) and field-cooled (FC in a 1 T field) modes were recorded.

First-order reversal curve (FORC) diagrams were generated via measurements performed at room temperature. A FORC diagram is derived from repeated measurement of $M(B)$ curves, by which, in addition to the major hysteresis cycle, minor loops (113 in this study) between a saturating positive field of 1 T and a number of reversed fields are measured. In a FORC diagram, the horizontal axis denotes the coercive field $B_c$ and is indicative of the grain size range, whereas the field $B_b$ plotted on the vertical axis indicates magnetic interactions. A detailed description of the method can be found elsewhere (Roberts et al., 2000). The data were analysed with a Matlab code (M. Winklhofer, personal communication, 2006).

In order to estimate the characteristics of the magnetic interaction in the bulk sample, a Henkel plot at 130 K was determined. At this temperature the requirement of unaxial anisotropy is fulfilled, such that the Stoner-Wohlfarth model for non-interacting particles can be used. Starting from the AC demagnetized state, an isothermal remanent magnetization (IRM) was imparted to the sample in a weak DC field. After measurement of the IRM, the sample was AC demagnetized completely. A stronger field was applied and the new IRM measured. This step-by-step procedure was repeated until saturation IRM was achieved. Next, DC demagnetization of saturation IRM was observed. The sample was given saturation IRM in a 1 T field, after which a field was applied in the reverse direction and the ensuing remanent magnetization was measured. The sample was again saturated and the procedure repeated with ever stronger reverse fields until the sample was saturated in the reverse field direction. These experiments were performed on a Quantum Design PPMS 9 magnetometer.

The same instrument was used for the saturation isothermal remanent magnetization (SIRM) conducted in a field-cooled and zero-field-cooled mode. In the latter mode the ZFC sample was magnetized in a 2.5 T field at 10 K and subsequently warmed in a zero field up to room temperature in steps of 5 K. In the FC mode, in contrast, the sample was exposed to a 2.5 T field upon cooling. The SIRM data were used for the delta-delta test of Moskowitz (Moskowitz et al., 1993) which quantifies the enhancement of the FC and ZFC curves below $T_v$, by defining the $\delta_{fc}/\delta_{zfc}$ ratio where $\delta = M_{80K} - M_{150K} / M_{80K}$.

The dynamic magnetization behavior of the sample was measured by means of AC susceptibility. The in-phase ($\chi'$) and the out-of-phase susceptibility ($\chi''$) were recorded at
different amplitudes ($B_{ac}$) between 0.1 and 1.2 mT and frequencies in the range from 200 Hz to 10 kHz.

For the FMR experiments freeze-dried intact magnetotactic bacteria were fixed in the glass tube with paraffin. The FMR spectra at room temperature were recorded on a Bruker EMX at a microwave frequency of 9.8 GHz, with a power of 0.06 mW, modulation amplitude of 0.1 mT, and a modulation frequency of 100 kHz. The angular dependence of the FMR spectra was determined by rotating the glass tube with a goniometer mounted on the top of the cavity. For the low-temperature experiment a Miniscope MS spectrometer was used with microwave frequency of 9.4 GHz, a power of 0.2 mW, and modulation amplitude of 0.2 mT. The FMR spectra were recorded after cooling the sample in the spectrometer cavity exposed to a 250 mT field. Because of the spectrometer design, the measurement at 77 K was conducted in a special dewar, after cooling the sample from 295 K to liquid nitrogen temperature in a 250 mT field.

For all FMR spectra, the effective resonance field ($B_{eff}$), the corresponding effective $g$-value ($g_{eff}$), and the linewidth $\delta B$ were determined (Fig. 4.7a). The $B_{eff}$ is defined as the field of zero-crossing in the derivative spectrum (Okamura, 1952; Weiss et al., 2004b). The effective $g$-value ($g_{eff}$) was derived from $B_{eff}$ using the resonance relation $g_{eff} = h \nu / \mu_b B_{eff}$, where $h$ is Planck’s constant ($6.626 \times 10^{-34}$ Js), $\nu$ is the microwave frequency, and $\mu_b$ is Bohr’s magneton ($9.274 \times 10^{-24}$ J/T) (Wertz and Bolton, 1972). In addition, the FMR data were classified by subdividing the spectra into a low-field side defined by an applied field $B < B_{eff}$, and the high-field side with $B > B_{eff}$ (Griscom, 1974).

The simulation of the FMR spectra was performed using the Matlab code written by Kopp et al. (2006b) for cubic or uniaxial systems or a linear combination of the two. The congruence of the experimental and simulated spectra was maximized by a non-linear least-square fitting procedure (Kopp et al., 2006b).

4.3 Results

4.3.1 Structural and morphological properties
Inspection of the sample under the TEM revealed intact chains of about 1 µm length containing about 20 to 25 magnetosomes (Fig. 4.1). The individual particles were nearly equidimensional and exhibited an average diameter of 35 ± 5 nm. Some smaller particles (diameter < 30 nm) were found. Given the millions of bacteria in the sample, however, the
grain size information reflects an estimate and not a statistical value. The spacing between magnetosomes in chains was less than 10 nm, whereas the spacing between chains was more than an order of magnitude larger. X-ray diffractometry of the bulk samples at RT showed a cubic phase with $a_0 = 0.83945 \pm 0.00001$ nm. The best congruence of the diffractogram pattern was obtained with the data for magnetite published by Wright et al. (2002). Apart from the peaks assigned to magnetite, no additional peaks were found. For the magnetosomes a cation deficiency $\Delta$ of 0.01 was deduced from the lattice cell parameter $a_0$.

![Figure 4.1: TEM micrograph of intact *M. gryphiswaldense* bacteria with intercellular chains of magnetite nanoparticles.](image)

### 4.3.2 Magnetic measurements

#### 4.3.2.1 Static magnetization

At room temperature, the magnetic moment against applied field ($B$), measured in sweeping mode, showed hysteretic properties for the magnetotactic bacteria with a coercivity ($B_c$) of 16.3 mT (Fig. 4.2a). The remanent magnetic moment was 7.44 $\mu$Am$^2$ and the saturation magnetic moment at 1 T was 16.91 $\mu$Am$^2$. The measured coercivity of remanence ($B_{cr}$) was 20.3 mT. Further, the remanence ratio $M_r/M_s$ was 0.44 and the coercivity ratio $B_{cr}/B_c$ was 1.25 were obtained (Table 1). The FORC diagram at room temperature displayed two features (Fig. 4.2b). The dominant feature spread along $B_c$, with a maximum at 19 mT and a relative narrow distribution along the $B_b$ axis. The interaction field was 7.4 mT as defined by the full width at half maximum of $B_b$ distribution along a profile through the peak of the FORC distribution (Muxworthy and Dunlop, 2002). The second feature spread along the $B_b$ axis, and $B_c$ was smaller than 2 mT.
Upon cooling to 60 K, the temperature behavior of $B_c$ could be divided into three ranges (Fig. 4.3). Between 295 K and 160 K an increase from 16.3 to 19.5 mT was observed, followed by a local minimum at 105 K with $B_c = 18$ mT. At lower temperatures, an increase was observed with $B_c = 23.1$ mT at 77 K (Table 1). The remanence ratio $M_r/M_s$ increased to 0.46 upon cooling to 200 K and remained stable down to 95 K. Below this temperature, a steep increase was found, and at 77 K $M_r/M_s$ was 0.5.
To detect further structural changes, high-field magnetization experiments up to 9 T were performed. Down to 70 K the slope of the high-field susceptibility was negative due to the diamagnetic contribution of the organic matrix. Between 70 and 40 K the slope of the high-field susceptibility at $B > 0.3$ T became positive, indicating that the high-field component of the magnetosomes had become dominant. To saturate the sample at 10 K a magnetic field of about 7 T was required and $M_s$ exhibited a strong increase (Fig. 4.4a). The contribution to $M_s$ of the magnetization induced in $B > 0.5$ T was about 50 % of the magnetization induced in $B < 0.5$ T. Hysteresis loops in a persistent mode revealed that the distinct increase in $M_s$ occurred simultaneously with the doubling of $B_c$ between 70 K and 10 K. The comparison of ZFC and FC hysteresis loops at 20 K exhibited neither a significant broadening nor a shift, but an increase of the remanent magnetic moment of about 20 % upon field cooling (Fig. 4.4b) The FC and ZFC SIRM curve upon warming revealed kinks at about 100 K and less distinctly at about 45 K (Fig. 4.4c). In the FC curve these kinks were more pronounced. The $\delta_{fc}/\delta_{zfc}$ ratio of 1.16 deduced from these curves clearly indicates that our *M. gryphiswaldense* failed the Moskowitz test, which generally yields a value of > 2 for magnetotactic bacteria.
(Moskowitz et al., 1993). A ratio > 2 was obtained if the low temperature values of $M$ were taken at 25 K.

The shape of the Henkel plot at 130 K (Fig. 4.5) deviated clearly from the ideal linear plot corresponding to Stoner-Wohlfarth conditions (Stoner and Wolfahrt, 1948). Two distinct departures were evident, at low and high fields, respectively.

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Figure 4.4: High-field magnetization of the bulk sample at 10 K (circles), at 40 K (squares), and at 70 K (triangles) (a); hysteresis loops after ZFC (open diamonds) and after FC to 20 K in a 1 T field (solid triangles) (b); normalized ZFC (open triangles) and FC (solid triangles) SIRM curves (c).
4.3.2.2 Dynamic magnetization

In the temperature range between 295 K and 5 K the AC susceptibility measurements exhibited in-phase ($\chi'$) and out-of-phase ($\chi''$) components (Figs. 4.6a,b). No amplitude dependence was found. By contrast, $\chi'$ revealed a frequency dependence over the whole temperature range. Upon cooling, $\chi'$ decreased and reached a local minimum at 250 K followed by a moderate increase down to 100 K. At lower temperatures a drastic decrease in $\chi'$ was found with a kink at about 65 K. The amount of the frequency dependence $\Delta\chi' = (\chi'_{0.5 \text{ kHz}} - \chi'_{10 \text{ kHz}}) / \chi'_{0.5 \text{ kHz}}$ also changed with $T$ (Fig. 4.6c). It increased between 295 K and 200 K and decreased down to 105 K, followed by a weak enhancement to 60 K and a pronounced peak at 40 K.

In the temperature range between 295 K and 150 K, broad peaks were observed in the out-of-phase component. Increasing AC frequency shifted this peak to a higher temperature. Between 150 K and 70 K no frequency dependence was detected. At lower temperatures a frequency-dependent local maximum was found at 45 K close to the peak of $\Delta\chi'$ (Fig. 4.6b, c).
Figure 4.6: Temperature dependence of the in-phase susceptibility $\chi'$ (a) and the out-of-phase susceptibility $\chi''$ (b) measured with variable frequencies and an amplitude of 0.3 mT; the shift of the peak in $\chi'$ is indicated by an arrow; (c) displays the frequency dependence of $\chi'$ expressed as $\Delta \chi' = (\chi'_{0.5\, \text{kHz}} - \chi'_{10\, \text{kHz}}) / \chi'_{0.5\, \text{kHz}}$ as a function of temperature.
4.3.2.3 FMR spectroscopy
At room temperature the FMR spectra displayed a line-shape with a sharp high-field and extended low-field absorption. The low field side of the spectrum exhibited two positive peaks and a shoulder. The linewidth (δB) was 183.8 ± 0.4 mT and \( g_{\text{eff}} \) was found to be 1.885 ± 0.007 (Fig. 4.7a). The \( g_{\text{eff}} \) and to a minor extent δB revealed a weak angular dependence. The maximum and the minimum values of \( g_{\text{eff}} \) varied by about 1% and were separated by 90°. In addition, the maximum of \( g_{\text{eff}} \) occurred simultaneously with the maximal height of the peak at lower resonance and the minimal height of the peak at higher resonance (Fig. 4.7b). It is well-established that a maximal \( g_{\text{eff}} \) corresponds to the parallel alignment of the easy axes to an external field (Bickford et al., 1950; Fischer et al., 2007). The simultaneous maximum of \( g_{\text{eff}} \) and the peak at lower resonance point to chains with their easy axis oriented parallel to the applied field. The maximal and the minimal \( g_{\text{eff}} \) were also separated by 90°, and the minimal value coexisted with the maximum of the peak at higher resonance and the shoulder. Therefore, it is feasible to assign the peak at high resonance and the shoulder to chains with their easy axis perpendicular to the applied field. The presence of coupled features in the FMR spectra suggests collective properties of the magnetosomes in the chains. Moreover, the weak angular dependence of \( g_{\text{eff}} \) provides clear evidence that a preferential orientation of the magnetosome chains in the bulk sample is negligible.

Figure 4.7: Room temperature FMR spectrum of \( M.\ gryphiswaldense \) (recorded with a Bruker spectrometer), the baseline, effective \( g \)-value, \( g_{\text{eff}} \), linewidth δB and the external field \( B \) are indicated. (a); Superposition of two spectra with maximal variations of the height of the low field peaks (b).
Measurements at room temperature on the Miniscope spectrometer yielded $g_{\text{eff}} = 1.867$ and $\delta B = 185.8$ mT. No significant changes in the spectral parameters were observed at RT after the low-temperature experiment. Upon cooling the line-shape revealed slight changes down to 133 K which are mainly characterized by the disappearance of the shoulder on the low-field side (Fig. 4.8).

**Figure 4.8**: Low-temperature FMR spectra recorded with a Miniscope spectrometer; the dashed line indicates the evolution of the two low-field peaks upon cooling to the isotropic temperature at about 133 K.

Between 133 and 103 K the peak at higher resonance became less pronounced. The low-temperature behavior of $\delta B$ showed a slight increase down to 243 K and a pronounced decrease of 30 mT between 213 and 133 K (Fig. 4.9a). At lower temperatures the decrease became shallower and at 103 K $\delta B$ was 160 mT. The decrease of $\delta B$ accompanied the shift of the peak at lower resonance to higher fields, whereas the peak at higher resonance showed only slight changes (Fig. 4.8). Between 295 K and 133 K the shift of the peak at lower fields was 10 %, similar to the change of $\delta B$, which was 12 %.
In addition, the change of $\delta B$ between RT and 133 K was similar to the development of the first-order magnetocrystalline constant $K_1$. A correlation coefficient between $\delta B$ and $K_1$ of 0.98 was calculated (Fig. 4.9b). The $g_{\text{eff}}$ values increased steadily from 1.885 at RT to 1.995 at 113 K. At $T < 113$ K, $g_{\text{eff}}$ even showed values of more than 2; at 77 K, $g_{\text{eff}}$ was 2.218 and $\delta B$ was 198 mT. To our knowledge, $g_{\text{eff}} < 2$ for SSD magnetite powder sample has been reported only for magnetosomes in chains of intact bacteria (Weiss et al., 2004b; Kopp et al., 2006a). The shift of $g_{\text{eff}}$ to higher fields indicates a relatively strong internal field with demagnetizing properties that had to be compensated by the external field to reach resonance conditions. The value of $g_{\text{eff}} > 2$ below 113 K hints to a decrease in this demagnetization effect (Fig. 4.8).

$$y = 2.6e+002 \times + 1.6e+002$$

$$r = 0.98$$

**Figure 4.9:** Comparison of the low-temperature behavior of $\delta B$ with $|K_1|$ (absolute values); $K_1$ is taken from Bickford et al. [39] (short-dashed line) and from Syono and Ishikawa [40] (long-dashed line) (a). Correlation between $\delta B$ and $|K_1|$ taken from Bickford et al. (b).

In the FMR simulation using the code written by Kopp et al. (2006b) it was not possible to reproduce all traits of the spectrum at room temperature. In contrast, using $K_1 \approx 0$ a reasonably good fit was obtained between experimental and simulated spectra at 133 K by
considering only a uniaxial system (Fig. 4.10). The best fit yielded $g_{\text{eff}} = 1.93$ and $\delta B = 150$ mT.

![Figure 4.10: Comparison of the measured and the simulated FMR spectrum at 133 K.](image)

**4.4. Discussion**

The following discussion of the magnetic properties of the magnetosome chains in *M. gryphiswaldense* is subdivided into three parts. First, the blocking behavior of magnetosomes is addressed. The second part examines the anisotropy fields generated by the magnetosomes. In the third part we consider the magnetic properties of the magnetosomes at $T < 100$ K, below the Verwey transition.

**4.4.1 Grain size distribution and blocking above 100 K**

The magnetosomes in this study exhibit similar morphology and size to those reported for magnetite particles generated in cultured strains of *M. gryphiswaldense* (Lang et al., 2007). This similarity corresponds to the well-established finding that magnetotactic bacteria of a specific species generate magnetosomes with a narrow size and shape distribution (Blakemore and Frankel, 1989). In our bulk sample the nanoparticles are embedded in organic matter with diamagnetic properties. Most of the magnetosomes are arranged in chains (Fig. 4.1). This arrangement can be considered as an interacting system of nanoparticles. Our magnetosomes generally show diameters of about 35 nm but smaller particles of less than 30 nm are also observed (Fig. 4.1). The larger particles are unambiguously in the SSD size range, whereas the smaller magnetosomes are close to the threshold between blocked and
superparamagnetic (SP) states (Dunlop and Özdemir, 1997). In a Day-plot ($M_r/M_s$ versus $B_c/B_e$) the bulk of the magnetosomes are located close to the field characteristic for uniaxial SSD magnetite (Day et al., 1977). The spread along the $B_b$ axis at $B_c < 2$ mT in the FORC diagram can be interpreted as caused by particles in SP state (Roberts et al., 2000). This interpretation is supported by the increase in $B_c$ upon cooling to 160 K. Moreover, the shift of the out-of-phase susceptibility $\chi''$ with increasing frequency at about 175 K (Fig. 4.6b) confirms that the smaller magnetosomes exhibit SP-like behavior. These magnetosomes are blocked at about 150 K, as indicated by the disappearance of the frequency dependence of $\chi''$ below this temperature. Blocking leads to a broader grain size distribution of SSD magnetite at $T < 150$ K compared to RT.

4.4.2 Magnetosomes and their anisotropy fields

Ferromagnetic resonance spectra of intact magnetotactic bacteria at RT are the results of a combination of anisotropy fields generated by magnetocrystallinity, shape and interactions (Kopp et al., 2006b). The contribution of the various anisotropies to a FMR spectrum has not been examined in detail until now, either experimentally, comparing intact and clumps of magnetotactic bacteria, or in FMR simulations. In the following the qualitative contributions of different anisotropy fields to the absorption spectra at low temperatures are discussed.

The departure from the Stoner-Wohlfahrt line of non-interacting, uniaxial SSD particles in the Henkel-plot at 130 K suggests that the interactions in our sample have mainly demagnetizing properties. Demagnetization can be caused by magnetostatic interactions between single magnetosomes. Moreover electron holography analysis clearly showed that the alignment of magnetosomes generates a stray field, i.e., demagnetizing properties. With this in mind it is likely that the magnetic behaviour observed for M. gryphiswaldense is dominated by dipole characteristics arising from the geometric arrangement of the magnetosomes in the cell, i.e., by the uniaxial shape originated from entire chain. This is supported by the FMR spectrum at RT with its extended low-field and sharp high-field absorption typical for magnetic phase with uniaxial positive anisotropy properties (Griscom, 1974). The failure to simulate all features of the spectrum at RT using the code of Kopp et al. (2006b) indicates, that the magnetosome chains cannot be described solely in terms of a uniaxial system. Magnetite has cubic magnetocrystalline anisotropy with a negative $K_1$ between RT and the isotropic point near 130 K (Bickford et al., 1957; Syono and Ishikawa, 1963). The high correlation coefficient of 0.98 for $\delta B$ and $K_1$ in the temperature range between RT and 133 K (Figs. 4.9a,b) indicates that the magnetocrystalline anisotropy field
(\(B_m\)) contributes significantly to the absorption spectrum. The effect of \(B_m\) is supported by the low-temperature variation of the hysteresis parameter \(B_c\) (Morrish and Watt, 1958). Considering the above argumentation, the anisotropy field \((B_a)\) in the bulk sample can be treated schematically as the sum of the magnetocrystalline anisotropy fields \(B_m\) of each particle and of the stray fields generated by aligned magnetosomes which can be considered as shape anisotropy field \((B_s)\). In addition, \(B_a\) is assumed to be proportional to \(\delta B\) (Griscom, 1974).

Comparing the FMR spectra at RT and the isotropic point at 133 K provides an insight into the anisotropy properties of the bulk sample. In this temperature range, where \(B_m\) decreases by 100\%, \(B_a\) is reduced by 12\%. Thus \(B_m\) makes only a minor contribution to the anisotropy properties of the bulk sample. One has to be aware, however, that in the same temperature range \(B_s\) increases because of the increase in \(M_s\). Using the relation \(M_s(T) \propto (1-T/T_c)^\gamma\) with the Curie temperature \(T_c\) and \(\gamma = 0.43\) for magnetite, an enhancement of about 13\% can be calculated for \(M_s\) (Dunlop and Özdemir, 1997). Therefore it can be argued that the less-pronounced decrease in \(B_a\) compared to \(B_m\) is a consequence of the changes in \(B_s\).

The Henkel plot at 130 K reveals demagnetizing properties for the bulk sample. Demagnetization generally increases the resonance field \(B_{eff}\) and as a result decreases the \(g_{eff}\) value (Vonsovskii, 1966). Bickford (1950) reported a \(g\)-value of 2.08 for single-crystal magnetite at the isotropic point. Comparing this value with \(g_{eff} = 1.95\) obtained in our sample, a distinct contribution of \(B_s\) to \(B_a\) may be postulated.

Between 130 K and 100 K, the decrease in \(B_a\) indicates a diminishing of the anisotropy field acting on the spins localized with Fe. Since the change in \(B_a\) occurs simultaneously with the increase in \(B_m\), it follows that \(B_s\) also decreases. An explanation for the reduction of \(B_s\) may be the shifting of the magnetic easy axes in the magnetosomes from [111] to [100] below the isotropic point at about 130 K. This departure of the easy axes from the chain axes weakens the dipole interactions of the magnetosomes, and subsequently \(B_s\). Evidence for such an effect is apparent in the smearing out of the two resonance peaks in the FMR spectra between 130 K and 100 K (Fig. 4.8). The concomitant decrease in \(B_a\) and \(B_s\) between 133 K and 100 K suggests that this masks the change in \(B_m\) in this temperature range. The vanishing of the two peaks in the FMR spectra at 77 K, however, indicates that the major contribution to \(B_s\) below 100 K arises from \(B_m\). The behavior of \(B_m\) agrees well with the increase in \(B_c\) and \(M_r/M_s\), as well as the SIRM increase and the drop in \(\chi'\). Such changes in the magnetic
parameters have been interpreted as characteristics of the Verwey transition (Özdemir et al., 2002; Kosterov, 2003).

### 4.4.3 Magnetic behavior of the magnetosomes below 100 K and the Verwey transition

Extensive studies on single crystals and magnetite powder have shown a Verwey transition at a temperature \( T_v \) near 125 K, which is about 10 K below the temperature of the isotropic point \( T_i \) of magnetite (Walz, 2002). Our hysteresis and SIRM data, however, indicate that the Verwey transition found for *M. gryphiswaldense* is smeared and shifted by about 20 K to a lower temperature. A Verwey transition at about 100 K has been observed for magnetosomes in various bacteria (Weiss et al., 2004b; Pan et al., 2005a), Prozorov et al., 2007, 2003). Pan et al. (2005a) mentioned that the low \( T_v \) may be an intrinsic property of magnetosomes. Off-axes holography of magnetotactic bacteria (Simpson et al., 2005) reveals that despite some undulation of the magnetic induction below the isotropic point due to tilting of the easy axes, there is still magnetic coherence between the magnetosomes. This agrees well with the dominance of \( B_s \) indicated by FMR spectral data. Therefore the occurrence of the Verwey transition at a lower temperature of about 100 K in magnetotactic bacteria may be affected by the persistence of the distinct contribution of \( B_s \) below the isotropic point.

The smearing of the Verwey transition has been explained by oxidation processes (Özdemir et al., 1993) or by cation substitution (Kakol et al., 1992). The latter can be neglected in the present case because the culture medium contains no cations which can substitute Fe\(^{III}\) or Fe\(^{II}\) in the magnetite lattice. Özdemir et al. (1993) compared non-oxidized and oxidized nano-sized inorganic magnetite powders and found that the departure from stoichiometry due to oxidation leads to drastic maghemitization and a subsequent gradient of the chemical composition between core and surface, which results in the smearing out of the Verwey transition. In oxidized magnetosomes Moskowitz et al. (Moskowitz et al., 1993) found an increase in SIRM at \( T < 50 \) K and interpreted this as blocking of small SP maghemite particles. Taking these findings into account, the magnetic behavior of *M. gryphiswaldense* at low temperatures could be explained by maghemitization of the magnetosomes. The XRD data, however, provide no indication of maghemite in our bulk sample at RT and the FMR spectra do not show evidence for SP maghemite (Gehring et al., 1990). Blocking of maghemite as a low-coercivity phase similar to magnetite cannot explain the high-field susceptibility of the magnetization curve, which occurs simultaneous to the
increase in SIRM. According to the above argumentation, maghemitization is unlikely to explain the low-temperature behavior of the magnetosomes.

Recently Faivre et al. (2007) found evidence for a ferritin-type compound in the membrane fraction of *M. gryphiswaldense*. Ferritin consists of an antiferromagnetic ferrithydrate (5 Fe$_2$O$_3$•9 H$_2$O) nanoparticle surrounded by a protein shell (Chasteen and Harrison, 1999). It is known that the blocking temperature of ferritin is below 20 K (Seehra and Punnoose, 2001; Brem et al., 2006). Since no peaks are found in the AC susceptibility in this temperature range, a significant contribution of ferritin compounds to the low-temperature behavior in our sample is ruled out. Hence, the magnetic behavior at $T < 50$ K is probably due to magnetite. This explanation is supported by the similarity of ZFC and FC hysteresis loops at 20 K; no broadening or shift of the loops are observed, which is therefore not consistent with exchange coupling of magnetite with an antiferromagnetic phase (Nogues and Schuller, 1999). Moreover, if an additional antiferromagnetic phase (e.g., ferrithydrate) causes the strong increase in the high-field susceptibility at $T < 40$ K (Fig. 4.4a) it should be present in XRD-detectable quantities in the bulk sample.

At low temperatures, the magnetite structure undergoes a rearrangement of electronic states in regions with inhomogeneous spin distributions (Kronmüller and Walz, 1980). Muxworthy and McClelland (2000) and references therein reported that decreasing temperature leads to a more pronounced Vonovskii exchange interaction between the localized inner electrons and the valence electrons of Fe cations. Ordering of the valence electrons generates the formation of e-sublattices which are antiferromagnetically coupled to B-sites of the spinel crystal structure with octahedrally-coordinated Fe$^{(III)}$ and Fe$^{(II)}$. The diminution of electron hopping due to ordering entails magnetic hardening of the material, since the A-sites of the magnetite with Fe$^{(III)}$ only become more pronounced. The high-field susceptibility and the doubling of $B_c$ between 50 and 10 K indicate such a hardening effect in our magnetosomes. The temperature range in which this effect occurs accords with the finding by Kronmüller and Walz (1980), who demonstrated that below 45 K electron hopping ceases. Since it is known that an external field can destroy e-sublattices (Muxworthy and McClelland, 2000), an increase in remanent magnetic moment and a decrease in $B_c$ are expected in the hysteresis loop after field cooling. The comparison of the ZFC and FC hysteresis loop at 20 K reveals just this effect (Fig. 4.4b). With this in mind, it can be postulated that the magnetic behavior (e.g., increase in SIRM and $B_c$) of the magnetosomes below 50 K is mainly affected by the ordering of electron spins in e-sublattices. Further
evidence for the ordering of inhomogeneously-distributed electron spins is provided by the distinct frequency dependence of $\chi'$ and $\chi''$ at about 50 K (Figs. 4.6b,c). Skumryev et al. (1999) showed that regions with inhomogeneous spin distributions could be domain walls, and that the frequency dependence is due to freezing out of defects and interstitials. The magnetosomes in this study, however, are of SSD size, and, therefore the inhomogeneity must occur within the grain core and its surface.

In a study of synthesized non-stoichiometric single magnetite crystals, Kakol and Honig (1989a) reported that a decreased $T_v$ is caused by cation deficiency ($\Delta$) in the magnetite structure ($\text{Fe}_{3(1-\Delta)}\text{O}_4$). Magnetite with $\Delta < 0.01$ has a lower $K_1$ than pure magnetite, but shows a similar temperature dependence with an isotropic point $T_i$ near 130 K (Kakol and Honig, 1989b). A Verwey transition is documented in the non-stoichiometric magnetite with $\Delta < 0.012$ (Kakol and Honig, 1989a). The XRD data of $M.\ gryphiswaldense$ reveal a $\Delta$ of 0.01. For such a value a $T_v$ of ca. 90 K was reported (Kakol and Honig, 1989a), which is close to $T_v \approx 100$ K found for $M.\ gryphiswaldense$ in this study. In contrast to the magnetite single crystal used by Kakol and Honig (1989a), the magnetosomes are in the nanometer range with large specific surface areas. Therefore it is feasible that the surfaces of the magnetosomes contribute significantly to the departure from stoichiometry. With this in mind, the magnetic behavior below the Verwey transition is most likely due to non-stoichiometry and subsequent rearrangement of electronic spins in the core and on the surface, and their freezing at $T < 50$ K.

4.4.4. Non-stoichiometry in the magnetosomes

Non-stoichiometry in the context of magnetosomes has generally been taken to be an effect of maghemitization and has been used to explain relatively low $\delta$-ratios (Moskowitz et al., 1993; Weiss et al., 2004b). Despite their low $\delta$-ratio, our magnetic and mineralogical data show no indication for oxidative alteration of the magnetosomes in $M.\ gryphiswaldense$. Hence it is feasible to argue that the non-stoichiometry in our case is the result of biomineralization. The details of the magnetite biomineralization are so far unresolved. Two processes can be suggested: the co-precipitation of $\text{Fe}^{(II)}$ and $\text{Fe}^{(III)}$ or formation via a ferrihydrite precursor. In the latter case the absorption of soluble $\text{Fe}^{(II)}$ would lead to the magnetite phase. High-resolution TEM data revealed twinning in magnetosomes, which suggests structural inhomogeneity in the nanoparticles (Devouard et al., 1998). Such inhomogeneity can be a growth phenomenon or the result of a phase transition. The latter possibility is supported by
the detection of a ferritin-type compound in magnetosome membranes of *M. gryphiswaldense* (Faivre et al., 2007). Therefore it is probable that, during the mineral transition, defect structures such as vacancies can be produced. Based on our data, however, an unambiguous interpretation of the non-stoichiometry of the nano-sized magnetosomes remains elusive. Nevertheless, the magnetic characteristics of the magnetosomes provide clear evidence that non-stoichiometry in these nano-sized particles may be an intrinsic property.

### 4.5. Conclusions

The experimental approach in this study, which combines static and dynamic magnetization and FMR spectroscopy, shows a superposition of magnetic characteristics in the low-temperature range for magnetosomes of *M. gryphiswaldense* which are summarized as follows:

1. At room temperature nano-sized magnetosomes aligned in chains, consist of single-domain and superparamagnetic magnetite nanoparticles. At 150 K all magnetosomes are blocked.
2. Stray fields of the dipoles formed by magnetosome chains generate the anisotropy field $B_s$ of the bacteria. This anisotropy field, dominant down to 100 K, masks the increase in $B_m$ between the isotropic point and the Verwey transition in intact magnetotactic bacteria.
3. Values of $g_{\text{eff}} < 2$ can be used as a proxy to detect magnetotactic bacteria even if they fail the Moskowitz test.
4. The magnetic parameters indicate a Verwey transition of the magnetosomes at about 100 K. The smearing of the Verwey transition associated with *M. gryphiswaldense* is caused by non-stoichiometry in the core and at the surface of the nano-sized magnetosomes. The departure from stoichiometry and the subsequent inhomogeneous electron spin distribution in the single-domain magnetosomes can also explain the distinct static and dynamic magnetic behaviour at $T < 50$ K.
5. The combined magnetic and spectroscopic information on the magnetosomes points to particular magnetic properties of biologically-controlled magnetite aligned in chains. Genetic information may be a key in linking the magnetic properties and the processes leading to biomineralization in cultured *M. gryphiswaldense*. 
Chapter 5

EPR evidence for maghemitization of magnetite in a tropical soil

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**Abstract**

Electron paramagnetic resonance spectroscopy (EPR) was used in combination with standard rock magnetic methods to study magnetic minerals in a tropical soil. The susceptibility and hysteresis measurements showed magnetite grains with a Curie temperature near 850 K as the dominant magnetic remanence carrier in the soil. A minor Ti content in the magnetite was found by energy dispersive X-ray analysis. In order to get insight into the weathering status of the magnetite, different chemical treatments, including oxalate and citrate-bicarbonate-dithionite (CBD) extraction, were applied to the soil samples. The hysteretic properties exhibited no significant differences between the untreated and the CBD or oxalate treated samples. By contrast, the comparison of the EPR spectra revealed a significant broadening of the linewidth ($\delta B$) and a shift of the g-values ($g_{eff}$) to lower fields after the CBD treatment. Furthermore, the spectral parameters $g_{eff}$ and $\delta B$ exhibited an angular dependence. At low temperature, the CBD treated samples showed a jump in $\delta B$ between 120 and 100 K, the temperature range characteristic for the Verwey transition in magnetite. The changes in the spectral properties after the CBD treatment which dissolves ferric oxides, were attributed to the removal of maghemite formed by the oxidation of magnetite, i.e., during the maghemitization of the magnetite grains.
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5.1 Introduction

Lithogenic magnetite is widespread in soils and often dominates their magnetic properties. During weathering, magnetite becomes oxidised, whereas under reducing conditions, as in waterlogged soils, it can undergo reductive dissolution (e.g., Henshaw and Merrill, 1980). The identification of such processes is important to deduce pedogenesis. Oxidation of magnetite can lead to the formation of maghemite or less crystallised ferric phases. Using XRD and microscopic analysis, Gallagher et al. (1968) could show on a well defined synthetic magnetite sample a topotactical conversion into maghemite. The conversion is known as maghemitization, and has been described also in natural systems such as pelagic sediments (Smirnov and Tarduno, 2000) and loess (Chen et al., 2005). In the first study, maghemite was detected by thermal demagnetisation, while in the second one it was observed under the transmission electron microscope. Under reducing conditions, magnetite is slowly dissolved. The rate is grain-size dependant and is generally much slower than for ferric oxides.

The aforementioned redox processes are surface controlled (Stumm and Morgan, 1996). The detection of the surface products with rock magnetic methods is difficult, because the magnetic signals are generally dominated by the bulk properties. Furthermore, magnetite and its oxidation product maghemite have similar magnetic properties (Dunlop and Özdemir, 1997). In the rock magnetic literature, there are several experimental approaches to detect maghemitization. Van Velzen and Dekkers (1999) proposed that heating to 150°C could be used to distinguish between maghemite and partially oxidised magnetite because such a treatment would selectively change the magnetic coercivity of the latter. Low temperature magnetic experiments offer another approach, in which the oxidation of magnetite is detected via the suppression of the so-called Verwey transition (Özdemir et al., 1993). This transition, however, is also suppressed in magnetite with Ti substitution (Kakol et al., 1992); therefore, ambiguity can remain when using such an approach.

Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool for studying paramagnetic cations such as Fe(III) in diluted systems (e.g., Meads and Malden, 1975; Angel and Vincent, 1978). A detailed description of the technique is given by Wertz and Bolton (1972). The method, however, has rarely been used to study phases carrying a remanent magnetisation. In such systems, strong dipole-dipole interactions or magnetic coupling can lead to intense and broad signals at room temperature (RT) that cannot be assigned unambiguously to a specific magnetic phase (Griscom, 1980; Gehring and Karthein, 1990).
Such broad signals are produced by ferromagnetic resonance (FMR). The basic principles of this phenomenon were described by several authors (Kittel, 1948; Bickford, 1950). Experimental studies on magnetite revealed that apart from the different anisotropies (e.g., magnetocrystalline) the skin effect can influence the FMR (Kittel, 1946). Such an effect is produced in electrical conductors where eddy currents limit the penetration depth of the electromagnetic radiation. For magnetite at RT, this depth is in the µm range, and, therefore is expected for multi-domain (MD) and larger pseudo-single domain (PSD) particles. By contrast, in single-domain (SD) particles, the electromagnetic radiation is uniform across the whole grain. Hence, for MD and larger PSD grains, the surface and the near-surface region contribute more strongly to FMR spectra.

With this in mind, it is conceivable that FMR properties of larger magnetite grains can be influenced by surface modifications caused by oxidation. In order to test this hypothesis, we applied EPR spectroscopy in concert with rock magnetic methods to lithogenic magnetite in a tropical soil which was subjected to different chemical treatments to selectively remove certain minerals or surface layers formed during weathering.

### 5.2 Methodology

#### 5.2.1 Sample preparation

The soil samples were collected from the top layers of an alluvial Vertisol in the Savannah woodland of southern Mali near the hamlet Kabogora (Gehring et al., 1997). The lithogenic magnetite is dispersed in the soil matrix which mainly consists of quartz and montmorillonite. For the chemical and magnetic analyses, the samples were dried at 60° and passed through a 2-mm sieve in order to remove larger grains and components such as plant residues.

Three different chemical extraction procedures were performed on the untreated sample (KA). Oxalate treatment following the recipe by Schwertmann (1964) was used to remove amorphous and poorly crystallised ferric oxides from the soil samples. The citrate-bicarbonate-dithionite (CBD) extraction was performed using a protocol modified from Mehra and Jackson (1960). Briefly, 2 g of sieved soil, 2 g of sodium dithionite, 10 ml of 1 M sodium hydrogen carbonate, and 150 ml 0.3 M sodium citrate were equilibrated at RT for 24 hours in dark bottles using an end-over-end shaker. The liquid phase was removed by filtration and the residue washed several times with doubly-deionised water. The acid treatment involved boiling the sample in a concentrated acid solution with a 19:1 ratio of HCl
to H$_2$SO$_4$ followed by magnetic separation (Goulart et al., 1994). The treated samples are referred to as KA$_{ox}$, KA$_{dith}$, and KA$_{acid}$, respectively.

### 5.2.2 Experimental methods

The morphology of magnetic separates was investigated under the scanning electron microscope (SEM), which for semi-quantitative chemical analyses was connected to an energy dispersive system (EDX). The magnetic susceptibilities ($\chi$) of the untreated and chemically treated specimens were determined on an AGICO KLY-2 Kappabridge. In order to determine inhomogeneity effects, the susceptibility was measured on ten specimens. For sample KA, the temperature dependence of $\chi$ between RT and 973 K was recorded with a heating rate of approximately 11° C/min. The hysteretic properties of all samples were analysed at RT by magnetisation vs. applied field experiments using a Vibrating Sample Magnetometer (VSM) from Princeton Corporation. Coercivity ($B_c$), remanent magnetisation ($M_r$) and saturation magnetisation ($M_s$) were determined from the hysteresis loops, after they were corrected for paramagnetic contribution with a factor of 0.7. In addition, first-order reversal curves (FORC) were measured with the same instrument, and the data were analysed with a Matlab code by Winkelhofer (personal communication).

The EPR spectra of the untreated and chemically treated samples (about 300 mg) were obtained at RT on a Bruker EMX 300 spectrometer. The X-band spectra were recorded at a microwave frequency of 9.77 GHz with a micropower of 0.2 mW, a modulation frequency of 100 kHz, and an amplitude modulation of 0.1 mT. The field strength was controlled by a Bruker NMR Gaussmeter ER 035M. In order to avoid movement of the magnetic particles due to alignment with the external field, the bulk sample in the glass tube was moulded in paraffin. The angular dependence of the FMR spectra was determined by rotating the glass tube in the EPR cavity with the help of a goniometer installed at the top of the cavity. The axis of rotation was perpendicular to the applied magnetic field. For each sample, the angular dependence was measured four times. The low temperature measurements were carried out on a Bruker Elesys spectrometer at a frequency of 9.5 GHz in a temperature range between 10 and 150 K. Prior to inserting the tubes into the spectrometer cavity, they were cooled in liquid nitrogen. The experimental parameters were the same as for the RT measurements.
5.2.3 FMR

Since FMR experiments have not often been used in geophysical research, the basics are summarised in the following paragraph. A detailed description can be found elsewhere (Kittel, 1948; Vonsovskii, 1966). In the presence of a magnetic field, the magnetic moments precess around the field direction with a frequency of $\omega$. The frequency increases with the field, according to Larmor’s law:

$$\omega = \gamma B$$

(5.1)

with $\gamma$ being the gyromagnetic ratio, and $B$ the applied field. Absorption occurs when this frequency is equal to the one of the microwave radiation ($\nu$). The resulting resonance condition can be written as

$$h\nu = g\mu_B B$$

(5.2)

assuming no anisotropy fields ($h$ is Planck’s constant, $g$ the splitting factor, $\mu_B$ Bohr’s magneton). Since anisotropies in FM phases create internal fields which add to the external one, the effective field ($B_{eff}$) is the sum of applied field and internal fields. The $g$-value calculated from equation 2 will therefore be modified to $g_{eff}$. Equation 2 becomes then

$$h\nu = g_{eff} \mu_B B_{eff}$$

(5.3)

Griscom (1980) describes four major anisotropy energies which can influence $B_{eff}$. The magnetocrystalline anisotropy results from the crystallographic structure, whereas the shape anisotropy is caused by the interaction of the magnetisation vector with the demagnetizing factor of the grain. For magnetite, shape anisotropy is dominant in small ($< 20 \mu m$) non-spherical particles, whereas for larger particles, magnetocrystalline anisotropy is prevailing (Dunlop and Özdemir, 1997). Furthermore, domain structure anisotropy considers the relative orientation of the microwave field to the domain walls. Finally, exchange anisotropy arises from the interaction between magnetic particles.

For large magnetite grains at RT, the microwave radiation penetrates generally to a certain depth only, because of its relatively high electrical conductivity. The depth at which the intensity of the microwave radiation is reduced to 37% is denominated the skin depth. The
skin depth is frequency-dependent and it is about 5 μm for pure magnetite at the X-band frequency (Griscom, 1974). Crystal defects or cation substitutions (e.g., Ti(IV) for Fe(III)) often found in natural magnetites, however, can significantly reduce the electrical conductivity, and, therefore, increase the skin depth. Hence, spectroscopic information stems from both near-surface regions and the bulk of the larger magnetite grains.

The absorption spectra are generally presented as their first derivative. For the description of the FMR spectra of magnetite, two empirical parameters have been put forward: $g_{\text{eff}}$ value ($g$-value at zero-crossing), and the peak to peak linewidth $\delta B$. For non-interacting SD grains, these parameters can be used to characterize the anisotropy field. For systems with MD and PSD particles, however, these parameters can only be understood in a general sense.

5.3 Results

5.3.1 Magnetic and microscopic properties

The mean susceptibility of KA was $69 \times 10^{-8}$ m$^3$ kg$^{-1}$ with a standard deviation ($\sigma$) of $4 \times 10^{-8}$ m$^3$ kg$^{-1}$. A mean $\chi$ of $77 \ (\sigma = 6) \times 10^{-8}$ m$^3$ kg$^{-1}$ was found for KA_ox, while that of KA_dith was $54 \ (\sigma = 2) \times 10^{-8}$ m$^3$ kg$^{-1}$. Upon heating KA to 973 K, $\chi$ remained relatively constant up to 510 K followed by a bump at 575 K and a decrease up to 775 K. A more pronounced decay was found between 793 and 850 K (Fig. 5.1). At higher temperature $\chi$ did not significantly change any more. Upon reversed cooling, $\chi$ increased drastically down to about 520 K followed by a slight decrease. The end value at RT was three times higher than the starting value.

The magnetisation vs. applied field plot (Fig. 5.2) revealed an open hysteresis loop for KA, KA_ox and KA_dith. By contrast, no significant hysteretic properties were found for KA_acid (Fig. 5.2). The coercivity ($B_c$) was 10 mT for KA and KA_dith, and 9 mT for KA_ox. The hysteresis loops for KA, KA_ox and KA_dith closed between 250-300 mT. The ratio of the remanent magnetisation ($M_r$) to the saturation magnetisation ($M_s$) was 0.15 for KA, 0.18 for KA_ox, and 0.17 for KA_dith.
The FORC diagram of KA revealed two features. The distribution along the \( B_c \) axis extended up to 50 mT with weakly diverging open contours (Fig. 5.3a); a maximum was observed at \( B_c \approx 10 \) mT. The second feature consisted of a distribution along the \( B_b \) axis for values of \( B_c < 5 \) mT. Chemical treatment did not significantly change the diagrams and both KA_ox and KA_dith displayed the same features as KA (Figs. 5.3b and 5.3c).
Figure 5.3: FORC diagrams (smoothing factor SF 3) of (a) KA (b) KA_ox, and (c) KA_dith.
Under the SEM, the magnetite grains were generally larger than 20 μm and exhibited variable morphologies. No significant change in the morphology was observed after chemical treatment (Fig. 5.4). Semi-quantitative EDX analysis revealed minor substitution of Fe by different cations, mainly Ti. A few magnetite grains contained an amount of substitution which was below the detection limits of the EDX analyses.

5.3.2 EPR measurements

The EPR spectra of the untreated, oxalate and the CBD treated samples recorded at RT were dominated by a broad signal (Fig. 5.5). This signal was missing in the KA_acid sample. All samples exhibited two additional signals, one at low field with $g = 4.3$ and the other at high field with $g = 2$. The resonance at low field could be assigned to Fe$^{3+}$ in distorted octahedral coordination sites, whereas the sharp signal at $g = 2$ is characteristic for a free radical (e.g., Meads and Malden, 1975). For the KA, the KA_ox, and the KA_dith samples the broad signal was different with respect to its spectroscopic parameters, $g_{\text{eff}}$ and $\delta B$. The untreated sample revealed a $g_{\text{eff}}$ of 2.119. A shift to higher value, i.e., to lower applied field, was observed in
chemically treated samples. For KA_ox, $g_{\text{eff}} = 2.145$ and for KA_dith, $g_{\text{eff}} = 2.29$ were determined. For KA and KA_ox, $\delta B$ was similar with values of 122 and 119 mT, respectively. In contrast, a higher $\delta B$ of 161 mT was found for KA_dith. Replicate measurements with removal of the samples from the spectrometer cavity between the runs led to slight changes in the FMR parameters. The variation was most pronounced in KA_dith.

Fig. 5.5: EPR spectra of KA, KA_ox, KA_dith and KA_acid

A similar effect was found when rotating the sample in the cavity. Figure 5.6 shows the measured $g_{\text{eff}}$ versus rotation angle for one replicate run of each sample. The replicates for each sample differed slightly, but the relative differences between the samples were the same in all cases. The $g_{\text{eff}}$-values revealed for all three samples an angular dependence with no overlapping values between the samples. Sample KA_dith exhibited the most pronounced angular dependence. In this sample, $g_{\text{eff}}$ was characterised by a mean value of 2.27 and $\sigma = 0.05$. A periodicity of 180° was found (Fig. 5.6). In the two other samples, the angular dependence was weak. For KA_ox the mean value for $g_{\text{eff}}$ was 2.142 with $\sigma = 0.004$, whereas in KA, the mean value for $g_{\text{eff}}$ was 2.119 with $\sigma = 0.008$. 
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Figure 5.6: Angular dependence of $g_{\text{eff}}$ for KA, KA\textsubscript{ox}, and KA\textsubscript{dith} with the minimum in $g_{\text{eff}}$ set at 0°.

Furthermore, an angular dependence was also found for $\delta B$ (Figure 5.7). In KA the mean $\delta B$ was 122 mT with $\sigma$ of 4.6 mT, while in KA\textsubscript{ox}, $\delta B$ was 121 mT with $\sigma$ of 2.2 mT. For KA\textsubscript{dith} $\delta B$ had a mean value of 164 mT with $\sigma$ of 20 mT. Upon rotation the $\delta B$ was characterized by broad maxima and minima and the occurrence of a shoulder as additional feature in the EPR spectra, indicating a superimposed signal (Figure 5.7b). This feature appeared simultaneously with the increase of the linewidth and was most pronounced where the $\delta B$ reached its maximum (Figure 5.7).

Figure 5.7: (a) Angular dependence of $\delta B$ for KA\textsubscript{dith} corresponding to that of $g_{\text{eff}}$ in Figure 6, and (b) two spectra when $\delta B$ is in (1) the maximum range (at 110°) and (2) in the minimum range (at 235°).
The KA spectra could be reasonably fitted with a single Lorentzian line, whereas the best fitting for chemically treated samples was obtained by a linear combination of Lorentzian and Gaussian lines. Sample KA_ox could be fitted well by using two components with the same \( g_{\text{eff}} \) and similar \( \delta B \). For the spectra of KA_dith revealing the additional shoulder, the best fit was achieved by a combination of components with different \( \delta B \) as well as \( g_{\text{eff}} \) (Fig. 5.8).

![Figure 5.8](image_url)

**Figure 5.8**: (a) Comparison of the measured (solid line) and the fitted (dotted line) spectrum of KA_dith. (b) The fitting consists of a broad Lorentzian (L) and a narrow Gaussian (G) component with different spectral parameters \( g_{\text{eff}} \) and \( \delta B \).

The EPR spectra at low temperature exhibited the expected increase in intensity for the paramagnetic signal and a slight decrease for the broad FMR (Figure 5.9). The lineshape of KA and KA_ox showed no significant change whereas \( \delta B \) increased at \( T < 100 \) K (Figure 5.9).
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Figure 5.9: Low-temperature EPR spectra of KA, KA_ox, and KA_dith.

Between 50 and 10 K the $\delta B$ of KA and KA_ox revealed a pronounced increase of about 60% and 30%, respectively (Fig. 5.10). The $\delta B$ of KA_dith exhibited a different behaviour. It increased slightly upon cooling to 120 K, then $\delta B$ almost doubled between 120 and 100 K, followed by a steady increase down to 10 K. Due to the superimposed paramagnetic signal, $g_{\text{eff}}$ for the FMR at low temperatures could not be determined exactly from the spectra.

Figure 5.10: $\delta B$ vs temperature for KA, KA_ox and KA_dith at low temperature.
5.4 Discussion

The hysteresis loop of the untreated sample shows that the remanent magnetic properties are dominated by a low coercivity phase. The $\chi$ vs temperature measurement shows that this phase has a $T_c$ of about 850 K, which is indicative of magnetite. The semiquantitative EDX analysis shows the presence of minor amounts of Ti in the magnetite grains. The Ti content, however, has to be relatively low, because it is not documented in a significant lowering of $T_c$ (e.g., Dunlop and Özdemir, 1997). The bump in $\chi$ at about 570 K is probably due to the conversion of ferric hydroxides into an oxide, most likely hematite. The lack of clear evidence for a Néel temperature of hematite in the $\chi$ at $T > 870$ K points to a very low concentration of this ferric oxide in the heated sample. Upon cooling the increase in $\chi$ indicates the generation of additional magnetite as a conversion product most likely of clay minerals.

The magnetite particles in the soil samples resist chemical treatment with oxalate and CBD as indicated by the hysteretic properties. This is supported by the similar morphologies of the grains under the SEM (Fig. 5.4). Gehring et al. (1997) showed that oxalate extracts about 10% of the total Fe in the sample. The oxalate extractable Fe can be attributed to poorly crystallised ferric oxides which do not significantly contribute to the magnetic remanence of the sample. The difference in $\chi$ between KA and KA_ox is smaller than the variability of $\chi$ in the original topsoil material ranging between 74 to 86 x 10^{-8} m^3 kg^{-1} (Gehring et al., 1997). With this in mind it is postulated that KA and KA_ox are similar with respect to their $\chi$. The CBD treatment is known to dissolve ferric oxides such as hematite and maghemite. Furthermore, CBD can also dissolve superparamagnetic (SP) and SD magnetite (Hunt et al., 1995; Van Oorschoot and Dekkers, 1999). In our soil sample, CBD extracts 25% of the total Fe (Gehring et al., 1997). The fact, that CBD extracts more Fe than oxalate, indicates a significant content of crystalline ferric oxides that contribute to the remanence of the sample. This agrees well with the decrease in $\chi$ in the CBD treated sample, which is most likely due to the removal of maghemite, since no clear indication for hematite has been found in the soil samples. The $\chi$ values are low compared to the bulk susceptibility of magnetite and titanomagnetite found in the literature (e.g., Peters and Dekkers, 2003). These authors reported average $\chi$ values of 67 x 10^{-5} m^3 kg^{-1} for magnetite, 42 x 10^{-5} m^3 kg^{-1} for titanomagnetite and 63 10^{-5} m^3 kg^{-1} for maghemite, which are about three orders of magnitude higher than the susceptibility of our soil sample. Therefore, assuming that susceptibility arises only from ferrimagnetic phases, a concentration of magnetite/maghemite of approximately 1 wt% can be deduced for it.
The hysteretic properties (i.e., $B_c$ and $M_r/M_s$) of KA, KA_ox, and KA_dith give clues to PSD magnetite, which is characterised by grain sizes in the range from 0.3 to approximately $20 \mu m$ (Dunlop and Özdemir, 1997). Parameters indicative of PSD grains are often found in soils and sediments and can also be produced by a mixture of particles with a wide variation of grain sizes (Roberts et al., 2000). Weakly diverging open contours in the FORC diagram as found for KA, KA_ox and KA_dith (Fig. 3) have been described for magnetite in PSD state (Carvallo et al., 2005). The spread along $B_B$ in the FORC diagram has been denoted as reversal ridge and can be generated by SP phases (Roberts et al., 2000) or by MD particles (Pike et al., 2001). Since SP magnetite is ruled out, the reversal ridge is most likely caused by MD particles. It follows that the magnetite grains in the soil can be considered as PSD to MD. This is in good agreement with the SEM observations which revealed magnetite grains of a size generally larger than $20 \mu m$. The similarity of the FORC diagrams, however, provides clear evidence that the grain size distribution of magnetite has not changed during the chemical treatments.

The EPR spectra of all samples except KA-acid are dominated by a broad signal characteristic for FMR, but they differ in their EPR parameters $g_{eff}$ and $\delta B$. It is well known that magnetite and maghemite can produce strong FMR signals (e.g., Griscom, 1984; Gehring et al., 1990). Other ferric oxides such as goethite and hematite can also cause a broad resonance (Angel and Vincent, 1978; Gehring and Karthein, 1989). Because the absorption intensity is proportional to the susceptibility, the EPR signal of these ferric oxides will be weak and hidden by the signal arising from magnetite/maghemite. Therefore the removal of goethite and hematite cannot account for the observed spectral changes upon CBD treatment. The observed changes could result from the dissolution of SD magnetite and maghemite or by partial chemical modification of MD or PSD magnetite. The similarity of the FORC diagrams before and after CBD treatment argues against significant changes of the magnetite properties, and thus in favour of the dissolution of the maghemite. The occurrence of a shoulder in the KA_dith FMR spectrum upon rotation suggests an additional directionally dependent absorption in the sample where maghemite has been removed. Schlömann and Zeender (1958) describe additional subsidiary peaks in polycrystalline ferrites occurring on the low-field side of the main resonance and explain them by strong magnetocrystalline anisotropy. Therefore, it is assumed that the shoulder found in the KA_dith spectra is caused by the magnetocrystalline anisotropy. With this in mind, a likely reason why the secondary absorption described above is clearly visible in the KA_dith only, is that maghemitization
reduces or masks the magnetocrystalline anisotropy. With other words, there is a link between CBD treatment and the increase of the magnetocrystalline anisotropy. Considering the maghemitization as a topotactical transformation (Gallagher et al., 1968), the dissolution of maghemite increases the Fe$^{(III)}/$Fe$^{(II)}$ ratio in the crystal structure. It is known that magnetocrystalline anisotropy energy in magnetite arises mainly from Fe$^{(II)}$ (e.g., Dunlop and Özdemir, 1997), and, therefore, the maghemitization, i.e., oxidation of Fe$^{(II)}$, reduces it, suppressing the secondary EPR absorption in KA and KA$_{ox}$. The angular dependence of this absorption, which is clearly visible for KA$_{dith}$, was not considered by Schlömann and Zeender (1958). Despite this fact, the behaviour of the secondary peak can be explained based on their findings. These authors showed for homogeneous polycrystalline systems a dependence of the intensity of the subsidiary absorption from the magnitude of the anisotropy and its influence on the effective field. In such a system, one can assume a randomized distribution of the anisotropies of the individual grains, and thus, of the corresponding easy axes. In natural samples, however, the magnetite grains are highly diluted in the soil matrix. In our experimental design, these magnetite grains in untreated and chemically treated samples are fixed relative to each other. As a consequence, the distribution of the easy axes has a given preferential orientation which leads to the angular dependence of the secondary EPR absorption indicated by $g_{\text{eff}}$. (Fig. 5.6) The angle where $g_{\text{eff}}$ has its maxima can be assigned to the configuration where most of the easy axes have the lowest angular departure relative to the applied field (e.g., Bickford, 1950).

The low temperature EPR data provide further evidence for the maghemitization of magnetite in our tropical soil. The jump in $\delta B$ for KA$_{dith}$ between 100 and 120K occurs in the same temperature range where the Verwey transition of magnetite has been observed. At this transition, the crystallographic structure changes from cubic to monoclinic (e.g. Muxworthy and McClelland, 2000). Only a few low-temperature EPR data are available on natural magnetite (Gehring and Karthein, 1989; Weiss et al. 2004b; Ananou et al., 2005; Kopp et al., 2006a). Weiss et al. (2004b) used the increase in $\delta B$ of 30 % between RT and 77 K as an indication for a Verwey transition. The samples KA and KA$_{ox}$, which show no jump between 120 and 100 K exhibit an increase between RT and 80 K by about 50 %. Hence, the broadening in such a temperature range cannot be taken as an unambiguous evidence for a Verwey transition. Ananou et al. (2005) published a sequence of low temperature EPR data of a tephra containing magnetite/maghemite and another ferric oxide, in which no spectral changes between 120 and 100 K were found. The EPR data on synthetic magnetite reported in
the literature show also no uniform picture of the Verwey transition. Different phenomena such as line broadening, loss of absorption or the appearance of new signals have been described associated with this transition (e.g., Bickford, 1950; Kale et al., 2001; Stankowski et al., 2006). A jump in linewidth as found for KA_dith was observed in a zero field cooled Fe₃O₄ crystalline film (Kale et al., 2001). These authors explained this phenomenon by an increase in possible easy axes caused by the crystallographic changes from cubic to monoclinic. With this in mind, we assume that the observed jump in δB indicates a Verwey transition in KA_dith. The absence of this jump in the spectra of the KA and KA_ox samples indicates a suppression of the Verwey transition. Such a suppression can be caused by either oxidation, i.e., maghemitization, defect structures (Özdemir et al., 1993), or by an increased Ti content (Kakol et al., 1992). The CBD treatment is known to dissolve maghemite (van Oorschoot and Dekkers, 1999), but leaves larger magnetite grains (> 20 μm) mainly unaffected (Hunt et al., 1995). Therefore, the visibility of the Verwey transition in KA_dith is most likely due to the removal of maghemite associated with the magnetite surface. Finally, such oxidation of the magnetite surfaces fits well in the depositional environment of a subtropical alluvial Vertisol which is characterized by relative fast weathering dynamics.

5.5 Conclusions
The combination of EPR spectroscopy and rock magnetic methods applied to untreated and chemically treated soil samples allowed to detect the maghemitization of magnetite. The rock magnetic methods identified magnetite as the only carrier of the remanent magnetisation at RT. The FORC diagrams showed that the different chemical treatments did not change significantly the magnetic properties of the magnetite grains. The EPR spectral properties of the CBD treated sample, from which maghemite was extracted, provided an indirect proof for the maghemitization of the magnetite surface. The elimination of the surface oxidation by removing the oxidation product increased the magnetocrystalline anisotropy of the magnetite at RT as indicated by the angular dependence of $g_{\text{eff}}$ and $\delta B$. At low temperature, the jump in $\delta B$ between 100 and 120 K indicating a Verwey transition in the magnetite is also visible after the removal of maghemite. The presented experimental approach clearly demonstrates that EPR spectroscopy can be an additional tool to detect maghemitization in natural samples.
Chapter 6 Magnetite weathering in a Vertisol with seasonal redox-dynamics

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Abstract

We investigated soil samples from a Vertisol in a flat lying flood plain in the savannah woodland of southern Mali, which is characterized by a water regime governed by regularly occurring wet and dry seasons. The soil was subdivided into four horizons which differed in the content and speciation of the redox sensitive elements and in the length of waterlogging. Magnetically, the profile could be subdivided into two parts. The magnetic susceptibility, the hysteresis parameters $M_r$, $M_s$, and $B_c$, as well as the coercivity of remanence $B_{cr}$, indicate that the upper two horizons differed from the lower two horizons by a higher content of magnetite and a larger contribution of multi-domain size magnetite grains as compared to single-domain size grains. A comparison of the chemical and magnetic data suggests that dissolution of magnetite in our soil is driven by a seasonal change between anoxic and oxic conditions.


6.1 Introduction

The magnetic properties in soils are often dominated by magnetite \([\text{Fe}^{2+}2\text{Fe}^{3+}]\text{O}_4\). This ferrimagnetic (FM) phase has a susceptibility that is several orders of magnitude higher than that of the antiferromagnetic (AFM) ferric oxides such as goethite and hematite, which generally occur in higher concentrations in soils and determine soil colours. The origin of the magnetite is lithogenic or pedogenic. The latter can be of inorganic or biogenic origin and is characterised by grain sizes in the single domain (SD) (≈ 0.03 - 0.1 μm) or superparamagnetic (SP < 0.03μm) ranges (e.g., Evans and Heller, 2003).

In soils, the top layers very often reveal an enhanced magnetic susceptibility caused by the increase in FM magnetite (e.g., Geiss and Zanner, 2006). This enhancement can be due to (a) the accumulation of magnetic particles from the parent rock during pedogenesis, (b) the input of atmospheric particulate fall-out of either natural or anthropogenic origin, or (c) the biogenic or inorganic neo-formation of magnetite during pedogenesis (e.g., Maher and Taylor, 1988; Fassbinder et al., 1990; Evans and Heller, 1994). The most extensively studied examples of an increased susceptibility due to pedogenic magnetite formation are loess/paleosoil sequences, which have been used as proxies to deduce paleoclimate oscillations (e.g., Heller and Evans, 1995). The above processes have in common that the accumulation of magnetite particles causes a relatively enhanced magnetic susceptibility in the top layers of a soil profile. By contrast, little is known about the effect of magnetite weathering on the magnetic pattern of soil profiles. Various authors have proposed that waterlogging in soils can lead to the reductive dissolution not only of ferric oxides but also of magnetite (e.g., Nawrocki et al., 1996; Maher, 1998; Hanesch and Scholger, 2005; Orgeira and Compagnucci, 2006).

On the other hand, laboratory experiments and theoretical considerations have provided evidence that the transformation of magnetite is an oxidative process involving a maghemite (\(\gamma\)-Fe2O3) phase under both oxic (e.g., Lindsey, 1976; Gallagher et al., 1968) and anoxic conditions (Jolivet and Tronc, 1988). Under oxic conditions this reaction can be written as (White et al., 1994):
2 \([Fe^{2+}2Fe^{3+}]O_4 + \frac{1}{2}O_2 \rightarrow 3\gamma[2Fe^{3+}]O_3 \) \hspace{1cm} (6.1a)

or

3 \([Fe^{2+}2Fe^{3+}]O_4 + \frac{1}{2}O_2 + 2H^+ \rightarrow 4\gamma[2Fe^{3+}]O_3 + Fe^{2+} + H_2O \) \hspace{1cm} (6.1b)

Equation (6.1a) denotes \(\gamma-Fe_2O_3\) formation by the incorporation of oxygen in a new oxide structure. In equation (6.1b) \(\gamma-Fe_2O_3\) is formed by an electron exchange with dissolved \(O_2\) to produce ferrous iron and water. A topotactical transition has also been achieved experimentally under anoxic conditions in an acidic medium (Jolivet and Tronc, 1988), conformal with the following equation (White et al., 1994):

\([Fe^{2+}2Fe^{3+}]O_4 + 2H^+ \rightarrow [2Fe^{3+}]O_3 + Fe^{2+} + H_2O \) \hspace{1cm} (6.2)

Experiments by White et al. (1994), based on these equations, showed that the oxidative dissolution under anoxic conditions is strongly pH-dependent and the rate is very low at near neutral conditions. A disagreement arises when comparing such slow dissolution rates of magnetite in laboratory experiments and the depletion of magnetite in gleyic soil horizons. There are, however, no mechanistic studies on the dissolution of magnetite in gleyic soil horizons, because of the difficulties arising from insufficient knowledge of the water regime which is strongly influenced by the topography and often irregular precipitation.

In this study, we present magnetic data for a Vertisol with a seasonally fluctuating water table in a flat lying flood plain in southern Mali. This soil was described in detail by Gehring et al. (1997) and Fischer et al. (2007); it is characterized by a water regime governed by regularly occurring wet and dry seasons. Furthermore, the subtropical climate with relatively high precipitation and temperatures accelerates weathering. We will show the effect of the regularly fluctuating water table on the magnetic characteristics of the soil profile.

### 6.1.1 Site characteristics

The Vertisol is located in the savannah woodland of southern Mali southeast of the village of Loulouni (Latitude 10° 55' 0 N, Longitude: 5° 40' 0 W). The climate is subtropical with wet and dry seasons referred to as the West African monsoon climate. Meteorological data for Sikasso, the regional centre about 80 km to the north, collected for a 51 year period (1950-
show a mean annual rainfall of 1186 mm distributed between a dry season (November to April) and a wet season (May to October). The mean average annual temperature is 27 °C with mean daily maximum temperatures ≥ 30 °C (see: http://www.worldweather.org). The Vertisol developed on alluvial material in a flat flood plain of the Bafini river. The soil was described in detail (Gehring et al., 1997) and the major features are summarized in the following. The Vertisol is a very fine clayey, montmorillonitic, non-acidic, hyperdemic Ustic Endoaquert (Soil Survey Staff, 1994). The profile exhibits a uniform dark-olive to black color. During the sampling (12th December 1993), the water-table was at a depth of 1.2 m and cracks extended to a depth of 0.2 m. The profile can be subdivided into four horizons: Ap, A2, A3, and Ag. The Ap and A2 horizons were intensively rooted. The A2 and A3 horizons exhibited a wedge-like structure. The Ag horizon was massive and below 1m had a plastic wet consistency. Reddish mottles with a diameter of approximately 1cm occurred in the Ag horizon.

6.2 Materials and Methods
Dried and sieved samples, stored at about 15°C and a humidity of 40-50 % at the WSL soil archive, were used. Soil chemical data were taken from Gehring et al. (1997). X-ray diffractograms were recorded on a Siemens D5000 diffractometer with a Cu Kα radiation. The morphology of the magnetite was analysed by scanning electron microscopy connected to an energy dispersive X-ray spectrometer (SEM/EDX). For the SEM analysis the soil samples were suspended in distilled water and the suspension was agitated with a magnetic stirrer. The magnetic particles that adhered to the stirrer were placed on a SEM holder.

Susceptibility measurements were used to determine the content of magnetic components. The susceptibility of magnetite or maghemite is several magnitudes higher than that of antiferromagnetic goethite and hematite or of paramagnetic clay minerals. Diamagnetic materials such as quartz have negative susceptibilities (Mullins, 1977). The ferrimagnetic phases magnetite and/or maghemite normally dominate the susceptibility of soil materials. Temperature dependence of magnetic susceptibility was measured on an AGICO KLY-2 Kappabridge coupled to a thermo-element in order to determine the Curie or Néel temperature of the magnetic carriers in the Vertisol. Above the Curie temperature a ferrimagnetic mineral becomes paramagnetic i.e., it loses its remanent magnetization. In order to prevent oxidative formation of hematite during heating, the measurements were performed in an argon atmosphere.
The frequency dependence of the susceptibility was measured on 5 samples per horizon between 0.3 and 5 kHz with an amplitude of 0.5 mT at RT using a Quantum Design PPMS 9 magnetometer with a detection limit of $2.5 \times 10^{-11}$ Am$^2$.

The hysteresis behaviour of the magnetic moment ($m = V \times M$ where $M$ is the magnetization and $V$ is the unknown volume) as a function of the magnetic field was measured up to 1 Tesla (T) with a Vibrating Sample Magnetometer (VSM, Princeton Measurements) on the same 20 samples as in the magnetic experiments above. All loops were started in a 1 T field and the elapsed time for one cycle was 245 s with measuring steps of 5 mT. The hysteresis loops were 70% slope-corrected for the paramagnetic constituents in the soil samples. This correction assumes that all remanence carriers are saturated in a field of 0.7 T. The remanent magnetization ($M_r$), the saturation magnetization ($M_s$), and the coercivity force ($B_c$) were obtained from the hysteresis loop. The zero crossings of the loop with the magnetization axis and with the axis of the applied field define $M_r$ and $B_c$, respectively. The magnetization at 1 T was taken as $M_s$. In addition to these parameters the coercivity of remanence ($B_{cr}$) was determined by the backfield demagnetization in steps of 2 mT of a saturation remanence magnetization acquired in a 1 T field. The following diagnostic tests were used to identify grain-size properties of the magnetite: (1) the $M_r/M_s$ and $B_{cr}/B_c$ ratios were plotted against each other (Day et al., 1977); (2) first-order reversal (FORC) diagrams were obtained. A FORC diagram is derived from repeated measurements of $M(B)$ curves, by which, in addition to the major hysteresis cycle, minor loops (113 in this case) between a saturating positive field of 1 T and a number of reversed fields are measured (e.g., Roberts et al., 2000). In a FORC diagram, the horizontal axis denotes the coercive field $B_c$ and is indicative of the grain size range, whereas the field $B_b$ plotted on the vertical axis is indicative of magnetic interactions. A detailed description of the method can be found elsewhere (Roberts et al., 2000). The data were analysed with a Matlab code by Winkelhofer (personal communication, 2006).

**6.3 Results**

X-ray diffractometry of the samples from all horizons revealed quartz and montmorillonite as major components and kaolinite and feldspar as minor components (data not shown). No significant variation in the mineralogical composition was found within the profile. All the magnetic phases were below the detection limit of x-ray diffraction. Under the scanning electron microscope particles consisting mainly of Fe and Ti and in grain-sizes of several tens
of microns occurred throughout the profile (Fig. 6.1a,b). Such a phase in the Vertisol was identified as hemo-ilmenite (Gehring et al., 2007). The magnetite revealed no clear morphology because of weathering and agglutination mainly with clay minerals and quartz (Fig. 6.1c). The microscopic detection of the weathered magnetite in the profile was supported by EDX analysis which revealed Fe as the dominant and Ti and V as minor phases (Fig. 6.1d). The weathered magnetite revealed striped or honey-combed features. Larger grains could be broken down mechanically into chemically identical fragments. Unaltered magnetite grains were only rarely visible.

Figure 6.1: SEM micrographs of a hemo-ilmenite grain from the Ap horizon (a); the circle indicates the area of the EDX analysis shown in (b); an assembly of weathered magnetite from the Ap horizon (c) and the representative EDX analysis (d) of the three areas marked in (c).

Within the profile the susceptibility $\chi$ varied between $5.5 \times 10^{-7}$ m$^3$kg$^{-1}$ in the Ap and $1.6 \times 10^{-7}$ m$^3$kg$^{-1}$ in the A3 horizons (Table 6.1). The values of $\chi$ were about a factor of three higher in the upper two horizons. The susceptibility in Ag was higher than in the A3 horizons.
Table 6.1: Chemical and magnetic key parameters. For the hysteretic parameters the minimum and maximum values are listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\chi$ [m$^3$kg$^{-1}$]</th>
<th>$B_{c_e}$ [mT]</th>
<th>$B_c$ [mT]</th>
<th>$B_{c_e}/B_c$</th>
<th>$M_r/M_s$</th>
<th>Mn [mg kg$^{-1}$]</th>
<th>Fe$<em>{ox}$/Fe$</em>{d}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ap</td>
<td>$5.5 \times 10^{-7}$</td>
<td>29.7 - 32.1</td>
<td>8.9 - 10.7</td>
<td>2.89 - 3.59</td>
<td>0.15 - 0.18</td>
<td>2080</td>
<td>0.38</td>
</tr>
<tr>
<td>A2</td>
<td>$4.2 \times 10^{-7}$</td>
<td>29.6 - 35.6</td>
<td>9.2 - 11.1</td>
<td>3.13 - 3.35</td>
<td>0.15 - 0.19</td>
<td>1550</td>
<td>0.44</td>
</tr>
<tr>
<td>A3</td>
<td>$1.6 \times 10^{-7}$</td>
<td>53.8 - 56.2</td>
<td>21.4 - 27.8</td>
<td>1.99 - 2.52</td>
<td>0.26 - 0.29</td>
<td>507</td>
<td>0.65</td>
</tr>
<tr>
<td>Ag</td>
<td>$2.4 \times 10^{-7}$</td>
<td>41.9 - 58.3</td>
<td>15.4 - 22.2</td>
<td>2.65 - 2.93</td>
<td>0.28 - 0.30</td>
<td>1950</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Upon heating the samples from the Ap, A2, and A3 horizons, $\chi$ remained stable up to 250°C followed by a slight increase with a maximum at about 300°C. This increase was more pronounced for sample A3 (Figure 6.2). Further heating led to a continuous decrease, which became more pronounced between 520° and 580°C. At higher temperature $\chi$ remained stable. The sample from the Ag horizon revealed a different behaviour upon heating. A weak shoulder at about 300°C was followed by a drastic increase up to about 420°C and a decrease up to 550°C. Upon cooling, all samples showed a drastic increase in $\chi$ at about 530°C, and the end value at room temperature was two orders of magnitude higher than the starting value. The frequency dependence of the susceptibility between 0.5 and 5 kHz was $5.3 \pm 0.8 \%$ for the Ap, $4.5 \pm 0.6 \%$ for the A2, $2.1 \pm 0.6 \%$ for the A3, and $4.1 \pm 0.3\%$ for the Ag horizon.

Figure 6.2: Magnetic susceptibility versus temperature for the soil samples.
The hysteresis loops of Ap and Ag samples are characterized by a low coercivity phase with a closure field of less than 0.5 T (Fig. 6.3). The coercive force ($B_c$) was similar in the upper two horizons and was increased by about a factor 2 in samples A3 and Ag (Table 1). A similar trend was found for remanence of coercivity ($B_{cr}$). The ratio of $B_{cr}$ to $B_c$ was higher in the upper two horizons (Table 1). The ratio between the remanent magnetization $M_r$ and the saturation magnetization $M_s$ was augmented by about 60% in the two lower horizons.

Presenting the hysteresis parameters in a Day plot (Fig. 6.4) showed two distinct set of clusters for the samples from the different horizons. All clusters were shifted with respect to the theoretical SD/MD mixing curve number 3 calculated by Dunlop (2002).

![Figure 6.3: Hysteresis loops of the Ap (a) and Ag (b) samples.](image-url)
The FORC diagram of the Ap and the A2 samples revealed two features. The distribution along the $B_c$ axis extended up to 60 mT with weakly diverging open contours; the maximum was observed at $B_c \approx 12$ mT. The second feature consisted of a distribution along the $B_b$ axis for values of $B_c < 5$ mT. The FORC diagram of the A3 and Ag samples revealed a more pronounced feature along the $B_c$ axis and a similar distribution along the $B_b$ axis (Fig. 6.5). Profiles along the $B_c$ axis of normalized FORC distributions revealed a much larger contribution of particles with a higher $B_c$ in the two lower horizons (Fig. 6.6).
Figure 6.5: FORC diagrams (smoothing factor SF 5) of the soil samples.
Chapter 6 Magnetite weathering in a Vertisol with seasonal redox dynamics

Figure 6.6: Normalised coercivity profiles along $B_c$-axis ($B_b = 0$) in the FORC diagrams.

6.4 Discussion

6.4.1 Soil formation factors and other constraints

The remote location of the sampling site suggests low anthropogenic input of magnetic particles. Because of the deposition of the Vertisol in a flat lying floodplain a significant topographic effect on the soil formation can be excluded.

The site near Loulouni is located in the Intertropical Convergence Zone (ITCZ). The north-south movement of the ITCZ in response to changes in the location of maximum solar heating controls the seasonality of the climate, which is known as the West African monsoon circulation (e.g., Gasse, 2000). The seasonality near the sampling site with summer rains and winter droughts is well documented for the last 50 years (see: http://www.worldweather.org). A longer term climate reconstruction over thousands of years is difficult because of the limited number of climate archives. Different models have been put forward to simulate the monsoon circulation in the latest Pleistocene and Holocene (e.g., Kutzbach et al., 1996; deMenocal et al., 2000). For Western Africa the best constraints for the climatic reconstruction are based on a large data set, including magnetic proxies, from Lake Bosumtwi in the lowland forest zone of southern Ghana (e.g., Shanaham et al., 2006; Peck et al., 2004; Maley, 1991; Talbot and Delibrias, 1980). These data provide evidence for a transition from cold arid grassland vegetation to warm drought-intolerant forest vegetation at about 10 kyr BP. The latter vegetation is similar to the present one in southern Ghana, and thus indicative of small changes in climate. The Vertisol site near Loulouni is located at about only four degrees of latitude north of lake Bosumtwi and within the migration path of the ITCZ, and there is no evidence that southern Mali was at any time not affected by this zone during the
Holocene. Thus, rather stable monsoonal conditions can be postulated for our site over the last thousands of years.

The stable seasonal pattern of precipitation and temperature and the location in a flat lying flood plain suggest a constant pattern of the water regime. Finally, the lack of vertical stratification within the profile, the overall mineralogical composition and the occurrence of weathering resistant hemo-ilmenite grains throughout the profile indicate a uniform source area, which led to a uniform parent material. Based on these considerations, we assume that the magnetic patterns within the profile are the result of pedogenesis rather than alluvial sedimentation. Furthermore, the distribution of redox-sensitive elements and the occurrence of redoximorphic features indicate prevailing reducing conditions in the Ag horizon, the redox cline in the A3 horizon, and a restriction of pedoturbation mainly to the Ap and A2 horizons (Gehring et al., 1997).

6.4.2 Magnetic patterns

Magnetite is the only remanence carrier in the soil profile since Gehring et al. (2007) showed that the hemo-ilmenite in the Ap horizon has a $T_c$ far below RT. The EDX analysis revealed a similar composition of the ilmenite in all horizons, and therefore it can be postulated that this phase is paramagnetic at RT. The magnetite in the soil profile contains a minor amount of Ti and V as indicated by EDX analysis. The relatively small deviation of the ordering temperature $T_c$ (520 and 570 °C) from the one of pure magnetite ($T_c \approx 580°C$) indicates that the Ti substitution is not very pronounced. The bump in the $\chi$ vs. $T$ diagram at about 300 °C in the samples of the upper three horizons (Fig. 6.2) suggests the formation of a new magnetic phase. This thermal effect is very strong in the samples from the Ag horizon. This increase in $\chi$ can be explained by the conversion of poorly crystallized ferric oxides such as ferrihydrite to maghemite or magnetite in the presence of soil organic matter (e.g., Hanesch et al., 2006). This interpretation is supported by the relatively high contents of organic carbon throughout the profile, which vary between 2.2 and 3.5% (Gehring et al., 1997). The subsequent decrease of $\chi$ above 460 °C is most likely due to the conversion of maghemite to hematite (Gehring and Hofmeister, 1994). On this basis, the strong thermo-magnetic effect in the Ag horizon can be explained by the predominance of ferric oxides in a poorly crystallized form. Gehring et al. (1997) reported such predominance based on the high ratio between the oxalate- and dithionite-extractable iron ($Fe_o/Fe_d$) (Table 6.1). The $\chi$ values at room temperature are low compared to the bulk susceptibility of magnetite cited in the literature (e.g., Peters and Dekkers, 2003). These authors reported an average $\chi$ value of $6.7 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ for magnetite.
which is about three orders of magnitude higher than the $\chi$ of our soil samples. Assuming that susceptibility arises only from ferrimagnetic phases, a concentration of magnetite of less than 0.1 wt % can be inferred. Furthermore, based on the values of $\chi$, the upper part of the profile contains more than twice as much magnetite as the A3 and Ag horizons.

The higher $B_{cr}/B_c$ ratios, accompanied by lower $M/M_s$ ratios, suggest larger particle sizes (e.g., unaltered cores) in the Ap and A2 horizons than in the lower part of the profile (Day et al., 1977). All samples are shifted towards higher $B_{cr}/B_c$ ratios with respect to the theoretical curve. Such a shift could be due to a contribution of SP magnetite or to a bimodal admixture of larger MD magnetite (Dunlop, 2002). Using low field susceptibility measurements at dual frequencies (0.47 and 4.7 kHz), a widely used tool to detect superparamagnetic magnetite (e.g., Thompson and Oldfield, 1986), Gehring et al. (1997) showed a negligible contribution of ultrafine grains in our samples. The current frequency measurements with a more sensitive magnetometer reveal similar values for the Ap, A2, and Ag horizons, and a lower value for the A3 horizon. The frequency dependence and the hysteretic properties as presented in the Day plot of the different horizons are incongruent under the assumption of the presence of SP magnetite. Therefore a significant contribution of SP magnetite to the magnetic properties of the different soil horizons is unlikely. According to Dunlop (2002), MD magnetite grains as found under the SEM, mainly in the Ap horizon, could be the reason for the observed shift. With this in mind, the $B_{cr}/B_c$ and $M/M_s$ ratios indicate that the contribution of MD grains is more pronounced for the Ap and A2 horizons than for the A3 and Ag horizons. Since $B_c$ represents the resistance to the change in magnetization and increases generally with decreasing magnetite grain sizes, the smaller contribution of multidomain grains in the lower part of the profile is confirmed by the FORC measurements (e.g., Dunlop and Özdemir, 1997; Roberts et al., 2000).

The contents of the redox-sensitive elements Mn and Fe (Table 6.1) indicate the redox cline within the A3 horizon (Gehring et al., 1997). In this horizon, the water table shows the largest fluctuations, as suggested by the minimum total Mn contents. This minimum is caused by the regular change between reductive dissolution during the rainy season and the removal with the receding water table. Furthermore, the $\text{Fe}_o/\text{Fe}_d$ ratio of approximately 1 in the mostly waterlogged Ag horizon suggests the occurrence of mainly amorphous Fe phases. The $\text{Fe}_o/\text{Fe}_d$ ratios of approximately 0.4 in the Ap and A2 horizons and of 0.65 in the A3 horizon indicate larger contributions of crystalline ferric oxides (Schwertmann, 1964). The comparison of $\chi$ with the chemical data reveals that the horizons with pronounced (A3) or
prevailing (Ag) reducing conditions contain less magnetite than the upper, mostly oxic horizons. Furthermore, the ratios of the hysteretic parameters and the FORC diagram suggest that the magnetite population in the A3 and Ag horizons has a larger contribution of smaller magnetite grains. These results argue in favour of a higher degree of magnetite alteration under anoxic conditions, which is in agreement with the postulate of reductive dissolution of magnetite (e.g., Hanesch and Scholger, 2005; Maher, 1998).

White et al. (1994), however, showed in laboratory experiments under anoxic conditions, that magnetite undergoes surficial maghemitization caused by the loss of structural Fe\(^{2+}\). They demonstrated that this process slowed down with time due to passivation by a reduced diffusion of Fe\(^{2+}\) through the topotactical maghemite. Furthermore, the rate of the maghemitization under anoxic conditions decreased drastically with increasing pH. This leads to the conclusion that in our Vertisol with a pH around 7 this mechanism would not lead to substantial dissolution of magnetite. By contrast, it is well known that ferric oxides can be reductively dissolved under natural anoxic conditions (e.g., Schwertmann, 1991; Stumm and Sulzberger, 1992). Such a surface-chemical process is significant at oxic/anoxic boundaries with a continuous production of reducible metal oxide surfaces, suitable ligands, and Fe\(^{2+}\).

With all this in mind, we postulate that pronounced magnetite dissolution in the lower horizons of our Vertisol occurs by a seasonal interchange of surficial maghemitization under oxic conditions and microbially induced reductive dissolution of this maghemite layer. This is supported by spectroscopic evidence for magnetite with surficial maghemitization in the Ap horizon (Fischer et al., 2007). Furthermore, these considerations are in good agreement with the findings of White et al. (1994), who extrapolated laboratory data to predict a mean residence time of \(10^7\) years for a sand-size grain under constantly anoxic conditions. Since the lower part of the profile contains fewer and much smaller magnetite particles, it can be postulated that the length of the waterlogged conditions is responsible for the degree of the reductive dissolution of the ferric oxides formed during the dry season, and, thus, determines the overall rate of magnetite alteration. This period is relatively short in the Ap and A2 horizons.

6.5 Conclusions

Magnetic and chemical data for a Vertisol in the savannah woodland of southern Mali exhibiting a seasonally fluctuating watertable indicate that dissolution of magnetite in
subtropical soils is driven by a seasonal change between anoxic and oxic conditions. This is reflected by the grain size distribution in the soil profile which shows a more pronounced presence of MD magnetite in the upper two horizons. The present occurrence of magnetite throughout the profile suggests that magnetite dissolution under changing redox conditions is a process occurring on the time scale of soil formation.
Chapter 7

Summary and outlook

The purpose of this thesis project, which consisted of four experimental studies, was to examine various types of mineral transformation of relevance for a better understanding of geological systems. These studies include the thermal transformation of Mg phyllosilicates in the presence of trace elements and polymorphic, as well as mineral chemical transformation of the mixed valence oxide magnetite. To investigate these transformations an experimental approach was used which combined mineralogical and chemical methods with EPR/FMR spectroscopy and magnetic analysis. Here the main results of the different studies are summarised and possible future research activities outlined.

In Chapter 3, the thermal stability of a synthetic hectorite in the presence of Cu(II) in concentrations similar to its occurrence in rock was studied with a two-step approach. First, the hectorite was loaded with Cu(II) in concentrations between 50 and 500 ppm using a hydrothermal treatment. Secondly, the thermal stability of Cu(II)-loaded hectorite was compared to untreated and hydrothermally-treated hectorite with no Cu(II). The thermal stability as detected by TG analysis exhibited that the breakdown of hectorite started at about 690 °C in the presence of Cu(II), which was about 30 degrees lower than for the Cu(II)-free samples. Moreover, XRD revealed that the presence of Cu(II) produces fluororichterite as an additional conversion product to the expected enstatite. The lower thermal stability is explained as an effect of structure-bound Cu(II), which exhibits typical Jahn-Teller distortion. The distorted Cu(II) configuration in Mg(II) octahedral layers of the hectorite can be considered as sites of lesser stability where the breakdown is triggered. This destabilisation effect of Cu(II) catalyses the formation of richterite which is mainly caused by the fluorine
added during the hydrothermal treatment in the first experimental step. This finding provides evidence that trace elements may affect the mineral formation in geological systems.

In order to approximate conditions in geological systems, future experimental study of thermal transformations should be expanded to include multimineral systems with different paramagnetic cations. For such studies, the experimental approach used in this thesis may be applied to analyse the overall mineral transitions. For a detailed study of the coordination properties and the fate of various paramagnetic cations in a multimineral system, advanced EPR techniques such as pulse EPR spectroscopy (Jeschke and Schweiger, 2001) should be considered. These applications (e.g., Electron Spin EchoEnvelope Modulation) can provide information on the nuclear spin environment of a paramagnetic center. Considering structure-bound Cu(II) in hectorite, it would be possible with pulse EPR to detect diamagnetic $^{25}$Mg ($I = 5/2$) or protons in the vicinity of the paramagnetic Cu(II) center. The few studies of multimineral systems demonstrate that pulse EPR spectroscopy, successfully used in physical chemistry, may also have potential in the earth sciences (Hoffmann and Schweiger, 1995; Schosseler and Gehring, 1996).

In Chapter 4, the low-temperature magnetic properties of nanophase magnetite ($\text{Fe}_3\text{O}_4$) in magnetotactic bacteria were studied as an example for low-temperature polymorphic transformation. Intact chains of $\text{Magnetospirillum Gryphyswaldense}$ were used as examples, and the magnetic properties were analysed by both FMR spectroscopy and static and dynamic magnetic measurements. The polymorphic transformation where the magnetite structure changes from cubic to monoclinic, known as the Verwey transition, occurs at 100 K. This temperature was about 20 K lower than the value for pure magnetite single crystals. The lowering of $T_v$ of magnetosomes was explained by non-stoichiometry, but it could also be the result of dominant shape anisotropy masking the distinct increase of the magnetocrystalline anisotropy at $T_v$.

Ferromagnetic resonance spectroscopy revealed the dominant contribution of the shape anisotropy to the total anisotropy due to the alignment of the magnetosomes in chains. This contribution was documented by the asymmetric FMR signal with an extended low field and a sharp high-field absorption component, $g_{\text{eff}}$ value < 2, and a $90^\circ$ angular dependence of the intensity of the two peaks on the low-field side. The temperature behaviour of the FMR signal between room temperature and 77 K suggests a significant contribution of the shape anisotropy down to the temperature of the Verwey transition $T_v$. Despite this fact, the smearing of the two low-field peaks and the shift of the $g$-value towards more than 2 below
130K point to the decrease in shape anisotropy below the isotropic point (first-order magnetocrystalline anisotropy constant \(K_1 = 0\)). This can be explained by the tilting of the magnetite easy axes from [111] to [100], which lead to the departure from the parallel orientation of the easy axes of the magnetosomes and the axes of their chain alignment. Moreover, with FMR it was possible to monitor the magnetocrystalline anisotropy with temperature by comparing \(K_1\) taken from literature and the measured linewidth \(\delta B\) between RT and the isotropic point at 130K. Between this point and \(T_v\) the expected increase of \(K_1\) is masked by the shape anisotropy, as indicated by \(\delta B\). This finding provides clues that shape anisotropy of the magnetosome chains can affect the detection of \(T_v\), but does not unambiguously explain the lowering of \(T_v\). Structural information obtained from X-ray diffraction showed that magnetosomes departed from ideal stoichiometry. Comparing this departure with the literature and the corresponding magnetic data, it was concluded that the lowering of \(T_v\) was due to non stoichiometry. This suggests that the \(T_v\) of the magnetosomes is probably an intrinsic property.

In addition to the magnetic identification of the Verwey transition, analysis of the magnetosomes provided further insight into their physical characteristics. Above \(T_v\) dynamic magnetization analysis revealed superparamagnetic (SP) properties between room temperature and about 150 K, i.e., at this temperature all magnetosome chains are blocked. The SP behavior was also indicated by the maximum coercivity in hysteresis measurements at \(T > T_v\). The occurrence of magnetosomes with SP characteristics was supported by transmission electron microscopy. Particles of less than 30 nm were attributed to main carriers of SP properties, and these particles generally appeared at the ends of the chains consisting of single-domain magnetosomes with an average diameter of 35 nm.

Below \(T_v\) static magnetization measurements revealed the generation of high field component at \(T < 50\) K which saturated in a 7 Tesla field and increased the saturation magnetization up to 50 % compared to that found at 0.5 T. This newly-formed magnetic phase occurred simultaneously with a peak in the ac susceptibility measurements. The anomalous behavior could be explained in the concept by Belov (1993). According to this concept, decreasing temperature leads to a more pronounced Vonsovskii exchange interaction between the localized inner electrons and the valence electrons. Ordering of the valence electrons generates the formation of e-sublattices which are antiferromagnetically coupled to B sites of the spinel crystal structure, with octahedral coordinated Fe(II) and Fe(III). This effect may explain the magnetic hardening of the magnetosomes, whereas the increase in the
saturation magnetization at T <50 K is not resolved in detail. The low temperature magnetic properties of *Magnetospirillum gryphiswaldense*, however, implied that electron ordering had a stronger effect on the magnetic properties than the structural change at the Verwey transition.

In a rock magnetic context, the above findings indicate that the Moskowitz test for detecting biogenic magnetite in geological systems, which uses the loss of remanent magnetization at the Verwey transition, is ambiguous. Future research should address the test’s robustness. This could be done experimentally by measuring the low-temperature FMR of different strains of cultivated and wild type magnetotactic bacteria which vary in magnetosome size and shape. Such a study should be completed by numerical simulations of the FMR spectra, as reported in literature for systems of competing uniaxial and cubic anisotropies (e.g., Kachkachi and Schmool, 2007). This could open the door for a quantification of the contribution of different anisotropies and might link the occurrence of $T_v$ associated with magnetotactic bacteria to a specific anisotropy configuration. Moreover, the use of FMR spectroscopy could be applied to unravel the 45 K anomaly in single-domain magnetite. It is worth noting that just such an anomaly at 50 K was reported for SP SD magnetite assemblage in brain tissue (Hirt et al., 2006). Since this anomaly occurs in biological material, it can be assumed that magnetite formation via ferrhydrite precursor is its potential cause (Faivre et al., 2007). Finally, the magnetic relaxation of magnetosome chains is not understood in detail (e.g., Prozorov et al., 2007). In this context, the question of importance could be whether the relaxation properties found at room temperature are related to a certain extend to the magnetotaxis.

Chapters 5 and 6 contain two studies of a Vertisol profile from western Africa as an example of a natural multiminerals system. Magnetite is the only remanent magnetization carrier at room temperature in this soil. An analytical approach is presented which combines rock magnetic tools, FMR spectroscopy and chemical extraction in order to detect maghemitization, i.e., partial oxidation of magnetite. This process was used as a proxy to deduce redox conditions in a geological environment. Since maghemitization leads to a suppression of the Verwey transition, low-temperature magnetic analysis has generally been used to detect this oxidation process in earlier studies.

In Chapter 5 maghemitization was detected by FMR spectroscopy and dithonite extraction samples from the top horizon of the Vertisol. Reducing agent dithionite selectively dissolves maghemite ($\gamma$-Fe$_2$O$_3$) in the presence of magnetite. A comparison of the FMR spectra of
magnetite in soil samples before and after dithonite treatment exhibited significant spectral changes. The \( g_{\text{eff}} \)-value, the linewidth \( \delta B \) and the angular dependence of these spectral parameters revealed a pronounced increase, which suggested that selective dissolution of the ferric oxide changed the magnetocrystalline anisotropy due to an enhanced \( \text{Fe(II)}/\text{Fe(III)} \) ratio in the magnetite particles. In contrast to the untreated samples, the chemically-treated samples exhibited a clear Verwey transition as indicated by a near-doubling of \( \delta B \) between 120 and 100 K. These results show clearly that the magnetite particles in the Vertisol are maghemitized and that FMR, in contrast to classical rock magnetic methods, can detect oxidation processes at room temperature.

The relatively easy procedure of dithonite treatment in combination with the rapid recording of room temperature FMR spectra makes this approach an alternative tool for studying maghemitization in environmental magnetism.

In Chapter 6, the effect of maghemitization on the grain size distribution of magnetite in the Vertisol with seasonal redox conditions was studied. From the above chapter it is known that in this soil the magnetite was partially oxidized and that reductive dissolution can erase the maghemitization. Further basic conditions in this study were stable seasonal climate conditions over thousands of years, which led to relatively controlled watertable fluctuation and redox conditions, respectively, and drainage systems in a nearly flat topography. Hysteresis parameters \( M_r/M_s \) and \( B_c/B_{cr} \) ratios and FORC measurements showed clearly that the two upper horizons (Ap and A2) contained larger magnetite grains than the two lower horizons (A3 and Ag). From data in literature the redox-cline in A3 is known. Under the assumption that the size distribution of magnetite grains in the alluvial Vertisol is determined by the conditions in the depositional environment, the following model which links grain size distribution with climate was proposed. During dry seasons exposure of the magnetite grains to the atmosphere oxidized their surfaces, and during waterlogging in the rainy seasons the ferric surface coating was dissolved. The generally smaller sizes in the lower two horizons indicate that reductive dissolution is the major determined effect for the slow magnetite dissolution via maghemitization. It is worth noting that the grain size effects of magnetite due to changing redox conditions can be detected when the above process has acted over thousand of years. Further investigations are required to verify the above model in different depositional environments on stable cratons. The finding, however, provides evidence that a more detailed knowledge of magnetite weathering has potential as an additional terrestrial proxy for climate reconstruction.
References


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