

Identification of magnetic Fe–Ti oxides in marine sediments by electron backscatter diffraction in scanning electron microscopy

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SUMMARY

In paleomagnetic and environmental magnetic studies the magnetomineralogical identification is usually based on a set of rock magnetic parameters, complemented by crystallographic and chemical information retrieved from X-ray diffraction (XRD), (electron) microscopy or energy dispersive spectroscopy (EDS) of selected samples. While very useful, each of these supplementary techniques has its limitations when applied to natural sample material which are related to low particle concentrations (down to the ppm range in marine sediments) and very fine grain sizes (down to the nm scale). Therefore, meaningful application of such techniques depends on sample quality. Electron backscatter diffraction (EBSD) of individual grains in scanning electron microscopy (SEM) enables mineralogical identification of grains down to ~0.2 micrometer and is particularly powerful when combined with EDS. In this study, we show the merits of EBSD for rock magnetic investigations by analyzing titanomagnetites and hemoilmenites of various compositions and submicron lamella of titanomagnetite–hemoilmenite intergrowths. Such particles often occur in natural marine sediments where EDS often has a semi-quantitative character and compositionally similar intergrowths may be difficult to distinguish. With the mineralogical information provided by EBSD unambiguous identification of spinel-type and trigonal oxides is obtained. Optimal EBSD patterns are gathered from smooth, polished surfaces, but here we show that interpretable EBSD patterns can be obtained directly from the surface of unconsolidated, so called 'non-embedded' particles from marine sediments. This information enhances the interpretative value of rock magnetic parameters.

Key words: electron backscatter diffraction (EBSD), energy dispersive spectroscopy (EDS), hemoilmenite, rock magnetism, scanning electron microscopy (SEM), titanomagnetite.

1 INTRODUCTION

Iron–titanium oxide minerals are fundamental to paleo-, rock and environmental magnetic purposes because they constitute the most common magnetic particles on Earth. Two Fe–Ti oxide solid solution series are relevant for magnetic studies, the titanomagnetite (TM) and the titanohematite–hemoilmenite series. Titanomagnetites, with their large compositional field, also play an important role (Fig. 1; *cf.* also O'Reilly 1984; Waychunas 1991; Dunlop & Özdemir 1997). TM is the cubic spinel series between the magnetite (Mt, Fe₃O₄) and ulvöspinel (Usp, Fe₂TiO₄) end-members. The general TM formula is Fe_{3–x}Ti_xO₄, where *x* is the mole fraction of the ulvöspinel component. Hereafter, TM compositions will be given as 'TM*x*%', for example TM60 for *x* = 0.6. Phases of the trigonal

α-oxide series between hematite (Hmt, Fe₂O₃) and ilmenite (Ilm, FeTiO₃) are called titanohematite or hemoilmenite, depending on their compositions, and will be here simply abbreviated as Hilm. Their general formula is Fe_{2–y}Ti_yO₃, where *y* is the mole fraction of the ilmenite endmember. Titanomagnetites (Tmh), which are generally formed by oxidation of TM at low temperatures, have a cubic crystal structure related to that of the spinels, but are characterized by variable concentrations of cationic vacancies (□) related to the charge-balanced substitution 3Fe²⁺ = 2Fe³⁺ + □. Consequently, their compositional field extends over a large range of Fe²⁺/Fe³⁺ and ΣFe/Ti values (Fig. 1). Although natural Fe–Ti oxides generally contain small amounts of other elements, such as Al, Mg or Cr, the general characteristics listed above are also applicable to naturally occurring compositions.

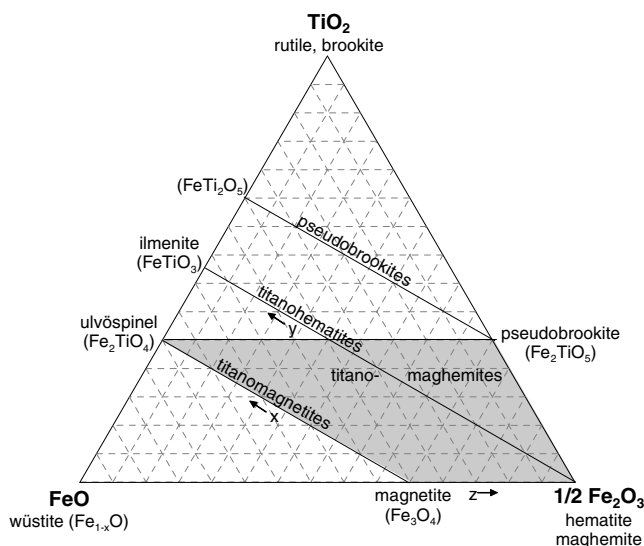


Figure 1 Ternary system of TiO_2 - FeO - $1/2\text{Fe}_2\text{O}_3$ (modified after Dunlop & Özdemir 1997) showing the titanomagnetite and titanohematite-hemoilmenite solid-solution lines and the titanomaghemite compositional field (grey). The mole fraction of the ulvöspinel end member is given by the parameter x with respect to the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ formula of the titanomagnetite solid-solution, the mole fraction of the ilmenite end member by the parameter y with respect to the $\text{Fe}_{2-y}\text{Ti}_y\text{O}_3$ formula of the titanohematite solid-solution. The degree of oxidation is measured by the parameter z . During high-temperature oxidation of titanomagnetites, their bulk compositions are shifted to the right, following the horizontal dashed lines and the resulting products are not single-phase titanomagnetites, but instead mixtures of TM and Hilm. During low-temperature oxidation ($<300^\circ\text{C}$) single-phase titanomaghemites are formed, but the Fe/Ti ratio usually decreases and the compositions follows an upwards sloping line in the ternary diagram (e.g. Feitknecht & Gallagher 1970; Petersen *et al.* 1979; Krása *et al.* 2005).

In contrast to most hard rock samples, the identification of the magnetic carrier minerals in marine sediments is often difficult, in particular for regions in the vicinity of the continental slopes. Various rock magnetic techniques and parameters are available to identify the magnetic Fe-Ti oxide minerals (e.g. low- and high-temperature magnetic remanence and susceptibility measurements, magnetic hysteresis, first-order reversal curve (FORC), anhysteretic (ARM) and isothermal remanent magnetization (IRM) determination). These magnetic techniques are very sensitive, comparatively rapid and in suitable combinations, particularly discriminating for fine, submicron sized grains and magnetically contrasting minerals. Rock magnetic parameters are therefore extensively used in stratigraphic correlations and paleoenvironmental proxy studies. However, the mixing of particles from various sources – which generally occurs in marine sediments – complicates the identification of the different magnetic components. After deposition, magnetic minerals may undergo a series of diagenetic reactions that alter the concentrations of magnetic particles and add more complexity to the interpretation of the magnetic signal. Independent information provided by non-magnetic methods is essential to reduce some inherent ambiguities of rock magnetic data and to gain an understanding of the state and origin of the different types of magnetic particles. Powder X-ray diffraction (XRD) is not suited to identification of individual magnetic minerals in marine sediments because concentrations of the complete magnetic assemblage are typically $<1\%$ by volume. Detailed mineralogical characterizations of magnetic particles by optical microscopic techniques have a long tradition (e.g. Lindley

1926; Ramdohr 1955; Petersen *et al.* 1979), but have limited spatial resolution. SEM with back scattered electron (BSE) imaging (Lloyd 1985) or energy dispersive spectroscopy (EDS) (Goldstein *et al.* 1992) are conventional techniques in petrology (Prior *et al.* 1999). Electron microprobe analysis (EMP) is able to yield the chemical composition of an excitation volume of about $5\text{ }\mu\text{m}$ in diameter.

Analytical transmission electron microscopic (TEM) techniques have been successfully applied in mineral magnetic studies to identify very small magnetic particles in natural samples. For example, Xu *et al.* (1994, 1996, 1997a,b); Shau *et al.* (2000) and Zhou *et al.* (1997, 1999a,b, 2001a,b) performed combined rock magnetic and TEM investigations on Fe-Ti oxides of Mid Ocean Ridge Basalts (MORB) using selected area electron diffraction or convergent beam electron diffraction. TEM methods are time-consuming in analysis (Kumar *et al.* 2001; Humphreys 2004) and TEM sample preparation is often not straightforward.

Feinberg *et al.* (2004) applied the electron backscatter diffraction (EBSD) technique for rapid and precise determination of lattice orientations (Randle & Engler 2000) of clinopyroxene-hosted magnetite inclusions. They describe EBSD as significantly less cumbersome and labour intensive compared to TEM and single-crystal XRD methods. EBSD is not yet well established in rock magnetic investigations, but offers a reasonable basis to identify the mineralogy/crystallography of single grains or grain sections within the spatial resolution of the technique (Humphreys *et al.* 1999; Kumar *et al.* 2001; Humphreys 2001, 2004). In principle, grains as small as $\sim 200\text{ nm}$ can be analyzed by EBSD, as shown by Ohfuji *et al.* (2005). They performed a detailed crystallographic study on microcrystals of natural pyrite framboids. Other work from El-Naggar *et al.* (2005) has even reported EBSD measurements on grains as small as 50 nm .

Here, we test the merits and limitations of the EBSD technique on examples of mineral phases from the Fe-Ti-O system. Several different sample types of synthetic and natural magnetic Fe-Ti oxides have been investigated with EBSD and EDS. We aim to demonstrate the usefulness of EBSD for magnetic carrier identification of marine sediments. Therefore, most analyses were performed on polished section samples, but a novel application of EBSD was also performed on magnetic particles extracted from unconsolidated marine sediments.

2 ELECTRON BACKSCATTER DIFFRACTION

2.1 The EBSD technique

The EBSD technique is briefly described below (for further information see e.g. Schwartz *et al.* 2000; Baba-Kishi 2002). We follow the terminology of Prior *et al.* (1999) using the term EBSD to denote the *diffraction* technique, and the term EBSP to refer to the individual diffraction *pattern*. The interaction of the incident electron beam with the specimen causes electron scattering over a wide range of angles. This omni-directional population of scattered electrons, derived from a small interaction volume, acts as a very small source of electrons, some of which are subsequently Bragg diffracted. The low-loss electrons that backscatter out of the uppermost layer ($10\text{--}50\text{ nm}$) of the sample give useful information for EBSD analysis. Diffraction cones of high intensity intersect with the phosphor screen producing a pattern of almost straight bands (Fig. 2). The weak EBSD signal is processed to improve

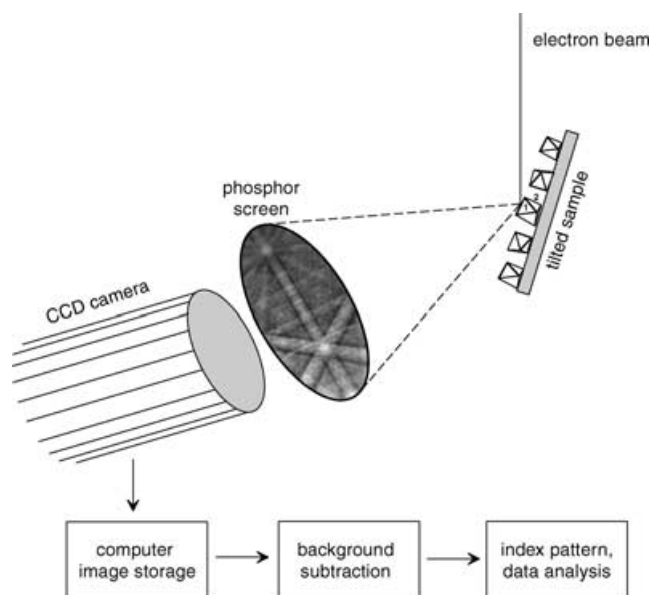


Figure 2. Sketch of the EBSD hardware set up (modified after Prior *et al.* 1999). The EBSD pattern is a projection of the spherical angles between the crystallographic directions onto the flat plane of the phosphor screen. Here, we show a schematic sample for non-embedded particles, position 1 is favourable and position 2 is not favourable for obtaining an EBSD signal of the particle. In standard EBSD, polished sections with smooth surfaces are used.

pattern quality before indexing. Pattern processing involves removal of a background signal followed by contrast enhancement. The selection of the appropriate background signal is crucial for achieving a reasonable EBSP (e.g. Baba-Kishi 2002). The geometry of the EBSD pattern is then calibrated.

The geometry of the diffraction bands in the EBSP is used to index patterns (Lloyd *et al.* 1991; Prior *et al.* 1999). The bands are identified using commercial software (Channel 5, HKL Technology) and compared to crystallographic information selected from the American Mineralogist database (Table 1), which included magnetite, TM (TM75, TM100) and titanomaghemite (Tmh42), hematite and ilmenite (Blake *et al.* 1966; Wechsler & Prewitt 1984; Wechsler *et al.* 1984; Collyer *et al.* 1988). In some cases, multiple solutions to an individual EBSP were possible and a best-fit solution was selected by inspection of the geometry, width and relative intensity of diffraction bands in the simulated and observed EBSP. In addition, the goodness of fit between the observed and the indexed EBSPs in the software was given by the mean angular deviation (MAD). A lower MAD value implies a better solution. Typically MAD values

<1.3° are considered acceptable for crystal orientation measurements. Details about software and pattern processing are given by Dingley (1984); Wilkinson & Hirsch (1997) and Day & Quesada (1999).

2.2 EBSD sample preparation

Highly polished sample surfaces are needed to optimize EBSD pattern quality. Furthermore, as the detector-sample geometry is highly directional, flat, smooth samples are required to improve the line-of-sight between the sample and the detector (Fig. 2). Therefore, most samples were mechanically polished to a 1 µm finish before chemical-mechanical polishing with colloidal silica (±0.03 µm) (Fynn & Powell 1979). To reduce charging in the SEM, large non-conducting areas surrounding the sample were coated with silver paint. Where possible, carbon coating was avoided, as any coating diminished the EBSD signal. Samples which contained many small magnetic particles (unconsolidated magnetic particles extracted from marine sediments, GeoB 6229-6, 655 cm) were first embedded in epoxy resin before polishing and carbon coating. Polished sections only succeeded when individual grains were numerous and large enough (≥100 µm). For other unconsolidated material (GeoB 4313-2, 130 cm), the material of interest was only available in very limited quantities and the very small grain size (down to a few nm) created problems for embedding and polishing, especially as the particles were magnetic and very difficult to disperse. For this sample, the extracted material was dispersed in propanol and a drop of this dispersion was applied to a carbon sticker on a standard SEM stub. After fluid evaporation, the sample was carbon coated. EBSD was difficult on this sample, in part because of the variable background scattering, but also because of the variable surface quality and limited line-of-sight for many of the particles (Fig. 2).

A FEI XL30 SFE scanning electron microscope was used, operating with beam currents between 2.11 and 2.41 nA and working distances between 15 and 20 mm. Acceleration voltages between 12 and 30 kV were used, balancing on the one hand weak pattern signals and on the other hand charging problems of the sample surface. For polished sections (see Section 3.2), lower voltages around ~12 kV gave reasonable EBSPs whereas higher voltages generally resulted in better EBSP signals for embedded and non-embedded particle samples.

2.3 Background signal

The normal approach for polished sections is to collect a background signal on the same sample over many grains. For the non-embedded particle sample (see Section 3.4) this method of background collection was not appropriate, because the sample was not flat and the 3-D topography of the individual grains produced large variations

Table 1. Chemical and crystallographical data of the mineral phases used to generate the simulated EBSD pattern solutions for this study, originating from the 'American Mineralogic database'. References: (1) Blake *et al.* (1966); (2) Collyer *et al.* (1988); (3) Wechsler & Prewitt (1984); (4) Wechsler *et al.* (1984).

Mineral phase	Structural formula	Space group	Ti [at%]	Fe [at%]	O [at%]	Ref.
Mt	Fe ₃ O ₄	Fd3m	0.0	42.9	57.1	4
Tmh42	Fe _{0.96} ³⁺ □ _{0.04} [Fe _{0.23} ²⁺ Fe _{0.99} ³⁺ Ti _{0.42} ⁴⁺ □ _{0.37}]O ₄	P4 ₃ 32	6.3	33.0	60.7	2
TM75	Fe _{1.75} ²⁺ Fe _{0.5} ³⁺ Ti _{0.75} ⁴⁺ O ₄	Fd3m	10.7	32.1	57.1	4
TM100	Fe _{2.0} ²⁺ Ti _{1.0} ⁴⁺ O ₄	Fd3m	14.3	28.6	57.1	4
Hmt	α Fe ₂ O ₃	R3c	0.0	40.0	60.0	1
Ilm	FeTiO ₃	R3c	20.0	20.0	60.0	3

in the background scattering. Here, a more uniform background signal obtained from the polished synthetic sample was found to be suitable for background subtraction of EBSPs from individual grains of the non-embedded sample.

3 SAMPLE MATERIAL

3.1 Sample selection strategy

Different types of samples were selected for this study, ranging from coarse-grained well-constrained synthetic materials to extracts of unconsolidated, fine-grained magnetic particles from marine sediments (Table 2). The coarse-grained synthetic samples were used to obtain high quality EBSPs from materials with a well-known structure and composition. A variety of sample preparation techniques were assessed (Section 2.2). The two samples described in Section 3.3 and 3.4 represent natural magnetic mineral assemblages from marine environments of the Equatorial and South Atlantic. Their composition is highly complex and depends on the degree of reductive diagenesis: the proportions of the different Fe–Ti oxides within the mineral assemblage were therefore expected to vary dramatically.

3.2 Synthetic Fe–Ti oxides from the Fe–Ti–O system (polished sections)

A polycrystalline sample consisting of a TM–Hilm assemblage with intermediate Fe-composition (sample 6F92×0.15; Tables 2 and 3) was synthesized at 1300°C in the Fe–Ti–O system. The starting materials for the synthesis were mixtures of Fe₂O₃ (99.9%; Alpha Products) and TiO₂ (99.9%; Aldrich Chemical Comp. Inc.) which were weighed, ground and mixed in an agate mortar under acetone and, after drying, pressed into a pellet. The pellet was fired for 24 h at 1300°C, at subsolidus conditions in a vertical furnace flushed with a CO/CO₂ gas mixture to control the oxygen fugac-

ity (*cf.* Deines *et al.* 1974). The synthesis experiment was terminated by drop-quenching the sample into water. More details about the synthesis are given in Lattard *et al.* (2005). The experimental material was characterized by XRD, SEM and EMP investigation. It consisted of polycrystalline, roughly equigranular aggregates, with a mean grain size between 10 and 50 µm. The modal proportions and the chemical composition of the Fe–Ti oxide phases within the synthetic sample are given in Table 3. Both TM and Hilm have very homogeneous chemical compositions within the crystals and over the whole sample pellet. The EBSD specimen was made from blocks of the pellet, approximately 2 to 3 mm in diameter, which were embedded in epoxy resin, sectioned and polished.

3.3 Natural Fe–Ti oxides (unconsolidated magnetic particles, embedded and polished)

Magnetic particles originating from hemipelagic sediment were chosen from sediment gravity core GeoB 6229-6, which was retrieved from the Western Argentine Basin (South Atlantic) during the *R/V Meteor* cruise M46/2 (Schulz *et al.* 2001). The sediment in 655 cm core depth is characterized by high hydrogen sulphide concentrations in the pore water released by anaerobic oxidation of methane between 4 and 6 meters depth, which caused diagenetic alteration of reactive iron phases (Riedinger *et al.* 2005). Due to this reducing chemical environment, Fe–Ti oxides, such as TM and Hilm, are dominant in the magnetic assemblage since they are more resistant to dissolution than pure Fe oxides (e.g. Karlin & Levi 1983; Canfield & Berner 1987; Karlin 1990a,b; Canfield *et al.* 1992). Magnetic mineral grains from this core depth were collected by magnetic extraction (after Petersen *et al.* 1986) and embedded in epoxy resin. After hardening, the section was ground down until grains were exposed at the polished surface. The resulting polished section (Table 2) was coated with carbon for SEM analysis (Garman *et al.* 2005, in rev.) and EBSD.

Table 2. Overview of the samples used in this study, their origin, mineral phases present and their sample preparation.

Sample name	Mineral phase	Origin	Sample preparation	Treatments
6F92×0.15	TM16 + Hilm42	Synthetic	Polished section	No coating, colloidal silica polishing (±0.03 µm)
GeoB 6229-6, 655 cm	TM, Hilm	Argentine Basin, South Atlantic	Polished section, embedded particles	Mechanically polished to 1 µm finish, carbon coating,
GeoB 4313-2, 130 cm	TM, Hilm, Mt	Mid Atlantic Ridge, Central Atlantic	Non-embedded loose particles	Carbon coating, no polish

Table 3. Modal proportions and chemical compositions of the synthetic Fe–Ti oxide phases, results from electron microprobe analyses. Vol.% are means over n image analyses, x(Usp) and y(Hilm) are means over N analyses.

Sample	Phases	n	Modal proportions				Chemical compositions					
			TM		Hilm		TM			Hilm		
			vol.%	σ	vol.%	σ	N	x(Usp)	σ	N	y(Hilm)	σ
6F92×0.15	TM+Hilm	6	86	2	14	2	10	0.161	0.002	10	0.419	0.002

3.4 Natural non-embedded particle sample (unconsolidated magnetic particles, unpolished)

The third sample originated from pelagic sediments of the central Equatorial Atlantic, from gravity core GeoB 4313-2 (Fischer *et al.* 1998). Magnetic extracts (after Dekkers 1988) (130 cm core depth; Table 2) contained Fe- and Fe–Ti oxides from different sources, such as detritus of the Amazon river, submarine basalt weathering products of Mid-Atlantic Ridge material or eolian dust input from the Sahelian Zone (Funk *et al.* 2004a,b; Franke 2006). We tested the EBSD method directly on the non-embedded magnetic grains dispersed on an SEM stub.

4 RESULTS

4.1 Discrimination between titanomagnetite and hemoilmenite

As shown in Fig. 3, the two mineral phases TM and Hilm present in the synthetic sample 6F92×0.15 were discriminated with standard BSE imaging (Fig. 3a) or from their EDS element spectra (Figs. 3c and d). The reason being that in the simple Fe–Ti–O system, TM always has much higher Fe/Ti ratios than the coexisting Hilm (e.g. Buddington & Lindsley 1964; Lattard *et al.* 2005). Consequently, the intensity ratios of the characteristic Fe K_{α} and Ti K_{α} peaks are significantly different in the EDS spectra of the respective phases. In standard BSE images, the TM phases display a lighter grey level which reflects the higher mean atomic number of this phase compared to that of Hilm. Orientation contrast imaging with

a forescatter geometry (Prior *et al.* 1996) shows the varying orientations of the grains, which have no preferred alignment. In these images, however, TM and Hilm cannot be discriminated (Fig. 3b).

Fig. 4 shows typical EBSPs acquired on both mineral phases of the synthetic sample 6F92×0.15. The observed EBSPs from TM grains clearly show a spinel pattern (Fig. 4a), those acquired from Hilm grains have trigonal patterns (Fig. 4b). Fig. 4c shows that the TM solution matches the geometry and width of all observed diffraction bands in the EBSP of Fig. 4a. There is no Hilm pattern solution that matches all of the bands in this EBSP. The same applies, vice versa, for Fig. 4d. An indexed solution is acceptable when all observed bands are matched by the solution and the MAD of the detected and calculated bands is less than a few degrees. The EBSPs obtained from the coarse synthetic samples are of high quality, displaying many relatively low-intensity diffraction bands and some higher order Laue zone (HOLZ) diffraction rings (Fig. 4a and b). Such HOLZ rings can be used to obtain data on lattice spacings (Michael & Eades 2000) that can assist in the discrimination of different phases with similar structures.

Fig. 5 shows two magnetic Fe–Ti oxide particles, extracted from the marine sediment sample from core GeoB 6229-6, 655 cm, and their respective EDS spectra. The relatively large grains (20 to 35 μm in diameter) contain visible exsolution lamellae in the submicron scale. In the grains the TM matrix is either partly or completely dissolved by reductive diagenesis (compare particles 1 and 2). The EDS spectrum of particle one (Fig. 5c) was taken from the inner part of the grain, where the mineral matrix seems to be less dissolved. The element spectrum suggests TM as the matrix phase because of the high Fe/Ti intensity ratio (somewhat lower than that of TM16

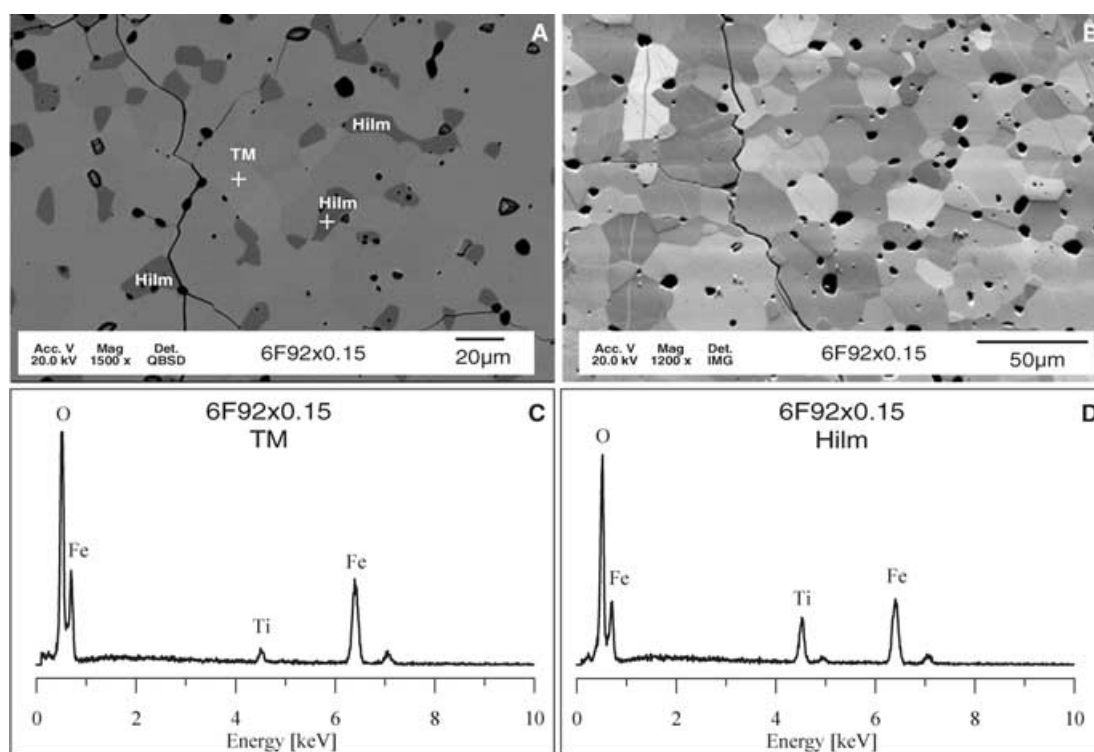


Figure 3. SEM images and EDS element spectra of a two-phase synthetic sample 6F92×0.15 containing 86 vol.% of titanomagnetite (TM16) and a relative small amount (14 vol.%) of Hilm. (A) BSE of part of the sample, obtained on the polished sample surface perpendicular to the electron beam. The grey tones reflect the different chemical compositions of the two phases, with lighter areas corresponding to TM (richer in Fe) and darker areas corresponding to Hilm (poorer in Fe). Black spots and lines are pores and cracks in the sample. (B) Orientation contrast image of forescatter electrons of another part of the same sample surface. The different grey levels show the different orientation of the individual crystals of TM or Hilm. (C) EDS spectrum of the TM phase from the spot marked in A. (D) EDS spectrum of the Hilm phase from the spot marked in A.

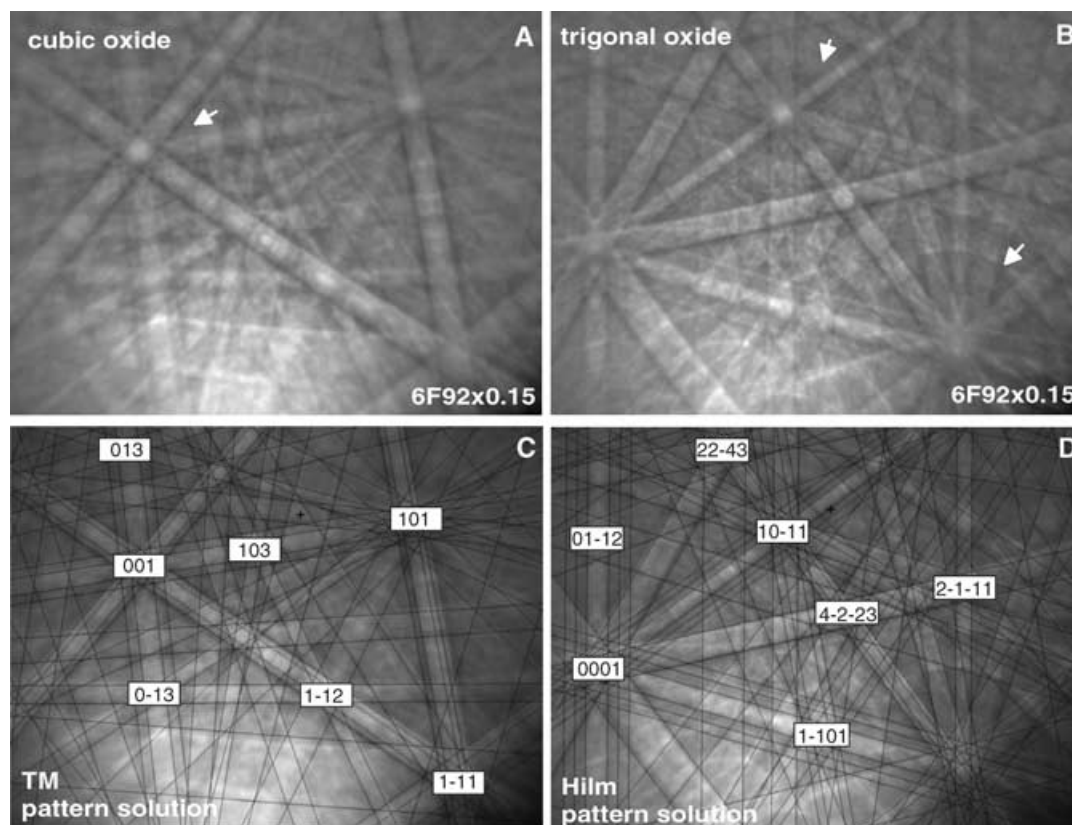


Figure 4. (A) EBSD obtained from the TM phase in the two-phase synthetic sample 6F92x0.15; white arrows show HOLZ rings, (B) EBSD obtained from the Hilm phase from the same sample. (C) EBSD solution of the TM phase. Zone axes are labelled using Miller indices. (D) EBSD solution of the Hilm phase. Zone axes are labelled using Weber numbers.

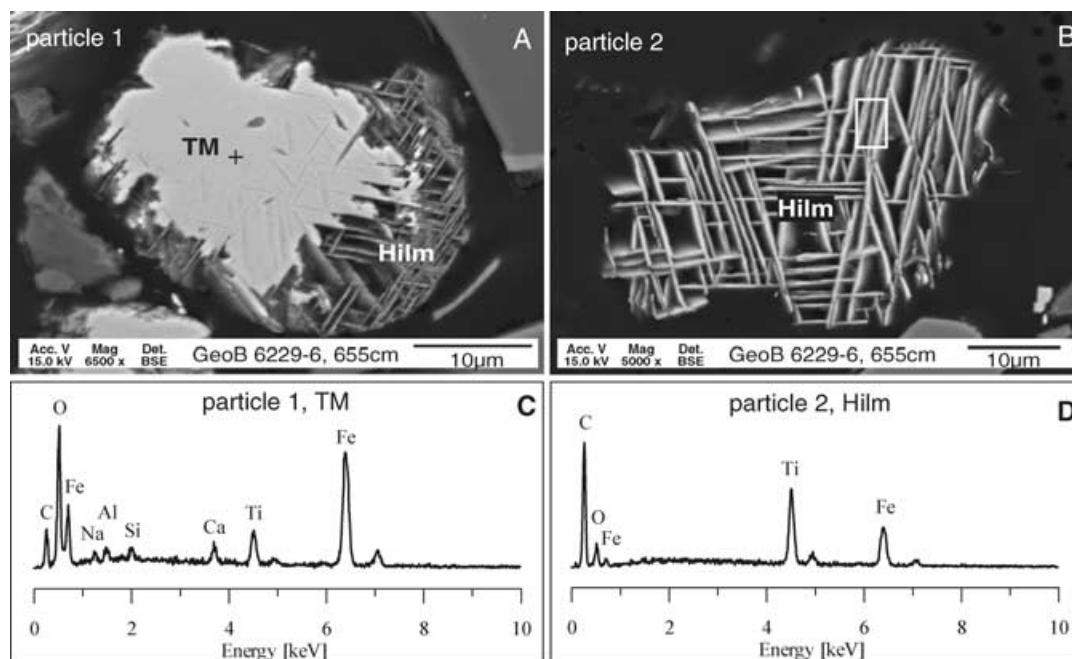


Figure 5. SEM images and EDS spectra of the natural sample GeoB 6229-6, 655 cm, (A) BSE of a TM grain (particle 1) with Hilm lamellae (dark background is due to the epoxy resin). The grain experienced partial, low-temperature dissolution in its reducing sedimentary environment, showing a porous region of thin lamellae and a solid matrix region in which fine-scale lamellae are also present. Exsolution features within the grain are relicts from former high-temperature oxidation processes in the source rock. (B) BSE of Hilm lamellae (particle 2) showing a more advanced stage of reductive diagenesis. (C) EDS spectrum of the spot marked in the TM matrix in particle 1: note that the small amounts of Na, Al, Si and Ca might be due to inclusions, C is due to the carbon coating. (D) EDS spectrum of the selected Hilm area marked in particle 2, C is due to the carbon coating.

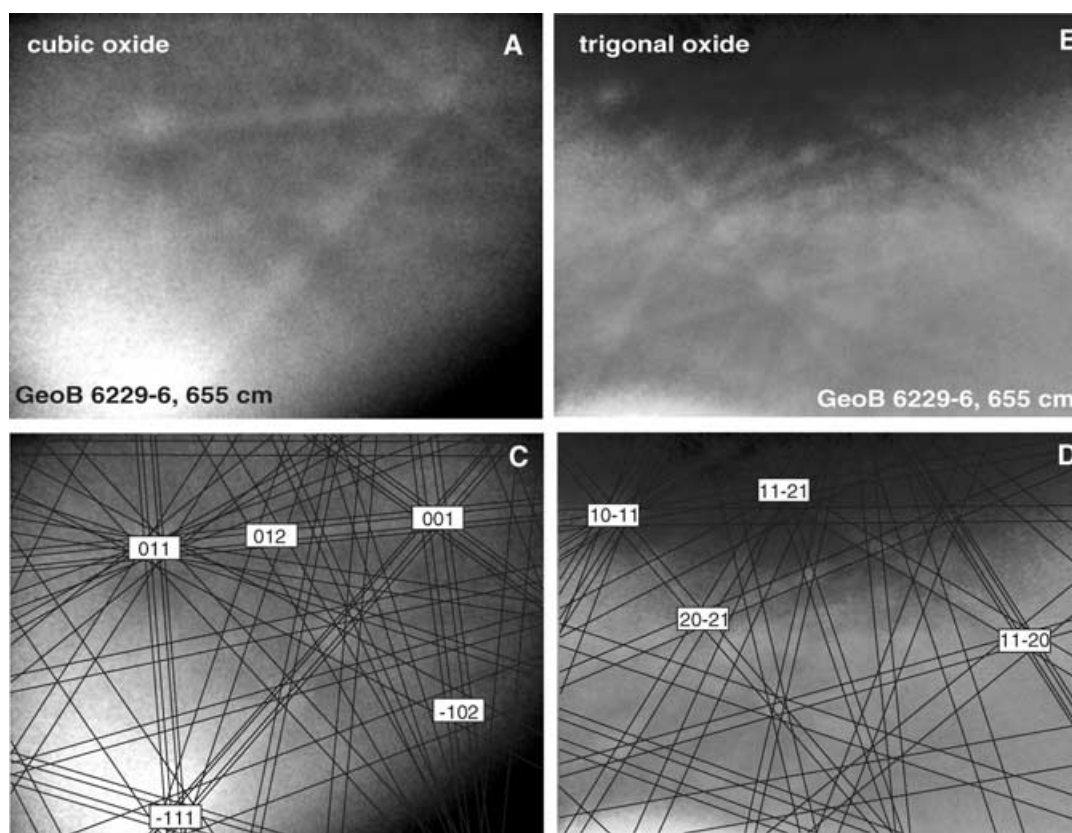


Figure 6. (A) EBSD obtained from the TM matrix phase of particle 1 from the same location as the EDS spectrum (see Fig. 5). (B) EBSD obtained from the lamellae of particle 2 from the same area as the EDS spectrum (see Fig. 5). (C) Miller indexed EBSD solution for TM. (D) Weber indexed EBSD solution for Hilm.

in sample 6F92×0.15, see Fig. 3c). It is clear, however, that the lamellae contribute to the EDS signal because they are present in the excitation volume of the electron beam. Since the TM matrix is completely dissolved in particle 2, an EDS analysis could be performed on a small selected area on the residual lamellae, providing an average element spectrum with a low Fe/Ti intensity ratio, which is typical for Hilm (Fig. 5d). However, only the EBSD analysis of both particles gave unambiguous crystallographic evidence of the presence of both TM and Hilm. Figure 6 shows the observed EBSDs of the Fe-rich matrix phase (Fig. 6a) and the Ti-rich exsolution lamellae (Fig. 6b). Presumably due to the carbon coating and the lack of a final polish with colloidal silica, the obtained EBSDs were weaker than from the non-coated synthetic samples. Indexing of the observed EBSDs yielded a spinel (TM) pattern solution for the matrix phase and a trigonal (Hilm) pattern solution for the lamellae.

4.2 Non-embedded particle sample

Despite dispersing the particles, the individual magnetic grains in sample GeoB 4313-2, 130 cm were randomly oriented and clumped together on the SEM stub (Fig. 7a). Although the sample had significant topography, and many of the particles were not in direct line-of-sight for the detector (compare Fig. 2, position 2), it was still possible to obtain EBSDs from a few regions at the edges of grain surfaces (Figs. 7a). This condition was fulfilled for only a few locations on grains (compare Fig. 2, position 1). Faceted grains gave a reasonable signal and information about the possible crystallography of the grain, but rounded grains, with less obvious shape

information, also gave reasonable EBSDs. The sample was rotated to obtain EBSDs from other particles which were not in direct line-of-sight to the detector.

The EBSDs from the non-embedded particles were generally weaker compared to those from the polished sections (Fig. 7c). Weaker EBSDs were, however, also obtained from the polished section of sample GeoB 6229-6, 655 cm, which although polished, was also carbon coated. The quality of the EBSDs obtained from both natural marine particle samples was comparable and we concluded that the weaker signal was mostly due to the carbon coating rather than due to the non-ideal sample surface of the non-embedded particles. The EBSDs contained the main bands and were of sufficient quality for the mineral identification (Fig. 7c and d). The best-fit for a pattern solution was found for a Ti-poor TM (Fig. 7d). This result is consistent with the particle's clear octahedral crystal morphology and its EDS spectra (Fig. 7b).

5 DISCUSSION AND PERSPECTIVES

Our results show that EBSD is a reliable tool to discriminate between magnetic spinel and trigonal Fe–Ti oxides. This is particularly helpful in combination with EDS analyses. In samples with submicron size particles, EDS information alone is often not sufficient to unambiguously identify the mineral phases, because of the very close chemical compositions of the mineral phases and the limited spatial resolution of the EDS. In this study we have obtained meaningful EBSDs from magnetite, TM and hemoilmenite grains in the range of 50 to 1 μm . The analyzed Hilm lamellae are submicron size

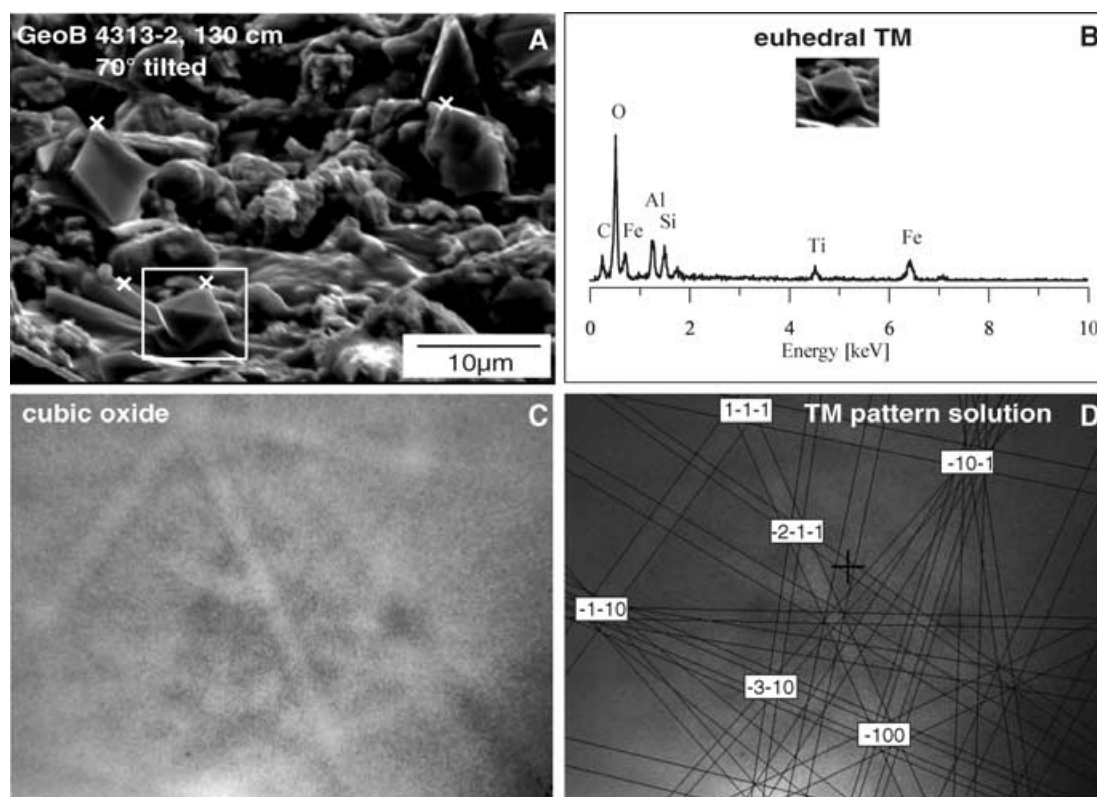


Figure 7. (A) BSE of the 70° tilted sample surface of GeoB 4313-2, 130 cm (carbon coated), EBSD signals could be obtained from marked areas (white cross symbols). (B) EDS spectrum of the euhedral TM crystal: note that the small amounts of Al and Si, might be due to clay mineral coating of the grain, C is due to the carbon coating. (C) EBSD pattern obtained from the euhedral TM crystal. (D) Miller indexed TM pattern solution of the euhedral crystal.

(~500 nm). In principle, mineral grains as small as 200 nm can be analyzed by EBSD using a FEG scanning electron microscope (Ohfuji *et al.* 2005). For the analysis of smaller magnetic oxide particles, TEM diffraction and analysis techniques should be used.

In open-ocean sediments, (titano-) magnetite is very often assumed to be the main magnetic mineral component carrying the paleo- and rock magnetic signal. For relatively simple compositions of the magnetic mineral assemblage, this assumption may be justified. Under more reducing conditions, such as at continental slope areas, however, the magnetic mineral fraction is often changed in composition during progressive sub and anoxic diagenesis (e.g. Riedinger *et al.* 2005; Garhing *et al.* 2005; Dillon & Bleil 2006). Other important magnetic mineral components might be present in addition to (titano-) magnetites, such as hemoilmenite of intermediate Ti-composition. When hemoilmenite and TM phases co-exist, interacting magnetic behaviour during low-temperature experiments was observed by, for example, Ishikawa *et al.* (1985) and Brown *et al.* (1993) for synthetic samples and, for example, Nagata *et al.* (1953), Heller *et al.* (1986), and Prévot *et al.* (2001) for natural hemoilmenites. McEnroe *et al.* (2002) described lamellar magnetism between intergrown mineral phases in natural crystalline rocks (Mid-Proterozoic anorthosite-norites from South Norway).

Flood basalts from the Paraná province in Argentina are the principal source for the sediments from the Argentine continental slope off the Rio de la Plata estuary (see also Section 3.3., Figs. 5 and 6). Main carriers of the natural remanent magnetization of these Mesozoic basalts are magnetite and slightly maghemitized low Ti TM (Kosterov *et al.* 1998; Tamrat & Ernesto 1999).

The mineralogical identification of the chemically very similar Fe–Ti oxide phases TM and hemoilmenite using EBSD is important for the interpretation of ambiguous rock magnetic data, for example in identifying exsolution features or paragenesis of different mineral phases, such as in sample GeoB 6929-6, 655. Low-temperature rock magnetic analysis provided a strong indication of a Hilm mineral phase being present in the TM grains of this sample by showing a remarkable partial self-reversal (Garhing *et al.* in rev.). Figure 5 shows the TM particles, which are derived from the Paraná volcanic province (Garhing *et al.* 2005). The intergrowths between TM matrix and Hilm lamellae result from high-temperature oxidation. After deposition in the marine environment, these particles experienced reducing conditions (Riedinger *et al.* 2005). The particles therefore evidently underwent strong reduction during diagenesis resulting in dissolution of the Fe-rich matrix phase (Garhing *et al.* 2005). The intergrown Hilm lamellae were more resistant to the Fe reduction. In Fig. 5b, the original TM matrix has been entirely dissolved and only the Hilm lamellae are left. Both Fe–Ti oxide phases were clearly identified by their EBSD pattern solutions (Fig. 6). Usually the identification of different mineral phases of close chemical compositions within a grain is very difficult. Here, the combination of EDS and EBSD enabled unambiguous phase identification.

So far, we tested the EBSD technique on a variety of magnetic Fe–Ti oxides. Most likely the application to the most common magnetic sulphides, such as greigite (43 at.% Fe; 57 at.% S) and pyrrhotite (47 at.% Fe; 53 at.% S) should lead to improved discrimination between these compositionally similar mineral phases. In marine sediment samples, these magnetic mineral phases are rather fine grained and not always easily identified using only EDS analysis.

Sometimes grains occur in different distinguishable morphologies (Roberts & Weaver 2005), but often their grain sizes are just at the edge of the SEM resolution. Additionally, greigite (cubic) and pyrrhotite (monoclinic) are precursors to pyrite and therefore they can occur sequentially next to each other in very similar grain size distributions and sedimentary settings. So far, EBSD textural and deformation studies have been carried out on micron- to submicron-sized natural pyrite crystals (e.g. Boyle *et al.* 1998; Freitag *et al.* 2004; Ohfuji *et al.* 2005).

We showed that sample preparation is crucial for the quality of the observed EBSD. The most suitable sample preparation for EBSD and EDS is a well-polished section without any additional (carbon) coating. Sometimes, surface charging effects are too strong and a thin carbon coating has to be applied to the polished section, especially when the grain size is very fine and application of silver paint coating around the particles is not practical. In samples with a limited abundance of material and very fine (submicron) grain sizes, the EBSD method can also be applied to non-embedded, unconsolidated particles. This might be suitable for extracts from marine sediments, loess or anthropogenic samples. In these types of samples, different cubic and trigonal oxides can be distinguished by EBSD, while EDS analysis can be used to distinguish between different spinel phases, such as Mt and TM or between Hmt and Ilm grains.

The application of the EBSD technique on unconsolidated, very fine-grained magnetic particles from the central Equatorial Atlantic, shown in sample GeoB 4313-2, 130 cm, enabled us to identify magnetic particles originating from different input sources. Here, the abundance of hemoilmenite in the complex magnetic mineral assemblage is a result of the source-to-sink relations in that region and not a result of enhanced dissolution of Fe-rich oxides (Franke 2006). The contribution of hemoilmenite to the bulk magnetic signal is difficult to identify with rock magnetic methods alone. Positive mineral identification cannot be obtained without the EBSD results.

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