## Pyrrhotite varieties from the 9.1 km deep borehole of the KTB project

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#### ABSTRACT

We used transmission electron microscopy (TEM) to study pyrrhotite from the German Continental Deep Drilling ("Kontinentale Tiefbohrung," KTB) project. Our goals were to determine the distribution of structure types with depth and to establish relationships between the bulk thermomagnetic behavior and the microstructures of pyrrhotite. In samples from the deep section of the borehole (9080 m below surface, which is equivalent to an in-situ temperature of ~260 °C), the dominant variety of pyrrhotite is 1C that has a mostly disordered vacancy distribution. Faint, diffuse superstructure reflections in the selected-area electron diffraction (SAED) patterns indicate some nC-like ordering occurs, probably in small domains. In addition to the disordered pyrrhotite, a 5C type is also present. According to bulk thermomagnetic measurements, pyrrhotite grains from 9080 m are antiferromagnetic at room temperature; we attribute this behavior to the dominance of the disordered 1C type. In the upper section of the hole (at 564 and 2325 m) several pyrrhotite varieties occur, but the 4C type is most common, in agreement with the ferrimagnetic character of most pyrrhotite grains.

Optical microscopy of pyrrhotite grains that are covered with a magnetic colloid reveal intergrown ferrimagnetic and antiferromagnetic lamellae. TEM images show that these grains are intergrowths of 4C, 5C, and nC types. We interpret these microstructural variations to be responsible for the variation in magnetic properties within single pyrrhotite grains.

#### INTRODUCTION

Pyrrhotite-type minerals include many varieties with Fe/S atomic ratios ranging from 7/8 to 1. Various ordered distributions of Fe-site vacancies produce superstructures that are either ferrimagnetic or antiferromagnetic. Pyrrhotite is a common mineral in igneous and metamorphic rocks and is the main carrier of rock magnetism in many rock types; therefore, it is important to understand how the distinct structure types are distributed in rocks and how this distribution affects the overall magnetic properties of the rocks.

Several pyrrhotite (Fe<sub>1-x</sub>S) superstructures exist in natural and synthetic specimens; all are based on a hexagonal NiAstype subcell (with a = 3.45 Å and c = 5.75 Å) in which Fe atoms occupy the octahedral interstices between the hexagonal close-packed S layers. Up to one fourth of these octahedral sites can be vacant within a metal layer (Bertaut 1953). The ordered arrangement of vacancies within defective layers and the various stackings of filled and vacancy-containing Fe layers along the **c** axis result in ordered superstructures. For a more detailed description of the structural principles of pyrrhotite, see Pósfai and Buseck (1997).

Theoretically, many superstructures can exist with the same c dimension and composition (Pósfai and Dódony 1990); how-

ever, only a few types seem to be common in nature (Table 1). Probably the most common is 4C monoclinic. The true symmetry of "hexagonal" pyrrhotites is orthorhombic, monoclinic (Morimoto et al. 1975a, 1975b), or even triclinic. When the weak superstructure reflections are not considered, the subcell diffraction spots of these varieties exhibit hexagonal symmetry; because the space groups and even the crystal systems are not known for "hexagonal" pyrrhotites, we follow the common practice and use a hexagonal cell for indexing our diffraction patterns. The conventional unit cells of 4C and "hexagonal" pyrrhotite, as well as that of troilite, are shown in Figure 1. The stability relationships of pyrrhotite varieties are discussed in a companion paper (Kontny et al. 2000).

To correlate magnetic measurements with characteristic pyrrhotite microstructures, we used TEM to study several pyrrhotite samples from the 9.1 km deep borehole of the KTB (the geological setting and general results of the deep drilling were described by Emmermann and Lauterjung 1997). Our goals were to identify what types of pyrrhotite superstructures occur as a function of depth and to determine whether the optically observed variations of magnetic properties within pyrrhotite grains are related to microstructural inhomogeneities. The high spatial resolution of the TEM allows for a detailed characterization of the distribution of various microstructures in pyrrhotite grains. X-ray powder diffraction (XRD), chemical, and thermomagnetic results are discussed by Kontny et al. (2000).

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TABLE 1. P	vrrhotite	types that	commonly	occur in	natural	specimens
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Туре	Composition	Structure (see Fig. 1)	Magnetic properties	Other names	References
2C	FeS	hexagonal, <i>P</i> 62 <i>c</i>	afm	troilite	1,2,3
4C	$Fe_7S_8$	monoclinic, F2/d	fm	monoclinic, Weiss-type, "normal"	4,5,6,7
5C, 6C, nC*	~ $Fe_9S_{10}$ to $Fe_{11}S_{12}$	"hexagonal", likely orthorhombic or monoclinic	afm	λ-type, peak-type, intermediate	8,9,10,11,7
nA†	~ Fe <sub>7</sub> S <sub>8</sub> to ~Fe <sub>9</sub> S <sub>10</sub>	"trigonal"	fm	"2A, 3C"	12,13,14,7

Note: afm = antiferromagnetic, fm = ferrimagnetic. 1 = Evans (1970); 2 = Putnis (1974); 3 = Töpel-Schadt and Müller (1982); 4 = Bertaut (1953); 5 = Tokonami et al. (1972); 6 = Nakazawa et al. (1975); 7 = Kissin and Scott (1982); 8 = Morimoto et al. (1975b); 9 = Engel et al. (1978); 10 = Pierce and Buseck (1974); 11 = Schwarz and Vaughan (1972); 12 = Morimoto and Nakazawa (1968); 13 = Francis and Craig (1976); 14 = Nakazawa et al. (1976).

\* nC structures have c dimensions that are non-integral multiples of the NiAs c parameter.

† The nA superstructure is characterized by a 3C periodicity along the c axis and a non-integral periodicity along a.



**FIGURE 1.** Conventional unit cells of the common pyrrhotite types, projected onto the (001) plane and compared to the NiAs cell. Dots represent Fe positions; 1, 2, 3, and 4 mark four possible positions of vacancies. In this case vacant sites are illustrated by the darker dots in position 2.

### **EXPERIMENTAL METHODS**

TEM specimens were prepared from samples obtained from the depths of 564, 2325, and 9080 m; these samples were chosen because optical, XRD, and thermomagnetic results suggested they represent the distinct pyrrhotite types in the KTB rocks. Pyrrhotite grains were crushed under ethanol and dispersed on holey-carbon Cu grids for TEM studies. Ion-milled samples were also prepared from grains that were selected by optical examinations of polished sections. We note that ion milling of pyrrhotites produced artifacts in some cases, as is discussed below; however, the identification of superstructures in this study is based on data obtained from crushed specimens. We used a Philips CM20-FEG electron microscope operated at 200 kV accelerating voltage and equipped with a Tracor analytical system for energy-dispersive X-ray spectrometry (EDS). Pyrrhotite structure types were identified on the basis of SAED patterns that were taken from directions perpendicular to their **c**\* axes. We obtained conventional and high-resolution images (HRTEM) from characteristic pyrrhotite types and their intergrowths. An objective aperture with  $r = 0.4 \text{ Å}^{-1}$  was used for high-resolution imaging. Electron micrographs and diffraction patterns for model structures were simulated using Cerius software.

We found that high-resolution imaging of pyrrhotite from the KTB borehole is difficult because of in situ contrast changes in the electron microscope. Vacancies tend to become disordered under the electron beam as previously observed by Nakazawa et al. (1975). Electron beam-induced disorder is most pronounced in nC and 5C types, whereas it is less obvious in well-ordered 4C. The 2C phase could be imaged most easily among the pyrrhotite modifications that were found in the KTB samples.

#### RESULTS

The KTB samples contain several pyrrhotite superstructures (Table 2). The dominant pyrrhotite modification is 4C in the samples from 564 and 2325 m, whereas in the 9080 m sample the major type has a basically disordered 1C structure in which an nC-like ordering of vacancies occurs in small domains. In addition to 4C, intergrowths of 4C, 5C, and nC are also found in the 564 m sample. The 9080 m sample contains minor 5C and nA in addition to the disordered type. In a few ion-milled specimens troilite (2C) occurs. Because troilite was only observed in ion-milled samples, we conclude that this 2C phase is an artifact produced by ion milling.

The periodic contrast in HRTEM images is dominated by the vacant Fe positions. We computed several series of images of ordered pyrrhotite superstructures for objective lens defocus values ranging from -300 to -1200 Å; the dominant features in these images are strong white spots forming patterns that fol-

Depth (m)	Temperature* (°C)	Pressure† (MPa)	Pyrrhotite modifications
564	20	NA	mostly 4C, lesser 5C, nC, and disordered 1C with domains
2325	70	40	4C and artifact 2C
9080	260	180	mostly 1C with nC-like domains, lesser 5C
Note: NA = not ava	ailable.		
* Clauser et al. 199	97.		
+ Brudy et al. 1997	7		

TABLE 2. Pyrrhotite types observed by TEM from three different depths of the KTB borehole

low the vacancy distributions of the model structures. Depending on the defocus value, the shapes of the white spots and their relative positions within the unit cell change but their ordered pattern remains basically the same. Therefore, the intense white spots in HRTEM images obtained over a wide range of defocus values can be interpreted as produced by vacant Fe positions along the direction of the electron beam. Our image simulations are consistent with the observations of Nakazawa et al. (1975), Pierce and Buseck (1976), Nguyen et al. (1985), and Pósfai and Buseck (1997). The HRTEM image in Figure 2a provides an example for the relationship between image contrast and vacancy distribution; the white spots represent vacant Fe positions in an ordered 4C crystal. The separation between adjacent white rows parallel to (001) is 5.8 Å; thus, the completely filled Fe layers are not resolved.

## 4C type

Twinning, stacking faults, and other, mostly unidentified defects are characteristic of 4C pyrrhotite from the KTB borehole. Lamellar, 60° twinning in 4C pyrrhotite was described in several studies (Bennett et al. 1972; Nakazawa et al. 1975; Nguyen et al. 1985; Putnis 1975). Twinning occurs on two different scales; the smaller lamellae are 100 to 200 nm, whereas the largest ones about 30 µm wide. A typical, twinned crystal is shown in Figure 2b; the twin lamellae are marked by their respective orientations ([110] and [010]) and the corresponding SAED patterns are shown in Figures 2c to 2d. [The difference between the two patterns arises from the fact that the topologies of vacancy-containing Fe columns are different in the two projections, as explained by Nakazawa et al. (1975) and Pósfai and Buseck (1997), among others.] The twin boundaries are only subparallel to (001) with steps along the interfaces (in some places marked by arrows), causing disorder in the vacancy arrangement along the a axis.

Crystals of 4C pyrrhotite are intergrown with each other in many places with the contact plane subparallel to (001). SAED patterns obtained from crystal parts on opposite sides of such boundaries show an angle of a few degrees between the two **c** axes, indicating the presence of subgrain boundaries. Such domain structures could affect the overall magnetic characteristics of the sample by changing both the sizes and the shape anisotropies of magnetic domains (Soffel 1977; Zapletal 1993). The twinning and defects in 4C suggest that this variety formed by solid-state transformation from precursor structures; this is discussed in more detail in our companion paper (Kontny et al. 2000).

## Intergrowths of 4C, 5C, and nC types

We observed fine-scale intergrowths of several pyrrhotite types in the 564 m sample. The optical micrograph in Figure 2a of Kontny et al. (2000) shows a pyrrhotite grain in polished section, after it was treated with a colloidal magnetic suspension. The colloidal suspension is attracted to ferrimagnetic regions, producing a light-dark lamellar pattern. On the basis of similar optical experiments (Schwarz 1975; Zapletal 1993; Halgedahl and Fuller 1981; Soffel 1977), the dark lamellae can be interpreted as domain walls, and the light areas as domains where magnetic moments are arranged parallel. Because in the central region of the grain there are no lamellae, that part is likely non-magnetic.

The pyrrhotite grain in Figure 2a of Kontny et al. (2000) was ion-milled and studied by TEM. The 4C pyrrhotite is intimately intergrown with ordered 5C (Figs. 3a and 3b) and nC types having non-integral (n) multiples of the NiAs *c* periodicity (Figs. 3c and 3d). A 1C-type pyrrhotite exhibiting shortrange vacancy ordering (see below) also occurs. The low-magnification image in Figure 4a shows an area of the 4C type, with twinning, stacking faults, and locally high densities of defects that appear to be dislocations. Wedge-shaped features in conventional TEM generally represent phase boundaries between 4C and other pyrrhotite types. Intergrowth also occurs between 4C and a long-period, non-integral nC superstructure (Fig. 4b).

Although a large difference exists in spatial resolution between the optical and the electron microscopes, we can state with certainty that the general direction of the ferrimagnetic lamellae, as observed in polished section, is parallel or subparallel to the (00*l*) planes of pyrrhotite superstructures as observed using TEM. The orientations of boundaries between different structure types seem to correspond to the orientations of boundaries between ferrimagnetic and antiferromagnetic areas in Figure 2a of Kontny et al. (2000). Several crystals of 4C and 5C, and some areas of nC pyrrhotites were analyzed by EDS. The differences between the compositions of 4C and other pyrrhotite types remained within analytical error (about  $\pm 1$  at%).

#### 5C type

A pyrrhotite variety with the same 5C superstructure occurs in the samples from 564 m and 9080 m. When the electron beam was parallel to a pseudohexagonal **a** axis, all studied grains of 5C pyrrhotite produced either of two distinct types of diffraction patterns (Figs. 3a and 3b). Although the tilt range of the specimen holder did not allow us to record both of these SAED patterns from the same crystal, it is likely that Figures 3a and 3b represent [010]- and [100]-type projections of the same 5C superstructure, respectively. A pair of identical SAED patterns were obtained from a 5C crystal by Dódony and Pósfai (1990), who determined the vacancy ordering scheme on the basis of the characteristic intensity distributions of reflections along the 01*l* and 10*l* reciprocal lattice rows. A comparison of



**FIGURE 2.** (a) HRTEM image of an ordered 4C crystal in [110] orientation. (b) HRTEM image of a twinned 4C crystal; the white arrows mark steps along the twin planes. (c to e) SAED patterns from 4C crystals in [110] (c) and [010] (d) orientations, and from a twinned crystal (e). (The SAED patterns are indexed according to the 4C monoclinic cell shown in Figure 1. All images and SAED patterns were obtained from crystals from the 564 m sample.)

experimental and simulated SAED patterns (Dódony and Pósfai 1990; Pósfai and Buseck 1997) indicates that the Fe layers are stacked in a 1020103040 sequence in this pyrrhotite type, where 0 denotes filled layers, and 1, 2, 3, and 4 stand for four different positions of vacancy-containing layers. Although this structure was originally described as hexagonal, the vacancy

distribution results in triclinic symmetry that accounts for the difference between the [100] and [010] zone-axis diffraction patterns.

The HRTEM image of a 5C crystal (Fig. 5) confirms the vacancy ordering scheme of Dódony and Pósfai (1990). Every second Fe layer parallel to (001) is resolved producing 5.8 Å



FIGURE 3. SAED patterns from 5C (a, b) and nC (c, d) crystals, indexed on the basis of the hexagonal cell that is shown in Figure 1. The white arrows in (c) and (d) mark satellite reflections that are typical of nC.

lattice finges, whereas within the close-packed Fe layers both vacant and filled positions are distinguishable in the form of white spots 3 Å apart. In some parts of the electron micrograph the strong white spots (vacant Fe positions as discussed above) clearly follow an AAABBAAABB... ordering scheme along the c axis, as marked by the broken line in the inset in the lower right corner. This type of ordering is consistent with a 1020103040 superstructure, because in [010] projection the vacant positions 1 and 2 line up along the same line (A), and positions 3 and 4 along another line (B) (see Fig. 1 and Pósfai and Buseck 1997). If our identification of the structure is correct, then this 5C variety has the same composition as 4C (near Fe<sub>7</sub>S<sub>8</sub>).

The image contrast is not uniform over the area shown in Figure 5. Within certain horizontal rows in Figure 5 (some marked by arrows), the regular alternation of intense and less intense white spots changes to a sequence of spots with weak and nearly uniform intensities. The change of contrast within Fe-deficient layers is probably caused by changes in the arrangement of vacancies along the **a** axis from ordered (two different intensities) to disordered (uniform intensity). Because the disordered vacancy distribution is present in certain areas of the crystal, the total number of vacancies and, consequently, the composition could deviate from the ideal Fe<sub>7</sub>S<sub>8</sub> formula of the 1020103040 structure.

#### 1C containing nC-type domains

Pyrrhotite grains from the deepest part of the borehole (9080 m) characteristically produce only very weak, smeared superstructure spots in their SAED patterns (Fig. 6). These spots indicate variable, non-integral c periodicities that range from ~3.2C to ~4.9C. The superstructure reflections in Figure 6 distinctly differ from those of the nC-type pyrrhotites from the 564 m samples (Fig. 3) in that their intensities are weaker relative to the substructure spots. Another difference between the two sets of SAED patterns is that the nC-types from 564 m have sharp satellite spots next to the subcell spots (Fig. 3), whereas such satellite reflections are absent from Figure 6. Similar diffraction characteristics were observed by Nakazawa and Morimoto (1971) and Kissin and Scott (1982) in single crystal X-ray diffraction patterns obtained from a high-temperature pyrrhotite modification; they termed this structure "mC" type. We interpret the faint superstructure reflections as caused by a poor ordering of vacancies; the overall structure is close to a 1C type with a disordered vacancy distribution.

SAED patterns obtained using the largest (Fig. 7a) and the smallest (Fig. 7b) selected-area apertures show that certain small regions of the crystal produce more distinct and relatively stronger superstructure reflections than a large, "average" area. (The SAED patterns in Fig. 7 represent projections that are not perpendicular to c.) If the barely visible superstructure reflections along the arrowed rows in Figure 7a are ignored, the structure can be regarded 1C; however, the more intense, split pairs of reflections along the same rows in Figure 7b indicate that an nC-like ordering of vacancies occurs in small domains. The TEM image in Figure 7c was obtained using only the direct beam and four superstructure reflections (circled in the inserted SAED pattern); the ripple-like features in the image reveal the domain nature of ordering in this crystal. The ordered domains produce more diffracted intensity within the aperture and therefore appear lighter in the image. The size of the domains is on the order of tens of nm, and their presence suggests that the vacancy ordering changes along c, as well as along a.

#### 2C (likely an artifact of ion milling)

A 2C superstructure occurs in some ion-milled specimens that were prepared from core samples obtained from the depths of 564 and 2325 m. The SAED patterns (Figs. 8a and 8b) can be interpreted as the [110] and [100] projections of troilite, respectively. The HRTEM image in Figure 8c matches a simulated electron micrograph that was computed on the basis of the troilite structure as determined by Evans (1970). EDS analyses gave compositions that are consistent with the FeS formula of troilite. We did not find the 2C type in crushed samples, suggesting that the 2C type is an artifact of ion milling.

Crystals of this 2C phase were studied again with the TEM a year after the ion-milled specimens were prepared; we found that troilite crystals invariably developed weak superstructure reflections at the positions belonging to nC or 4C pyrrhotites. Diffuse nC reflections (Fig. 8d) appear along the 01*l* and 02*l* reciprocal lattice rows (cf. Fig. 8b); in addition, weak spots appear at 3C positions along the 00*l* row, indicating the presence of a 3C superstructure.

The 2C troilite in some ion-milled specimens could have formed from Fe-deficient pyrrhotite. According to Schwarz and Harris (1970), sulfur loss occurs when pyrrhotite is heated in an Ar atmosphere. Because we used Ar ions for the sample preparation, we probably converted some pyrrhotite into troilite. Interestingly, the transformation in the ion mill seems to affect only certain pyrrhotite grains; at present, we do not have



**FIGURE 4.** Bright-field TEM images of typical features in the pyrrhotite grain of Figure 2a of Kontny et al. (2000). (**a**) 4C pyrrhotite displaying a narrow twin lamella; the lower twin boundary is connected to a wall of dislocations (marked by the white arrow). (**b**) An intergrowth of twinned 4C and nC regions.

an explanation for this behavior. In an earlier TEM study, Putnis (1975) found coexisting troilite and 4C pyrrhotite in ion-milled samples. His published diffraction patterns mimic Figure 8; it cannot be ruled out that the 2C phase observed by Putnis (1975) may also be an artifact of ion milling.

## DISCUSSION

#### **Reliability of TEM results**

The contrast of some pyrrhotite grains changed in the electron beam, indicating that the vacancies (or rather the Fe atoms) moved during irradiation. We minimized such changes by using a low beam current. Because some structure types consistently gave the same SAED patterns and we never observed the transformation of one ordered structure into another under the electron beam, we conclude that the observed superstructures (as in Table 2) were originally present in the samples.

We observed differences in superstructure distributions in crushed and ion-milled specimens that were prepared from the same hand specimens, particularly in the samples from 2325 m depth. Therefore, we only regarded pyrrhotite superstructures



**FIGURE 5.** HRTEM image of a 5C pyrrhotite crystal viewed along [010], with the corresponding SAED pattern in the upper left. The area outlined in white is enlarged in the lower right corner. The arrows mark (001) planes containing non-uniform vacancy distributions (see text).

in ion-milled samples as original, if the same superstructures were found in crushed samples as well.

Our observation that the artifact 2C pyrrhotite partly transformed into nC and 4C over 12 months raises the question as to whether other varieties may have changed during sample storage. TEM studies were performed from half a year to about four years after the samples were brought to the surface. The same TEM specimens were studied several times within a period of 18 months; the main superstructures (as given in Table 2) did not show major changes over this time. Optical microscope studies and thermomagnetic experiments were done within a few days after sample recovery (Kontny et al. 2000). Because the interpretation of our TEM data is consistent with the results of optical and magnetic studies, we believe the original superstructures have not converted into other varieties during sample storage.

Kontny et al. (2000) proposed that pyrrhotite types may transform during recovery by drilling. The pyrrhotite-bearing rocks went through several metamorphic cycles, with a peak temperature of ~720 °C (Emmermann and Lauterjung 1997). Because these host rocks have been in their present tectonic positions for at least 20 million years (Emmermann and Lauterjung 1997), the pyrrhotite types presumably attained



**FIGURE 6.** [100] SAED patterns of 1C-type pyrrhotite crystals containing regions that exhibit nC-like vacancy ordering, as indicated by faint reflections along the arrowed reciprocal lattice rows.

equilibrium at the temperatures corresponding to their depths below the surface (up to 260 °C at 9080 m). According to Kissin and Scott (1982), 1C pyrrhotite, which is stable above 308 °C, is unquenchable, whereas other modifications (including those in Table 2) are readily quenchable. Because all KTB samples were subjected to the same quick cooling (by the drilling mud and then fast uplift, see Kontny et al. 2000), the distinct differences in the distributions of pyrrhotite structure types reflect the differences that were present in the samples when they were in their original locations below the surface. Therefore, we interpret most of the observed structure types as original pyrrhotite modifications.



**FIGURE 7.** 1C-type pyrrhotite containing vacancy-ordered domains. (**a**) Typical SAED pattern that was obtained using a large selected-area aperture (indexed according to a hexagonal cell, zone axis is  $[0\bar{1}2]$ ), showing very weak superstructure reflections; (**b**) SAED pattern from a small area (less than 0.1  $\mu$ m in diameter) of the same crystal as in (**a**), showing stronger superstructure reflections; (**c**) diffraction contrast image showing ripple-like features that are likely related to changes in vacancy ordering. Inset shows the corresponding SAED pattern.

#### Superstructures and stabilities

From published phase diagrams (Kissin and Scott 1982; Nakazawa and Morimoto 1971; Grønvold and Stølen 1992), at 260 °C (corresponding to 9080 m in the KTB borehole) and for the typical compositions of pyrrhotite grains at this depth (see Fig. 4b in Kontny et al. 2000), the presence of either the nA (with c = 3C) or the mC (with 3 < m < 4) pyrrhotite type is expected. Because the observed superstructure domains in the 1C-type pyrrhotite can have c parameters as large as  $\sim$ 4.9C, these structures do not match exactly the mC type described by Nakazawa and Morimoto (1971) and Kissin and Scott (1982). They cannot be identified as nA either, because the characteristic 3C periodicity was observed in only one grain, and even that crystal produced stronger supercell reflections at ~3.7C positions (Fig. 9). To avoid further complication of the pyrrhotite terminology, we refer to the typical structure type from the 9080 m sample as "1C-type pyrrhotite with nClike domains."

Domain-like ordering of vacancies in pyrrhotite was described in several studies. Francis and Craig (1976) interpreted the structure of nA pyrrhotite as consisting of domains in which



**FIGURE 8.** [110] (**a**) and [100] (**b**) SAED patterns of troilite; (**c**) HRTEM image of troilite in [100] projection; (**d**) SAED pattern of altered troilite, showing diffuse reflections along the arrowed reciprocal lattice rows. (The SAED patterns are indexed on the basis of the troilite cell in Fig. 1.)

the ordered vacancy distribution produces 3C periodicity. In synthetic Fe<sub>7</sub>S<sub>8</sub> that was quenched from 340 °C, Li et al. (1996) observed the formation of 3C and 4C domains that were about 170 Å long along the **a** axis. Similarly, short-range ordering of vacancies was found in synthetic selenian pyrrhotite, in which the ordered domains grew with decreasing temperature and a spontaneous ferrimagnetic moment appeared below about 300 °C (Ericsson et al. 1997). As we discussed above, the 1C-like pyrrhotite with the domain structure may be related to the mC structure of Nakazawa and Morimoto (1971) and Kissin and Scott (1982); the domains that were revealed by TEM could not have been observed by these authors who used X-ray diffraction.

Based on the phase relations determined by Kissin and Scott (1982), it is surprising that nA pyrrhotite is only a minor phase in the 9080 m sample. Because nA pyrrhotite was observed in quenched synthetic samples (Morimoto and Nakazava 1968) and in natural hydrothermal ore specimens (Kissin and Scott 1982; Pósfai and Buseck, unpublished results), it is unlikely that original nA pyrrhotite transformed into other pyrrhotite types during sample recovery. If the 1C-like pyrrhotite modification with the domain structure is identical to the mC variety of Kissin and Scott (1982), then the phase boundary between mC and nA pyrrhotite may be at a temperature lower than 262 °C (the value determined experimentally). Kissin and Scott (1982) used a confining pressure of 61 to 890 bar in their experiments, and reported no measurable effect of pressure on the phase boundaries; however, because our sample from 9080 m was subjected to a pressure of about 1800 bar, the stability field data may not be directly applicable to the deepest KTB samples. The difference between results from experimental studies and from natural specimens could also arise from the fact that the preservation of metastable pyrrhotite structures is more likely in shorter duration laboratory experiments than in nature. In any case, the domain-bearing, 1C-like pyrrhotite (whether or not identical to mC) can be regarded as a structurally and thermodynamically transitional modification between 1C (with completely disordered vacancy distribution) and nA.

Perhaps the most enigmatic pyrrhotite variety from the KTB borehole is the 5C type. Several studies describe 5C as having a composition of Fe<sub>9</sub>S<sub>10</sub>, and regarded as a low-temperature variety within the phase field of NC pyrrhotites (where N is an integer; Morimoto et al. 1970; Engel et al. 1978; Kissin and Scott 1982). However, based on our interpretation of SAED patterns and HRTEM images, the observed 5C variety has a vacancy ordering scheme that results in a composition close to  $Fe_7S_8$ ; thus, it is nearly isochemical with 4C. It cannot be ruled out that among the many theoretically possible 5C superstructures (Pósfai and Dódony 1990) there are at least two specific and compositionally different varieties that are common in natural pyrrhotite specimens. The presence of 5C pyrrhotite with the same type of superstucture in both the 9080 m and the 564 m samples, and its occurrence in two different hydrothermal ore deposits (Dódony and Pósfai 1990; Pósfai and Buseck, unpublished results) indicates that the 5C, Fe<sub>7</sub>S<sub>8</sub> variety could be relatively widespread. The stability relations of this 5C variety remain unknown, but it seems to be stable up to at least 260 °C, the highest temperature in the KTB hole.

Monoclinic 4C pyrrhotite is the major pyrrhotite type in the KTB samples from depths of 564 and 2325 m. Twinning and subgrain boundaries (Fig. 3) suggest that some 4C crystals are the products of transformation from high-temperature modifications (Kontny et al. 2000). Optical studies show that ferrimagnetic (supposedly 4C) pyrrhotite forms rims around cores of some antiferromagnetic pyrrhotite (Kontny et al. 1997), where the 4C type seems to have formed by oxidation of more Fe-rich pyrrhotite. The presence of nC types intergrown with 4C in the 564 m sample is consistent with the phase diagrams of Kissin and Scott (1982) and Grønvold and Stølen (1992). Such intergrowths have been commonly observed in natural pyrrhotite specimens and may be exsolution products of hightemperature phases with compositions between  $Fe_7S_8$  and  $Fe_9S_{10}$ . The stability of 4C pyrrhotite is discussed further by Kontny et al. (2000).

# Correspondence between structure types and magnetic properties

Our TEM results indicate that a direct relationship exists between the variations of magnetic properties and the structures of pyrrhotite grains from the KTB borehole. TEM observations show 1C (with nC-like, vacancy-ordered domains) as the dominant phase at 9080 m, whereas 4C is the major pyrrhotite phase in the upper section of the rock sequence. The thermomagnetic curves of all specimens from depths greater than 8080 m show the dominance of antiferromagnetic pyrrhotite (Kontny et al. 2000). We assume that the domain-bearing 1C phase that we identified in the 9080 m sample is responsible for the antiferromagnetism of pyrrhotite samples from below 8080 m (> $220 \degree$ C).

The structure of the 1C-like, domain-bearing pyrrhotite is consistent with an antiferromagnetic character. The ~10 nm sized vacancy-ordered regions are likely in the superparamagnetic size range (Clark 1984). In addition, the overall structure has a mostly disordered vacancy distribution (as indicated by Fig. 7a), resulting in antiferromagnetic behavior at room temperature. The structural character of the 1C-like variety could also explain the nature of the so-called  $\lambda$ -transition (Li and Franzen 1996; also see Kontny et al. 2000).

Type 5C pyrrhotite is generally assumed to be antiferromagnetic; according to Schwarz and Vaughan (1972), an essential feature of the structure model is that every second vacant Fe layer is followed by two consecutive filled Fe layers. Such a model explains the antiferromagnetism of 5C, because the structure can be regarded as consisting of two interpenetrating, vacancy-containing Fe sublattices that have equivalent but oppositely directed magnetic moments that cancel each other (Schwarz 1975). This 5C model is also consistent with the stoichiometric Fe<sub>9</sub>S<sub>10</sub> composition that has been reported by several authors (Corlett 1968; Morimoto et al. 1970; Engel et al. 1978; Pierce and Buseck 1976).

As discussed above, our HRTEM images and SAED patterns obtained from 5C pyrrhotite from the KTB samples do not confirm a model that contains adjacent filled Fe layers; instead, they support a 1020103040-type vacancy distribution. Because every second layer contains vacancies, by analogy to 4C, this superstructure should be ferrimagnetic. However, the contrast features in Figure 5 indicate that the vacancies in 5C crystals are partly disordered; this irregularity of the structure could result in a weaker magnetic moment than that of ordered 4C. The lack of pronounced lamellar domain structures (as in 4C) is probably responsible for the diffuse accumulation of the magnetic fluid to some ferrimagnetic regions within polished sections (see Fig. 2c in Kontny et al. 2000). From the above discussion, we believe that in the deepest section of the borehole antiferromagnetic, 1C-like pyrrhotite is the major phase, and the observed minor ferrimagnetic contribution likely comes from the 5C type.

Rock magnetic parameters, such as coercivity and magnetocrystalline and shape anisotropy, are affected by the fine-scale microstructural variations and the sizes and shapes of regions that exhibit different superstructures (Dekkers 1988; Zapletal 1993). The intergrown 4C and nC regions in Figure 4 (see also Fig. 2a of Kontny et al. 2000) indicate that in many places the ferrimagnetic 4C crystallites are separated by antiferromagnetic lamellae. In such areas contiguous 4C regions are smaller than 3 µm, the approximate upper limit of the magnetic single-domain range (Clark 1984). Soffel (1977, 1981) observed that intergrowths of pyrrhotite varieties with only slightly different chemistries are responsible for entirely stationary "pseudo-domain walls;" in contrast to real domain walls, the "pseudo-domain walls" do not move when the applied magnetic field changes. Even though the grain size spectrum ranges from 10 to 500 µm, in many places the presence of twin boundaries and intergrowths creates smaller 4C domains that may be responsible for the observed high coercivity and pseudo-



**FIGURE 9.** SAED pattern from a pyrrhotite grain that exhibits some nA-like ordering, as indicated by the faint, off-axis reflections at 3C positions along **c\*** (marked by white arrows). The strong supercell reflections indicate that this crystal has primarily an nC-type, incommensurate superstructure with a ~3.7C periodicity.

single domain behavior of KTB pyrrhotite (Worm and Rolf 1994).

The lamellar arrangement of ferrimagnetic and antiferromagnetic pyrrhotite regions should contribute to the magnetic anisotropy of KTB rock samples. According to de Wall and Worm (1993), pyrrhotite grains from the KTB paragneiss samples are elongated along the plane of foliation, and the axis of minimum magnetic susceptibility is perpendicular to the foliation. Our observations also show that the pyrrhotite lamellae are preferentially oriented, with their magnetically "hard" **c** axes roughly perpendicular to the elongation direction (Fig. 4). Thus, owing to the crystallographic orientation of the elongated pyrrhotite grains, the effects of magnetocrystalline and shape anisotropies reinforce each other.

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