

IRON OXIDES AND PYRRHOTITES FROM IGDLUKUNGAQ, DISKO ISLAND, GREENLAND

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ABSTRACT

Magnetite, stoichiometric iron oxide, maghemite, troilite, and intermediate pyrrhotite occur in a massive sulfide showing at Igdlukunguaq, Greenland, in association with pentlandite, chalcopyrite, siderite and spinel. Minor-element substitutions may have stabilized stoichiometric iron oxide and maghemite. Troilite and intermediate pyrrhotite form an extremely fine-grained intergrowth which corresponds to the α - β lamellae commonly reported in pyrrhotite. Peculiar sulfide-oxide textural relations seem to be related either to cotectic crystallization or to solid-state exsolution.

SOMMAIRE

La magnétite, un oxyde de fer stoechiométrique, la maghémite, la troilite, et une pyrrhotine intermédiaire se trouvent dans une venue de sulfures massifs à Igdlukunguaq, Groënland, associés avec la pentlandite, la chalcopyrite, la sidérite et du spinel. Il se peut que la stabilisation de l'oxyde de fer stoechiométrique, et de la maghémite soit causée par la substitution d'éléments traces. La troilite et la pyrrhotite intermédiaire forment des intercrossances extrêmement fines qui correspondent aux lamelles α - β communément observées dans la pyrrhotine. D'étranges relations texturales entre sulfures et oxydes semblent indiquer soit une cristallisation cotectique ou une exsolution à l'état solide.

(Traduit par la Rédaction)

INTRODUCTION

Disko Island, Greenland, is best known for the occurrence of terrestrial native iron, formed (Pauly 1969) through assimilation of bituminous sediments by Tertiary basalts, with a consequent reduction of the oxygen fugacity of the basaltic melts. The major locality for this native iron is Uivfaq, on the west coast of Disko Island.

In a similar geological setting at Igdlukunguaq, on the east coast of Disko Island, there is an occurrence primarily of sulfides (pyrrhotite, pentlandite, chalcopyrite) with minor siderite and iron oxides. This mineral assemblage is

found as small pellets and as a large block (1.7 m by 3.3 m by 1.3 m) in the middle of a Tertiary basalt dyke 3.3 to 5.3 m wide (Pauly 1958). The detailed mineralographic description by Pauly (1958) includes mention of peculiar rounded zoned magnetite grains. The textures and zoning exhibited by the magnetite are so striking in Pauly's illustrations (see also Fig. 1) that it was thought that a re-examination of the material using electron microprobe and X-ray diffraction techniques might be of interest. The pyrrhotite phases present were also re-examined in the light of recent studies of this complex group of minerals (Morimoto *et al.* 1970, 1971, 1975; Vormo 1970).

EXPERIMENTAL TECHNIQUES

After preliminary optical identification, the various phases were analyzed using an Applied Research Laboratories AMX electron microprobe equipped with a Tracor-Northern NS-880 energy-dispersive spectrometer. Operating conditions were: excitation voltage 15 kV, specimen current about 1.0 nA, beam diameter about 2 μ m.

The reference standards used were: Si - SiO₂; S - Fe₇S₈ (synthetic); Ni - Ni metal; Mn - Mn metal; Fe - Fe₇S₈ (synthetic) as standard for iron sulfide analyses, or wüstite (synthetic) as standard for iron oxide analyses. Fe₇S₈ was synthesized by R. G. Arnold, using the same methods which were used to produce the synthetic materials on which Arnold's (1956) d_{102} determination curve for pyrrhotite compositions is based. This material has been checked by the author, using X-ray diffraction, wavelength-dispersive, and energy-dispersive techniques. All these tests indicate that the composition of the material is 60.4 \pm 0.3% Fe, 39.6 \pm 0.1% S. The only other element detected by wavelength-dispersive techniques, and then only in a few analyses, was nickel, maximum 0.3% (detection limit 0.1%). Thus the synthetic pyrrhotite is homogeneous with respect to iron and sulfur within the limits of error for the analytical method, and repeated analyses provide an experi-

mental measure of the precision of this analytical method. Wüstite, supplied by P. L. Roeder, was synthesized in equilibrium with metallic iron at 1200°C. Its composition (76.95% Fe) is taken from the experimental data for the Fe-O system (Darken & Gurry 1946) and has been confirmed by X-ray diffraction and by microprobe analysis, using Fe metal as a standard.

All data points for iron sulfide analyses were chosen at random; for comparison, 52 analyses were also made of the homogeneous Fe₇S₈ standard. The iron oxide analyses include 13 analyses made on 4 different grains, and 40 analyses selected from 60 analyses made at 2 μm intervals across two grains. The 20 iron oxide analyses excluded were of grain boundaries, core-rim boundaries, and cracks. The emission spectrum (0 to 10 kV range) for each data point was collected for 120 seconds (13 iron oxide analyses) or 200 seconds (all other analyses), then analyzed using a multiple least-squares fitting technique developed by F. H. Schamber, Tracor-Northern Laboratories. The resulting apparent concentrations ("k" values) were corrected for absorption, secondary fluorescence, and atomic number effects using a standard ZAF correction program.

Several different methods were used to obtain X-ray data for the various zones in the magne-

tite grains. Individual grains were plucked from the polished section and mounted in a Gandolfi camera. The entire polished section was mounted in a diffractometer. A magnetic separate was prepared from crushed material and examined using diffractometer and Guinier techniques. As will be discussed later, no conclusive X-ray evidence supporting the existence of chemically distinct iron oxide phases could be obtained.

RESULTS

Optical properties

The zoned grains range in diameter from 10 to 50 μm and characteristically exhibit a droplet shape. These droplets are usually arranged in regular fan-like patterns, reminiscent of the plagioclase-quartz myrmekite texture. Larger irregular magnetite grains are also present, but they do not appear to be zoned.

Pauly (1958) identified two types of zoned magnetite grains in polished sections from this locality. The first has an inner core which he described as being sometimes darker and sometimes lighter than the surrounding rim, and displaying a distinct, but not pronounced, anisotropy. These inner cores are often euhedral, and are browner than magnetite. The second type has a mottled blue-grey core, which Pauly interpreted as indicative of maghemitization of the magnetite. These two types of zoned grains may occur in close proximity in the same polished sections; one grain was found which contained all three phases.

No attempt in this study was made to etch the pyrrhotite to verify the presence of α and β lamellae observed by Pauly (1958). It was thought that any etching method might alter the chemical composition, and/or the crystal structure of the phases, and thus affect the subsequent chemical and X-ray data.

Chemical composition

Microprobe analyses of the iron oxide grains indicate that three chemically distinct phases are present (Fig. 2). Three clusters of Fe values occur, corresponding roughly to the theoretical Fe values for maghemite (69.94% Fe), magnetite (72.36% Fe), and stoichiometric FeO (77.73% Fe). The complete analyses include minor amounts of Ni, Si, S, and Mn. All of these elements are present in some analyses in amounts in excess of their detection limits; the limits for these minor elements, taken as 3σ above the background radiation level, are: Ni, 0.4%; Si, 0.1%; S, 0.1%; Mn, 0.2%. The precision for each of these minor elements is ±0.1% (limited

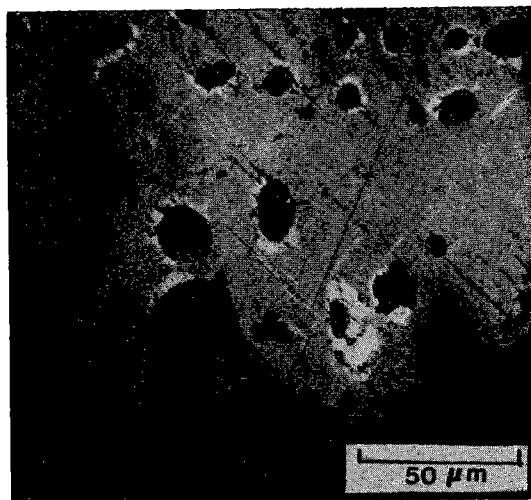


FIG. 1. Rounded zoned iron oxide grains (dark grey), Igdlukunguaq, Disko Island. Each grain is surrounded by a fine-grained chalcopyrite-pentlandite intergrowth (white); the major mineral present is pyrrhotite (light grey). The zoning in the iron oxide grains is barely discernible in black and white photographs, although differential plucking of the inner zones from some of the smaller grains may be observed.

in the case of Si and S by the three-figure output of the analytical program). All of these peaks, moreover, were visible in the spectral displays during the analyses.

Scattering of electrons and of X-rays in a specimen may generate additional X-ray signals in the specimen, at some distance from the focal point of the electron beam. In wavelength-dispersive X-ray spectrometry, such signals are to some extent screened out, since they do not impinge on the analyzing crystal at the required Bragg angle θ . In energy-dispersive X-ray spectrometry, however, all X-rays leaving the sample in the solid angle seen by the detector are counted. Thus the minor amounts of Ni and S in the analyses could be due to excitation of the surrounding sulfides; the Si signal could represent excitation of the detector itself.

In such cases the intensity of the spurious signals should be constant, corresponding to widespread low-level generation of X-rays in the specimen, the specimen chamber, and/or

the detector, or it should be greater near grain margins, representing excitation of the immediately adjacent material. Magnetite and stoichiometric FeO spectra contain constant, low-level Si and S signals; these are interpreted as due to excitation of X-rays away from the incident electron beam. Examination of the analyses, however, shows that in all other cases the minor elements are present in core, rather than rim, analyses. This indicates that these elements are actually present in the core phases, since a reverse pattern would be expected if the reported minor elements were due to excitation of the surrounding sulfides.

Of the 60 analyses made at 2 μm intervals across two zoned oxide grains, only 1 or 2 data points at each core-rim boundary showed transitional analytical values. This indicates that the effective spatial resolution for these elements at this low operating voltage (15 kV) and low electron flux (1.0 nA specimen current) is approximately 5 μm .

The average atomic ratios (Fe+Ni+Mn)/(O+S) are: magnetite rims, 0.741; mottled blue-gray cores, 0.646; brown cores, 1.006. These ratios correspond to magnetite (metal:oxygen = 0.750), maghemite (0.667), and stoichiometric FeO (1.000). This last composition has never been attained experimentally in the pure FeO system (see Levin *et al.* 1956; Cirilli *et al.* 1970; Aubry *et al.* 1970). The crystallochemical role played by Si in maghemite is not known; thus it was left out of the atomic ratio calculations. This may explain the deviation of the average atomic ratio from the theoretical value.

The detection limit for Ni under these analytical conditions is high (0.4%). Thus, as expected, the analyses of the Fe_7S_8 standard showed only Fe and S. In comparison, the pyrrhotite from Igdlukunguaq contains Ni in amounts ranging from below the detection limit to 1.0%. No correlation of Ni content with Fe content was noted. No other elements were found to be consistently present in the analyses; very occasional low Cu values are attributed to the presence of chalcopyrite in the analyzed volume, and low Co and Zn values are due to the poor peak resolution for higher atomic number elements at this low operating voltage.

The scatter in the metal:sulfur ratios for pyrrhotite may be compared with the analytical scatter for homogeneous Fe_7S_8 (Fig. 3). This comparison indicates that the pyrrhotite in question is inhomogeneous, and probably consists of a fine intergrowth of troilite and of pyrrhotite, possibly $\text{Fe}_{11}\text{S}_{12}$. These two compositions have been found in lamellar intergrowths by Vormá (1970).

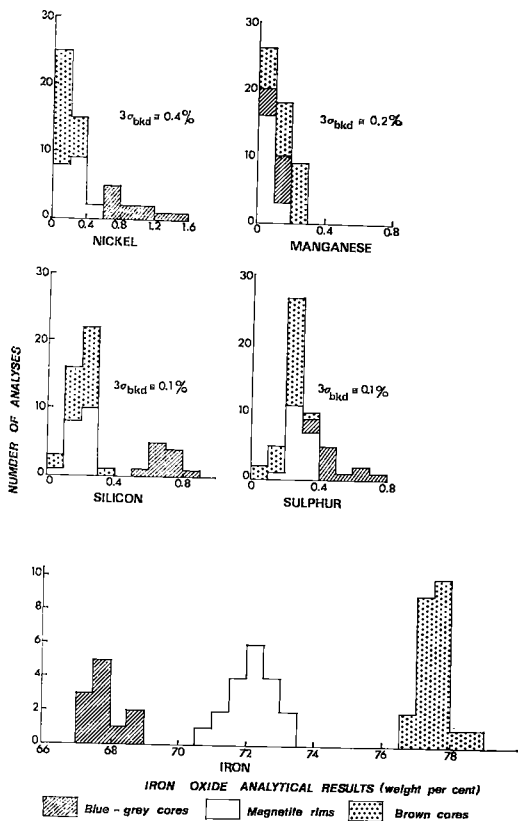


FIG. 2. Iron oxide analytical results, expressed in terms of frequency versus weight percent element. The calculated value 3σ for the background is taken as the detection limit for minor elements.

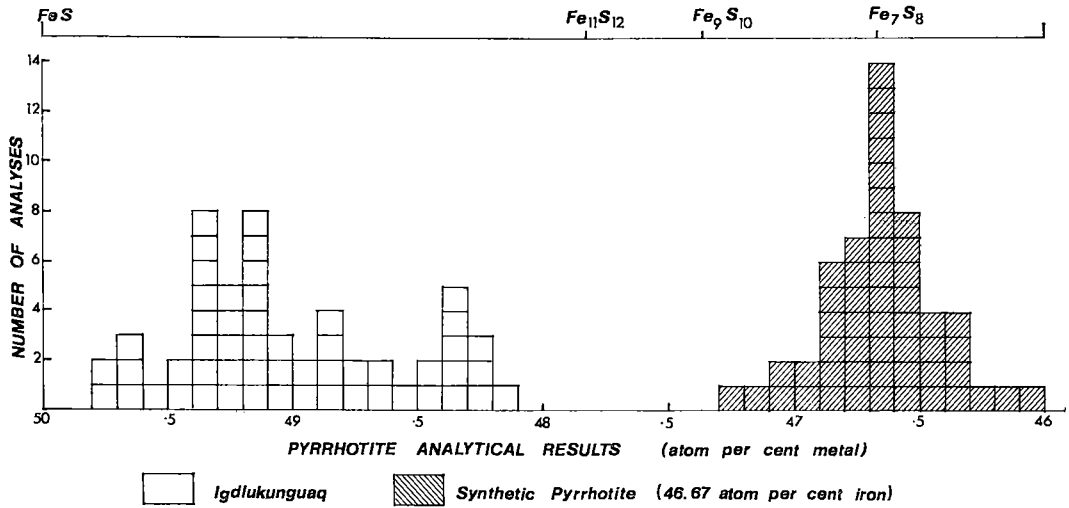


FIG. 3. Scatter in pyrrhotite analytical data, expressed in terms of frequency versus atom per cent metal. The data from the homogeneous synthetic analytical standard (52 data points) indicate the amount of scatter assignable to the analytical method; the greater scatter in the Igdlukunguaq data (54 data points) is due partly to real variations in chemical composition.

X-ray diffraction data

The best data were obtained from Guinier photographs of the most magnetic fraction of the material. This magnetic separation was made

in an attempt to obtain a sufficiently high concentration of zoned magnetite grains to produce detectable X-ray diffraction lines from the inner-core material. Although a clear set of magnetite lines could be identified on the photograph (Table 1), no lines were found which could be attributed to other known iron oxide phases. It seems that the volume ratios (a) core to rim in zoned grains, and (b) zoned to unzoned magnetite, are both too low to allow detection of these extra diffraction lines. Other minerals present in this most magnetic fraction and contributing to the X-ray diffraction pattern are troilite, pyrrhotite, siderite, pentlandite, and chalcopyrite. Several of these minerals are non-magnetic, and their presence in this concentrate is indicative of fine-grained intergrowths. One additional unidentified line at $d=2.130\text{\AA}$, will be discussed later. Unit-cell parameters calculated for magnetite, troilite and pyrrhotite are given in Table 2, together with pertinent data from the literature.

TABLE 1. X-RAY DIFFRACTION DATA FOR MOST MAGNETIC FRACTIONS

	1	2	3	4	5	6	7
<i>d</i>	<i>r</i>	<i>d/r</i>	<i>d/r</i>	<i>d/r</i>	<i>d/r</i>	<i>d/r</i>	<i>d/r</i>
4.832	10	4.85/8					
3.040	80b					3.03/100	3.03/80
2.985	80		2.981/80	2.98/70			
2.968	80	2.967/30					
2.786	10				2.79/100		
2.656	50		2.656/90				
2.648	50			2.64/90			
2.533	100	2.532/100					
2.427	5	2.424/8					
2.130†	5						
2.099††	80	2.099/20					
2.093	80		2.091/100				
2.069	70			2.067/100			
1.938	20b		1.936/60				1.93/50
1.863	20b					1.85/80	
1.779	20b						1.76/100
1.722	70		1.722/70	1.720/80			
1.715	30	1.715/10					
1.617	50	1.616/30					
1.485	50	1.485/40					
1.2812	10	1.281/10					

† Observed on 1 of 2 sample preparations.
 †† Interference with Si peak; line position taken from a photograph without an internal standard.

- Magnetic fraction, Igdlukunguaq. Guinier camera, $\text{CuK}\alpha_1$ radiation. Silicon internal standard; visual intensities.
- Magnetite PDF 19-629. Diffractometer, $\text{CuK}\alpha_1$ radiation.
- Troilite, Del Norte, California. Guinier camera, $\text{FeK}\alpha_1$ radiation; quartz internal standard; visual intensities (strongest lines only).
- 5c-pyrrhotite. PDF 22-358. $\text{FeK}\alpha$ radiation. Spinel used as internal standard; visual intensities (strongest lines only).
- Siderite. PDF 8-133. $\text{CoK}\alpha$ radiation; visual intensities (strongest lines only).
- Chalcopyrite. PDF 9-423. $\text{FeK}\alpha$ radiation; visual intensities (strongest lines only).
- Pentlandite. PDF 8-90. $\text{CuK}\alpha$ radiation; visual intensities (strongest lines only).

TABLE 2. CELL PARAMETERS FOR MAGNETITE, TROILITE, AND PYRRHOTITE

	magnetite		troilite		pyrrhotite (subcell parameters)		
	Igdlukunguaq	PDF 19-629	Igdlukunguaq	Del Norte	Igdlukunguaq	Japan†	Finland††
$a(\text{\AA})$	8.401	8.396	5.964	5.961	3.445	3.4475	3.4470
$c(\text{\AA})$			11.750	11.750	5.744	5.7530	5.7501

† 6c pyrrhotite, Chichusa, Makimine mine, Japan (Morimoto *et al.* 1975).
 †† 5.53c pyrrhotite, Luikonlahti mine, Finland (Morimoto *et al.* 1975).

DISCUSSION

Magnetite

The optical, chemical, and X-ray data for the magnetite from Igdlukunguaq are normal, although the textural relations suggest an unusual mode of formation. Pauly (1958 pp. 86-87) considers that

"Evenly distributed in the molten sulfide mass there was apparently a substance which now can be recognized only in the magnetite. During the FeS crystallization the sulfide was first able to push this substance right outside of the solid phase. Gradually as crystallization advanced, large quantities of the substance collected in the 'crystallization front' and assumed the form of drops; then came a moment when the FeS structure was no longer able to keep them out, they became included in the solid phase as 'vacuoles' in the sulfide. The longer the advance of the crystallization front, the larger became the drops of the repelled substances. When these large drops became in-bedded, they became moulded into shape by the crystallizing mass, chiefly by being pressed out in the direction of the crystallization; hence the familiar elongated shape and the claviform grains."

Pauly has enlarged on this interpretation (personal comm. 1977). He considers that the oxidic material (which he prefers to think of as regions rich in elements substituting for S) was caught in the solid sulfide while it (the oxidic material) was still in a liquid or semi-solid state. Such a widespread, evenly distributed compositional fluctuation in a liquid is characteristic of spinodal decomposition, and is therefore an exsolution phenomenon — that is, he regards the texture as indicative of liquid immiscibility in the melt.

If the Igdlukunguaq material is projected into the Fe-S-O ternary system (Naldrett 1969), the present bulk composition falls very close to the position of pyrrhotite, within the field of primary crystallization of pyrrhotite and well outside the boundary of the two-liquid field. In view of this recent experimental work, liquid immiscibility no longer seems a reasonable explanation for the observed textural relations. Two other suggestions may be made:

(1) As pyrrhotite crystallization proceeded the composition of the remaining liquid moved toward one of the cotectic lines pyrrhotite-magnetite or pyrrhotite-wüstite. When the line was reached, crystallization of an oxidic phase began. The texture thus represents cotectic crystallization in a ternary system.

(2) The original pyrrhotite contained oxygen in solid solution, substituting for sulfur. This solid solution broke down at lower temperatures into pyrrhotite and an oxidic phase. The texture thus represents exsolution in the solid state. Texturally, the intergrowths resemble myrmekite, which is thought to be a product of such a solid-state decomposition (although not necessarily in a closed chemical system).

Similar textures have been variously attributed to both origins (see, for example, Edwards 1954). A choice between them may require re-examination of the Fe-S-O system, specifically of the oxygen content of early-formed pyrrhotites.

Stoichiometric FeO

The chemical analyses indicate that the brown cores are composed of stoichiometric FeO. The highest Fe:O ratio for pure wüstite grown in the pure Fe-O system (Darken & Gurry 1946) is $\text{Fe}_{0.953}\text{O}_{1.000}$ (23.10 wt. % O). Aubry *et al.* (1970) synthesized stoichiometric iron-rich monoxide phases with the wüstite structures in several systems, among them Fe-Mn-O; however, stoichiometry is attained only when there is significant incorporation (>50 mole %) of MnO in the phase. They reported that this stoichiometric monoxide phase is stable even at room temperature, whereas wüstite synthesized in the Fe-O system is stable only above 560°C, below which it breaks down to metallic iron plus magnetite. Although some of the analyses presented here show minor amounts of Mn, no larger-scale substitution has been found; the phase appears to be stoichiometric FeO. Even more surprising, this FeO is coexisting with magnetite; previous experimental studies (Levin *et al.* 1956; Cirilli *et al.* 1970) indicate that the most iron-rich "monoxide" phase in equilibrium with magnetite contains 23.3 wt. % O ($\text{Fe}_{0.943}\text{O}$). One can suggest that minute amounts of manganese may be sufficient to stabilize the stoichiometric monoxide, and allow it to coexist with magnetite at low temperatures. In the absence of X-ray diffraction information, one can also suggest that this mineral, stoichiometric FeO, may not be wüstite but rather a new phase.

The unidentified line in the X-ray diffraction pattern ($d=2.130\text{\AA}$) cannot be assigned to any of the minerals identified here. Weak lines at 2.154 and 2.140 \AA in the Del Norte troilite pattern are near this line; the strongest line in a "stoichiometric wüstite" pattern would also be in this region ($d=2.170\text{\AA}$, by extrapolation from the data of Cirilli *et al.* 1970). However, the angular separation obtained with the Guinier camera ensures that this line is not due to troi-

lite or to "stoichiometric wüstite".* Indeed, if it were due to a cubic iron oxide, the d -value (again by extrapolation from the data of Cirilli *et al.* 1970) would correspond to the composition $\text{Fe}_{0.88}\text{O}$, clearly at variance with the chemical analytical results.

Maghemite

The cation:anion ratios obtained for maghemite indicate that it is the pure γ -phase, showing no solid solution toward magnetite. The definite enrichment of this phase in Si, S, and Ni compared with the other oxide phases requires further comment. Si, reported as SiO_2 , is commonly present in maghemite analyses (see Deer *et al.* 1962; Palache *et al.* 1944); the results of this microprobe study indicate that Si is present as part of the iron oxide phase, rather than as inclusions. This element may be necessary to stabilize maghemite with respect to magnetite and hematite. Also, the amount of Ni in maghemite is high, especially when compared with the low-Ni troilite and pyrrhotite. The presence of these elements in maghemite must be dealt with in any attempt to trace the origin and history of this mineral assemblage.

Pyrrhotite

The compositional range in pyrrhotite, as well as the X-ray data, indicate that two pyrrhotite phases are present in the specimens. The lack of a distinct bimodal distribution in the analytical data indicates that the two phases are very finely intergrown; likely they correspond to the α - β lamellae mentioned by Pauly (1958). The X-ray data, supported by the chemical data, indicate that these two phases are troilite and intermediate pyrrhotite.† Similar intergrowths are mentioned by Morimoto *et al.* (1975) and Vormaa (1970).

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This most interesting and scarce material was made available to the author by Hans Pauly;

*A difference of 0.01 Å in the d -value in this range corresponds (for $\text{CuK}\alpha_1$ radiation) to a difference of 0.4 mm in the film position. With a well-aligned Guinier camera, a reliable internal standard, a well-prepared specimen mount, and reasonable care, film positions may be measured to ± 0.05 mm.

†The " d_{102} " line (i.e. the strongest line in the pyrrhotite powder pattern), compared with the Morimoto *et al.* (1975) data, and the compositional range, indicate that the pyrrhotite is either of the $5.5n\text{C}$ or 6C variety. Without single-crystal data or well-defined low-angle lines it is impossible to distinguish between these superstructures.

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