

X-ray diffraction and magnetic studies of altered ilmenite and pseudorutile

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SYNOPSIS

IT was not until 1966 that pseudorutile was first defined. Earlier, its X-ray diffraction spectrum had been confused with that of rutile and, to a lesser degree, with those of hematite and ilmenite. Subsequent work has shown that pseudorutile has a world-wide distribution in detrital ilmenite-bearing heavy mineral deposits. The present work has confirmed its magnetic susceptibility and density. In addition pseudorutile is shown to be a magnetic spin glass with a peak susceptibility at 23 °K.

Altered ilmenites, in which pseudorutile occurs as a secondary alteration product, display a range of chemical composition and magnetic susceptibility. The most highly magnetic fractions are not necessarily those containing the least-altered ilmenite,

and in material from Capel, Western Australia, the most highly magnetic fractions were those containing grains of ferrimagnetic ferrian ilmenite.

Quantitative X-ray diffraction has shown that West Australian altered ilmenite contains significant amounts of amorphous ilmenite, pseudorutile, and rutile. The magnetic susceptibility of paramagnetic fractions of altered ilmenite from Capel, Western Australia, can be calculated from normative compositions based on chemical analyses.

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Introduction

Ilmenite grains in beach sands are almost invariably altered. The alteration initially involves the removal of iron and the formation of a mineral phase having the approximate composition $Fe_{0.7}Ti_2O_5$. The name pseudorutile has been suggested for this phase (Teufer and Temple, 1966); its chemical composition matches that of arizonite (Overholt et al., 1950; Kerkkanavala, 1959) and proarizonite, but none of these mineral names has been internationally recognised (Fleischer, 1967). Although the chemical compositions of these three minerals are very similar, their X-ray diffraction spectra are reportedly different. In addition, the X-ray diffraction spectrum of pseudorutile has been confused with the spectra of ilmenite, rutile and hematite (Fig. 1), especially when these minerals occur together in the same samples. Thus, Lynd et al. (1954) noted that weakly magnetic fractions of ilmenite concentrates gave rutile-like spectra yet did not show the main peak of rutile; the broad maximum peak found by Lynd et al. at $d = 1.698 \text{ \AA}$ was reinterpreted as being the main peak of pseudorutile ($d = 1.688 \text{ \AA}$).

Nominally pure pseudorutile has only been reported from South Australia (Larrock and Spencer, 1971), but X-ray diffraction peaks attributable to this mineral are found in the spectra of detrital ilmenite from many localities. It is difficult to determine accurately the amount of pseudorutile in altered ilmenite grains; this paper describes an attempt to quantify this value by a combination of X-ray diffraction results and chemical analyses.

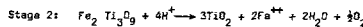
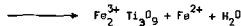
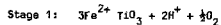
The magnetic susceptibilities of various altered ilmenite fractions have also been determined, and the results are interpreted in terms of their calculated mineralogical compositions.

Geographical distribution of pseudorutile

In addition to the South Australian locality, it has been shown that pseudorutile occurs in altered ilmenite grains from Capel, Western Australia (see below, and Gray and Reid, 1974), and that slightly impure pseudorutiles, containing traces of ilmenite and rutile, occur in detrital specimens from Indonesia (Gray and Reid, 1975). The present authors have confirmed that the mineral occurs in altered ilmenite from Eneabba, Western Australia (Lissiman and Oxenford, 1975, p.1068); in ilmenite concentrates from eastern Australia; and from Pulmoddi, Sri Lanka (Fig. 2). It has also been shown (Teufer and Temple, 1966) that pseudorutile occurs in Florida, in Brazil, and at Quilon in Southern India.

Chemical Studies

The complex chemical processes accompanying the alteration of ilmenite can be simplified to two major reactions (Dizanche and Bartholomew, 1976) that take place sequentially.



In stage 1 the ilmenite changes to pseudorutile by the loss of one third of the total iron and the oxidation of the remaining iron to the ferric state. Stage 2 involves the removal of the remaining iron and the loss of some oxygen to form rutile.

These alteration stages can be deduced qualitatively from the changes in mineral proportions revealed by the diffraction spectra of magnetic fractions of altered ilmenite grains. The proportions of ilmenite, pseudorutile and rutile were estimated by Gray and Reid, (1974) using X-ray diffraction calibration curves based on nominally pure, natural pseudorutile and on synthetic ilmenite and rutile. The results were similar to those obtained by normative calculation from chemical assays by allocating all the FeO and MnO to ilmenite, the Fe_2O_3 to pseudorutile, and any remaining 'unaccounted' TiO_2 to rutile. This normative calculation gives poor results if the titanium-rich minerals are markedly non-stoichiometric or if there are other minerals present. Furthermore, the normative values will not be matched by the X-ray diffraction results if the pseudorutile standard is poorly crystalline.

Altered ilmenite from Capel, Western Australia, was carefully separated into magnetic fractions of progressively decreasing susceptibility using a Cook magnetic separator with a six slope of 70 degrees. These fractions were hand-picked to remove silicates, and then chemically analysed. Table 1 and Figure 3 show the results of this analysis.

TABLE 1 ANALYSES OF MAGNETIC FRACTIONS OF ALTERED ILMENITE FROM CAPEL, W. AUSTRALIA

Sepn Current A	Cook $\frac{L \times X}{JT^2 Mg^{-1}}$	Analysis, wt. %							
		TiO ₂	Tot. Fe	FeO	Fe ₂ O ₃	Cr ₂ O ₃	V ₂ O ₅	MnO	MgO
0.05	2737	55.8	30.0	19.7	20.9	0.04	0.13	1.33	0.18
0.10	703	55.1	30.3	21.4	19.5	0.04	0.15	1.47	0.16
0.15	317	55.4	31.1	22.3	19.7	0.04	0.14	1.49	0.18
0.20	180	55.4	30.3	23.2	17.6	0.04	0.13	1.47	—
0.25	115	55.0	31.5	25.2	17.0	0.04	0.15	1.52	0.13
0.30	81	55.7	30.3	25.7	14.8	0.04	0.13	1.68	—
0.35	60	57.4	28.6	18.3	20.6	0.05	0.13	1.66	0.17
0.40	46	61.5	23.7	10.2	22.6	0.07	0.17	1.48	—
0.45	37	63.2	21.5	5.2	25.0	0.29	0.16	1.28	—

Analyses by Tioxide International Limited

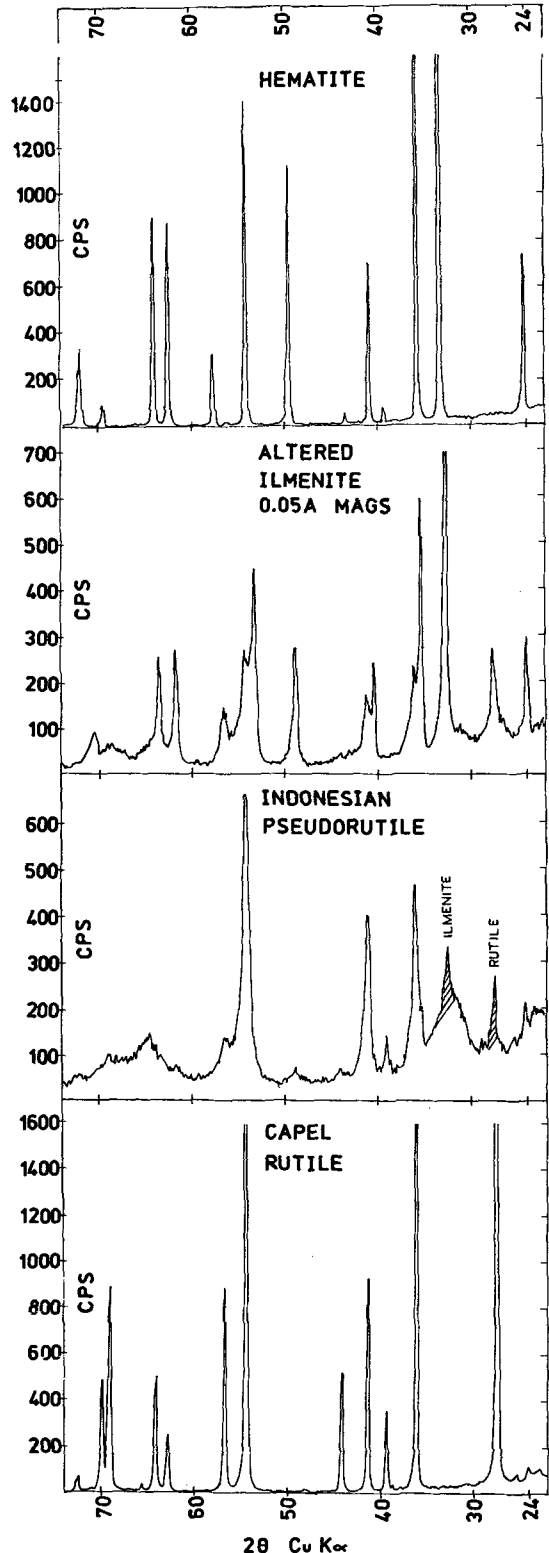


Fig 1. Comparison of the X-ray diffraction spectra of hematite, altered ilmenite, pseudorutile and rutile.

TABLE II COMPARISON OF APPARENT MINERAL COMPOSITIONS FOR MAGNETIC FRACTIONS OF ALTERED CAPEL ILMENITE, OBTAINED BY NORMATIVE CALCULATION AND BY QUANTITATIVE X-RAY DIFFRACTION.

Sep'n Current A	Normative Comp'n %			Comp'n by Chung XRD method			
	ILM	PSR	RUT	ILM	PSR	RUT	AMORPH
0.05	45	52	1	31	24	4	41
0.10	49	49	1	38	30	3	29
0.15	51	49	-1	50	32	3	15
0.20	52	44	1	48	30	2	19
0.25	57	42	-1	41	29	2	28
0.30	58	37	3	61	25	2	12
0.35	42	52	4	39	42	3	16
0.40	25	57	14	16	51	4	29
0.45	14	63	23	10	66	7	16

The mass magnetic susceptibilities of the fractions collected at low separation currents are much higher than the susceptibility of pure synthetic ilmenite ($\chi_{11} = 95 \times 10^{-2} \text{ JT}^{-2} \text{ Kg}^{-1}$). The qualitative behaviour of grains in these fractions is ferromagnetic, which is explained by the fact that the high FeO contents observed include solid solution of hematite in ilmenite. Such solid solution is known to produce a highly magnetic, ferrimagnetic structure (Nagata, 1961; Stacey & Banerjee, 1974) for compositions in the range 45 - 100 molar % ilmenite. Thus, the trend of the curves in Figure 3 over the range 0.05 - 0.30A can be interpreted as being due to magnetic fractionation, of relatively unaltered grains, according to the composition and amount of ilmenite-hematite solid solution. Curves of a similar trend have been published, though without this interpretation, for a Quilon ilmenite concentrate (Lynd et al., 1954).

The proportion of ilmenite falls steadily in the fractions 0.3 - 0.45A. This is shown by the steady decrease in the height of the main ilmenite X-ray diffraction peak and a corresponding decrease in FeO content, (Figure 4).

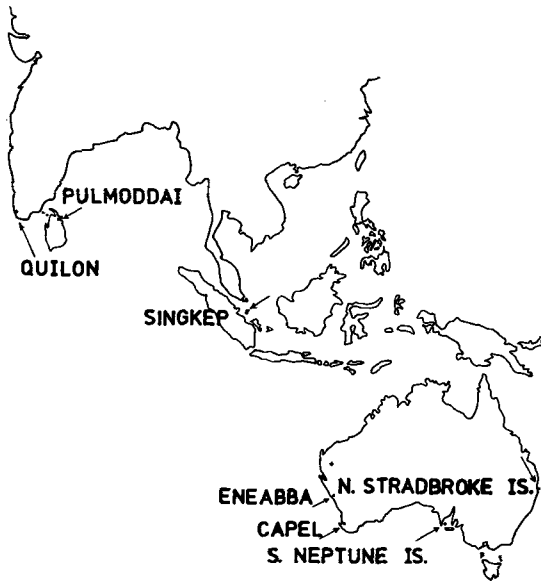


Fig 2. Some occurrences of pseudorutile

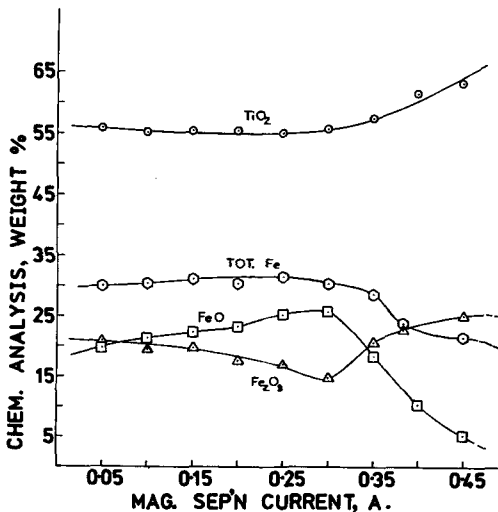


Fig 3. Chemical Variation of magnetic fractions of altered ilmenite from Capel, Western Australia.

The normative mineral compositions calculated from these analyses are given in Table 2. FeO and Fe₂O₃ were added to the FeO for calculating the ilmenite content.

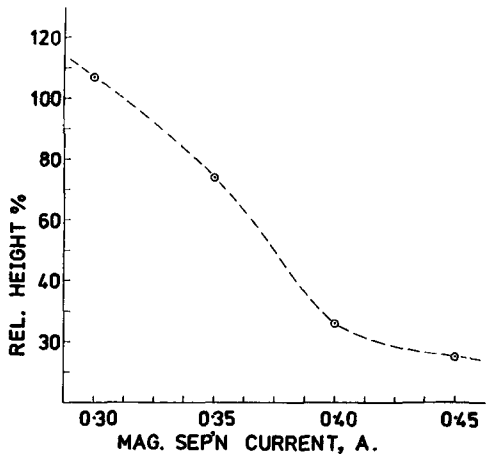


Fig 4. Height of main ilmenite peak relative to Fe internal standard as measured from X-ray diffractograms.

X-ray diffraction studies

The Chung (1974) method of quantitative X-ray diffraction analysis assumes that the identities but not the quantities of the crystalline phases in a mineral mixture are already known. Reference mixtures are made up from a pure specimen of each phase mixed in equal proportions by weight with a suitable internal standard (such as pure metallic iron powder). These reference mixtures are then used to prepare X-ray diffractograms in which the intensities corresponding to a selected line of the mineral phase and of the standard are noted, and the intensity ratio of mineral phase to standard is calculated. It is normally assumed that the degree of crystallinity of the mineral phase used to prepare the reference mixtures matches the crystallinities of the mineral phases in the natural mixtures. However, when the method is used specifically to determine the amorphous content of a specimen, the minerals used to prepare the reference mixtures must be of known crystallinity - preferably highly crystalline.

A diffractogram is prepared from the natural mixture into which a known weight of the internal standard has been blended. The intensities of selected peaks for each phase are noted together with the intensity for the internal standard. The data so obtained are substituted in the Chung working equation, which is calculated for each component in turn.

$$X_i = \frac{W_i}{I_i} \frac{I_c}{K_i}$$

$\cdot 10^{-2} \text{ JT}^{-2} \text{ Kg}^{-1}$ (S.I.) = $10^{-6} \text{ erg Oe}^{-2} \text{ g}^{-1}$ (cgs) (Craniole, 1977)

where X_i = Wt. fraction of phase i
 I_i = Intensity of X-rays diffracted by a selected plane (hkl) of phase i in the mixture.
 I_c = Intensity for a selected plane (hkl) of the internal standard.
 K_i = Ratio of the intensities of the selected peak of component i to the selected peak of the internal standard, as measured from the 50/50 reference mixture.
 X_c = Wt. proportion of the internal standard added to the mixture being analysed.

Even if all the standards are highly crystalline, the sum of the X_i terms does not equal 100% when X-ray amorphous matter is present in the unknown specimen, and the amount of amorphous material can thus be determined by difference. However, this calculated figure also becomes a repository for errors in the individual X_i terms.

In this work, high purity iron (produced from iron carbonyl) of high crystallinity was used as the internal standard since its lines do not interfere with those of ilmenite, rutile or pseudobrookite. The iron was added to the diffraction samples in the ratio 1:1 by weight. The other standards were synthetic ilmenite, synthetic rutile, and carefully cleaned Indonesian pseudobrookite.

The mineral proportions obtained using the Chung technique are given in Table II. In the absence of amorphous phases and where all phases are approximately stoichiometric, the proportion of a mineral calculated by this method will match that obtained from a normative chemical calculation.

TABLE III. CALCULATED AND MEASURED MASS MAGNETIC SUSCEPTIBILITIES FOR MAGNETIC FRACTIONS OF ALTERED ILMENITE FROM CAPEL, W. AUSTRALIA

Sample	Cook	Normative Compn.		Calc.	Actual
Current A	$R \times 10^2$	% ILM	% PSR	$\times 10^2 \text{ JT}^{-2} \text{ Kg}^{-1}$	$\times 10^2$
0.05	2737	45	52	3	170 F
0.10	703	49	49	2	115 F
0.15	317	50	49	1	100 F
0.20	180	52	44	3	84 F
0.25	116	57	43	-	82 F
0.30	81	58	37	3	75 P
0.35	60	43	52	4	57 P
0.40	46	25	57	14	41 P
0.45	37	14	63	23	31 P

F = Ferromagnetic P = Paramagnetic

‡ = These figures are used to normalise the chemically calculated composition to 100% minerals. This procedure brings the rutile contents closer to the XRD determinations.

Note

- (1) Susceptibility values used to calculate X were ilmenite 96, rutile 1.2 and pseudobrookite $34.5 \times 10^{-2} \text{ JT}^{-2} \text{ Kg}^{-1}$ respectively.
- (2) Apparent susceptibilities as determined in low fields by a Cook isodynamic separator for ferromagnetic fractions are higher than other determinations on account of the field-dependence of the susceptibility of ferromagnetic materials.

For the 0.05 - 0.25A magnetic fractions, the normative contents of pseudobrookite are higher than expected because the mineral proportions were calculated using the whole of the Fe_2O_3 whereas part of the Fe_2O_3 occurs in solid solution in the ilmenite. These high pseudobrookite figures also "consume" extra TiO_2 , and result in lower calculated rutile figures than those determined by X-ray diffraction. (The normative mineral proportions are not normalised and were calculated from chemical analyses that did not add up to exactly 100%).

Within the 0.05 - 0.25A range, the most highly magnetic fractions have the highest amorphous mineral content, suggesting that these fractions are the most altered. In addition the results suggest that fractions that contain more Fe_2O_3 tend to weather more quickly. Both the amorphous content and the Fe_2O_3 content are at a minimum in the 0.30A fraction for which reflected-light examination has revealed the highest proportion of relatively unaltered 'pink' ilmenite. A tendency for ferric ilmenite to become strongly altered has been noted elsewhere (Rumble, 1976).

The 0.30A fraction gave the highest ilmenite diffraction intensities and the lowest content of Fe_2O_3 (Table I) and estimates of ilmenite content obtained by the diffraction and normative calculation methods agree closely. This suggests that in this fraction virtually the whole of the ilmenite is crystalline and that most of the indicated amorphous content is attributable to pseudobrookite. Because of the unknown, but probably low degree of crystallinity of the Indonesian pseudobrookite that was used as a standard, both the amount of pseudobrookite and the content of amorphous material are approximations only. This is because the Chung working equation only indicates amorphous content over and above any amorphous material present in the standards.

Measurements of the width of the main pseudobrookite peak at half-height indicates the size of the X-ray diffracting particles, (Cullity, 1959, p.99, 262). In the samples studied, the crystallite size was estimated to be about 10 nm.

General properties of pseudobrookite

In the past, the difficulties encountered in the study of pseudobrookite were due to its tendency to form intergrowths with relict ilmenite and secondary rutile. The unusual feature of the South Australian, and to a lesser extent, the Indonesian specimens of pseudobrookite is that the second stage of alteration (forming rutile) did not proceed although the first stage (ilmenite to pseudobrookite) went virtually to completion.

Chemical and microprobe analyses (Larrett and Spencer, 1971) show that the composition of the pseudobrookite from South Heptuna Island, South Australia, departs noticeably from the theoretical formula $\text{Fe}_2\text{Ti}_2\text{O}_9$. The specific gravity of this mineral is 4.2 and the mass magnetic susceptibility (X) falls between 25 and $40 \times 10^{-2} \text{ JT}^{-2} \text{ Kg}^{-1}$. Our own measurements on the Indonesian pseudobrookite give a specific gravity of 4.10 and a mass susceptibility value of $34.5 \times 10^{-2} \text{ JT}^{-2} \text{ Kg}^{-1}$. Pseudobrookite from different localities need not, of course, have identical properties, but these results show that the South Australian and the Indonesian samples have closely similar magnetic susceptibilities and densities.

A general feature of altered ilmenite grains is that an optically isotropic alteration product can often be seen. This product includes material that gives a pseudobrookite X-ray diffraction pattern as shown by the South Australian specimens. Pseudobrookite has a hexagonal crystal structure (Taufel and Temple, 1966; Grey and Reid, 1975). Since hexagonal minerals are markedly anisotropic, it is concluded that the pseudobrookite specimens are so fine grained with respect to the wavelength of light that they behave as if they were optically isotropic. This conclusion is supported by the 3 nm granularity observed in specimens of pseudobrookite by electron microscopy (A.K. Temple, 1966).

Indonesian pseudobrookite is not pure and shows weak peaks of ilmenite and rutile. Also, the peak intensities of the pseudobrookite are very low and it is probable that much of this mineral is of very low degree of crystallinity with possibly a significant X-ray amorphous component. The published molecular formula $\text{Fe}_{2.74}^{\text{Fe}}\text{Ti}_{1.75}^{\text{Ti}}\text{O}_9$ (Grey and Reid, 1975) does not include any correction for the presence of the ilmenite and rutile and consequently implies a lower degree of stoichiometry in the pseudobrookite than is actually the case. The allocation of manganese to the divalent state is also not unequivocal, since Mn has a wide range of possible valences, and it is very difficult to ascertain the oxidation state of this element in a solid phase. While Mn is known to be incorporated into the structure of many natural ilmenites, where it is divalent, much less is known about its valence once the ilmenite becomes largely altered to pseudobrookite. However, it is unlikely that the Mn remains in a divalent state except in small areas of relict ilmenite. The high Mn-Fe ratio suggests that much of the Mn has in fact entered the pseudobrookite structure, and no areas free of Mn could be detected by our electron probe microanalysis.

The published diffractogram for South Australian pseudobrookite shows no detectable peaks for ilmenite or rutile, and the implicit conclusion that these phases are absent is supported by the apparent chemical homogeneity of the grains (Larrett and Spencer, 1971). However, a mixture of 86% stoichiometric pseudobrookite, 9% rutile and 5% ilmenite, would yield a similar molecular formula ($\text{Fe}_{2.71}^{\text{Fe}}\text{Ti}_{1.73}^{\text{Ti}}\text{O}_9$) to that for the South Australian material ($\text{Fe}_{2.74}^{\text{Fe}}\text{Ti}_{1.75}^{\text{Ti}}\text{O}_9$). Such quantities of rutile and ilmenite would escape detection if they were X-ray amorphous.

Magnetic properties of altered ilmenites

Magnetic fractions were prepared from a West Australian (Capel) ilmenite sample using a Cook isodynamic separator employing a side-slope of 10 degrees. After removal of impurities by hand-picking, the magnetic susceptibilities of these fractions were determined using the Faraday method (Cullity, 1972, p.76); this method is applicable to both paramagnetic and ferromagnetic materials and can give accurate determinations of ferromagnetic susceptibility. The results were interpreted in terms of the normative mineralogical compositions derived from the chemical analyses (Table III). As partly discussed in the earlier section on Chemical studies, the high-susceptibility ferromagnetic fractions (marked F) suggest the possible presence of hematite in solid solution in ilmenite, since their measured susceptibility values were much higher than those calculated from the normative compositions. (The actual values given in Table III for the ferromagnetic fractions have been extrapolated to infinite field). Further evidence linking the Fe_2O_3 in the chemical analyses with the observed ferromagnetic behaviour was obtained by preparing magnetic sub-fractions of the 0.05A magnetites; these sub-fractions were chemically analysed and their X-ray diffractograms displayed peak shifts similar to those expected for different members of the hematite-ilmenite solid-solution series (Fig. 5). However, it has not yet been shown that the ferromagnetism in these fractions is wholly accounted for by hematite-ilmenite solid solution.

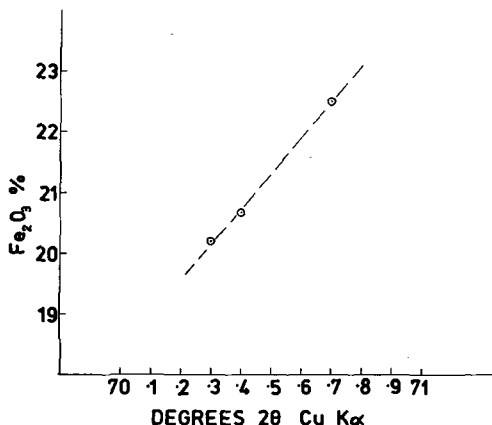


Fig. 5: Correlation of peak position for the 70.24° ($\text{CuK}\alpha$) line of ilmenite with changing Fe_2O_3 content of the magnetic fraction.

For the paramagnetic fractions, it was found that the susceptibility values calculated from the chemical analyses agree reasonably well with the measured values. The calculations were made using measured mass susceptibility values of 96, 34.5 and $1.2 \times 10^{-2} \text{ JT}^{-2} \text{ Kg}^{-1}$ for pure synthetic ilmenite, Indonesian pseudorutile and clean natural Capel rutile respectively.

Magnetic properties of pseudorutiles

A concentrate of Indonesian pseudorutile was carefully cleaned by hand-picking to remove all obvious impurities. Its mass magnetic susceptibility, determined by the Gouy method (Cullity, 1972 p.76) at natural grain size, was $34.5 \times 10^{-2} \text{ JT}^{-2} \text{ Kg}^{-1}$. The Gouy method was chosen because it can give highly accurate measurements in the paramagnetic regime, and no significant ferromagnetic component had been detected in this specimen at room temperature.

Mössbauer spectroscopy determinations were carried out on this Indonesian pseudorutile at 293°K and at 80°K and these show a simple ferric ion doublet with a very minor contribution from ferrous ions, (Fig. 6). The curve represents the best fit which could be obtained on the basis of two sites, using a Mössbauer least-squares fitting program developed in the Chemistry Department at Imperial College. These results indicate that no magnetic ordering is exhibited by pseudorutile at temperatures down to 80°K.

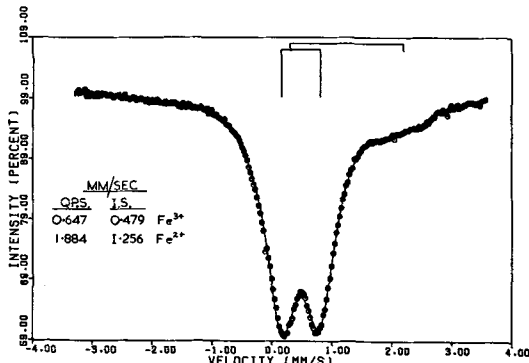


Fig. 6 Mössbauer spectrum of pseudorutile at 80°K.

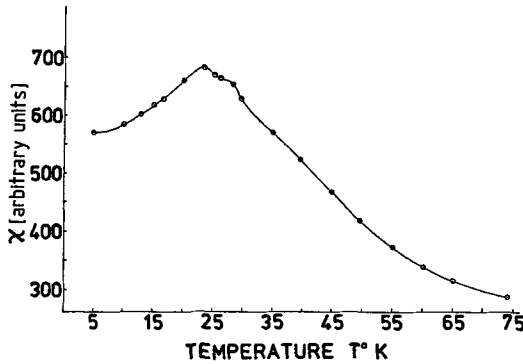


Fig. 7. Low-temperature susceptibility of Indonesian pseudorutile.

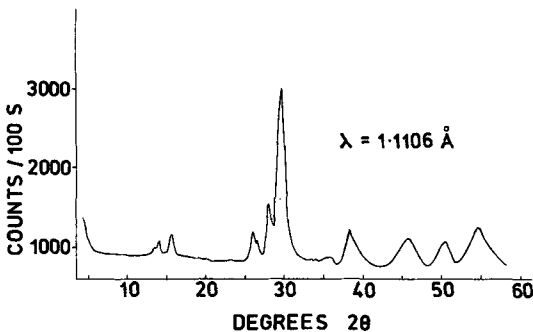


Fig. 8: Neutron diffraction spectrum of pseudorutile at 4°K.

Susceptibility measurements (Fig. 7) made with an a.c. induction bridge showed an apparent magnetic ordering at 23°K but the peak mass susceptibility value is not accurately known at yet. The shape of the curve suggests that the mineral is either antiferromagnetic, or a magnetic spin glass (Sherrington, 1975). However, when antiferromagnetic materials are examined by neutron diffraction at temperatures below their Néel point they normally display superlattice lines of magnetic origin, but, when pseudorutile was examined by neutron diffraction, even at 4°K, it did not show any magnetic superlattice lines, (fig. 8). Consequently, the magnetic ordering is insufficiently long-range to produce these superlattice lines. Because of this lack of long-range order, we conclude that pseudorutile is a naturally occurring example of a magnetic spin glass.

Conclusions

Since 1967 when the mineral pseudorutile was regarded as a doubtful new species by Flaischer (1967), additional data have been obtained which taken together, argue strongly that it is a genuine phase. In this paper it is assumed that pseudorutile should be accorded this status.

Quantitative X-ray diffraction demonstrates the presence of significant amounts of amorphous material in altered "ilmenite" grains that contain ilmenite, pseudorutile and rutile. However, it is not possible to apportion this amorphous material accurately among the mineral phases that are present.

The crystallite size of the X-ray diffracting pseudorutile is approximately 10 nm. The observed optical isotropism of pseudorutile is probably due to this very small crystallite size.

The density and magnetic susceptibility values established for pseudorutiles match those found in the literature.

Low temperature magnetic susceptibility measurements, considered together with the results of neutron diffraction, indicate that pseudorutile is a naturally occurring magnetic spin glass with a susceptibility peak at 23°K. The combined magnetic and other properties of pseudorutiles are not found in any other mineral.

Many commercial ilmenite concentrates contain significant amounts of pseudorutile and the presence of this mineral has important implications for the titanium dioxide pigment industry.

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