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Compositional, structural, and magnetic variations in Waipipi titanomagnetites

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Abstract The structural and compositional variations of titanomagnetites derived from New Zealand ironsands were investigated utilising XRD and electron probe techniques. This in-depth analysis is correlated with the magnetic properties of the titanomagnetites, determined by the use of a saturation magnetisation balance. The ulvospinel content, titanium and magnesium analyses, and lattice parameter are demonstrated to be strongly related to a magnetic parameter defined as magnetic fraction.

Keywords titanomagnetite; ironsands; molecular structure; iron-rich composition; magnetic properties; magnetic minerals; analysis

INTRODUCTION

For over a century the black sand beaches of New Zealand have held the interest of the mineral industry. In the late sixties the significance of the titanomagnetite deposits on the west coast of the North Island was realised when commercial mining operations commenced to support a domestic direct reduction iron industry and an export trade to Japan. The Waipipi Ironsands Ltd operation produced its first titanomagnetite concentrate for export in 1971 after upgrading the raw sand from 15-25% soluble iron to 56% soluble iron by magnetic and gravity separation processes. The Waipipi operation, situated 50 km north of Wanganui and a similar distance south of Mt Egmont, currently exports over 1.5 million tonnes of titanomagnetite concentrate to Japan annually, and the introduction of a second cutter-suction dredge for mining the raw sand has provided the potential for increased production rates.

In this region the ironsands (Hutton 1940; Foley-Fisher 1975) are dominated by titanomagnetite and the basic ferromagnesians with minor amounts of

quartz, calcite, and feldspar. The heavier minerals tend to report in the finer size fractions (0.075-0.150 mm) whilst the lighter minerals are found in the coarser fractions (0.150-0.250 mm), which indicates that the sands have been classified during deposition. Volcanic Mt Egmont is considered to be the source of the ironsand deposits (Gow 1967) and the sands are therefore products of weathered andesites which have been transported, attrited, and sorted hydraulically, before being laid down as beach sand (Fleming 1946).

The New Zealand titanomagnetites are members of the magnetite-ulvospinel solid solution series with minor elemental substitution of aluminium, magnesium, and manganese within the cubic lattice (Wright 1964). The composition of these titanomagnetites generally ranges from 70/30 to 80/20 magnetite/ulvospinel, and there is evidence that other spinels and also various oxidation products are present (Wright & Lovering 1965).

The assessment of titanomagnetite reserves, production, and concentrate grade in New Zealand has traditionally been in terms of iron content which has been shown not to be a direct measure of titanomagnetite (Foley-Fisher 1975). Subsequent development of assessment based on the magnetic properties of titanomagnetite has been encouraging (Watson 1979). However, the use of a magnetic parameter for assessment has shown that the magnetic properties of the Waipipi titanomagnetites are variable and this has complicated the choice of a standard for comparative purposes. Therefore an investigation of the magnetic properties of these titanomagnetites has been undertaken with respect to composition and structure.

Previous work on titanomagnetites has been hampered by an inability to isolate specific titanomagnetite compositions for analysis. This problem has been overcome by the utilisation of a magnetic hydrodynamic elutriator (Martin 1960), which is capable of discarding most composite grains and sorting a titanomagnetite concentrate into fractions of differing magnetic properties. The detailed structural analysis of these fractions has been undertaken using an electron probe microanalyser and X-ray diffractometer. An in-depth chemical analysis has been achieved providing considerable new data on the extent of compositional variation within titanomagnetites and the relation of this variation to structural and magnetic properties.

In order to measure the magnetic properties of the titanomagnetite fraction a saturation magnetisation balance (Outokumpu 1973) was utilised because of its use in the preceding magnetic assessment of iron sands from which this present investigation had arisen. This balance measures the ratio of magnetic and gravitational forces acting on a sample in a saturating magnetic field, and the ratio may be directly related to the weight fraction of the magnetic material present (i.e., magnetic fraction). To determine the magnetic fraction of an iron sand sample, the Satmagan reading must be divided by the reading produced by a magnetically pure sample which exhibits equal gravitational and magnetic mass when tested in the saturation magnetisation balance. In practice the magnetic fraction of a sample drawn from the beneficiation process will vary between 0.05 and 0.85 depending upon the degree to which non-magnetic and composite grains have been removed during magnetic and gravity concentration. In this investigation all titanomagnetite samples are magnetically pure and hence capable of performing as a standard. However, to illustrate the changing magnetic properties in terms of magnetic fraction, all Satmagan readings are divided by the standard Satmagan value derived from a previous investigation (Watson 1979). This standard is based upon a sample which exhibits the lowest Satmagan reading commensurate with magnetic purity and grain homogeneity under an optical microscope.

It is apparent from the theoretical analysis of forces acting on a sample in the magnetic balance that the magnetic fraction determined is affected by the saturation magnetisation value of the magnetic mineral. If this value changes for any reason then the Satmagan reading will reflect this change. Hence, since the standard Satmagan sample assumes a given constant saturation magnetisation, the magnetic fraction can exceed 1.0 if the saturation magnetisation of the titanomagnetite sample increases relative to that of the standard Satmagan sample.

EXPERIMENTAL PROCEDURE

Sample preparation

All titanomagnetite samples are derivatives of borehole samples collected from the site of the Waipipi operation. Initially the samples were magnetically concentrated to remove the gangue minerals and then the concentrates were fractionated by means of a magnetic hydrodynamic elutriator (MHE). The MHE effectively sorts titanomagnetites into fractions according to the magnetic properties of individual grains and hence

discriminates between grains exhibiting varying proportions of exsolutions and gangue minerals. Homogeneous grains are taken to represent grains which have no gangue minerals present and hence include grains with exsolutions.

The magnetic concentrates were sized at $-100+150$ BSS mesh and $-150+200$ BSS mesh and 50-g samples of each size fraction were elutriated in the MHE. Samples for magnetic analysis were produced by the variation of elutriation time whilst maintaining constant conditions of magnetic field strength (12.6 gauss) and water flow (5.3 l/min). Sample set A was produced from the $-100+150$ BSS mesh size fraction, and set B from the finer fraction. To establish the homogeneity of the samples produced by the MHE, a polished section point count of set A materials was undertaken with 500 grains being counted in each analysis.

Magnetic analysis

The magnetic properties of the titanomagnetites were measured in terms of magnetic fraction using the saturation magnetisation balance. The Satmagan requires a sample of constant volume which is measured by means of a sample spoon, and great care is necessary in producing the small sample to avoid segregation and to maintain a representative derivative. All determinations were carried out in duplicate and the balance was calibrated to a set of standard samples at regular intervals.

XRD and electron probe analysis

Structural analysis of the titanomagnetite unit cell was carried out on an X-ray diffractometer using silicon as an internal standard. Samples were reduced to minus 20 μm by ring grinding, and balanced proportions of titanomagnetite and standard were used for each analysis. Lattice parameters were calculated from 12 or more measurements of the $\{311\}$ peak which is the major reflection from the cubic lattice. The operating conditions of the X-ray set were 40 kV potential and 16 mA current using a copper tube.

All chemical analyses were carried out on the electron microprobe unit using an accelerating potential of 15 kV on the primary beam with a beam width of 1–3 μm . The full use of 3 spectrometers permitted analysis of 12 elements arranged in 4 runs comprising Al, Ti, Fe; Mg, Ca, Mn; Na, K, Ni; and Si, V, Cr. This arrangement diminished errors relating to carbonisation, current drift, and vapourisation.

All analyses with recalculated totals (Carmichael 1967, p.39) in the range 99.0–101.0 wt.% were accepted as being meaningful for the purposes of this investigation, and approximately 25 homogene-

Fig. 1 Weight distribution for magnetic elutriation, with respect to time, of titanomagnetite concentrates.

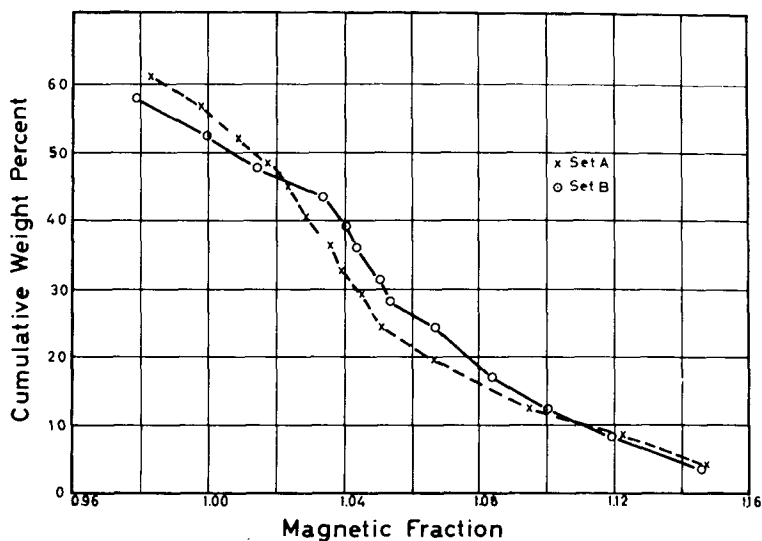
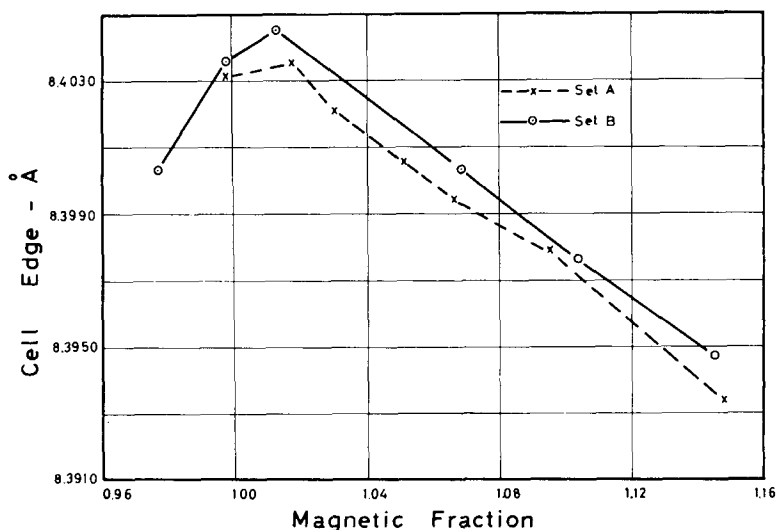


Fig. 2 Variation of titanomagnetite lattice parameter with magnetic fraction.



ous titanomagnetite grains were analysed per sample for the 12 elements with all subsequent calculations being based on averaged analyses.

RESULTS AND DISCUSSION

The progressive magnetic elutriation of sample sets A and B into discrete fractions is illustrated in Fig. 1 and the plots may be interpreted as indicating that the mode for the magnetic fraction of these "pure" titanomagnetites lies in the region 1.03–1.05. The plots illustrate that magnetic fractions in excess of 1.0 can be isolated, and from the analysis of the forces operating in the saturation magnetic balance,

these increases may be attributed to a change in the saturation magnetisation value of the titanomagnetite material. In turn this change indicates a variation in structure and composition between the standard "pure" sample and the discrete fractions under investigation. It has been demonstrated (Akimoto 1954; Akimoto et al. 1957; O'Reilly & Banerjee 1965) that the saturation magnetisation and saturation moment are inversely related to ulvospinel content for a range of synthetic titanomagnetites.

The XRD analysis examined the cell edge of the samples in sets A and B and the results are plotted in Fig. 2. It is evident that a linearity exists for samples exhibiting magnetic fractions in excess of 1.02; this is

confirmed by a regression analysis which calculates the correlation coefficients for both plots in excess of 0.995. Below a magnetic fraction of 1.02 the linearity does not apply and the lattice parameter is seen to diminish rapidly. The lattice parameters of titanomagnetite from the region of the Waipipi operation are, as noted by Wright (1964), close to pure magnetite (8.396 Å) whilst Fig. 2 illustrates variations from 8.404 Å to 8.394 Å. To explain these variations it is necessary to consider the lattice parameter of the other end member of the solid solution series (i.e., ulvospinel 8.530 Å). Since the cell edge is decreasing with increasing magnetic fraction (or saturation magnetisation) it may be argued that the ulvospinel content of the titanomagnetite is decreasing correspondingly. However the titanomagnetites are, as shown later, in the range 20–30 mole% ulvospinel, and, hence, to produce the measured cell edge, there must be another phase of much lower cell edge present. This is possibly an aluminous spinel ($a = 8.103 \text{ \AA}$) in solid solution, and then the variation of either the aluminous spinel or the ulvospinel, or both, could produce the observed results.

The breakdown of the linearity below 1.02 magnetic fraction is thought to be the result of composite grains entering the elutriated fractions. The point count undertaken on sample set A and reproduced in Table 1 illustrates the appearance of composite grains as the magnetic fraction falls, but it does not indicate a sudden change in composite nature below a magnetic fraction of 1.02. It is apparent that most composite grains contain less than 10% gangue, and higher gangue contents are only evident at the lower magnetic fractions. Overall, the non-titanomagnetite material content of set A samples may be calculated to be within the range 0.3–1.3% for samples with magnetic fractions in excess of 1.0. This small variation in gangue content would contribute slightly to the overall properties of a sample.

Table 1 Point count (as percentage of 500 grains) of Sample Set A.

Magnetic Fraction	Composites		Homogeneous Grains %	Estimated Gangue Content %
	>10% Gangue	<10% Gangue		
1.15	0	6	94	0.3
1.12	0	10	90	0.5
1.10	0	6	94	0.3
1.07	2	8	90	0.7
1.05	4	12	84	1.2
1.04	4	13	83	1.3
1.02	4	13	83	1.3
1.00	4	10	86	1.1

The results of the analysis by electron probe of sample set A give the average chemical composition of titanomagnetite (together with approximate ranges) reported in Table 2, where the average iron content is given as $61.3 \pm 1.4\%$. The potential normative compositions given in Table 3 indicate that the average ulvospinel content of the titanomagnetite is $22.7 \pm 3.3 \text{ mole\%}$. A full statement of the chemical analysis for sample set A is given in Appendix 1.

Table 2 Chemical analyses¹ of Waipipi titanomagnetites (Sample Set A).

Oxide	Weight percent		
	Average	Minimum ²	Maximum ²
TiO ₂	8.1	5.28	16.19
SiO ₂	0.1	0.02	0.26
Al ₂ O ₃	3.9	1.20	8.13
Cr ₂ O ₃	0.1	0.00	2.66
MgO	3.2	1.15	6.07
MnO	0.6	0.30	1.15
V ₂ O ₃	0.2	0.13	0.39
NiO	tr	0.00	0.11
FeO	33.9	30.20	42.92
Fe ₂ O ₃	49.9	37.02	55.90
(Fe)	61.3	59.30	62.36
Total	100.0		

¹Oxidation states of Fe calculated using method of Carmichael (1967, p. 39).

²Maximum and minimum values refer to the extreme values determined from the analyses of all grains contributing to each sample in Set A.

Table 3 Potential normative composition¹ of Waipipi titanomagnetite (Sample Set A).

	mole %
MgO.Al ₂ O ₃	8.9
2FeO.TiO ₂	20.1
FeO.Fe ₂ O ₃	63.2
2RO.TiO ₂	2.6
RO.Fe ₂ O ₃	5.2

If the spinel is considered as being substituted in the magnetite solid solution, the average composition may be simplified to: Magnetite, 77.3%; Ulvospinel, 22.7%.

¹Calculated using the method of Buddington & Lindsley (1964, p. 328).

The various analyses have been recalculated (as in Carmichael 1967, p. 39) as divalent, trivalent, and quadrivalent ions and plotted together with FeO and Fe_2O_3 against magnetic fraction in Fig. 3. The quadrivalent ions (Ti^{4+} , Si^{4+}) display an inverse correlation with magnetic fraction whilst Al^{3+} , Cr^{3+} , and V^{3+} show only a slight decrease with increasing magnetic fraction. The main divalent ions (Mg^{2+} , Mn^{2+}) display a similar relationship to the R^{4+} ions, and from the chemical analyses it is apparent that apart from the iron, the important elements influencing magnetic fraction are titanium and magnesium.

The variations of Fe^{2+} and Fe^{3+} with magnetic fraction are opposed with the Fe^{3+} showing a positive linear correlation. When iron content is plotted against magnetic fraction (Fig. 3) the correlation is again linear and reflects essentially the Fe^{3+} plot. If all the analyses are recalculated as potential normative compositions (Buddington & Lindsley 1964, p. 328) then Fig. 4 results, illustrating the major relationship between magnetic fraction

and composition of the magnetite-ulvospinel solid solution. The relationship demonstrates that magnetic fraction is proportional to magnetite content and inversely proportional to ulvospinel content.

The magnetic properties of magnetite are attributed to the difference in magnetic moment between the A and B cation layers within the reverse spinel structure $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4^{2-}$. The magnetic moment of Fe^{3+} is larger than that for Fe^{2+} and for magnetite there is an imbalance between the magnetic moments of cation layers. In the case of ulvospinel $\text{Fe}^{2+}(\text{Fe}^{2+}\text{Ti}^{4+})\text{O}_4^{2-}$ the magnetic moment of Fe^{2+} is the same in both layers and hence ulvospinel, unlike magnetite, is not strongly magnetic. Since magnetite and ulvospinel form a solid solution series $(1-x)\text{Fe}_3\text{O}_4 : x\text{Fe}_2\text{TiO}_4$, the magnetic properties of any titanomagnetite in this series will be related to the ulvospinel content. This is confirmed by Fig. 4 and may be explained in terms of the distribution of Fe^{3+} and Fe^{2+} between the cation layers as Ti^{4+} is introduced into the structure.

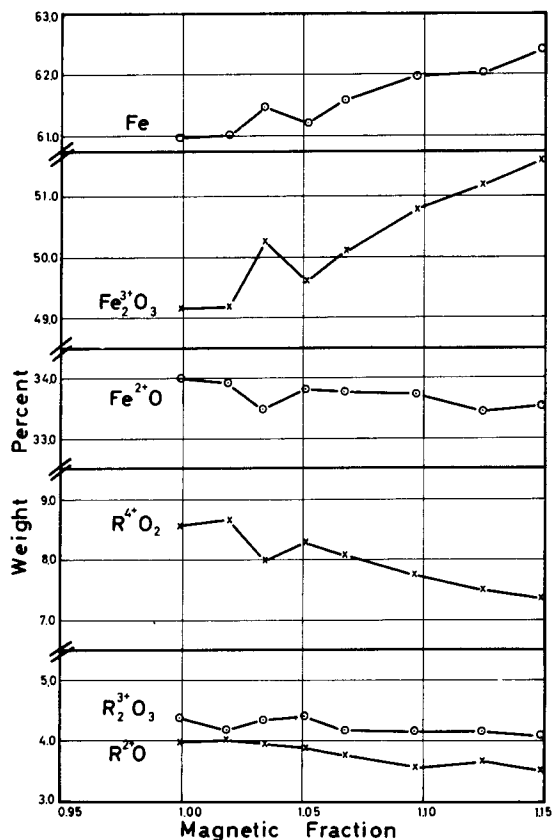


Fig. 3 Oxide weight variation with magnetic fraction for titanomagnetites.

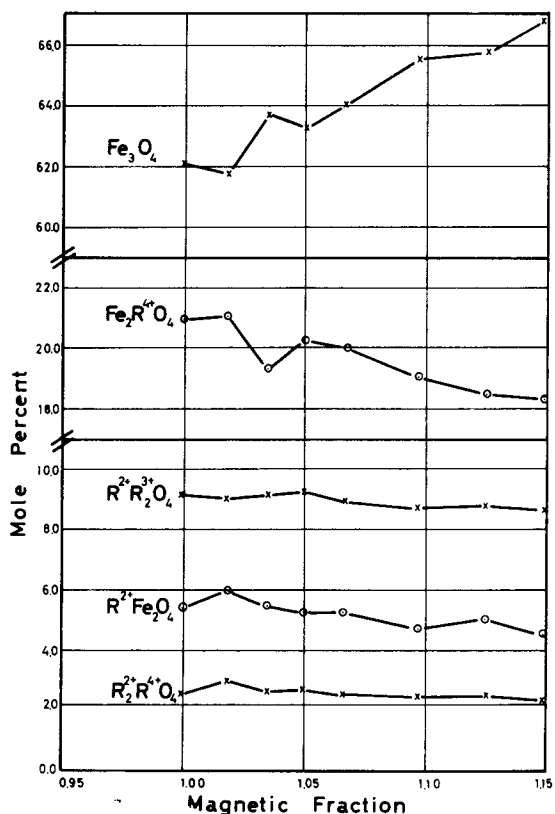
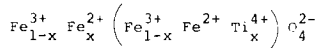
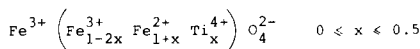


Fig. 4 Molecular variation with magnetic fraction for titanomagnetites.

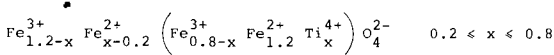
The simplest model (Akimoto 1954) assumes that Fe^{3+} has been replaced in both layers, but the replacement is effectively by Fe^{2+} in the A layer, or tetrahedral sites, and by Ti^{4+} in the B layer, or octahedral sites. The effect of this will be to reduce the imbalance of the magnetic moments between the layers, and hence the magnetic properties will be inversely related to the titanium content. The structure of this simple model may be written



If the replacement of Fe^{3+} occurs only in the B layer (Neel 1955) the structure becomes



Again, as x increases, the magnetic moment imbalance reduces and the relationship between ulvospinel content and magnetic property may be explained. A further model (O'Reilly & Banerjee 1965) provides an intermediate structure based on saturation magnetisation measurement and it may be written as

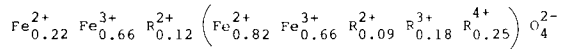


The effect of impurity cations (R^{2+} , R^{3+}) on the titanomagnetite structure has been investigated (Richards et al. 1973; Creer & Stephenson 1972; Pickart & Turnock 1959) and it is generally agreed that trivalent ions enter the B layer displacing Fe^{2+} to the A layer. The effect of this is to decrease the magnetic properties, but since the variation in R^{3+} is less than 0.5% for the titanomagnetites examined the results do not illustrate the expected relationship. If the divalent ions are simply considered to displace Fe^{2+} in both layers then the magnetic properties would not be altered, but the replacement of Fe^{2+} preferentially in 1 layer would influence the magnetic moment imbalance. Creer & Ibbetson (1970) have shown that Mg^{2+} substitutes preferentially in the B layer and as a result the magnetic properties decrease. In the titanomagnetites under investigation, the variation in R^{2+} is less than 1% and hence the indicated relationship between R^{2+} and magnetic fraction has only minor significance compared with the R^{4+} relationship outlined above.

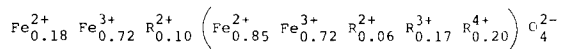
To construct a structural picture of the titanomagnetites from the Waipipi site it is necessary to consider the molecular assemblage in the light of the variations in cell edge and magnetic properties. To maintain the consistently low cell edge the presence of spinel is required and this is illustrated by the compositional data given in Table 3. If all the R^{3+} enters the spinel as B layer cations then it follows that R^{2+} will enter the A layer. In addition with the formation of R_2^{2+} R^{4+} O_4 and

R^{2+} Fe_2^{3+} O_4 it is apparent that R^{2+} occurs in both cation layers but predominates in the A layer. Thus the following formulae, derived from Fig. 4 data in the light of the above comments, may be postulated to describe the 2 end members of the titanomagnetites investigated.

Magnetic Fraction = 1.00



Magnetic Fraction = 1.15



The structure of the 2 end members illustrates the imbalance between Fe^{2+} and Fe^{3+} and the replacement of Fe^{3+} by R^{4+} is seen to be the major contributor to the imbalance. A linear regression analysis applied to the variation of ulvospinel content (u) with magnetic fraction (m) suggests the following relationship which has a correlation coefficient of 0.910 (see Fig. 4).

$$m = 2.13 - 5.44u \quad 0.18 < u < 0.25$$

If the magnetic fraction of pure titanomagnetite is related to saturation magnetisation, as suggested earlier, then the above equation may be modified to a form similar to that described by Akimoto et al. (1957), where saturation moment is equal to $4.0 - 6u$. It is also possible to relate the cell edge (c) to ulvospinel content by virtue of the appropriate plots illustrated in Fig. 2 and 4, and the resultant equation has the form

$$c = 0.413u + 8.318 \quad 0.18 < u < 0.25$$

When compared with the titanomagnetite data of Akimoto et al. (1957) the experimental line not only plots much lower, due to the influence of the spinel, but also has a steeper slope for the narrow range of compositions examined.

Akimoto et al.

$$c = 0.142u + 8.391 \quad 0 < u < 1.0$$

CONCLUSIONS

It is evident from this study that the titanomagnetites derived from Waipipi ironsands exhibit a range of structures, chemical compositions, and magnetic properties. Relationships have been established between the magnetic fraction of titanomagnetite and cell edge, ulvospinel content, and titanium and magnesium contents. It is concluded that the variation in magnetic property is related to the ulvospinel content and that an inverse relationship exists between magnetic property and ulvospinel content. Polished section point counts, however,

have indicated the presence of non-titanomagnetite material up to levels of approximately 1%, but this gangue material is unlikely to influence magnetic properties to a significant extent.

The effect of divalent, trivalent, and quadrivalent ions substituting in the titanomagnetite lattice has been related to the variation in the imbalance of the magnetic moments of Fe^{2+} and Fe^{3+} in the A and B cation layers in the reverse spinel structure of the titanomagnetites. Two extreme structures, which illustrate the effect of substituting ions on magnetic moment imbalance, have been postulated for the Waipipi titanomagnetite, and it is apparent that the ion of major importance with respect to magnetic properties, in this study, is titanium. The lattice parameter of the titanomagnetites is shown to be linearly related to magnetic fraction and hence to ulvospinel content, and the lower range of values observed are explained in terms of a constant, substitution of spinel in magnetite.

If magnetic fraction is plotted against total iron content (Fig. 5) for a series of ironsands produced by the beneficiation of raw sands (Watson 1979) and including the pure titanomagnetites investigated in this study, a discontinuity is evident in the region of 61% Fe and 1.0 magnetic fraction. It is suggested that this discontinuity is a result of variations in saturation magnetisation value (Msat) of the

titanomagnetite such that at magnetic fraction values in the region of 1.0 the standard sample Msat utilised for the raw sands is no longer applicable. However, since the use of magnetic assessment is largely for magnetic fractions less than 0.85, it is evident that variations in the Msat values of the pure titanomagnetites in the sample are unlikely to be a major problem, and the original titanomagnetite standard sample does represent the limit of the linearity between total iron and magnetic fraction in the area of interest with regard to assessment.

Thus, the titanomagnetites derived from the site of the Waipipi Ironsands Ltd operations display a range of magnetic properties which may be related to structure and composition, but which do not invalidate the standard titanomagnetite sample utilised in the magnetic assessment of these ironsands.

ACKNOWLEDGMENTS

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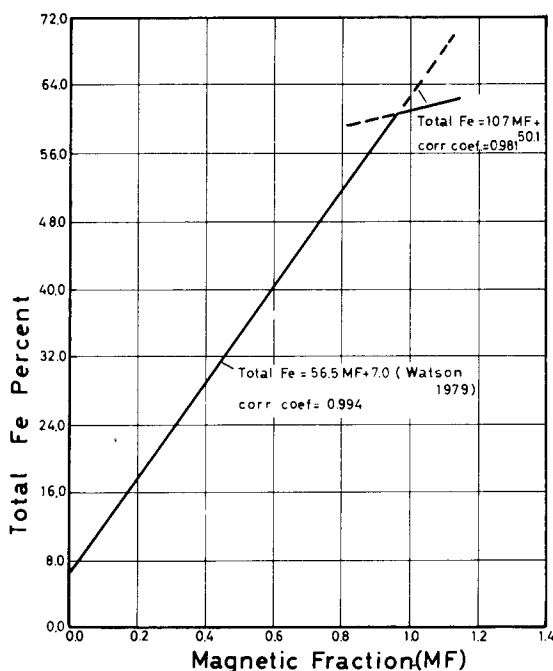


Fig. 5 Variation of total iron content with magnetic fraction for Waipipi ironsands.

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APPENDIX 1 Normalised microprobe analyses¹ of Sample Set A. (All analyses in wt.% oxide.)

Magnetic fraction	1.15	1.12	1.10	1.07	1.05	1.04	1.02	1.00
No. grains	25	26	26	25	25	26	24	22
SiO ₂	0.15	0.12	0.10	0.12	0.14	0.13	0.15	0.11
Al ₂ O ₃	3.68	3.84	3.80	3.87	4.09	4.04	3.92	4.05
TiO ₂	7.17	7.39	7.61	7.96	8.11	7.84	8.49	8.43
Fe ₂ O ₃	51.59	51.23	50.81	50.18	49.63	50.26	49.19	49.14
FeO	33.54	33.45	33.75	33.80	33.83	33.50	33.96	33.99
MnO	0.68	0.62	0.64	0.64	0.58	0.65	0.58	0.61
MgO	2.77	3.01	2.91	3.09	3.26	3.26	3.40	3.31
CaO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cr ₂ O ₃	0.11	0.06	0.09	0.08	0.05	0.05	0.04	0.06
NiO	0.04	0.02	0.02	0.03	0.03	0.02	0.03	0.02
V ₂ O ₃	0.25	0.26	0.26	0.22	0.27	0.22	0.23	0.27
Orig. total	99.70	99.74	100.01	99.67	99.44	99.86	99.94	99.75
% Fe	62.36	62.04	61.98	61.58	61.21	61.40	61.01	60.99
Mole% ulvo-spinel	20.31	20.76	21.30	22.29	22.69	22.03	23.81	23.47

¹The analyses represent the average composition derived from the number of grains detailed for each magnetic fraction.