A THERMAL-MAGNETIC INVESTIGATION OF THE MAGNETITE-ULVOSPINEL SERIES

by

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ABSTRACT

This thesis is concerned with the thermo-magnetic properties of natural and synthetic titanomagnetites, part 1 dealing with synthetic samples and part 2 with natural samples. A review was made of the methods of preparation of synthetic titanomagnetites and samples were prepared by a sintering process. The effect of oxidation on samples in the ulvospinel-magnetite series was investigated and a thermal chemical remanent magnetisation obtained.

Thermal and partial thermal remanent magnetisations were measured for unoxidised samples and samples oxidised to varying degrees, and a region of oxidation was found in which reversal of the partial thermal remanence occurred. The dependence on composition, degree of oxidation and other parameters was found and different possible mechanisms discussed. It was concluded that the effect was due to negative interaction probably of magnetostatic origin between two phases caused by a different degree of oxidation in large grains or between a metastable oxidised state and a highly oxidised state.

It was found possible to reduce synthetic titanomagnetites by heating above 800°C in the absence of air. Exsolution and homogenisation problems were reviewed and investigated.

Part 2 deals with the thermal treatment of rocks. One sill was investigated in detail and a lowering of the curie point was observed on heat treatment. The dependence on position in the sill, temperature and time of heating was found and petrological changes observed. Reduction of oxidised titanomagnetites was found to be the probable cause.

Thermal demagnetisation curves of rocks in air and in the absence of air were measured and support found for a metastable oxidised state. A theoretical explanation of the proposed metastable state was discussed. Weak field behaviour of rocks was investigated and reversal tendencies similar to those shown by synthetic samples were observed.

Finally a comparison of the thermomagnetic properties of natural and synthetic samples was made.

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CHAPTER 1.

Introduction

1.1 Rock Magnetism

Rock magnetism is concerned with the measurement of the fossil magnetisation of rocks. The fossil magnetisation can be due to thermal remanent magnetisation[1,2] (T.R.M), chemical remanent[3,4] magnetisation (C.R.M) or depositional magnetisation.

On the assumption that the earths magnetic field has remained almost a dipole and that the rocks have faithfully retained their direction of magnetisation, the latitudes of the rocks on acquisition of their remanent magnetisation can be found. Results were shown to support the theory of continental drift[5]. It has been shown that the ancient field was probably about the same magnitude as the earths field today[6] and many tests of stability have been introduced to test the second assumption.

Another result which emerged from the measurement of fossil magnetisation was that almost 50°/o of all rocks measured, both igneous and sedimentary were found to have their magnetic moment in the opposite direction to the other 50°/o. Often this would occur in a succession of lava flows. Such cases of normal and reversed remanent magnetisation have been reported by Roche[7] (1951), Hospers[8] (1954) and many other workers. There were two theories to account for these observations both consistent with the earths field remaining a dipole. Either the earths field had remained in the same direction as at present and the rocks were all self reversed or the dipole field had at times in the past reversed. The second theory implied some of the reversed rocks were not self reversed and that the earths field had changed direction many times.

Neel[9] (1951) considered the theoretical possibilities of self reversal and postulated four ways by which a rock could acquire a reversed remanent magnetisation and since then other possible mechanisms have been suggested by Verhoogen[10] (1956). These theories and their applicability will be discussed in detail later, together with the interactions which may cause reversals. The discovery of rocks which self reversed in the laboratory by Nagata[11] et al (1951) and Carmichael[12] (1961), the reversal of the direction of magnetisation of a crystal of magnetite at low temperatures by Nagata[13] (1963) and the reversal of synthesised lithium ferrites by Gorter et al[14] (1953) seem to support the theory of self reversal. But for no field reversal to have taken place all reversed rocks must be self reversed and as yet most of the reversed rocks have not been shown to be self reversed.

Graham[15] (1949) found sedimentary rocks of the same age with normal and reversed directions and Edwards[16] (1963) investigated the properties of an iron grit 6 inches thick which contained normal and reversed polarities and which changed in a few millemeters from normal to reversed and back again. Using the accepted rates of sedimentation, time of deposition was 10^3 years and estimates of the time between field reversals given by Cox[17] et al (1963) were of the order of 10^6 years it seemed likely that this was a case of self reversal. Yet Edwards carried out almost every conceivable laboratory test but found no difference between normal and reversed specimans and the problem remained unresolved.

Convincing evidence was given by Wilson[18] (1962) in support of field reversal. He made a survey of the direction of magnetisation of rocks baked by dykes and sills and found in 49 cases out of 52 the baked county rock was magnetised in the same direction as the dyke or sill, whether it was normal or reversed. This seemed to support field reversal and showed self-reversal to be a rare occurance.

Recently Ade-Hall and Wilson[19] (1963) have found petrological differences in the series of normal and reversed Mull lava flows and in other cases reversely magnetised rocks have been found which differ strikingly in petrological properties from normal rocks. Petrology seems to be a somewhat unexplored tool in helping to elucidate the question of field or self reversal. The probable truth is that both field and self reversal has occurred and new techniques may be able to identify much more clearly than is at present possible which rocks belong to each class.

It is clear that before rock magnetism can proceed any further a clear understanding of the mechanism of acquiring the remanent magnetisation has to be understood and to do this a knowledge of the properties of the magnetic constituents in rocks has to be known.

1.2. Magnetic minerals.

It has been found that there are three main groups of magnetic minerals present in varying forms in varying amounts in rocks. These are the cubic titanomagnetites having the general chemical formula $(1-x)Fe_3O_4.xFe_2TiO_4$ (and their oxidation products), the rhombohedral ilmenohaematite series (1-y) $Fe_2O_3 + yFeTiO_3$ and the iron sulphides, pyrite and pyrrhotite. A review of their minerology was given by Nicholls[20] (1955).

1. Titanomagnetites.

The solid solution series between magnetite (Fe_3O_4) and ulvöspinel (Fe_2TiO_4) produces probably the most important magnetic constituent as it comprises 90°/o of the magnetic minerals in rocks. It is almost completely responsible for the remanent magnetisation in igneous rocks. The titanomagnetites are ferrimagnetic~~es~~ with an inverse spinel type crystal structure. The difference between a ferro- and a ferrimagnetic material lies in the fact that a ferromagnetic material has a parallel alignment of all the atomic magnetic moments due to exchange interaction but in the ferrimagnetic the atomic magnetic moments belong to two sublattices A and B which are interwoven and interact negatively. All the moments of sublattice A are aligned parallel to each other but antiparallel to the ones on the B sublattice. The smallest cell with cubic symmetry consists of eight molecules of Fe_3O_4. The two types of interstital sites, the A (tetrahedral) and the B (octohedral) are surrounded by 4 and 6 oxygen atoms as nearest neighbours respectively. In the unit cell there are 64 A sites with 8 occupied and 32 B sites with 16 occupied. Magnetite has been shown to have an inverse special structure in which the Fe^{3+} ions occupy the A sites and half the B sites and the Fe^{2+} are on the remaining B sites. As Ti^{4+} ions enter the lattice with increasing percentage ulvospinel the Ti^{4+} enter the B sites and the valancy balance is maintained by an increase of Fe^{2+} at the expense of Fe^{3+}. Since Ti^{4+} has no magnetic moment pure ulvospinel $Fe^{2+}(Fe^{2+}Ti^{4+})O_4^{-2}$ is non magnetic. Thus we get an intermediate compound

$Fe_1^{3+}\ [Fe_{1-2x}^{3+}\ Fe_{1+x}^{2+}\ Ti_x^{4+}]\ O_4$ for $x < 1/2$

and $Fe_{2-2x}^{3+}\ Fe_{2x-1}^{2+}\ [Fe_{2-x}^{2+}\ Ti_x^{4+}]\ O_4$ for $x > 1/2$.

The spontaneous magnetisation, curie point and cell size vary approximately linearly with composition as shown by Akimoto[21] (1957). The series exhibits complete solid solution at high temperature and there have been two solvus curves suggested for the sub-solidus region below 600°C. Phillips and Vincent[22] (1954) suggested an eutectoid curve in their early work but later Vincent et al[33] (1957) decided on a hoop shaped solvus curve similar to that suggested by Kawai et al[24] (1954). Kawai placed the maximum at 800°C but later[25] corrected it to 600°C. The phase splitting below this temperature is reported to be very slow and at room temperature is on a geological time scale. It does explain very nicely the occurrance in nature of rocks with two curie points.

Natural titanomagnetites are often found in an oxidised state[26] but still retaining their spinel structure. In these cases there are more Fe^{3+} ions present and the valancy balance is maintained by vacancies in the lattice sites as in pure maghemite. It has been shown by Henry and Boehm[27] (1956) that vacancies occur on octahedral sites for maghemite and it can be expected therefore that in the oxidised titanomagnetites the vacancies will be on the octahedral sites. Some of the effects of oxidation on the properties of synthetic titanomagnetites have been investigated by the Japanese workers including Akimoto et al[28] and they have investigated the change of curie point, cubic cell size and saturation moment with oxidation. The possible effect of oxidation producing an unstable remanent magnetisation has also been discussed by Akimoto[29] (1960).

It has been suggested mainly by mineralogists that there may be a solid solution between magnetite and ilmenite. The discussion of such a possibility is given by Nicolls[20] and Vincent[23]. The possibility of a cubic form of ilmenite $\gamma FeTiO_3$ has also been considered as a possible end member by Banerjee[30] (1963). It is clear that the oxidised region covers the region of this supposed solid solution except near the ilmenite end where no cubic spinel has been identified. Crystallographic arguements make a solid solution between cubic magnetite and rhombohedral ilmenite unlikely though Chevallier et al[31] (1950) has reported such a solution up to 37°/o

Thus in natural samples it seems likely they may be found in an oxidised state, containing vacancies on the octahedral sites.

2. Ilmenite-Haematite series.

This series has as its end members rhombohedral haematite (Fe_2O_3) and either rhombohedral or hexagonal ilmenite ($FeTiO_3$) in which the position of the oxygen atoms are slightly distorted. Its interest is contained in the variation of magnetic properties through the series[32]. The general formula is $(1-y)Fe_2O_3\ y\ FeTiO_3$. Ilmenite ($y = 1$) is antiferromagnetic above 55°K and in the region $1 > y > .45$ it is ferrimagnetic, caused by the Ti ions occupying one of the sublattice sites only. Between $.45 > y > 0$ it is antiferromagnetic with a weak parasitic ferromagnetism superimposed. This is similar to pure haematite where the two sublattices are not perfectly balanced.

The important magnetic properties associated with this series are the cases of reversed thermal remanence reported by Nagata et al[11] on the famous Haruna dacite. They found a reversed T.R.M. near the region of $y = .5$. Uyeda[32] (1958) has also found a region giving a reversed T.R.M. between $.5 < y < .65$ in synthetic specimans. Vlasov and other Russian workers[33] (1963) have also reported reversal of the T.R.M. in a synthetic sample which was empirically 50°/o $FeTiO_3$. A new reversal region was found by Carmichael[12] in the range 25 to 15°/o ilmenite in haematite.

Carmichael also confirmed a hoop shaped solvus diagram and showed complete solid solution at temperatures above 1000°C.

3. Iron sulphides.

The only ferrimagnetite sulphide is pyrrhotite, FeS_{1+x} where x goes from 0 to 0.14. This can exist in many forms at room temperature but it is not of great importance to rock magnetism. It does show self reversing properties[34,35,36] similar to those found by Carmichael in the Allard Lake ilmenohaematites and is of interest from this point of view.

1.3. Thermomagnetic properties of rocks.

In order to reduce the scatter of results and obtain a more accurate result for the direction of the true fossil magnetisation techniques of alternating field demagnetisation and thermal demagnetisation have been used. Using these techniques it is hoped that secondary magnetisation may be removed and the fossil magnetisation unmasked. Wilson[37] (1962) has described an instrument for measuring the thermal demagnetisation of natural specimens in three directions.

Measurements of curie points and thermal demagnetisation curves have been used extensively to give information on the magnetic constituents. This has been done by Akimoto[38], Cox and Doell[39] and other workers and it has proved an important tool in investigating the magnetic materials and their magnetic state. Kawai[24] first suggested his hoop shaped solvus curve in the Fe_3O_4 - Fe_2TiO_4 series after measuring the distribution of curie points in natural rocks. He also began to heat-treat samples at temperatures much greater than their curie point and began investigating solid phase transformations and exsolution problems[40], and their effects on rock magnetism.

The formation of the magnetic phases in igneous rocks has been the cause of much discussion. Ramdohr's[41] book shows the many types of different intergrowths which can be found and with the increased linking of petrology and rock magnetism, the origin and effects of different intergrowths and exsolution lamallae and their thermal properties has become a very interesting but difficult problem.

Intergrowths of magnetite-ulvospinel, magnetite-ilmenite, magnetite-ilmenite-ulvospinel have been reported in natural titaniferous magnetites by Vincent et al[23]. They heat-treated these samples in a vacuum at high temperature and attempted to homogenise the different intergrowths into the host. This they succeeded in doing in the case of magnetite-ulvospinel but found difficulty in the case of ilmenite-magnetite. They also produced heating curves of the samples heated for different times showing the changes in the curie point and measured the cell size of the cubic magnetite, which also varies approximately linearly with the increase of titanium in the lattice. Nickel[42] (1961) has published electron-microscope photographs of ulvospinel showing that it exists as a very fine microtexture. New techniques such as ~~the~~ electron probe microanalys~~er~~is will be of great assistance in solving these problems.

In igneous rocks free ilmenite also appears after magmatic crystallisation but there are conflicting ideas on the presence of ilmenite intergrowths in the magnetite host. Direct exsolution from the magnetite host is one possibility similar to the suggested mechanisms for the ulvospinel intergrowths, or the ilmenite intergrowths may arise from oxidation of the ulvospinel intergrowths.

At least two oxidising reactions have been considered.

$$3Fe_2TiO_4+O \Rightarrow 3FeTiO_3+Fe_3O_4$$

and

$$Fe_2TiO_4+Fe_2O_3 \Rightarrow Fe_3O_4+FeTiO_3$$

According to Vincent the ilmenite present is almost 100°/o $FeTiO_3$ and so no contribution is made to the magnetic moment of the rock.

The question of oxidation in the magmatic cooling process is very complicated. Vincent[22] et al discussed the possibilities but the conditions determining whether an oxidising or reducing atmosphere is present have not yet been completely elucidated. However many workers have reported the existance of titanomaghemites (oxidised titanomagnetites) in nature and Verhoogen[44] (1962) has shown it is likely that iron oxides in the magnetite-ulvospinel-ilmenite range undergo oxidation during cooling in the presence of magmatic gases or air.

A knowledge of the thermal properties of the magnetic minerals in the rocks is vitally important in establishing the validity of the results of rock magnetism.

1.4. Thermomagnetic properties of synthetic material.

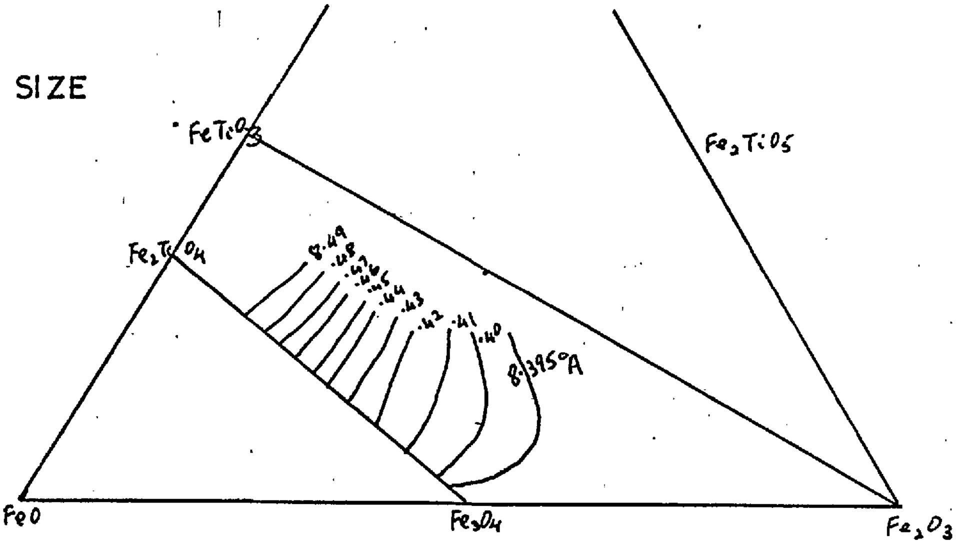
In order to investigate the thermomagnetic properties of titanomagnetites without the added complications due to other minerals being present many workers have prepared and used synthetic samples. The largest contribution in this field has been by the Japanese workers and Akimoto[28] et al have measured the variation of curie point, cubic cell size and saturation magnetisation with composition and oxidation. The most recently published curves are shown in Fig. 1. Kawai[45] claimed to have confirmed his hoop shaped solvus diagram with synthetic specimens and obtained exsolution down to 300°C. Lindsley[46] investigated the phase relation between various members and showed that ilmenite intergrowths are formed by the oxidation of ulvospinel. Ishikawa[47] et al prepared, measured and discussed the properties of the ilmenite-haematite series and also[48] discussed order disorder phenomena in this series.

It was therefore decided to prepare synthetic samples in the magnetite ulvospinel series and further investigate the thermomagnetic properties of the series, especially with regard to oxidation and its effect on the magnetic properties and to measure properties of the series in weak fields. In the light of these experiments on synthetic materials it was hoped to eludiate the results obtained from thermal treatment of natural igneous rock.

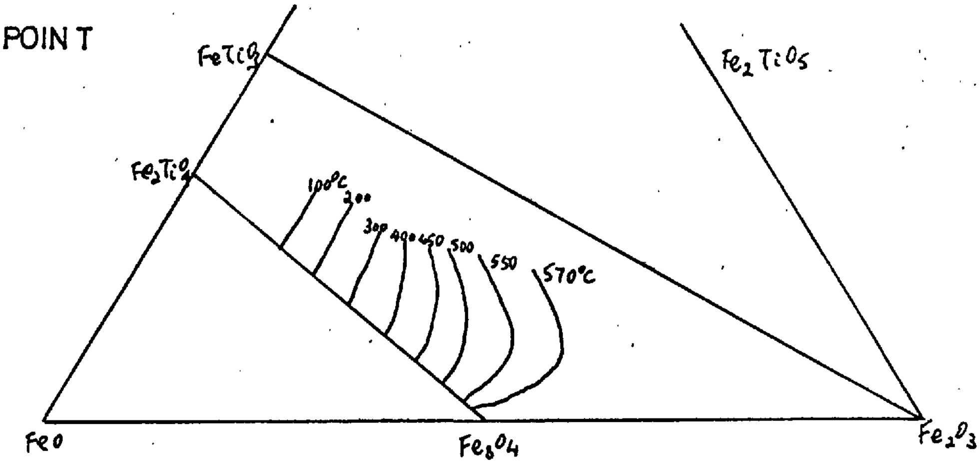
FIG. I

VARIATION WITH CHEMICAL COMPOSITION OF

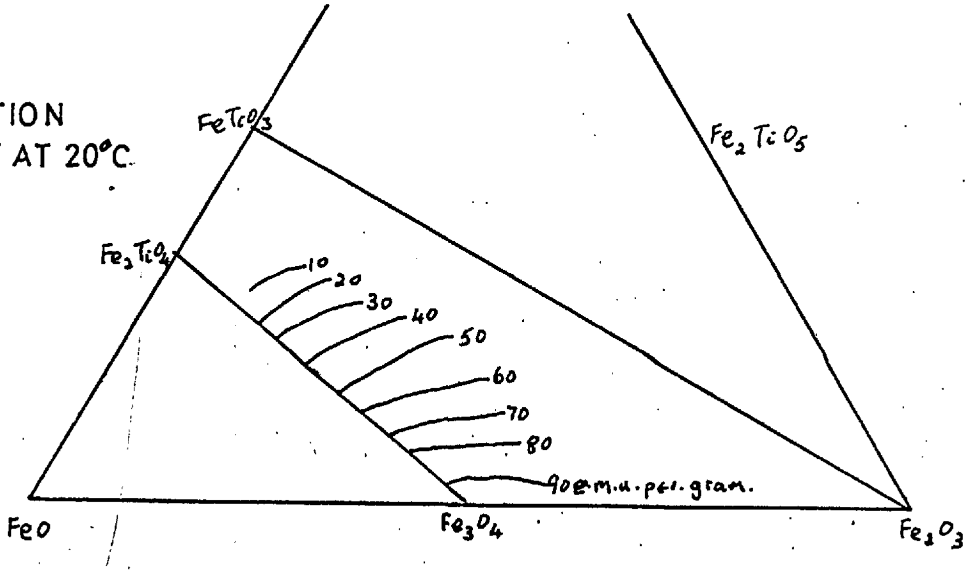
1. CELL SIZE



2. CURIE POINT



3. SATURATION
MOMENT AT 20°C



PART ONE

SYNTHETIC TITANOMAGNETITES

CHAPTER 2.

Preparation of synthetic samples

2.1. Methods of Preparation.

Iron lies in the middle of a transition series in the periodic table and because of this the crystal chemistry of the iron oxides is very complicated. The method principly used in producing iron-titanium oxides over a wide range of composition has been a sintering process but it is not surprising to find impurities present in the form of higher oxides because of irons complicated crystal chemistry.

When Pouillard[49] synthesised titanamagnetites with up to 42°/o ulvospinel he used two methods. Mixtures of TiO_2 and Fe_3O_4 were heated in an evacuated furnace at 900°C for one hour and he also tried reducing a mixture of TiO_2 and Fe_2O_3 with hydrogen gas at 450°C. In both cases his product contained other phases and he attempted to estimate the amount of $TiFe_2O_4$ from the cell size.

Akimoto[28] and his co-workers used a sintering process and used Fe_2O_3, TiO_2 and electrolytic iron as their starting point. A mixture in the correct proportion was sealed in an evacuated silica tube and quenched from

1150°C after a six hour heating. A single phase spinel resulted and impurities due to the ilmenite-haematite series, when present, were less than 10°/o. Chemical analysis of the samples showed that most of the samples prepared were slightly away from the ulvospinel-magnetite series, towards the oxidised region.

The method used for preparation by Kawai[45] was slightly different. He started with TiO_2 and powders of Fe_3O_4 and FeO. The latter two were prepared by reduction of haematite by $CO-CO_2$ mixture at 1300°C. The appropriate mixtures was sealed in an evacuated silica tube and given a prolonged heat treatment at 900°C.

A more involved method was used by Lindsley[46] to prevent oxidation of the iron sponge used. He analysed his iron sponge for oxygen and corrected for this when preparing his mixture of Fe, Fe_2O_3 and TiO_2. The material was mixed by grinding under acetone or toluene to make sure the sponge iron did not further oxidise at this stage. He then sintered the samples at 1000°C in an evacuated silica tube or at 1200°C in an atmosphere of nitrogen and hydrogen.

Although the ulvospinel magnetite series is the primary concern, it is interesting to note Vlasov's[33] method of preparing synthetic specimens. He began with Fe, Fe_2O_3 and TiO_2 and the mixture was briquetted and maintained at 1200°C for a few hours. The specimens were formed into prisms under high pressure (1500 Kg./cm^2) and heated to over 1150°C in a evacuated quartz furnace for a further 8 hours before being slowly cooled. But they still found two phases present, one cubic and fairly close to pure magnetite and one rhombohedral. Ishikawa and Akimoto[50] simply mixed haematite and ilmenite together and sintered the mixture at high temperatures in an evacuated tube to obtain their samples for their work on the ilmenite-haematite series.

2.2. Method of preparation used.

It was decided to use the sintering process and to use as the starting material TiO_2, Fe_2O_3 and iron sponge. The three constituents were pure to 300 p.p.m. in the case of TiO_2 and 50 p.p.m. for Fe and Fe_2O_3. The calculated mixture of total weight one gram was mixed in an agate morter and when thoroughly mixed sealed in an evacuated quartz tube. Care was taken during the evacuation to shake the powder up, making sure no air pockets exist, before packing the material with quartz wool and sealing under a vacuum of 10^{-3}cm. mercury. The temperature of sintering used in the first set was 900°C and samples were heated to this temperature for 48 hours. The furnace was specially constructed so that the samples could be quenched by dropping them into water. Eleven samples along the series were made in this way.

The samples appeared as fine grained black powders and the following experiments were carried out to verify that spinels had been produced. Thermal demagnetization curves of the saturation moment ^{J}sat. were measured in a vacuum to determine the curie points and X-ray photographs taken and the cell size determined. It was found from the X-ray photographs that a single cubic spinel had been produced and also lines due to a rhombohedral phase appeared. The amount of rhombohedral phase present varied from less than 5°/o in the case of pure magnetite to 10-15°/o for pure ulvospinel. There were not sufficient lines present to be able to calculate the rhombohedral cell size but an approximate estimate of the position in the ilmenite-haematite series was made by comparing with films of pure haematite and ilmenite. However a correction for the presence of the rhombohedral phase to this extent only changed x in the expression $(1-x)Fe_3O_4xFe_2TiO_4$ by up to .03.

The cubic lines were very sharp and there were no more additional lines and therefore almost all the TiO_2 and Fe was considered homogenized. Only one curie point was observed in every case and so the small amount of rhombohedral phase present did not seem to effect the magnetic properties in any way and could be neglected. The curie points plotted against x all appeared higher than the accepted values reported by Akimoto[28]. This was almost certainly due to the fact that the very fine sponge iron oxidised very quickly in air even in the short time between the weighing, mixing and sealing the samples. The cell size also verified that the samples were slightly oxidised. It was a very difficult problem to overcome and Akimoto's[28] samples made in a similar way were also found to be just off the ulvospinel magnetite line and Lindsley went to great pains to avoid trouble from oxidation. Further annealing at 750° for 7 days brought all the curie points much closer to the accepted value and further heating for 80 hours at 900°C on two samples brought the curie points very close to the accepted values. Fig. 2 shows these results. These points are discussed later.

Polished surfaces of a few samples were made by setting the grains on an organic resin and polishing in the usual way. The grain size varied from 200 microns down to a few microns. The most striking feature was the fact that many appeared isotropic on the periphery and anisotropic in the centre. Fig. 3 shows photographs taken of a typical grain (magnified x450) taken in ordinary light and with the nichols almost crossed. The anisotropic areas can clearly be seen.

The same polished surface was then examined by the electron probe microanalyser and spot tests taken of the percentage iron and titanium in the isotropic and anisotropic material. The anisotropic material was found to be exactly 100°/o ilmenite and the isotropic material between $x = .50$ and $.55$ compared with the corrected value of $x = .57$. The large error was due to the relatively low amount of titanium present. Also found in the material were a few very small regions which corresponded to almost pure TiO_2. In the sintering process small pockets of TiO_2 were left and this would also have the effect of increasing the curie point above the accepted value and on further heating as all the titanium went into the lattice then the curie point reached the accepted value. The amount of free TiO_2 must have been small as it did not appear in x-ray photographs.

Thus although the samples prepared seemed to contain a few percent rhombohedral material it appeared that it did not contribute to the magnetic properties and could be neglected. The cubic material which was the series of spinels of interest appeared to be slightly oxidised, due to iron contamination during preparation but as most of the experiments to be performed involved oxidation to a much greater extent, the samples and the method of preparation were considered to be good enough and more elaborate methods and techniques in preparation of synthetic samples were not considered to be worthwhile.

The samples along the ilmenite-haematite series were prepared in a similar way again starting with TiO_2, Fe_2O_3 and iron sponge. The only differences were that all the ilmenite-haematites were sintered at 1150°C for six hours and allowed to cool slowly in the furnace. X-ray photographs, and heating curves of the thermal remanent magnetisation generally showed only one rhombohedral phase but in one sample a large amount (25°/o) of cubic material, corresponding to almost pure magnetite was found.

FIG. 2 CURIE TEMPERATURE against COMPOSITION

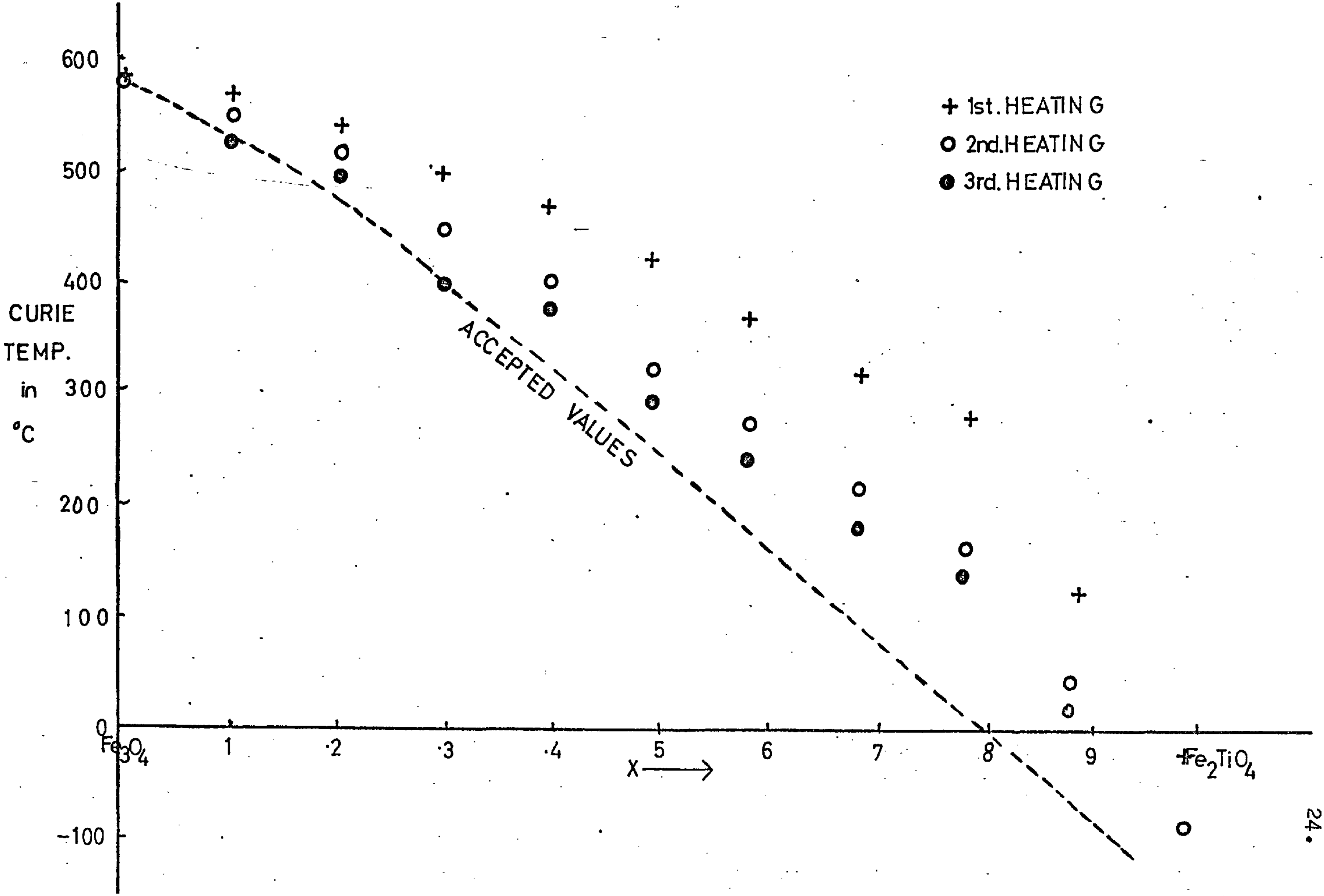


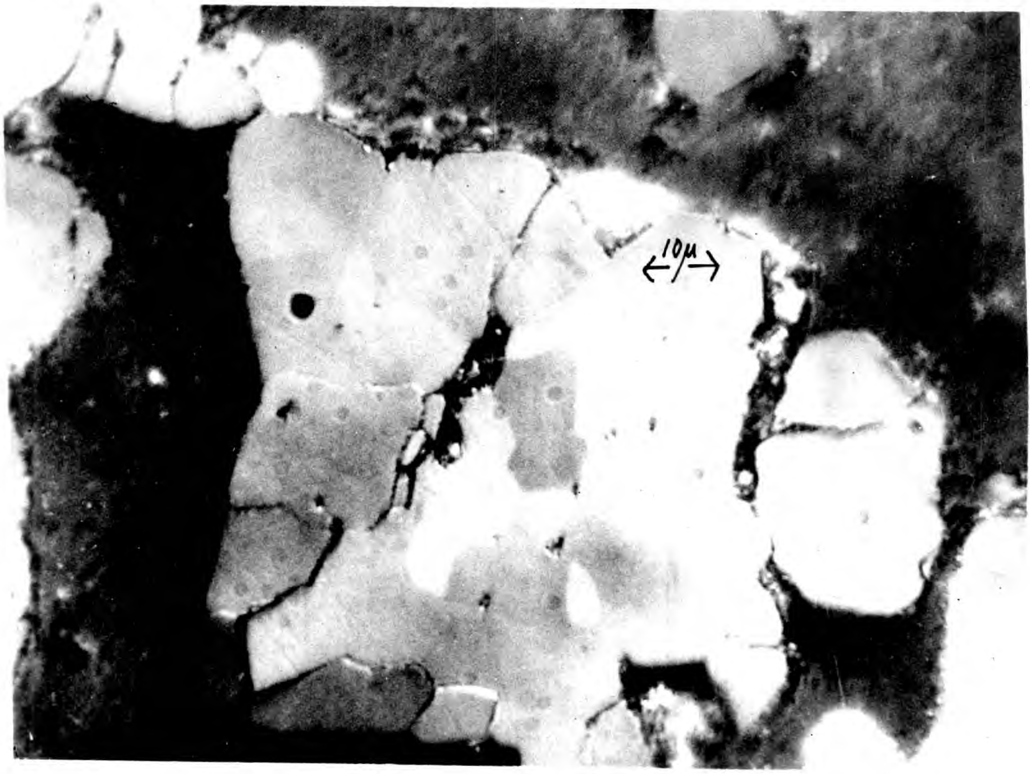
FIG. 3a

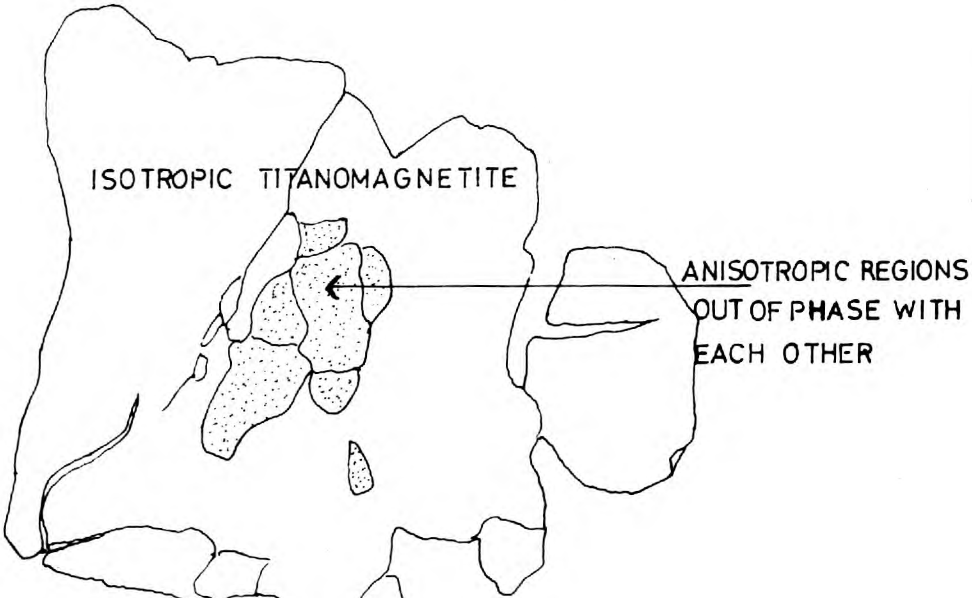
UNOXIDISED GRAIN OF SYNTHETIC MATERIAL (X=·57)

IN ORDINARY REFLECTED LIGHT

FIG 3b

IN POLARISED LIGHT WITH THE NICOLS 5° OFF CROSSED





CHAPTER 3.

Thermal Demagnetisation and oxidation.

3.1. Experimental Procedure.

The thermal demagnetising curves of saturation moment J_{sat} and also the corresponding cooling curves were measured for the 11 samples prepared in the ulvospinel-magnetite series under two conditions. The samples were measured after being sealed in an evacuated quartz tube and also curves taken of the samples heated in air. Some typical curves are shown in fig. 4a to 4f. The heating and cooling curves were measured on a curie balance designed by Wilson and Smith which allowed the change of J_{sat} to be followed from - 190°C to 600°C. The field obtained in this instrument was 6000 oersteds and specially shaped pole pieces ensured a large field gradient. The calibration was by means of a small coil of known area and number of turns but could not be considered accurate to more than 5 to 10°/o as the position in the field was critical and the number of turns small. It took 30 minutes to reach 600°C at a steady rate of heating and the samples varied from .01 gram for magnetite to .03 gram for the sample with 97°/o ulvospinel.

The rate of oxidation of the synthetic samples was also measured by heating samples with low curie points to a given temperature in air and with the temperature held constant the moment was observed to grow with time. This is similar to an experiment by Nagata[51] and he called the moment so acquired thermochemical remanent magnetisation. The new curie point was determined by cooling the sample to room temperature, sealing in an evacuated quartz tube to prevent further oxidation taking place and reheating J_s. Curves are shown in Fig. 5a to 5f. This series of experiments was carried out in curie balance designed by Kawai which unfortunately could not be calibrated absolutely. On this instrument it again took 30 minutes to reach 600°C and again samples of approximately .01 to .02 grams were used.

3.2. Comparison of thermal demagnetisation curves in air and vacuum.

Curves for six of the synthetic specimens are shown in Fig. 4a to 4f, and the remaining specimens gave similar results and fell into the same general pattern. Many important observations can be made from a study of these curves.

Both the heating curves in air and in vacuum were identical up to about 300°C and it was above this temperature that oxidation effects began. The two curves sometimes had different room temperature values of J_{sat} e.g. Fig. 4c and this was due to the slightly different positions the samples were placed in the instrument. This was quite critical and the descrepency in the readings gave an idea of the accuracy of the calibration, and was about 5 to 10°/o.

The curves obtained for the samples in a vacuum repeated exactly on cooling in all cases and successive heatings gave the same curves. In all cases there was only one curie point and this implied that the small percentage of rhombohedral material, shown to be present in x-ray photographs, had no effect on the magnetic properties. The curves for $x = .97$ fell slightly at low temperature and this was compatible with the idea that pure ulvospinel $Fe^{2+}[Fe^{2+}Ti^{4+}]O_4$ should have no moment at 0°K in a perfectly ordered state.

In air however the moment above 300°C was affected by oxidation and depending on the original curie point, fell less quickly ($x = .2$) leveled out or even increased i.e. $x = .57$ and $x = .77$. This was due to ferrimagnetic oxidised titanomagnetites being produced with a curie temperature greater than the oxidising temperature. Thus curves similar to the ones for $x = .57$ did not correspond to two components being present originally but to the original low curie temperature component being oxidised to a high temperature component.

In the case of $x = 0$ and .1 another process was happening. The cooling curves showed that both samples were non-magnetic and when heated in air the moment fell more quickly than in vacuum. In both these cases the oxidised magnetite has been converted to haematite. X-ray photographs taken after heating for $x = 0$ and $x = .1$ showed only haematite lines.

In the other cases from $x = .2$ to .97 the curie point had risen to 550°-600°C as shown by the cooling durves and was independent of the composition. This has important consequences as it may explain in many cases the large grouping of curie points of natural specimens around 500° to 600°C, irrespective of composition. The value of J_{sat} of the oxidised sample was interesting. The case of $x = 0$ and .1 has been discussed. For $x = .2$ and .295 the moment acquired was less than the original J_{sat} at 20° but for samples with x greater than .395

the moment had increased. In many cases (4 out of 7) x-ray photographs showed a second rhombohedral phase to be present up to 5 to 10°/o and so the result for $x = .2$ and .295 might be due to the decrease in cubic material present but it was only by about 10°/o and as the drop in the moment is 40°/o, the effect seemed real. So oxidation caused J_{sat} at 20°C to increase for $x > .35$ and decrease for $x < .35$.

3.3. The Rate of oxidation at different temperatures.

As in the previous section the heating curves were found to level out or even rise during heating and when held at a fixed temperature this increase in moment could be observed with time. Various temperatures from 250° to 550°C were used and sufficiently long times used to give a large increase in moment and curie point. At 225°C the rate of oxidation was too slow to be of interest but from 300°C upwards the rate of oxidation was on a laboratory time scale. The moment acquired was due to the production of a ferrimagnetic oxidised titanomagnetite with a curie point above the oxidation temperature as explained previously and the moment was found to grow steadily at first but the rate dropped and the increase became much slower, as if it was reaching a limiting degree of oxidation at a given temperature. The curves obtained are shown in Fig. 5a to 5f and the results tabulated in Table 1.

Table 1. Oxidation at different temperatures.

Original curie point in °C	Oxidising Temp °C	Oxidising Time in mins.	New Curie point.
100	225	2580 (43 hrs)	150°
290	300	950	420
290	350	1050	500
290	400	275	500
340	450	157	540
370	500	30	530
370	550	6	550

The only annomalous curve obtained was the one for oxidising at 550°C. Here the moment grew for 3 minutes but after 5 minutes was reducing again, because after three minutes the sample began to revert to a rhombohedral form with increased oxidation.

3.4. Conclusions.

It is clear that above 300°C when heated in air, oxidation effects are important. The curie points rise on oxidation and irrespective of composition will reach 500° - 600°C except in the case of pure or nearly pure magnetite which reverts to haematite. The moment J_{sat} at 20°C for oxidised samples is greater than for unoxidised samples for $x > .35$ but is less for $x < .35$.

The oxidation time varies from 15 to 17 hours at 300°C to a few minutes above 500°C and prolonged heating at the higher temperature has the effect of producing a rhombohedral phase. This was for fine grained powders up to 100 microns and in natural samples may not be as rapid. The results of this chapter agree fairly well with the results obtained by the Japanese workers and Fig. 6 shows the continuation of the lines of constant curie point to meet the oxidation line of ulvospinel, and also shows the region where oxidised magnetite reverts to rhombohedral haematite.

THERMAL DEMAGNETISING CURVES IN AIR AND IN VACUUM FOR SYNTHETIC TITANOMAGNETITES

FIG 4a

X = 0

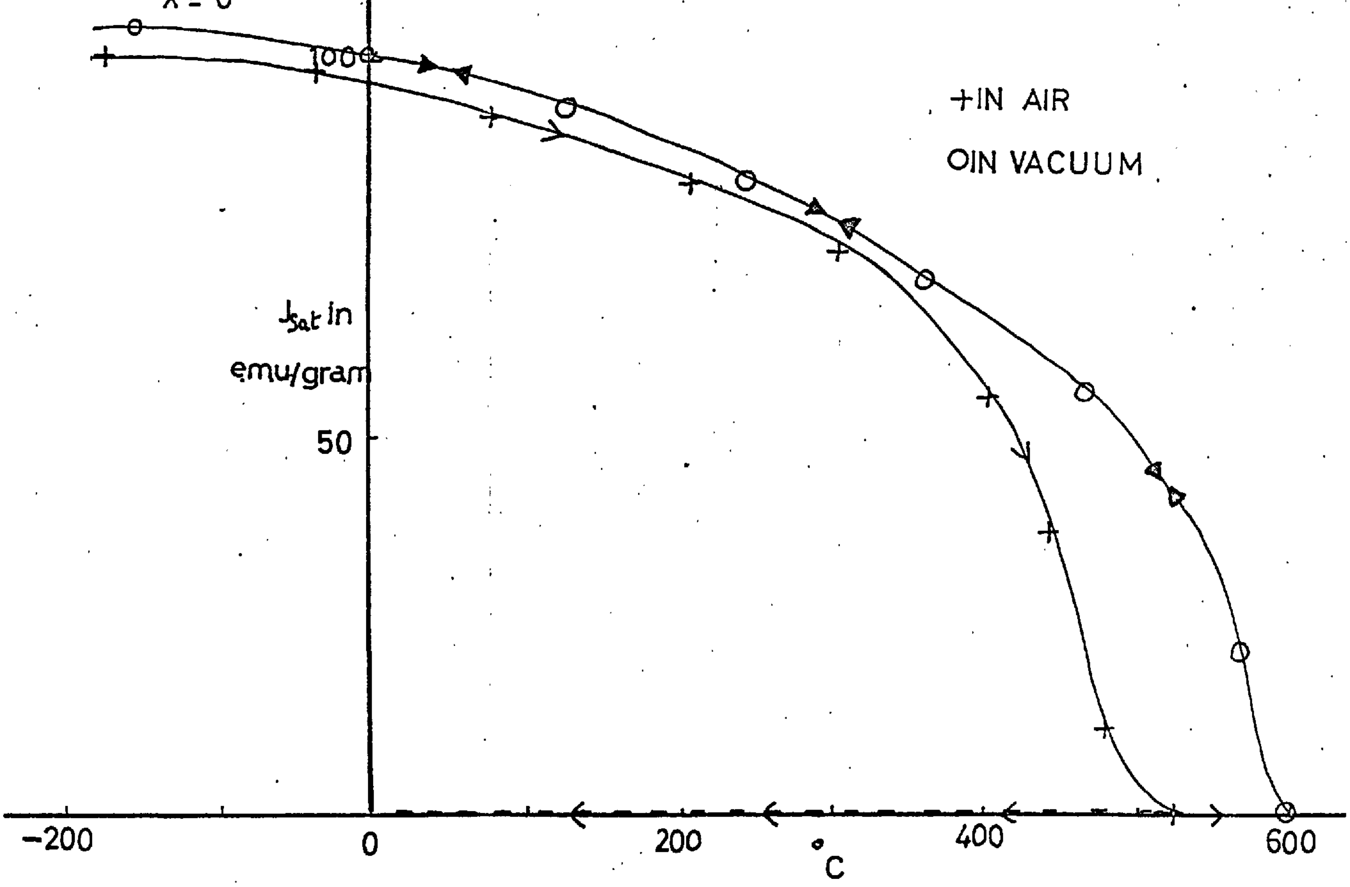


FIG. 4b X = ·20

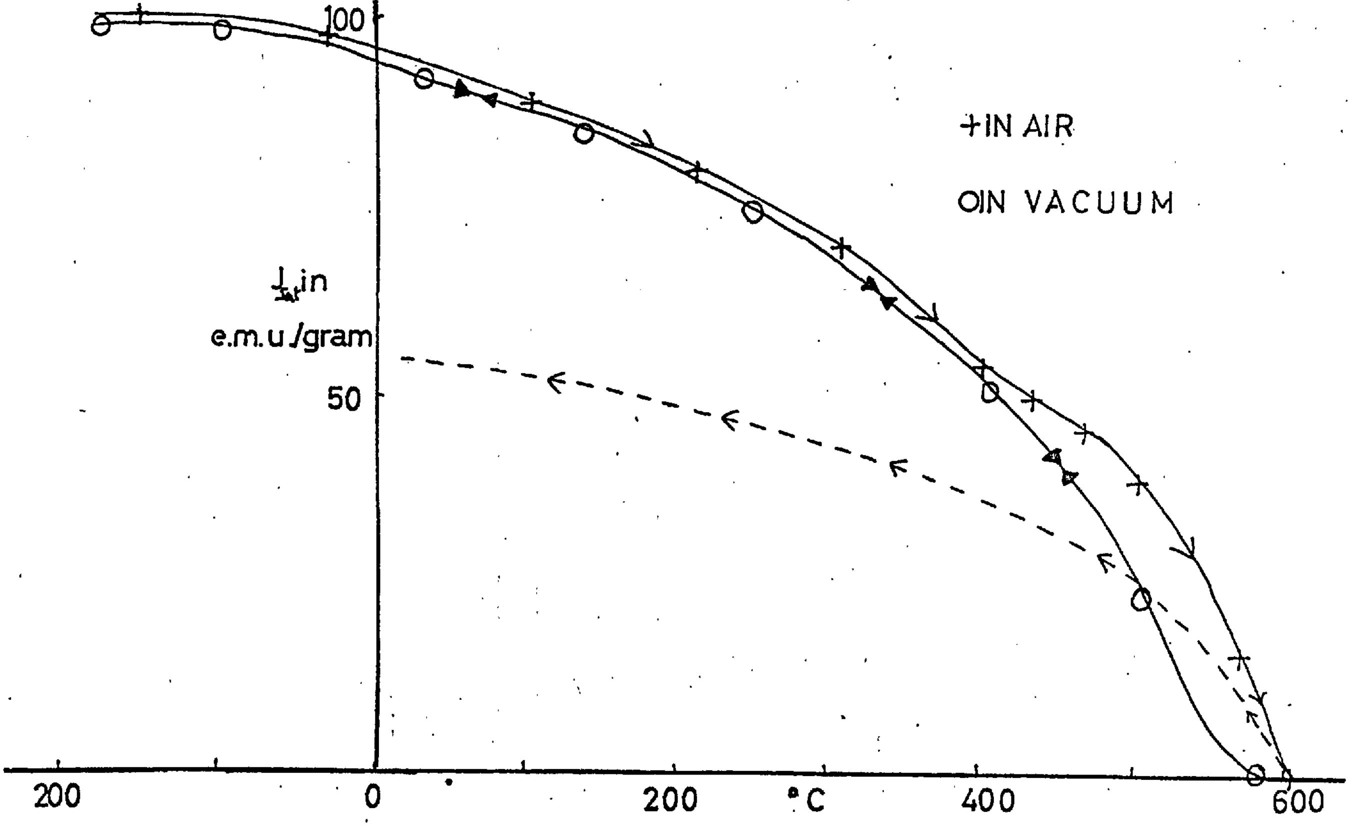


FIG 4c X = ·395

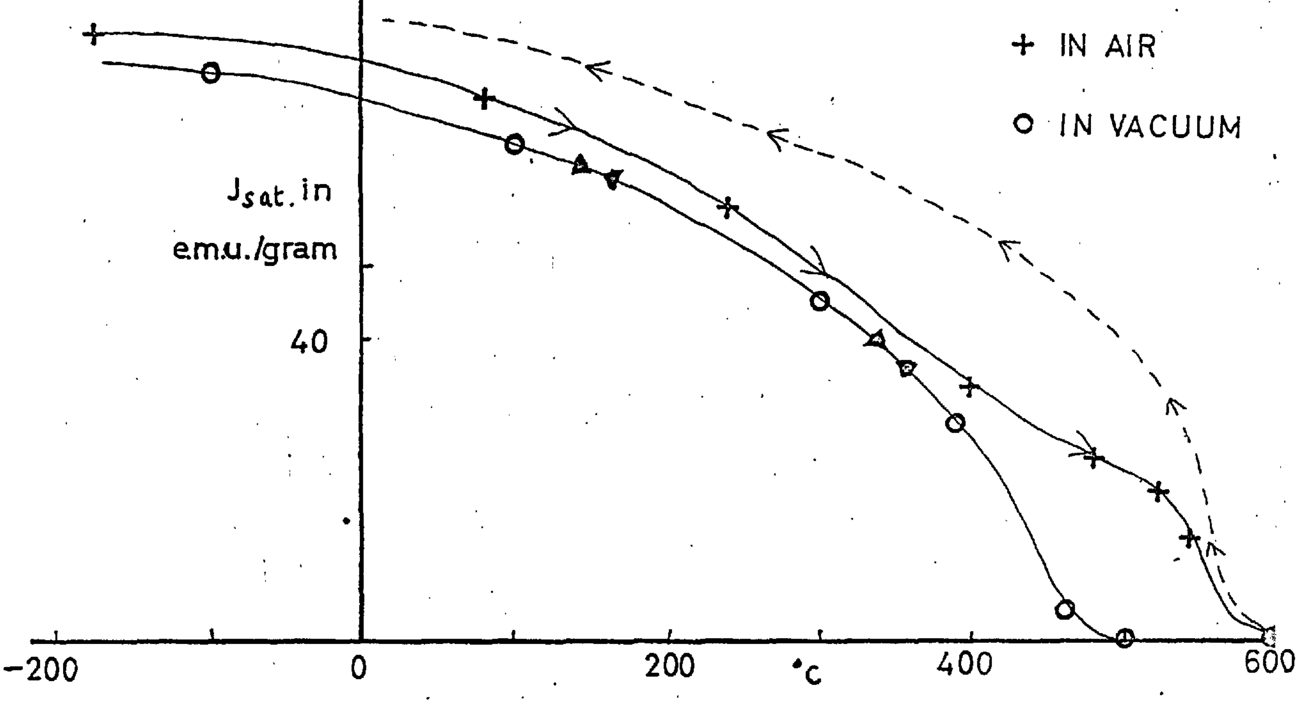


FIG.4d X = ·57

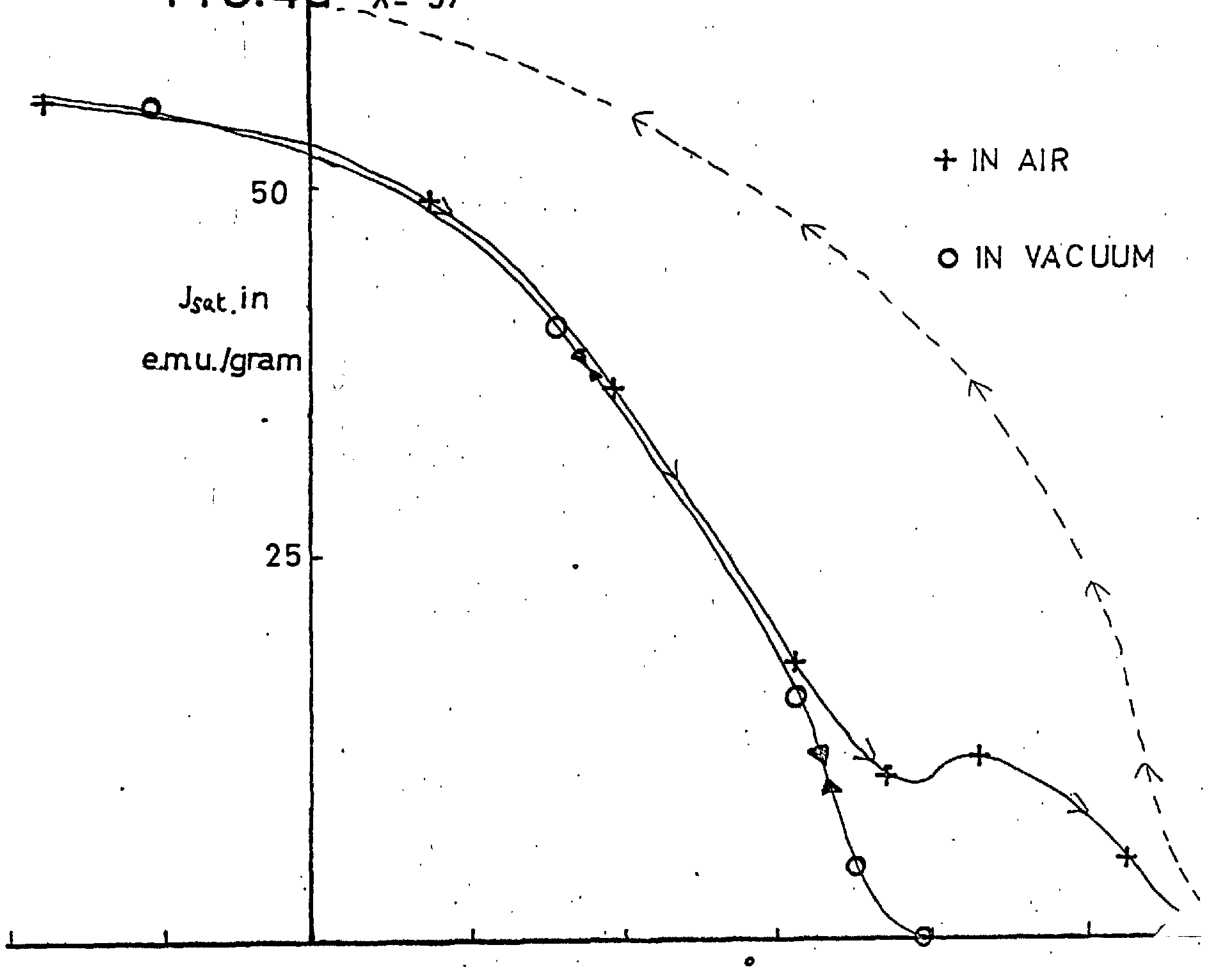


FIG.4e X= ·77

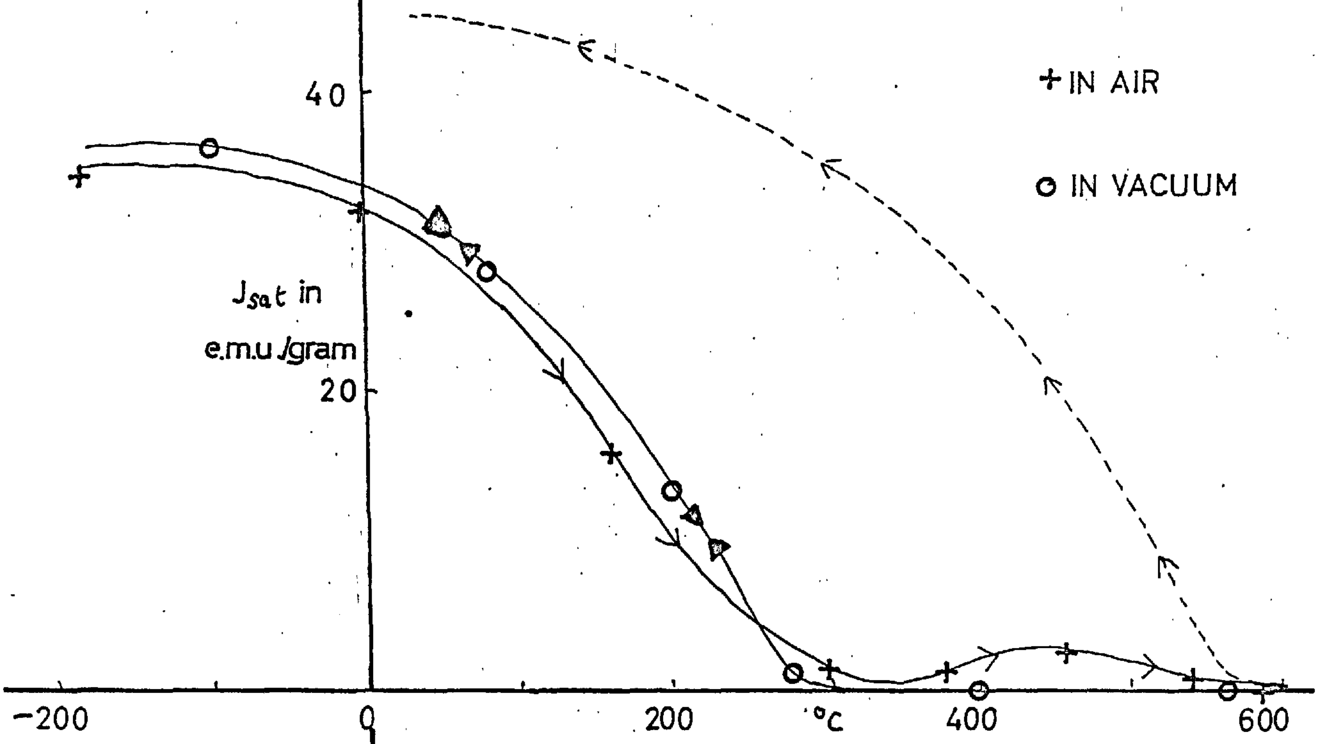
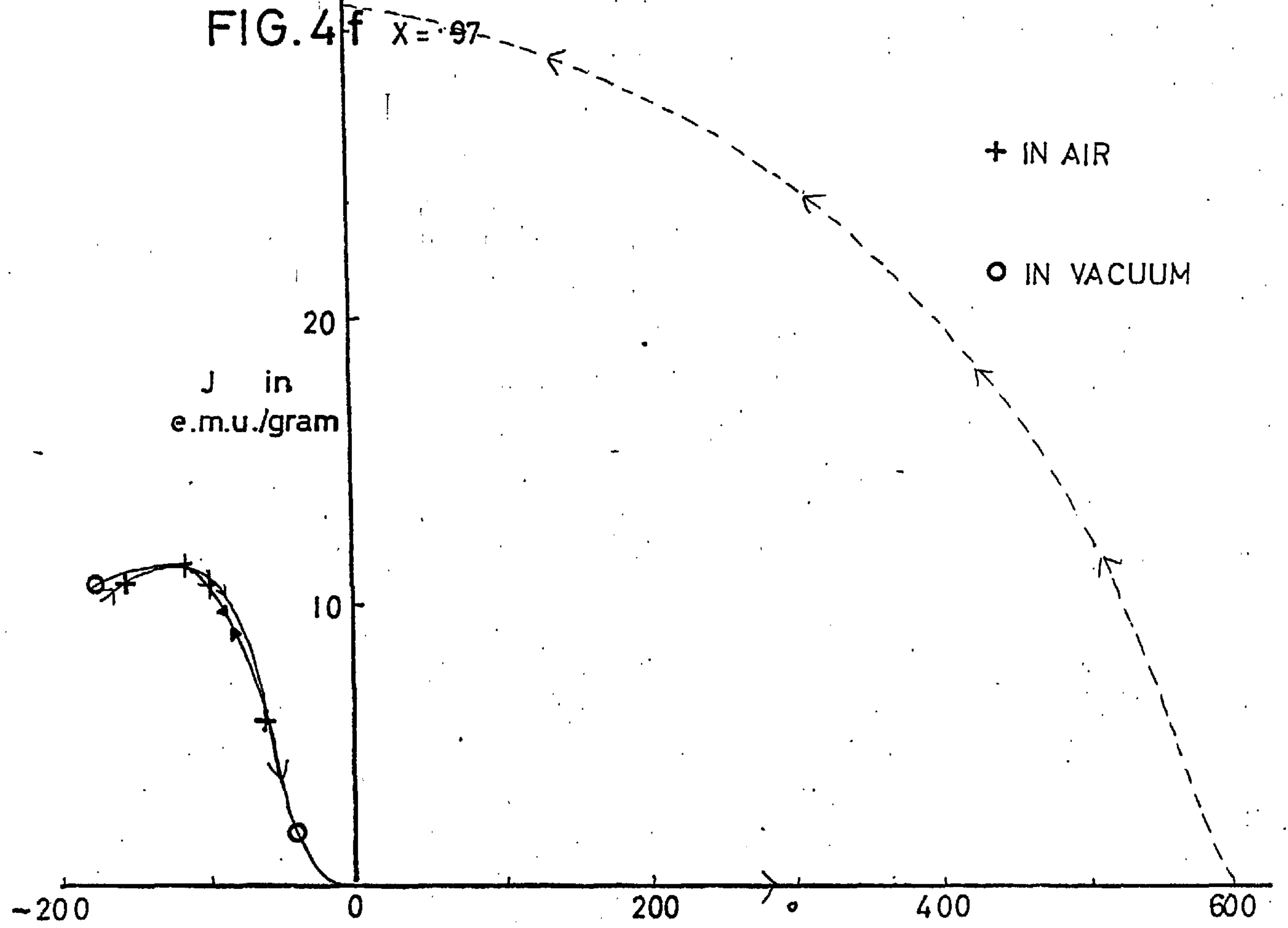


FIG.4f X= ·97



OXIDATION RATES AT DIFFERENT TEMPERATURES

FIG. 5a OXIDATION AT 300°C (X= ·77)

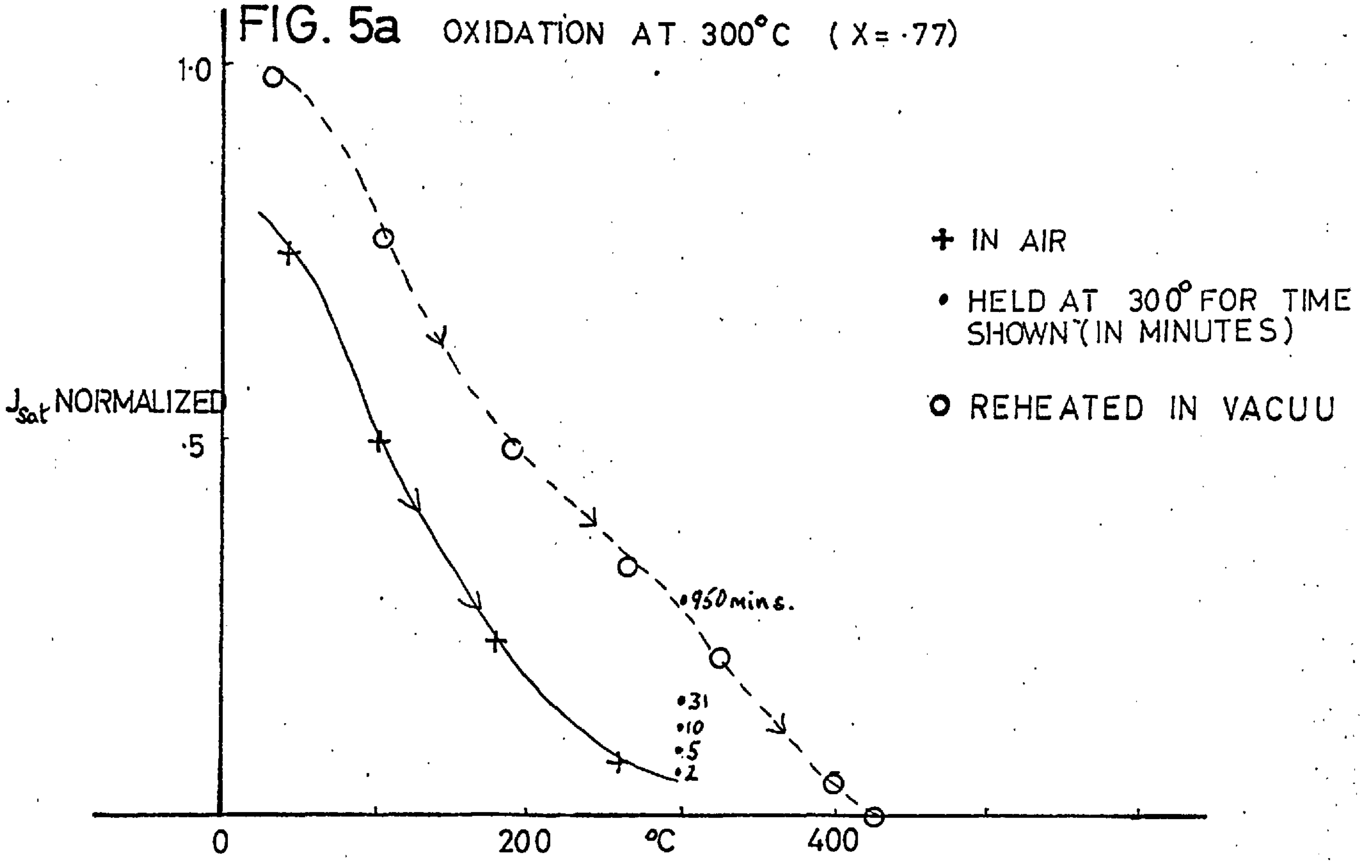


FIG. 5b OXIDATION AT 350°C (X= ·77)

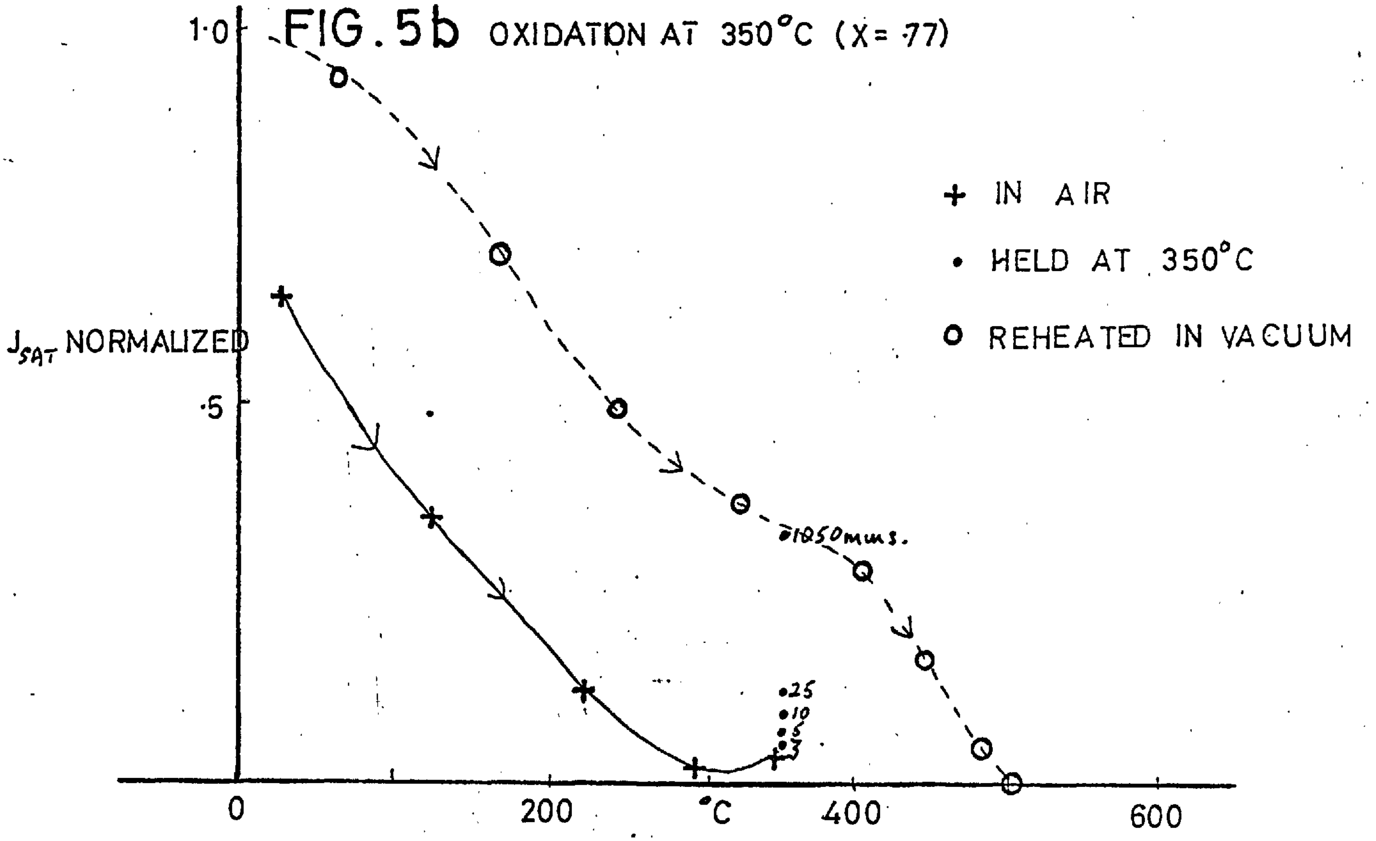


FIG. 5c OXIDATION AT 400°C (X= ·7)

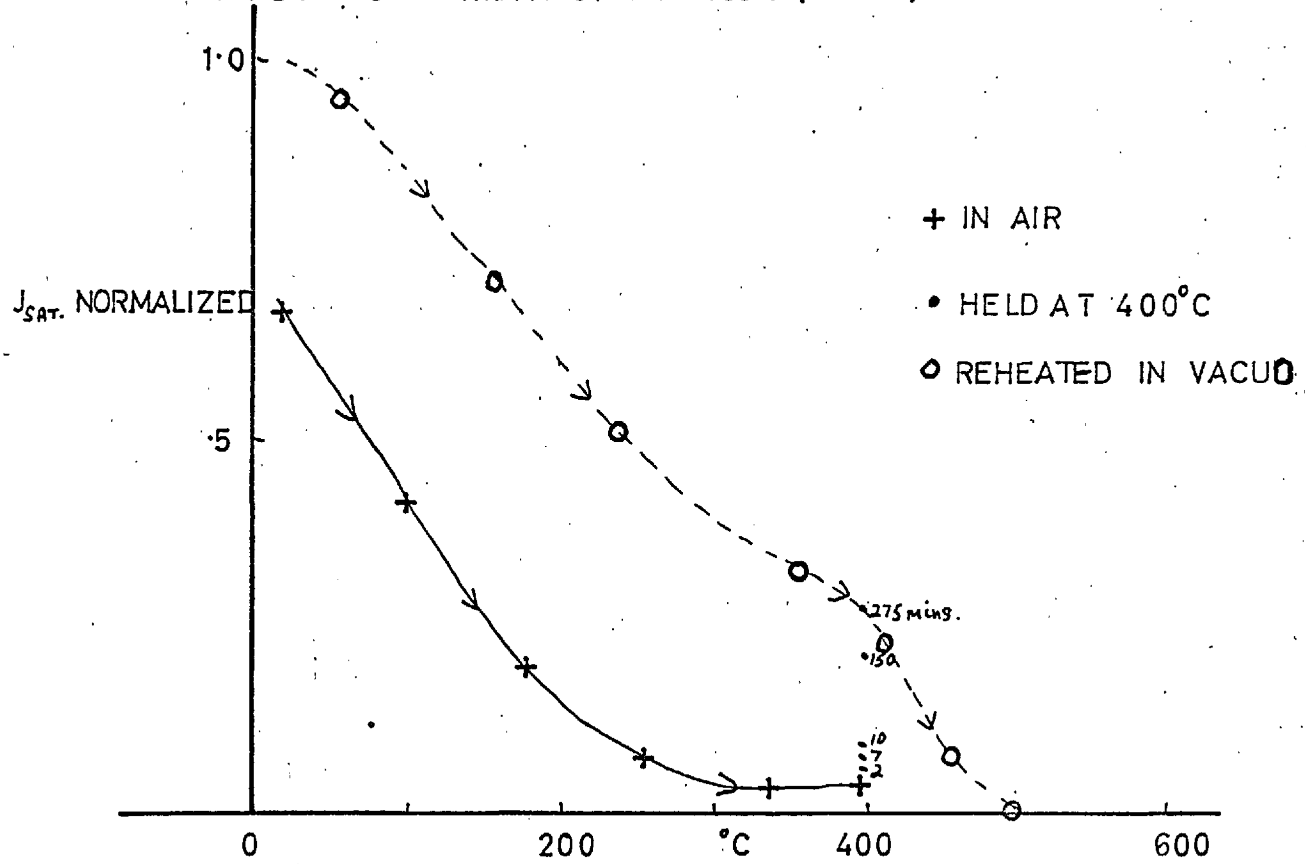


FIG. 5d OXIDATION AT 450 C (X =·67)

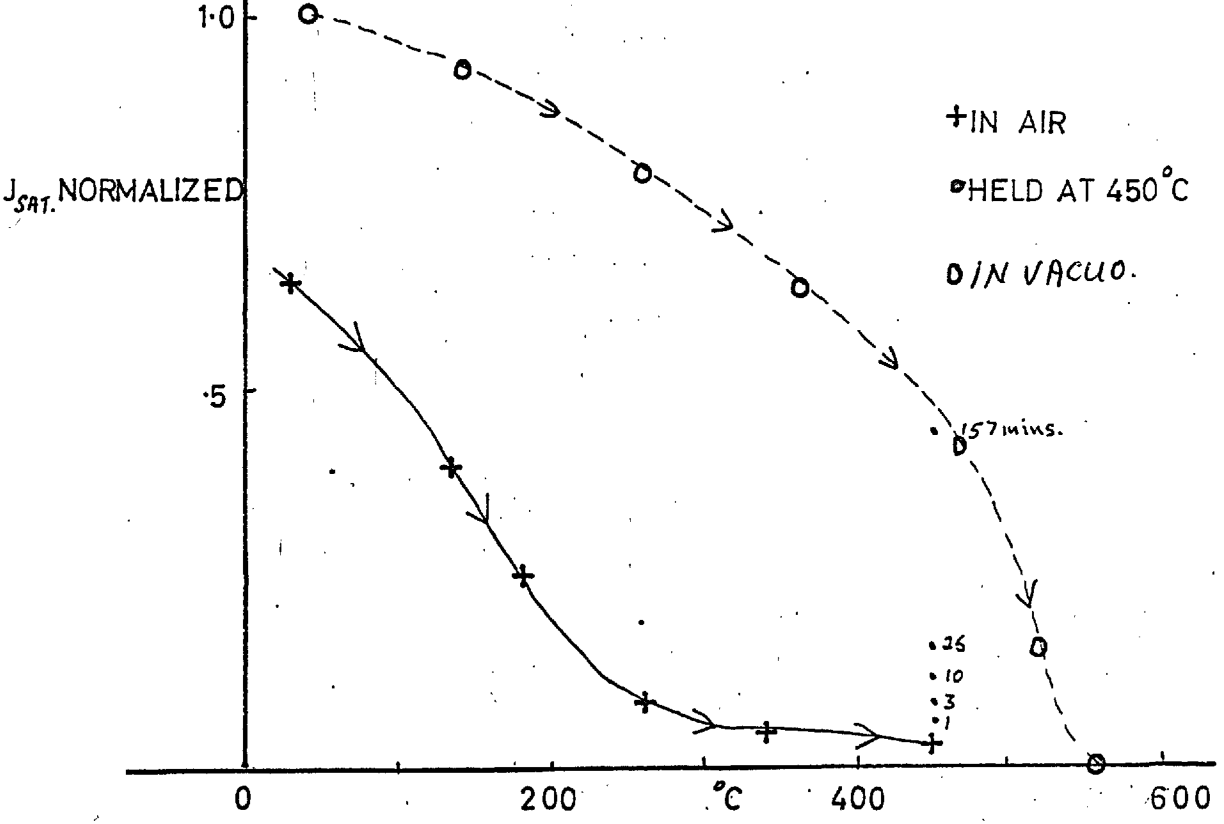


FIG. 5e OXIDATION AT 500°C (X=·57)

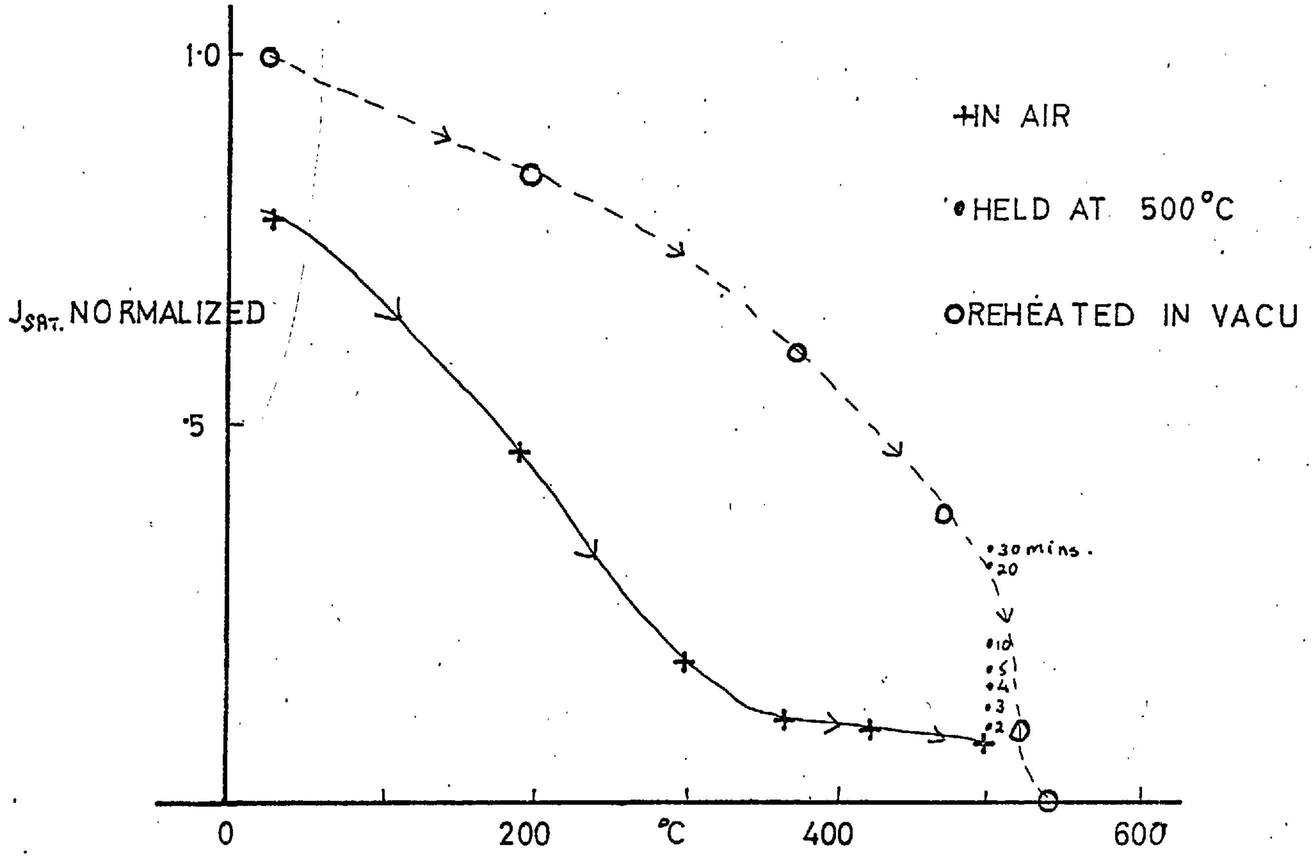


FIG. 5f OXIDATION AT 550°C

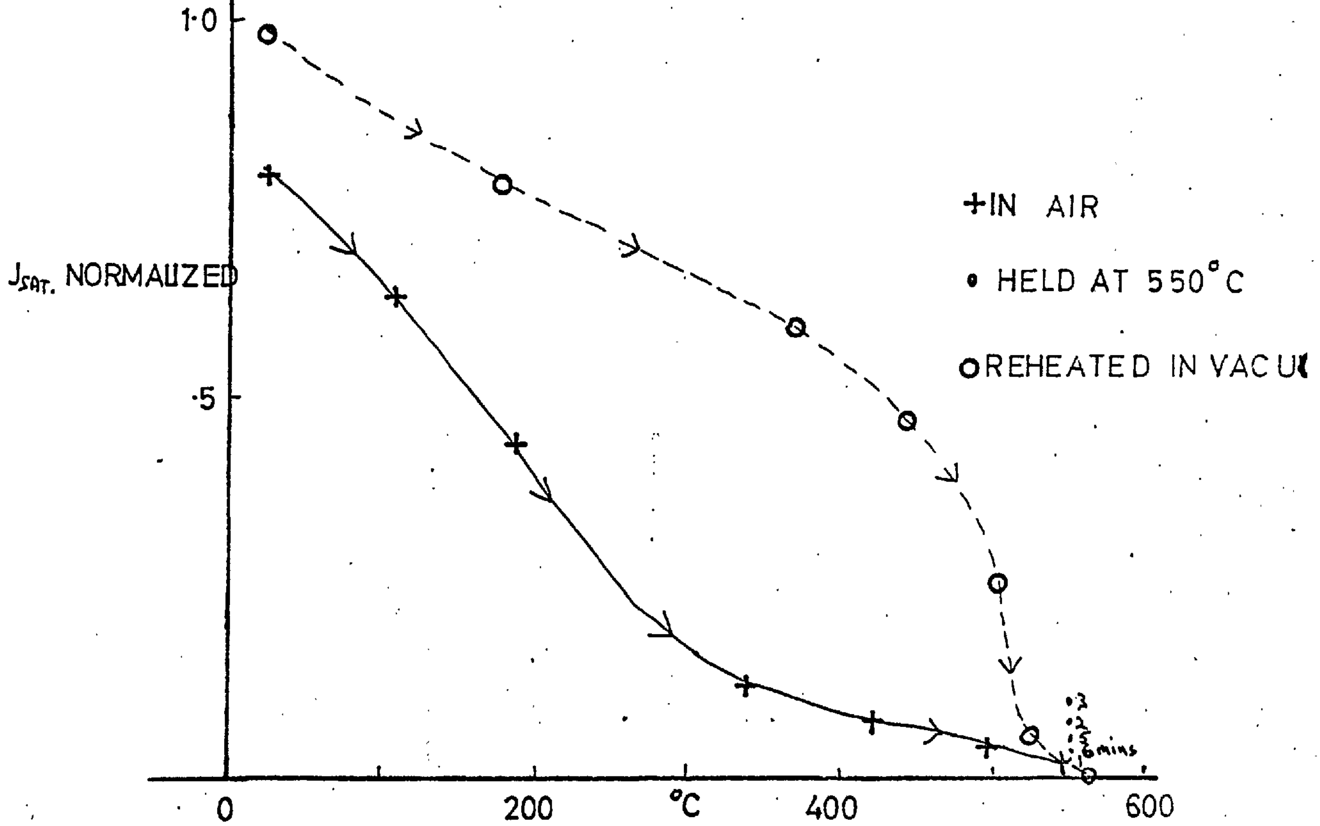
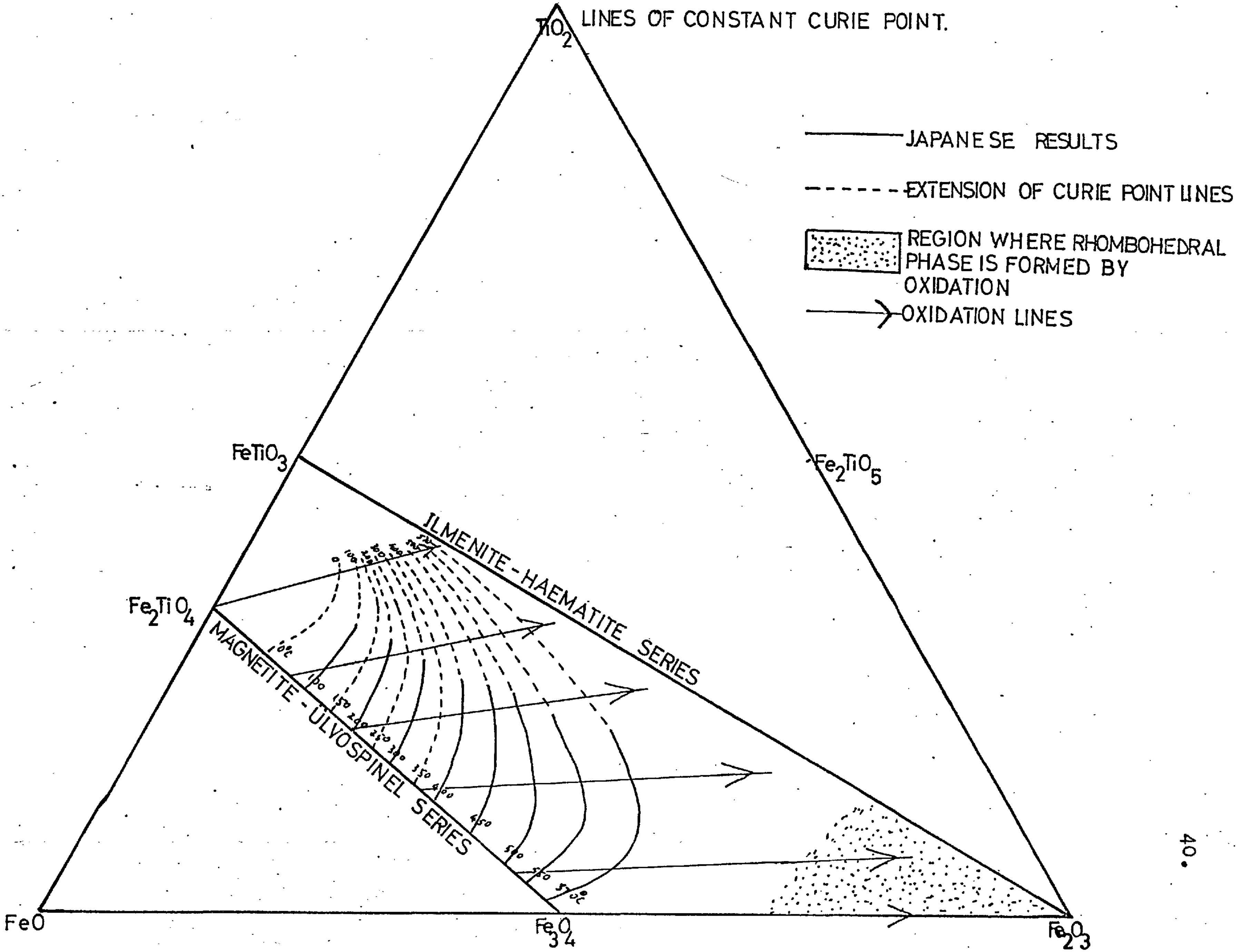


FIG. 6 TERNARY DIAGRAM SHOWING THE EXTENSION OF THE LINES OF CONSTANT CURIE POINT.



CHAPTER 4.

Thermal remanent magnetisation and partial thermal remanent magnetisation of synthetic titanomagnetites.

4.1. Introduction.

Although titanomagnetites and oxidised titanomagnetites form a large percentage of the magnetic constituents of rocks and the remanent magnetisation of igneous rocks is usually thermal remanence, very little work seems to have been carried out on low field thermal remanent magnetisation (T.R.M.) and partial T.R.M. of synthetic titanomagnetites. Partial T.R.M. (P.T.R.M.) occurs when a sample is cooled through its curie point to a temperature T_i in a field and cooled from T_i to room temperature in different or zero field. Bhimasankaram[35] and Charmichael have shown that low field interactions between two magnetic phases can cause reversal of the P.T.R.M. in the case of pyrrhotite and ilmenohaematite and Lewis[52] has shown a similar effect to be present in natural titanomagnetites from an Indian lava in the Deccan Traps. It was decided to investigate the T.R.M. and P.T.R.M. in low fields of unoxidised and oxidised samples.

4.2. Experimental procedure.

In order to be able to measure the T.R.M. and P.T.R.M. while cooling in a field and heating in zero field a new instrument was constructed and placed at the side of an astatic system allowing the moment to be measured by a vertical movement of the sample. A detailed description is given in Appendix 1.

To avoid further oxidation taking place during the measurement of the heating curve all the specimens used were sealed in evacuated tubes. The samples weighed up to 0.1 gram. It took 30 minutes to heat to 600°C and it was possible to cool the samples in a field of up to 2 oersteds.

The general order of events was as follows. The sample was heated to 560°C in zero field and cooled in a field of .4 oersted to room temperature, thus acquiring a T.R.M. The variation of T.R.M. with temperature was then measured in a zero field up to 560°C and the sample cooled in .4 oersted to a temperature T_i, which was always approximately 100°C below the curie point. At T_i the field was changed to zero and the sample cooled to room temperature. The variation of the acquired P.T.R.M. with temperature was then measured in zero field up to 560°C and the process repeated using different fields below T_i if necessary. It was found that repeated heatings and coolings gave identical curves.

4.3. T.R.M. and P.T.R.M. of unoxidised samples.

The samples used had a range of curie points from below room temperature to 560°C and T_i was chosen 100° below the curie point in most cases. Two sets of curves are shown in Fig. 7a and 7b. In both cases the variation of T.R.M. and P.T.R.M. with temperature was very similar. The P.T.R.M. acquired was less than the T.R.M. acquired and using THELLIERS ~~Nagatas~~[illegible] addition law for P.T.R.M. a slight spread of blocking temperatures below T_i can be inferred from the result. The P.T.R.M. acquired by cooling in a field of .2 oersted below T_i was between the T.R.M. and the P.T.R.M. in zero field and agreed with the result obtained using THELLIERS ~~Nagatas~~ law. Similar curves to those shown in Fig. 7a and 7b were obtained for all samples measured. (All samples with curie points > 200°C.)

4.4. T.R.M. and P.T.R.M. of oxidised samples.

Samples which had been heated to 600°C in air and then sealed in evacuated quartz tubes were also measured in a similar way, T_i being 400° in all cases. Whereas all the unoxidised samples gave similar results the curves obtained from the oxidised set of specimens fell into three groups.

Five samples gave similar curves to the unoxidised samples with the P.T.R.M. acquired less than the T.R.M. (Fig. 8a). Three samples acquired P.T.R.M.'s which were identical to the T.R.M. irrespective of the field applied below T_i. Clearly in these cases there was no blocking temperatures below 400°C. However two samples acquired P.T.R.M.'s in zero field below T_i which decreased on cooling below T_i and the corresponding heating curve showed a maximum (Fig. 8b). For this sample the P.T.R.M. acquired in .2 oersted below T_i remained constant on cooling.

No real pattern emerged from the values of x in the different cases. The P.T.R.M. curves which fell on cooling, occurred for x = .2 and .77 and the curves which coincided with the T.R.M. for x = .48, .57 and .87.

The drop in the P.T.R.M. can only be due to some negative interaction causing the moment to fall.

4.5. T.R.M. and P.T.R.M. of partially oxidised samples.

A similar series of experiments was carried out on samples oxidised at lower temperatures for longer times. These were called partially oxidised to differentiate them from the samples heated to 600° which were previously discussed.

Three samples with $x = .77$ were heated to 300°C for 950 minutes, 350°C for 1050 minutes and 400°C for 250 minutes and the T.R.M. and P.T.R.M. heating curves were measured after sealing in an evacuated quartz tube. The P.T.R.M. of the sample heated at 400° was similar to the unoxidised samples but the other two were found to have reversed P.T.R.M. One is shown in Fig. 9a. The T.R.M. curves showed that two components were present and the P.T.R.M. curves showed that the negative interaction between them was about 0.2 oersted since the P.T.R.M. in a field of 0.2 oersted did not rise or fall below T_i.

The samples with $x = .57$ which were heated to 500°C for 17 minutes and 550° for 6 minutes also showed a reversed P.T.R.M. and both differed from the previous case in that the T.R.M. showed a negative interaction to be present. The T.R.M. heating curve fell with temperature up to 300°C and then rose sharply before disappearing at 550°C. The curve for the sample heated to 500° for 17 minutes is shown in Fig. 9b. The other sample was very similar but the rise at 300° less pronounced. The T.R.M. in 1 oersted on this sample again showed this effect and the reversed P.T.R.M. was reproducable after a number of heatings. Fig. 10 shows the P.T.R.M. acquired by cooling in a field of 0.4 oersted applied over 50° intervals for a partially oxidised sample with $x = \cdot 57$. It shows the distribution of blocking temperatures and very clearly shows the existance of two phases.

4.6. Variation of P.T.R.M. with composition.

The last section has shown reversal of the P.T.R.M. to have taken place for samples heated at temperatures between 300° and 550°C. for hours and a few minutes respectively. Samples having a wide range of compositions were heated for various times in air at different temperatures and the most interesting results were obtained on the T.R.M. and P.T.R.M. of samples heated between 450° and 500°C. for up to 10 minutes. Table 2 gives the list of compositions, time and temperature of oxidation and information about the T.R.M. and P.T.R.M. curves for interesting cases.

Table 2.

T.R.M. and P.T.R.M. of partially oxidised samples

x	oxidation temp. and in °C.	Time in mins.	PTRM cooling below T_1 in zero field	T.R.M. on heating	New Curie point in °C .
.2	500	2	levels out	falls steadily	540
.396	450	6	falls slightly	falls steadily	500
.57	360	1020	reverses	two components seen	250,460
.67	450	10	falls to zero	two components seen	250,470
.67	490	10	falls to almost zero	maximum at 260	500
.67	550	10	increases as TRM	falls steadily	530
.77	350	720	falls slightly	falls steadily	425
.87	500	2	falls	two components	250,400
.87	500	10	just reverses	two components	300,500
.87	500	20	levels out	falls steadily	500
.97	500	1	reverses	maximum at 370	550
.97	500	2	reverses	maximum at 360	550
.97	500	5	levels out	falls steadily	560

It is clear from this table and the previous section that reversal of the P.T.R.M. has been found in all samples with $x > .5$ and that a negative interaction, although not large enough to always cause a reversal, occurs in all samples with $x > .2$.

4.7. Variation of P.T.R.M. with oxidation.

It was decided to investigate more fully the changes of P.T.R.M. with the degree of oxidation and a series of experiments was carried out on a sample with $x = .57$. Firstly a suitable temperature had to be used so that oxidation did not take place too quickly. Samples were heated to 500° for 1 minute and 30 minutes and the curves for the first sample showed the P.T.R.M. to have fallen to zero at room temperature and the T.R.M. heating curve to level out between 200 and 300° before falling to an upper curve point of 500°. After 30 minutes heating in air the P.T.R.M. curve was similar to the T.R.M. curve which fell steadily to an upper curie point of 550°C. Heating to 500° for 5 minutes produced an intermediate result with the P.T.R.M. still decreasing below T_i on cooling but not reversing. The T.R.M. still levelled out between 250 and 300°C but this was less pronounced than in the first case.

Microscopic examination of the grains showed a size distribution up to 200 microns and in order to obtain a more uniform rate of oxidation it was decided to separate the grains into large and small grain sizes. The grains were separated by a sedimentation process and the large grains obtained were between 50 and 200μ and the small grains between 1 and 50μ.

Samples from each size range were heated to 500°C for 2 minutes and measured. The P.T.R.M. of the large grains was found to just reverse while that of the small grains just levelled out below T_i (Fig. 11a and 11b). The small grains had a higher curie point showing that they are more oxidised than the larger grains as might be expected. It was not known whether this difference in the P.T.R.M. was due to the difference in size or just to the fact that smaller grains oxidised more quickly. In order to investigate this and the effect of oxidation it was decided to carry out a series of experiments at 450° and to successively oxidise the same sample and measure the T.R.M. and P.T.R.M. (in an evacuated quartz tube every time) at every stage in the oxidation. The oxidation took place too quickly at 500° so 450° was used to enable the time scale to be extended. However it was found that even at 450° oxidation took place fairly rapidly but interesting and informative curves were obtained.

At first the larger grains gave a P.T.R.M. which decreased with increase of oxidation time and reverses after 2 minutes. The R.P.T.R.M. increased with oxidation time up to 10 minutes but then began to decrease and the P.T.R.M. became normal again. After heating for a total of 60 minutes at 450° the P.T.R.M. no longer fell when cooled below T_1. Fig. 12a and 12b show the T.R.M. and P.T.R.M. for the sample heated for 4 minutes and 60 minutes and Fig. 13 shows a graph of the room temperature value of the P.T.R.M. against oxidation time. The maximum R.P.T.R.M. occurs after 10 minutes and clearly there is a region where a R.P.T.R.M. is produced. A blocking temperature diagram for the reversing sample oxidised for 4 minutes is shown in Fig. 14 and clearly shows the existance of two phases.

Thermal demagnetising curves of J_{sat} in a curie balance are shown in Fig. 15 for the unoxidised, partially oxidised reversing sample and the oxidised sample which no longer reversed. No indication of two components or any negative interaction was seen in these curves.

The curie point was seen to rise with oxidation.

The small grained material was also given a similar oxidation treatment at 450°. Fig. 16a and 16b show the T.R.M. and P.T.R.M. for the sample after heating for 4 minutes and 10 minutes. The variation of P.T.R.M. at room temperature with oxidation time is shown in Fig. 17. The most significant points about this curve are that the P.T.R.M. just reverses after 4 minutes but after 10 minutes it does not even fall on cooling below T_1. On comparison with the curve for large grains it can clearly be seen that the reversal properties are more pronounced in the large grains.

4.8. Variation of P.T.R.M. with geometric configuration.

A sample with $x = .87$ showed a drop in the P.T.R.M. below T_1 on cooling after being partially oxidised at 500° for 2 minutes. The sample was mixed with three times its volume of non-magnetic magnesium oxide and heating curves of the T.R.M. and P.T.R.M. remeasured. It was then mixed with nine times its volume and the curves repeated. All three sets of curves were practically identical and the conclusion drawn that the interaction did not depend on the geometric positions of the grains with respect to each other but occured inside the individual grains.

4.9. Comparison with the ilmenite-haematite series.

The reversal of the T.R.M. in synthetic ilmenite-haematites containing 60°/o ilmenite has been reported by Uyeda[32] and Vsalov[33] and a R.P.T.R.M. has been reported by Carmichael in the region of 20°/o ilmenite. It was decided to prepare synthetic samples in this series and to investigate the T.R.M. and P.T.R.M. to see if the reversals found had similar features to those already described for the ulvospinel-magnetite series.

Ten samples were prepared and the T.R.M. and P.T.R.M. thermal demagnetising curves measured. A reversal of the T.R.M. was found for the samples containing 60 and 70°/o ilmenite. The heating curve of the T.R.M. for 60°/o ilmenite is shown in Fig. 18a. This is the region in which the Japanese and Russian workers obtained their reversals. Unlike the magnetite ulvospinel series the T.R.M. reversed and the heating curve showed the R.T.R.M. to fall from 386×10^{-3} emu/gram at 20°C and became normal at 200°C but only to reach a value of 2.8×10^{-3} emu/gram before reaching the curie point at approximately

250°C. In low fields up to 2 oersteds the R.T.R.M. increased with field and after measuring in a ballistic magnetometer the T.R.M. was plotted against applied field (Fig. 19a). A field of 200 oersteds was required to produce a normal T.R.M. and so the interaction causing this reversal was much stronger than the .1 to .2 oersted in the oxidised titanomagnetites. An x-ray photograph showed only one rhombohedral phase and no cubic phase present.

The sample with 70°/o ilmenite also showed a reversed T.R.M. with a 200° curie point. It just became positive in a similar way to the sample with 60°/o ilmenite but the intensity was much less as shown in Fig. 18b. In this case a field of less than 10 oersteds produced a normal T.R.M. (Fig. 19b). The existance of a small positive moment near the curie point is very important as it suggests that a two component system with the curie points of the components differing by only 10 to 20°C and with a large negative interaction, is responsible for the reversed T.R.M.

The interaction producing this effect was clearly very sensitive to compositional changes. The Russians found 25 oersteds and the Japanese over 1600 oersteds was necessary to produce a normal T.R.M. Yet it is extremely unlikely that one small compositional range around

$60^{o}/o$ ilmenite can have more than one reversal mechanism so the dependence of this interaction on composition is critical. It is impossible to rule out this mechanism when considering the possible mechanism which may be the cause of the R.P.T.R.M. in the ulvospinel magnetite series but it does appear unlikely to be the cause.

The rest of the series had normal T.R.M. and P.T.R.M. and the samples with more than $85^{o}/o$ ilmenite were non-magnetic at room temperatures.

4.10. Summary and discussion of results.

A review of the factors and parameters which influence the P.T.R.M. and the R.P.T.R.M. must now be made before the possible mechanisms causing this effect can be discussed.

1. The completely unoxidised and highly oxidised samples have a normal P.T.R.M. which does not decrease on cooling below T_1. The T.R.M. heating curve and x-ray data show only one cubic component to be present in both cases.

2. There exists a region of partial oxidation where the sample is partially oxidised when the P.T.R.M. is reversed. Around this region of oxidisation the P.T.R.M. falls on cooling below T_1 but does not reverse.

3. The T.R.M. curves and blocking temperature diagrams indicate clearly the presence of two components in the samples having R.P.T.R.M. although the original titanomagnetite and the end product of oxidation show only one.

4. The reversals seem to occur when the highest ~~curve~~ Curie point is about 500°C and the lower component between 220° and 350°C.

5. This effect does not appear to be very critically dependent on the original composition of the titanomagnetite

and reversals are found in the compositional range $x > .5$ and the negative interaction in the range $x > .2$.

6. The reversals do not appear to be dependent on the rate of oxidation. It does not appear to matter whether long times at low temperatures (15 hours at 300°C) or a few minutes at 500°C are used. Only the degree of oxidation appears critical.

7. The interaction does not appear to be dependent on the geometrical position of the grains. Mixing the powdered titanomagnetite with nine times the volume of magnesium oxide has no effect on the P.T.R.M. Thus both the interacting components must be contained within individual grains.

8. A considerable dependence on grain size was found. For instance the production of a R.P.T.R.M. was much more pronounced in samples with a large grain size, (50 to 200 μ) than in samples with small grain sizes (1 to 50μ) and the difference could not be accounted for simply by the fact that the small grain oxidise more quickly. The interaction was not absent in small grains but it was considerably weaker.

9. The production of the R.P.T.R.M. by oxidation is not a reversible chemical process. In Chapter 6 which

deals with the process of reduction, it is shown that after being reduced by heating at 800°C for 92 hours in an evacuated quartz tube three samples, originally partially oxidised and showing a drop in the P.T.R.M. on cooling below T_1 had identical normal T.R.M. and P.T.R.M.

10. The reversal of the T.R.M. in the ilmenite-haematite series appears to be of an entirely different nature. It is very critically dependent on composition and the magnetitude of the magnetic interaction can vary by orders of magnetitude for small compositional changes.

11. The R.P.T.R.M. of synthetic partially oxidised titanomagnetites appears to be similar to that found in pyrrhotite and ilmenohaematite (20°/o ilmenite). This suggests the mechanism is of a general nature and not due for instance to specific crystal structures. Such general mechanisms may include magnetic interaction between regions of order and disorder or between regions with different distribution of vacancies or regions of varying cation composition and so on.

The results summarised for the R.P.T.R.M. indicate very strongly the existence of two components A and B with a negative interaction. Defining B as having the higher curie point, on cooling component A acquires a moment due to the resultant of the external field and the reversed field due to B. This is similar to Neel's mechanism. However before a detailed discussion of the probably mechanism can take place a review of the possible reversal mechanisms already postulated and their applicability to the ulvospinel magnetite series will be made.

T.R.M. AND P.T.R.M. THERMAL DEMAGNETISATION CURVES FOR UNOXIDISED SYNTHETIC TITANOMANETITES

FIG. 7a X = ·1

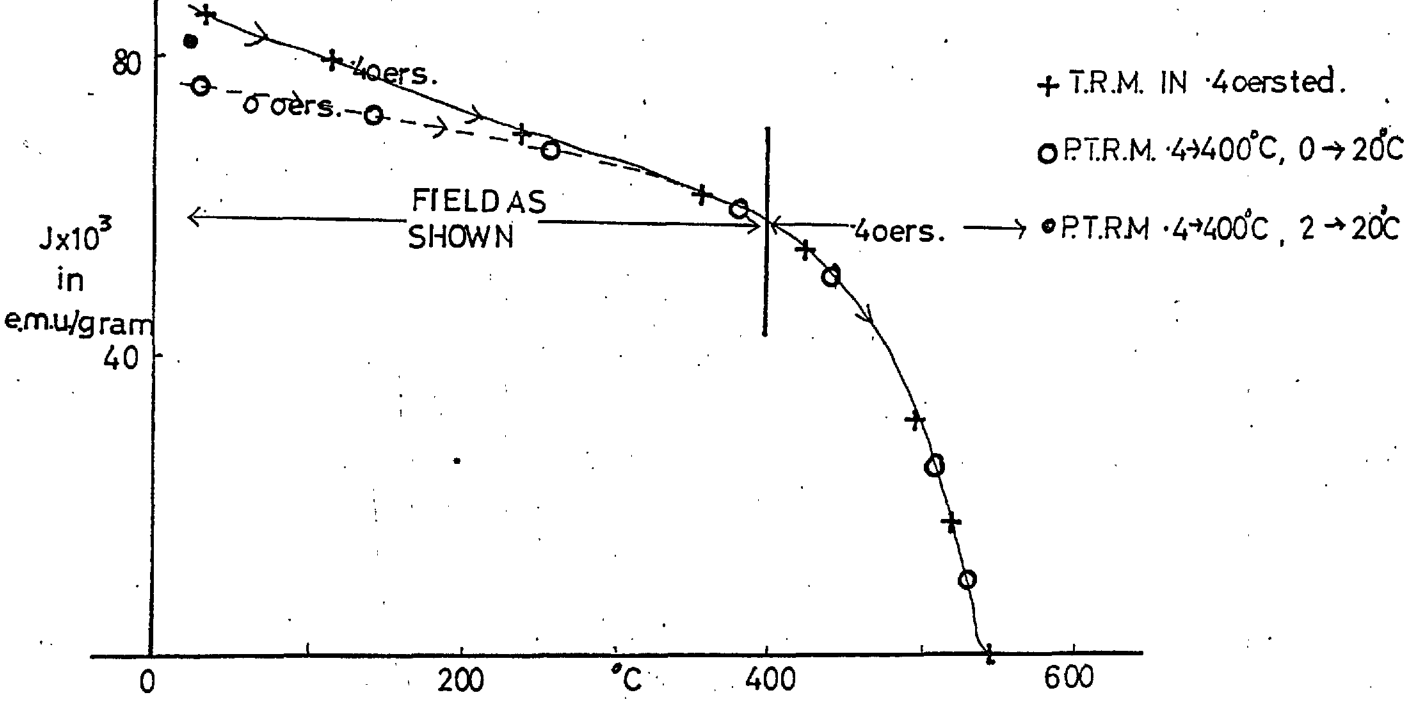
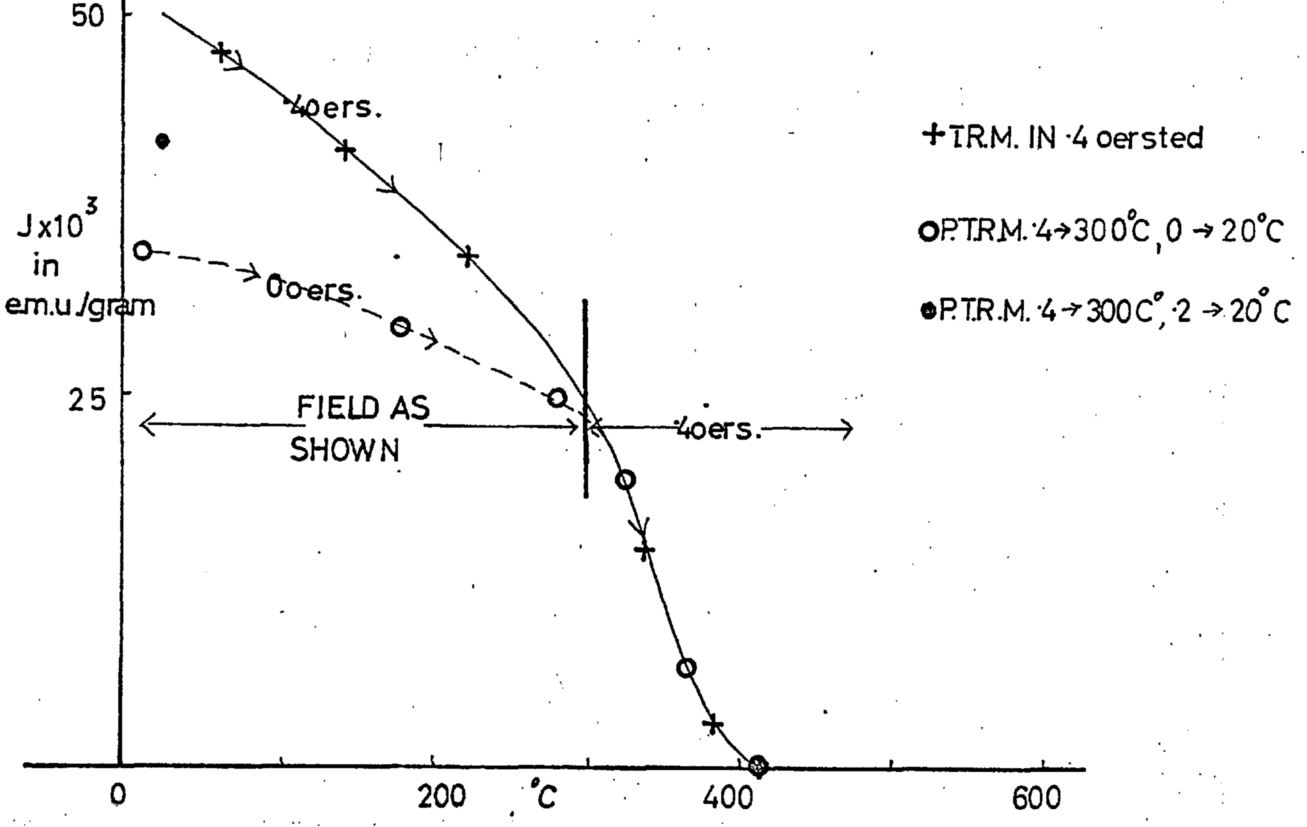


FIG 7b X = ·39



T.R.M. AND P.T.R.M. FOR OXIDISED SYNTHETIC TITA O A T T

FIG. 8a X= ·67

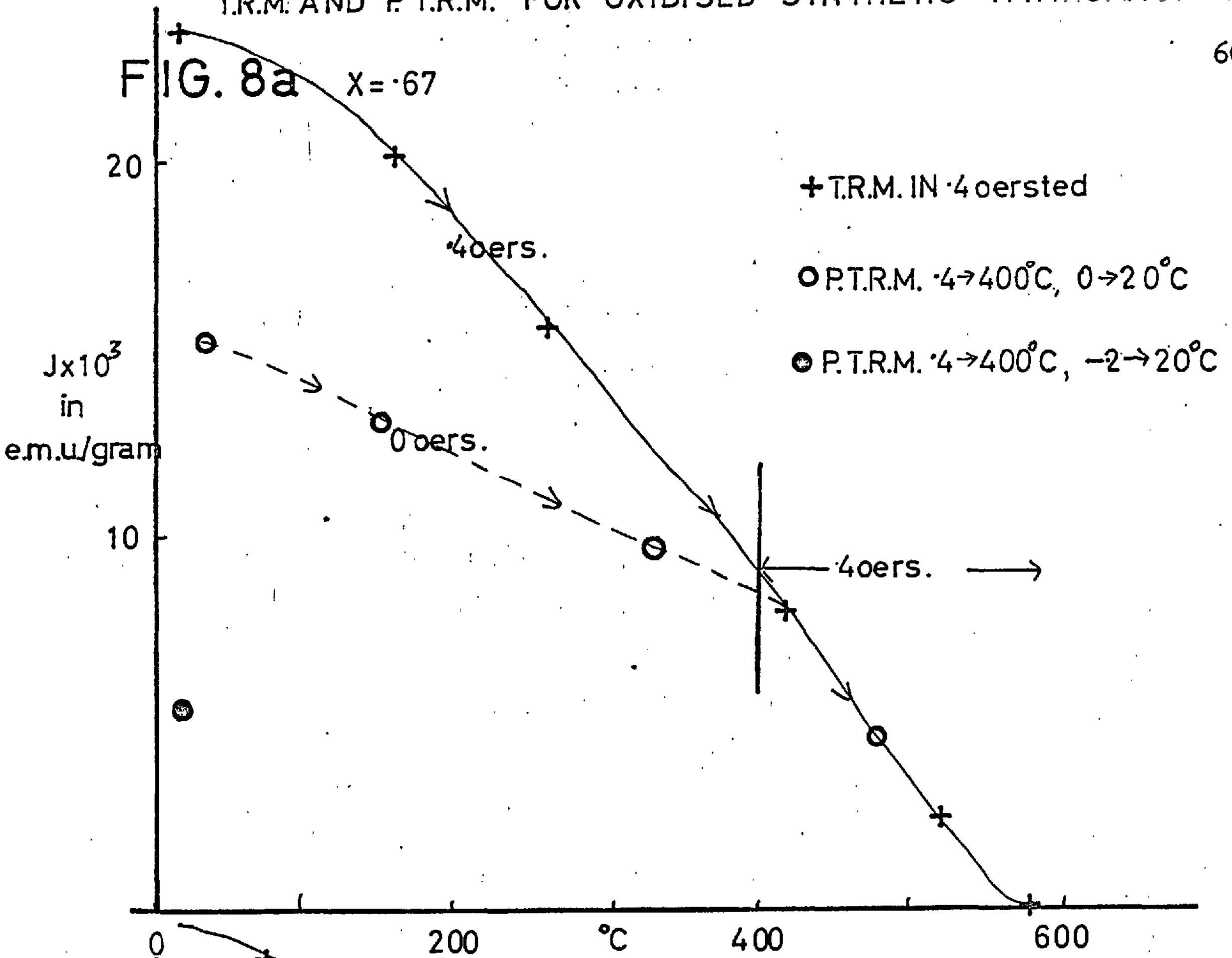
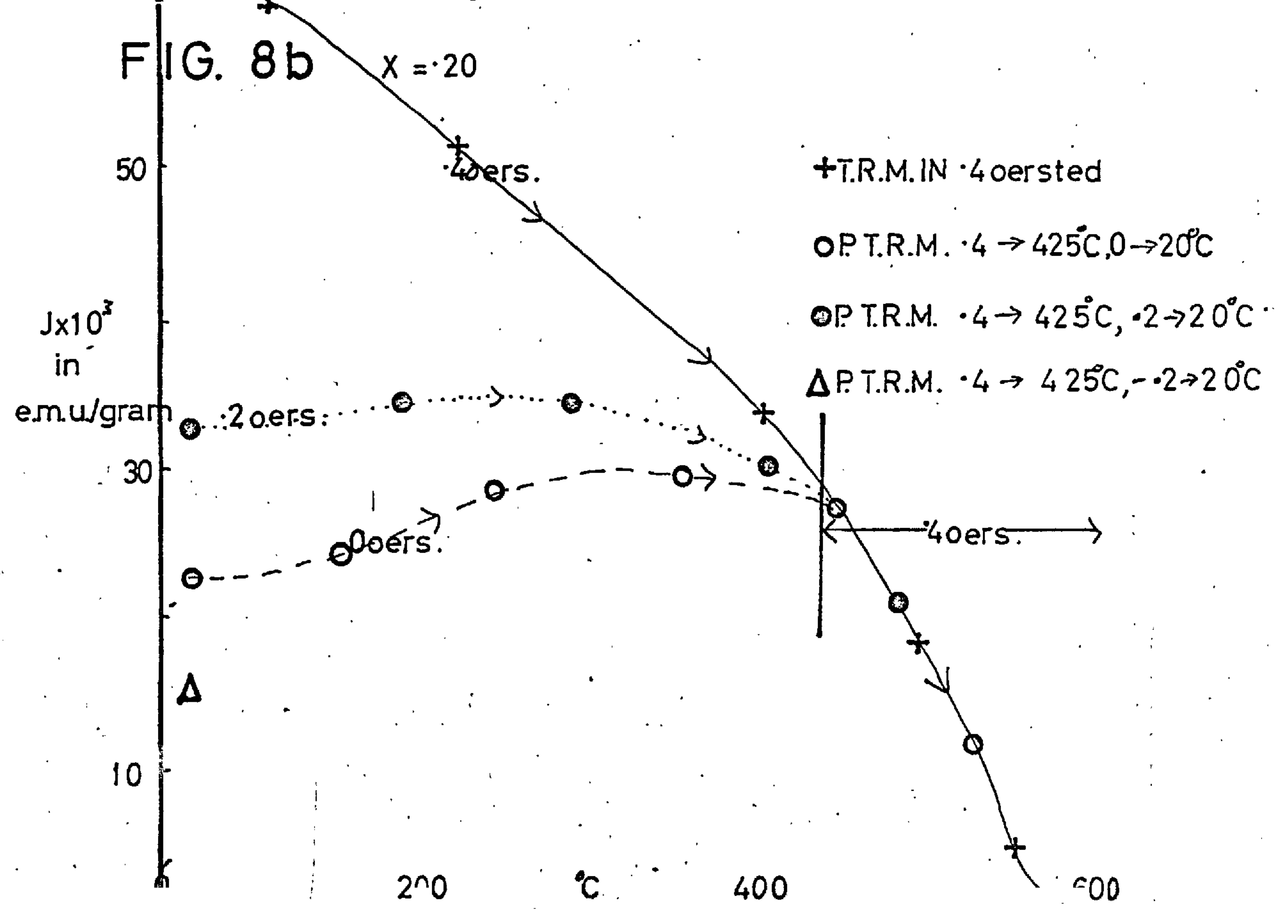


FIG. 8b X = ·20



T.R.M. AND P.T.R.M. FOR PARTIALLY OXIDISED SYNTHETIC TITANOMAGNETI

FIG. 9a X = ·77

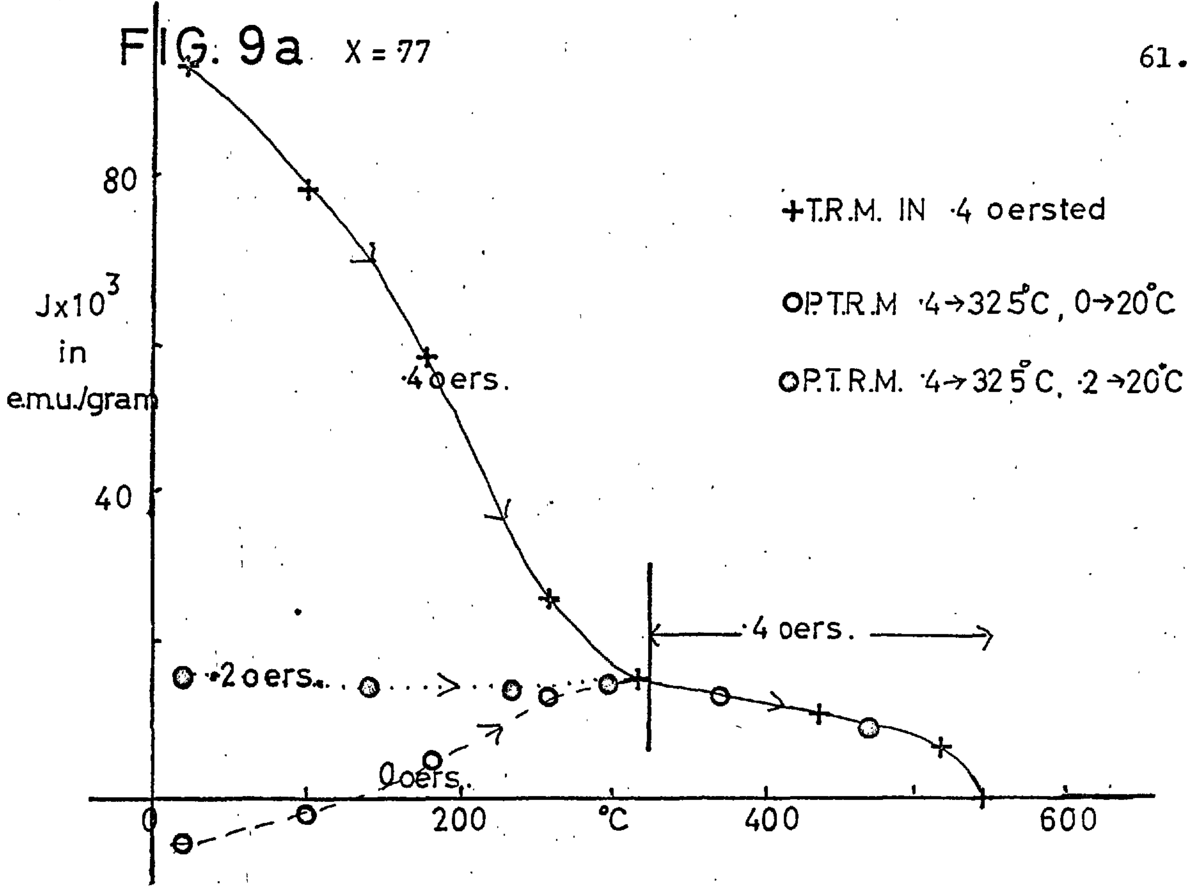


FIG. 9b X = ·57

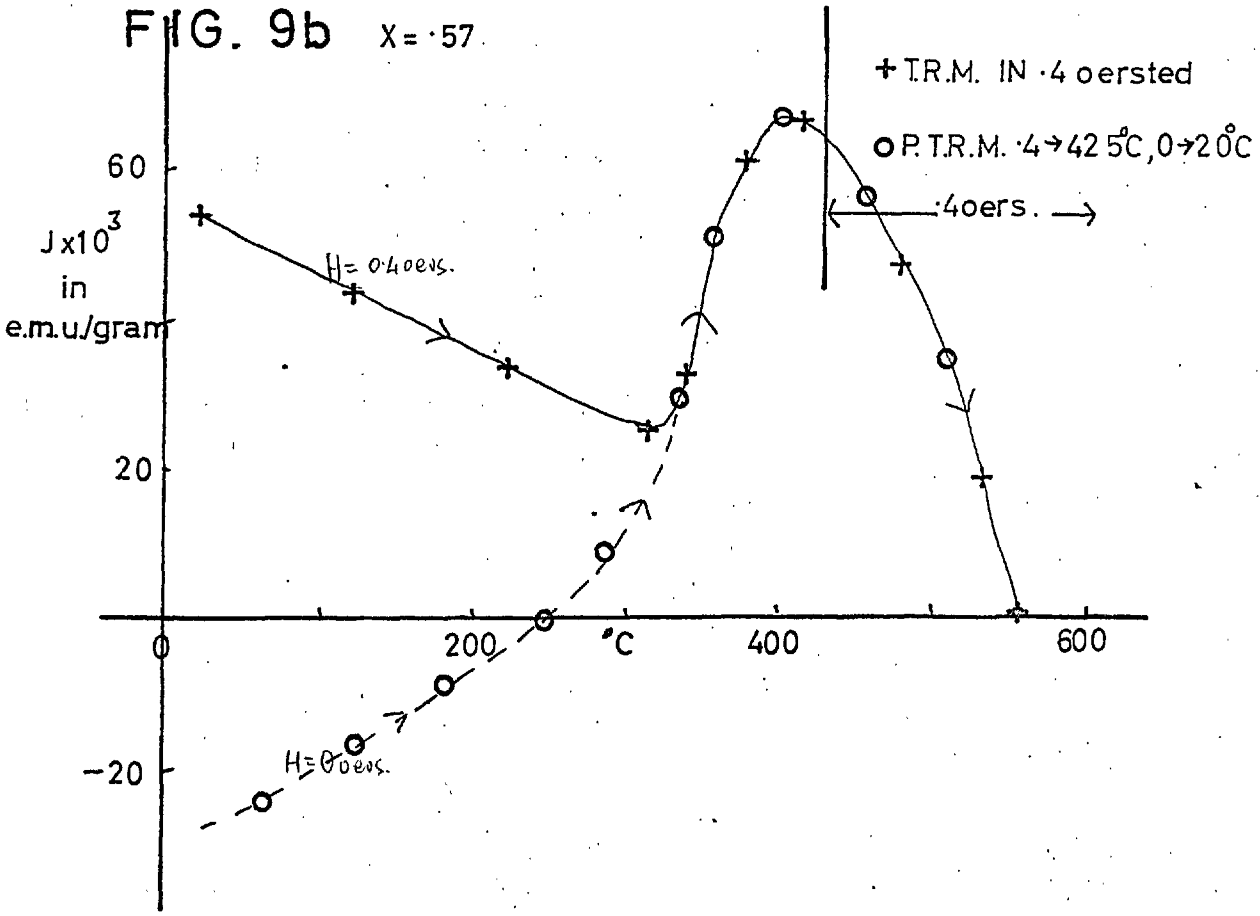
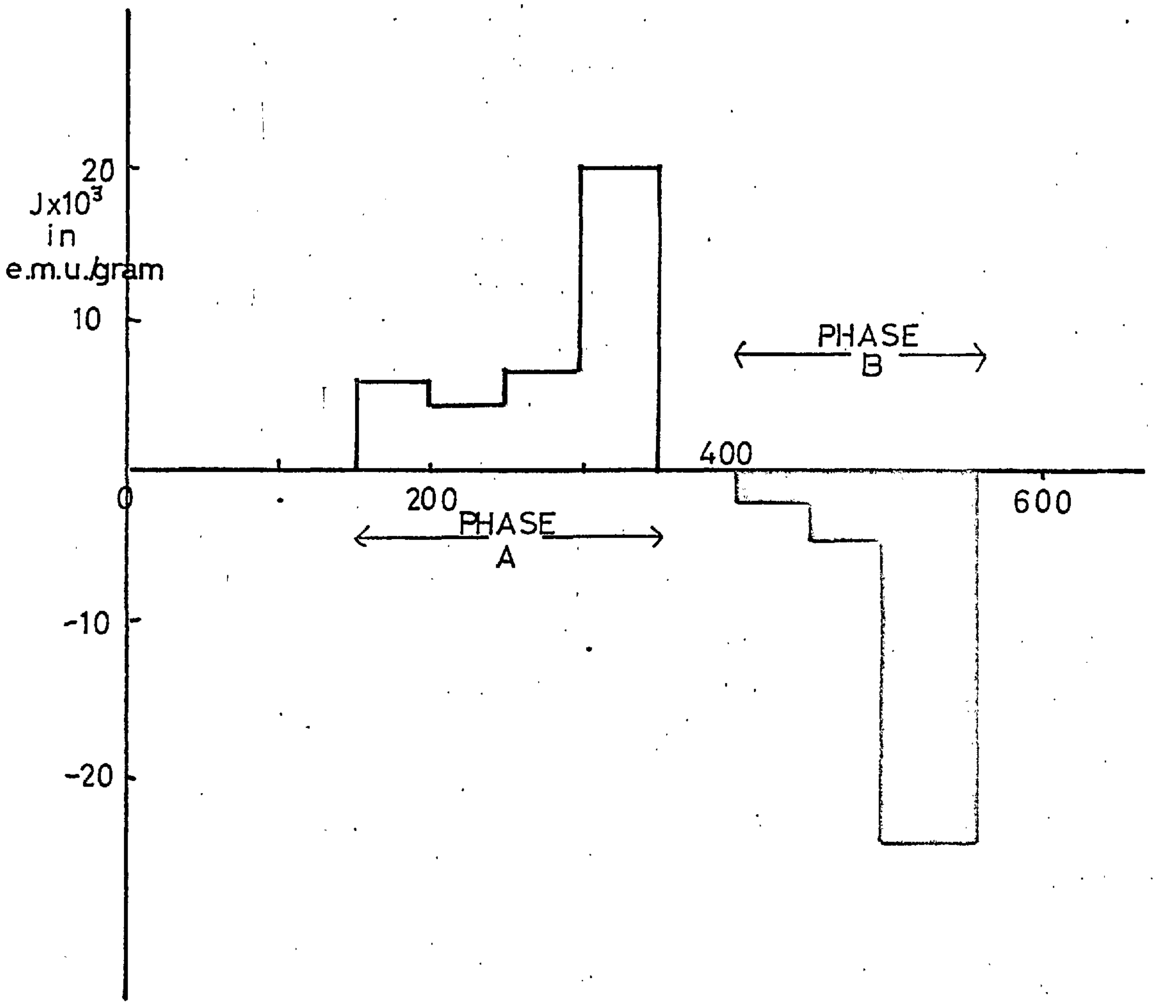


FIG. 10

$J_{P.T.R.M.}$ AT 20°C FOR ·4 oersted APPLIED OVER REGION SHOWN

FOR X = ·57 PARTIALLY OXIDISED



T.R.M. AND P.T.R.M FOR LARGE AND SMALL GRAINS
PARTIALLY OXIDISED At 500°C for 2mins.

FIG 11a LARGE GRAINS (X= ·57)

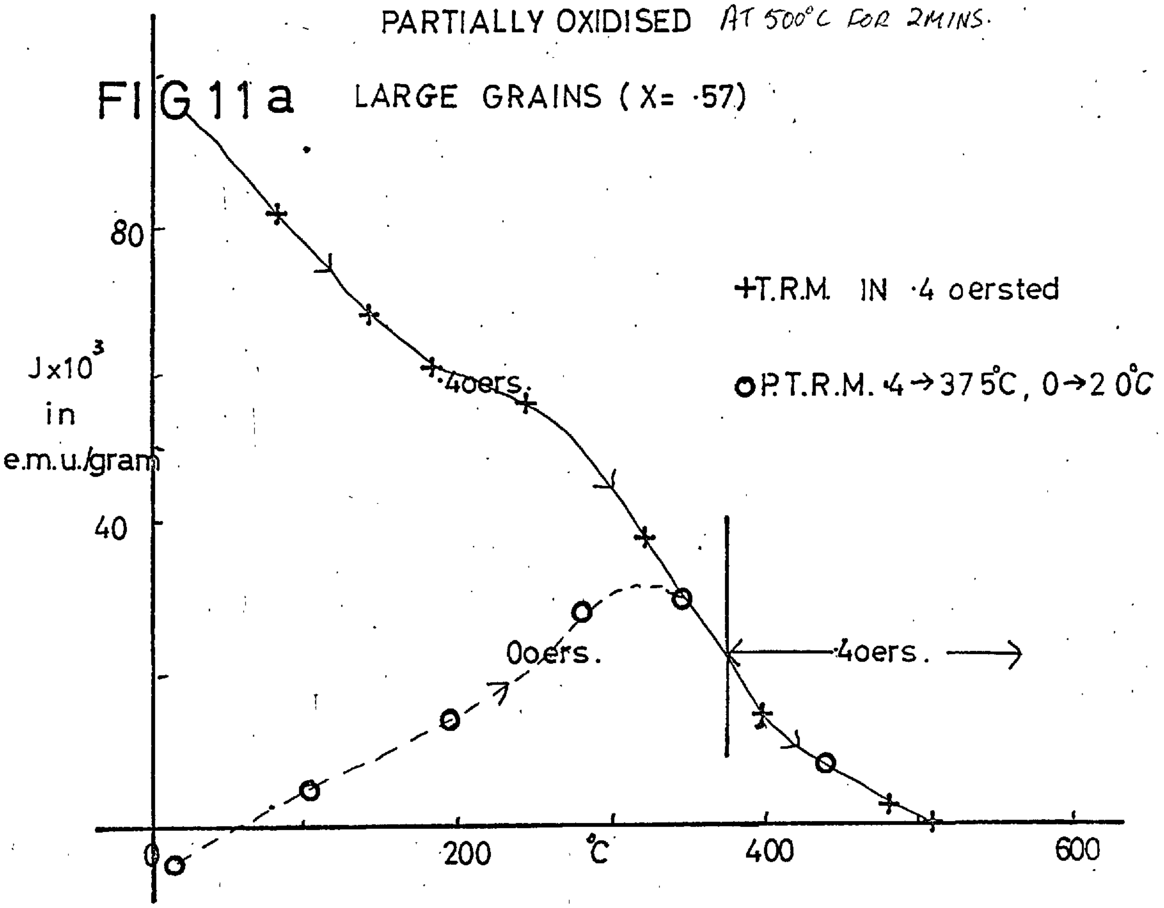
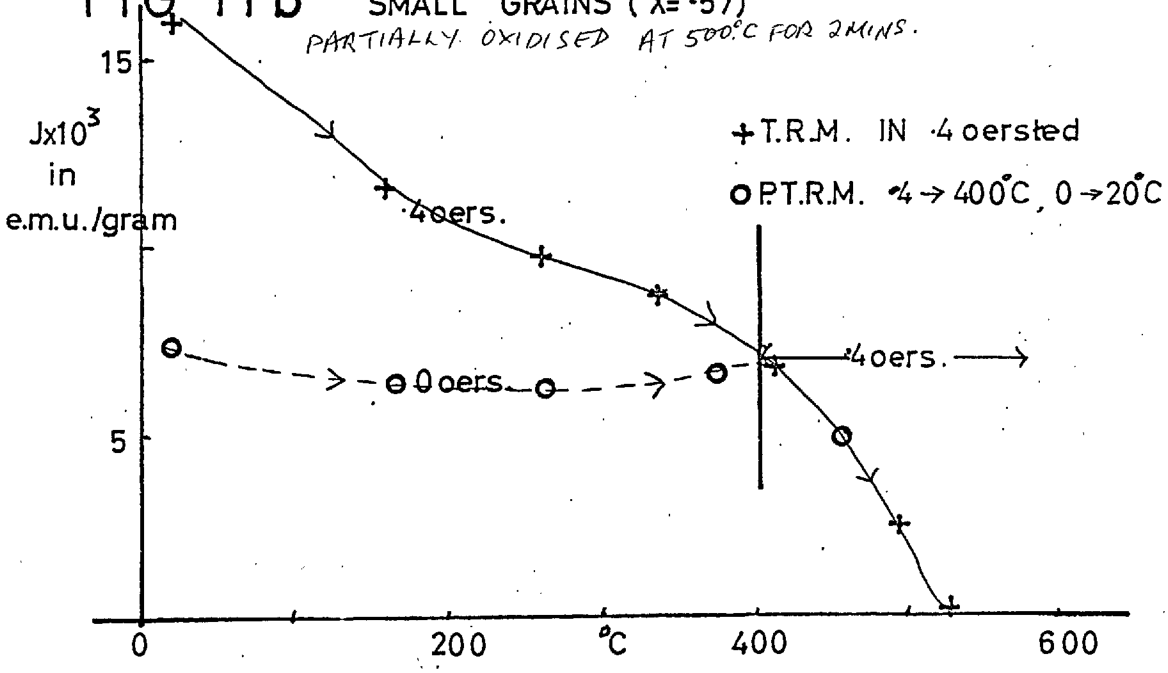


FIG 11b SMALL GRAINS (X= ·57)
PARTIALLY OXIDISED AT 500°C FOR 2MINS.



T.R.M. AND P.T.R.M. FOR LARGE GRAINS OXIDISED FOR DIFFERENT TIMES AT 450C

FIG. 12a X= ·57after 4 mins. AT 450°C

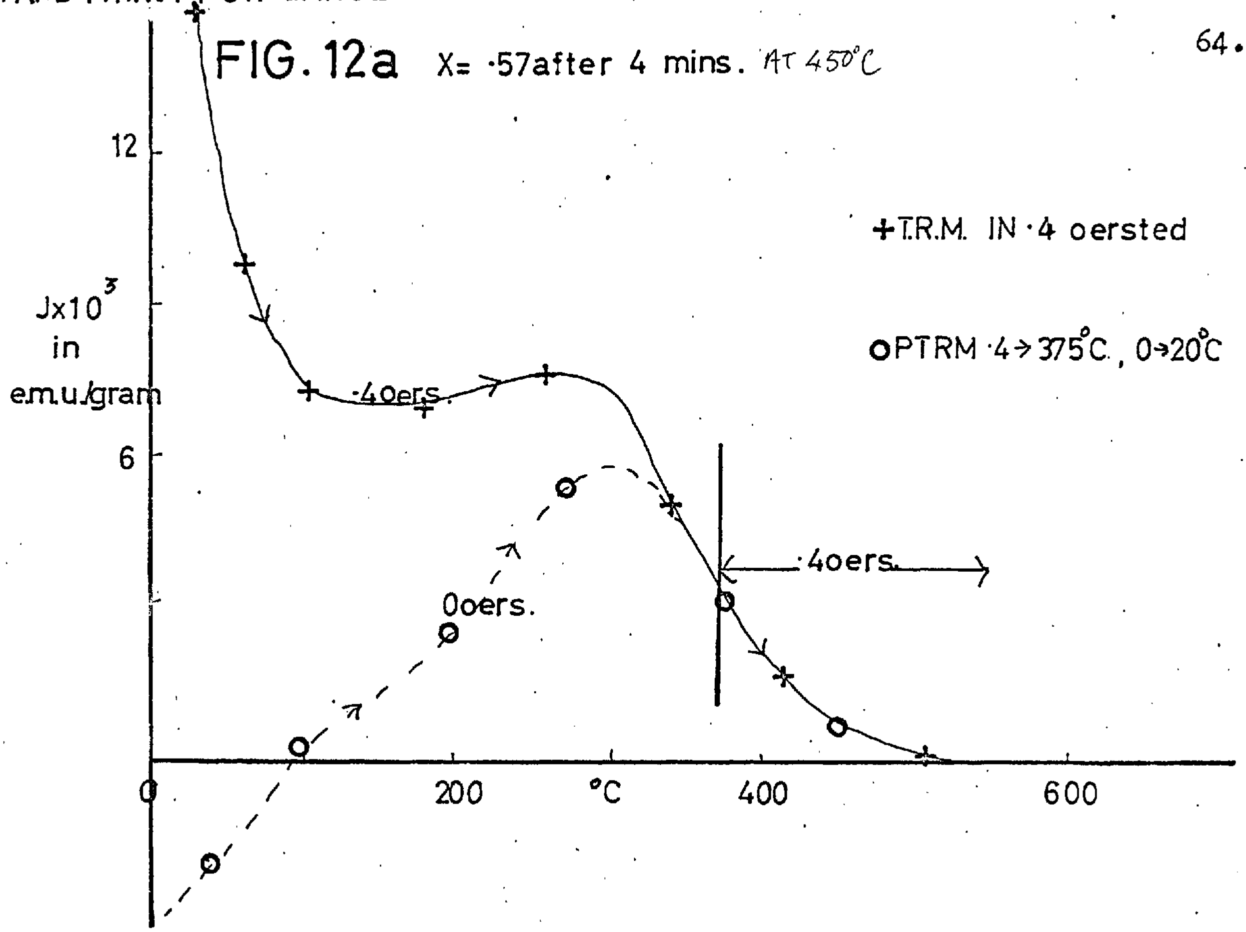


FIG 12b X= ·57 after 60 mins. AT 450°

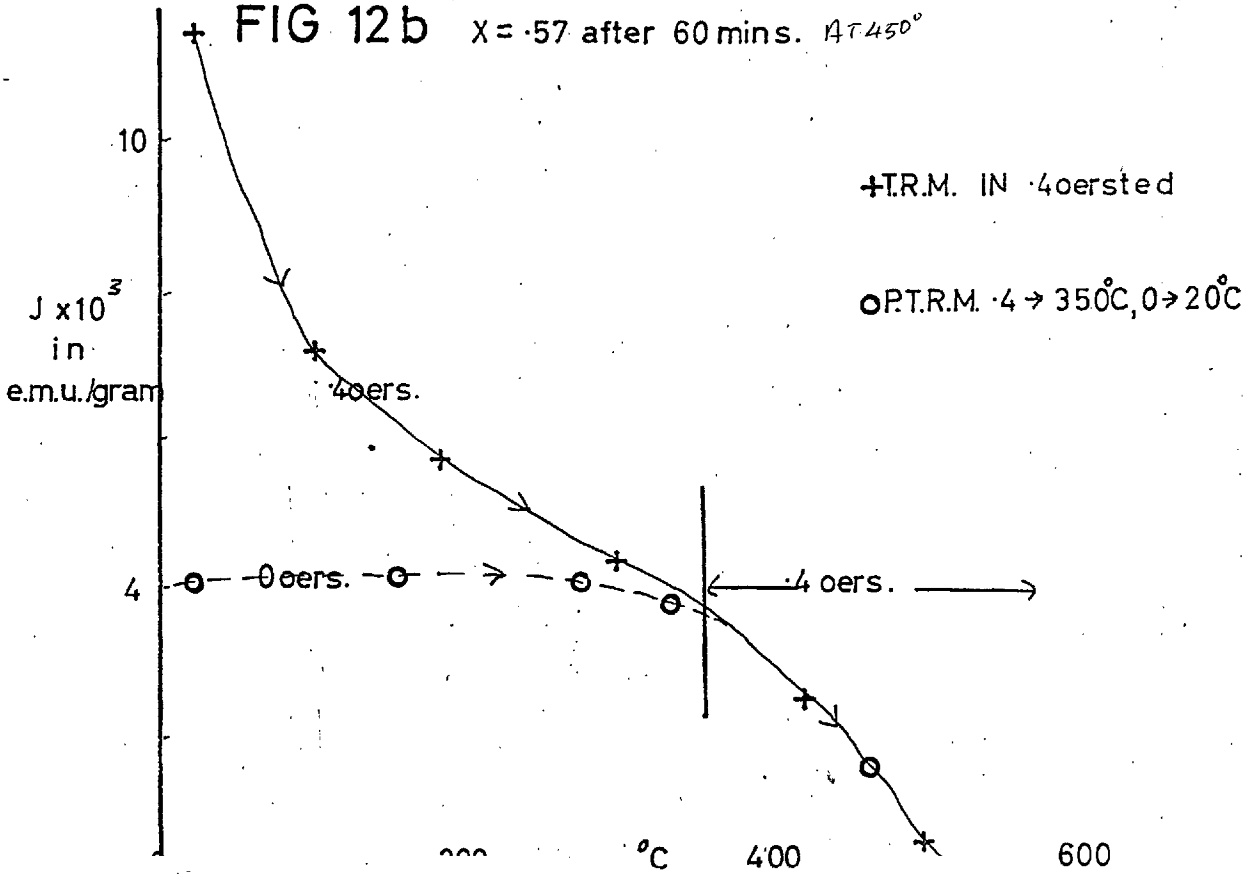


FIG. 13 P.T.R.M. AT 20°C AGAINST OXIDATION TIME AT 450°C FOR LARGE GRAINS

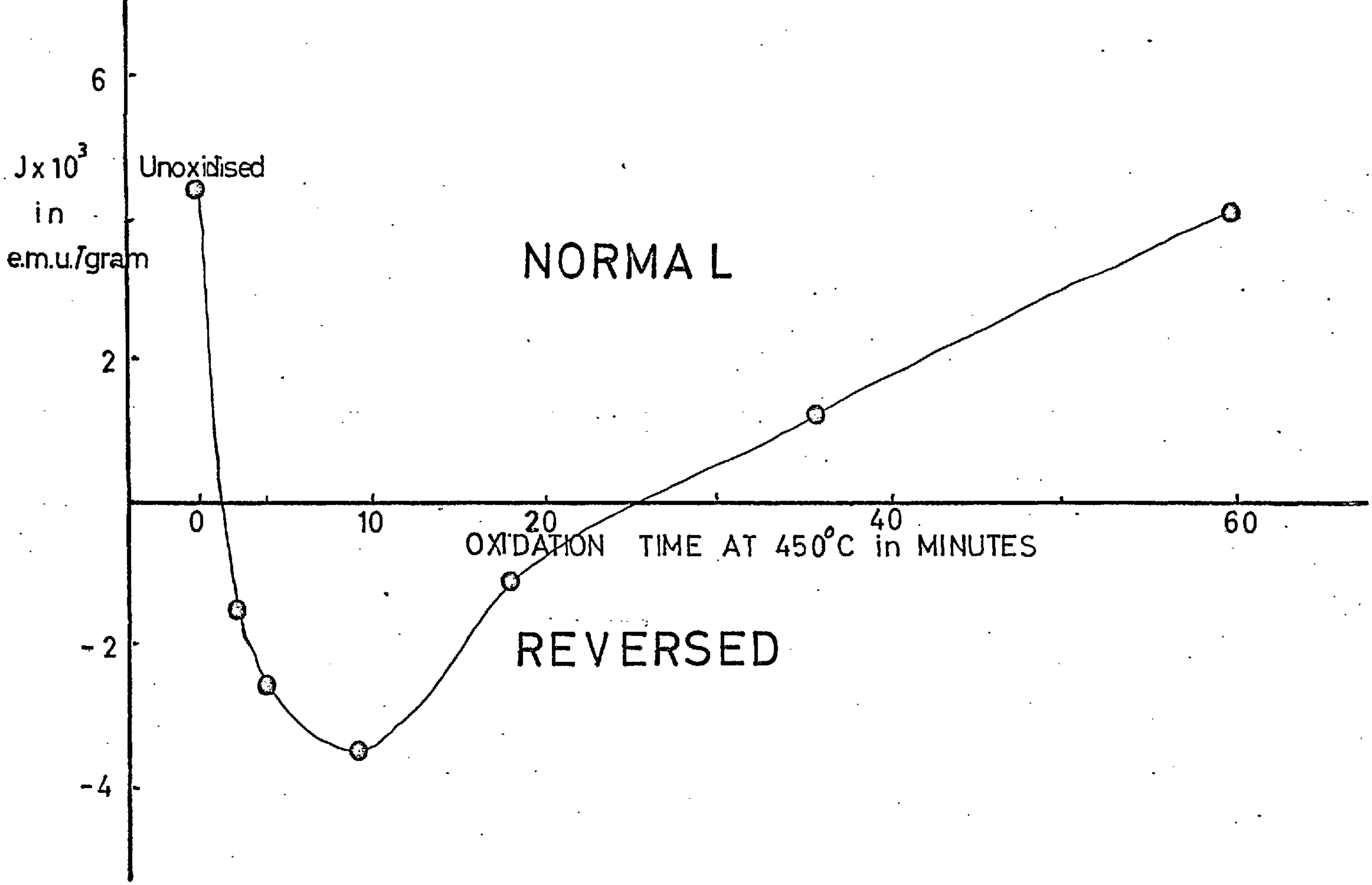


FIG. 14 $J_{P.T.R.M.}$ AT 20°C FOR ·4oersted APPLIED OVER REGION SHOWN

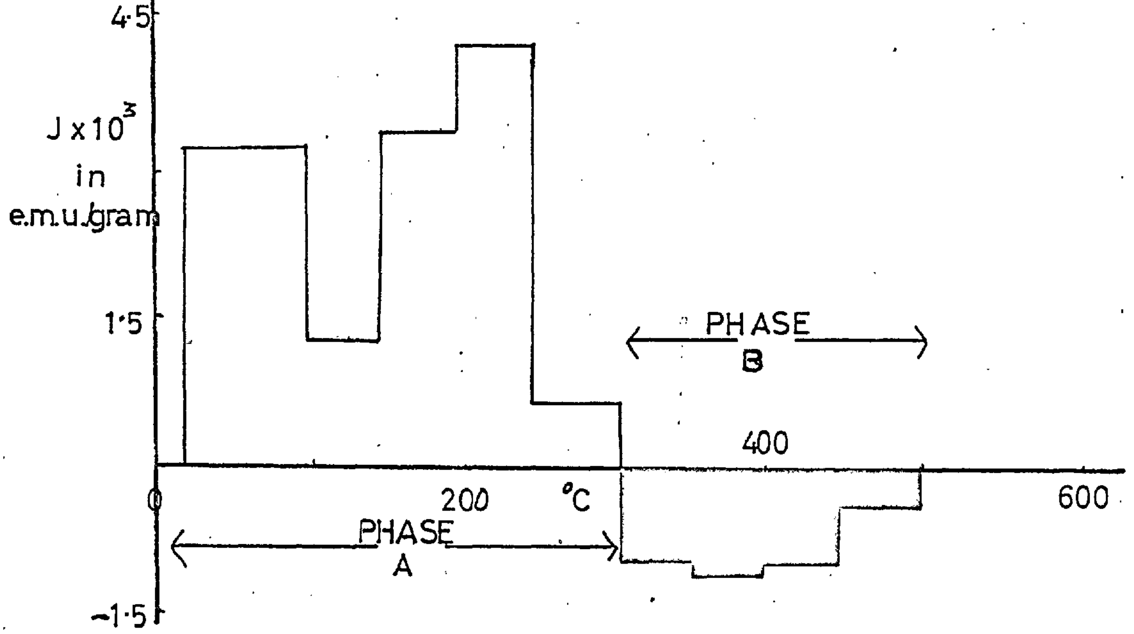
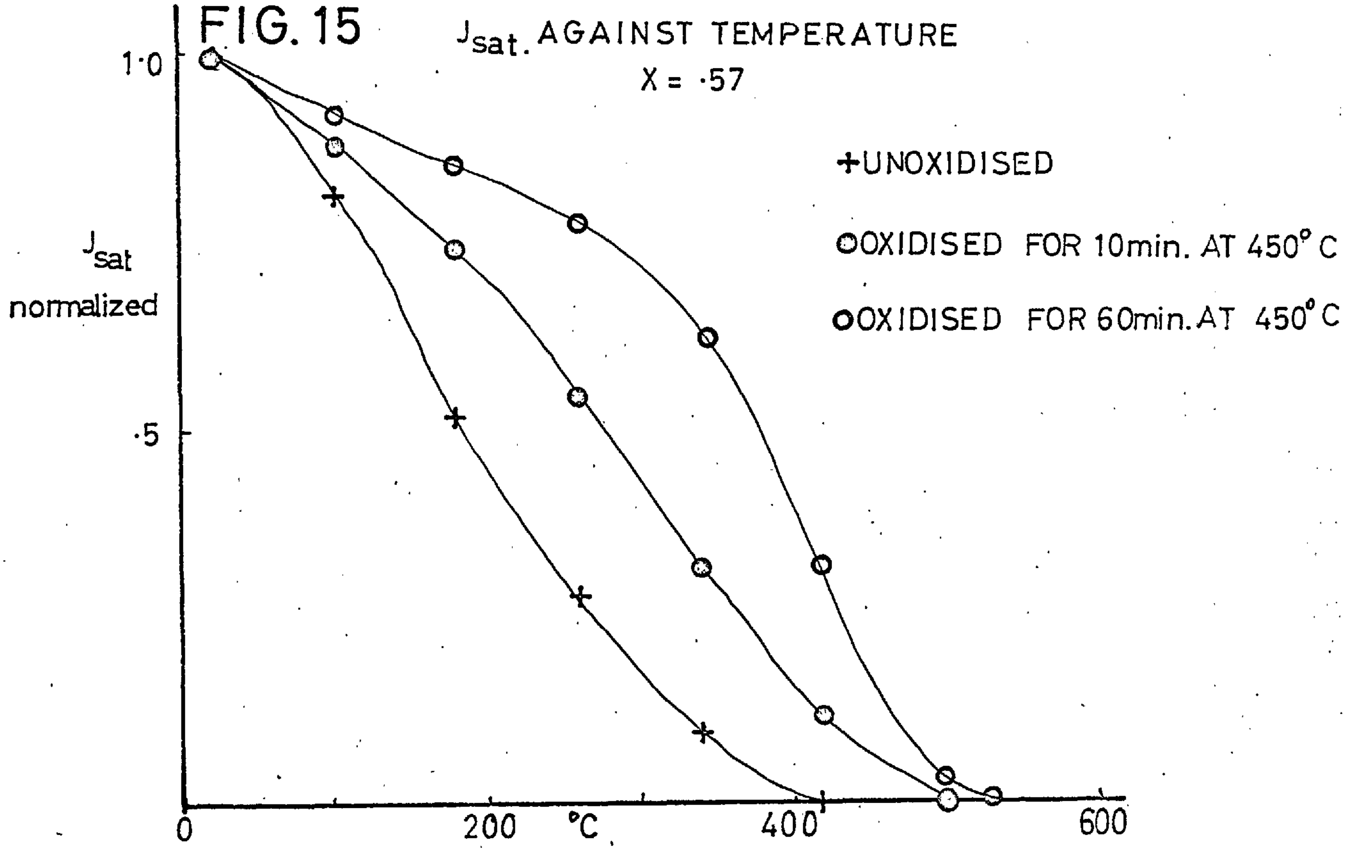


FIG. 15 $J_{sat.}$ AGAINST TEMPERATURE

X = ·57



T.R.M. AND P.T.R.M. FOR SMALL GRAINS OXIDISED FOR DIFFERENT TIMES AT 450 C

FIG. 16a X = ·57 AFTER 4 mins.

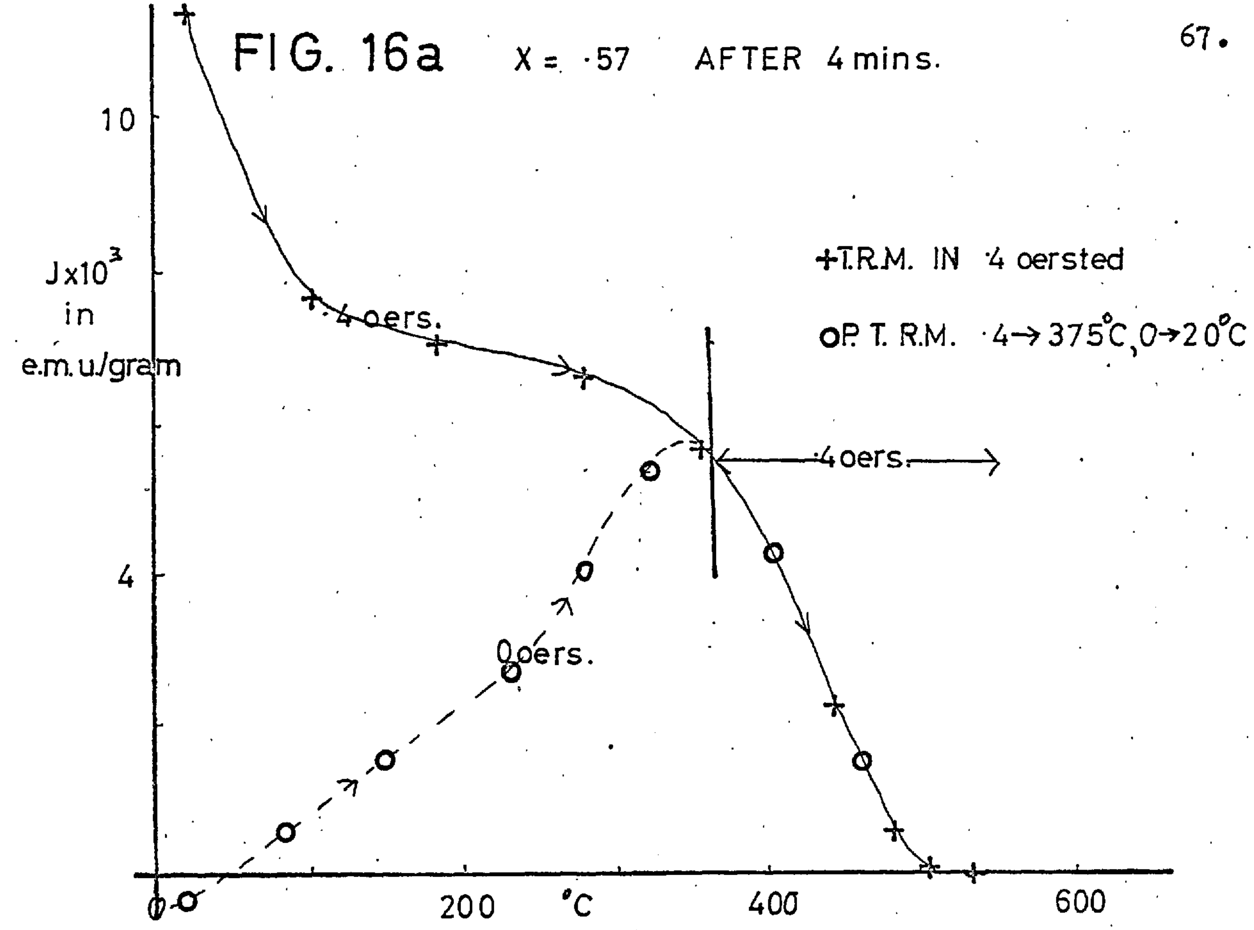


FIG. 16b X = ·57 AFTER 10 mins.

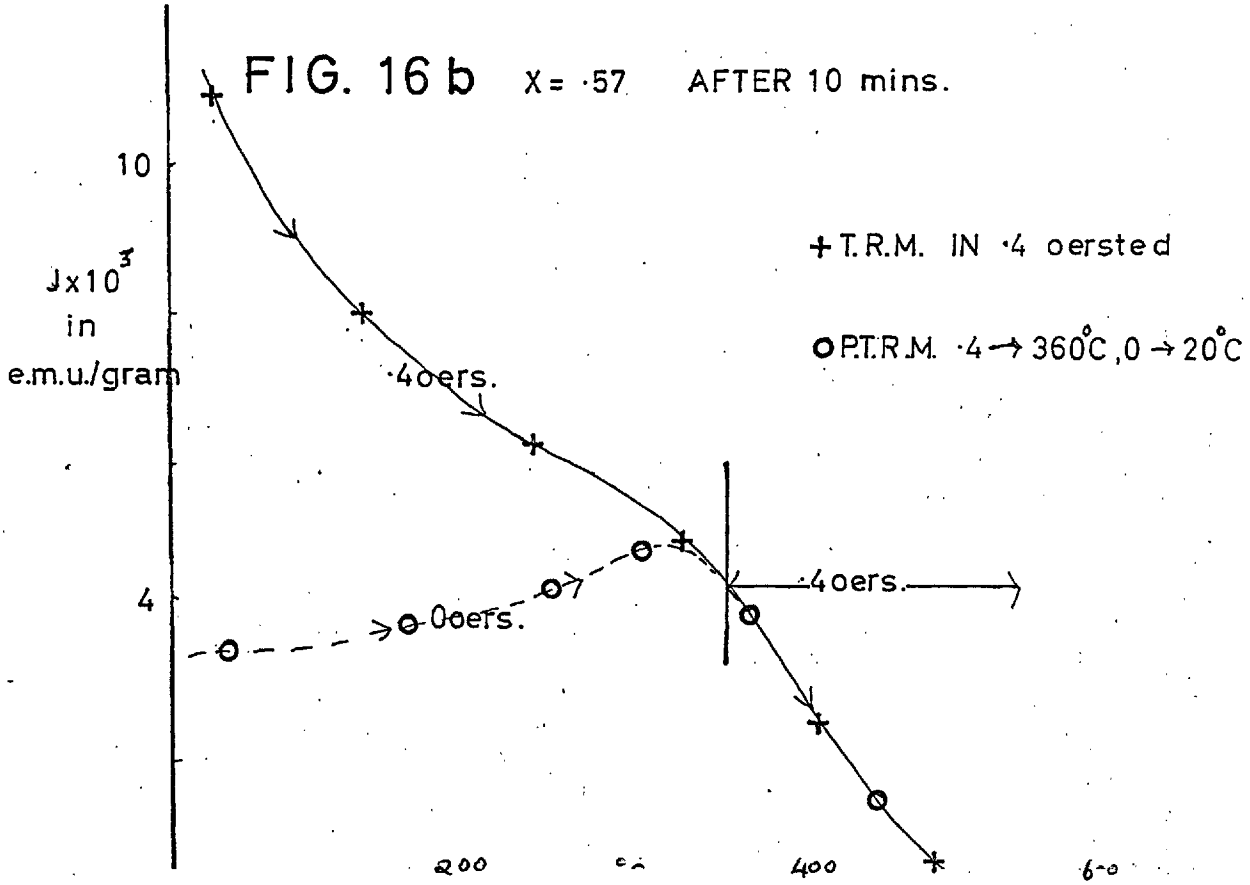
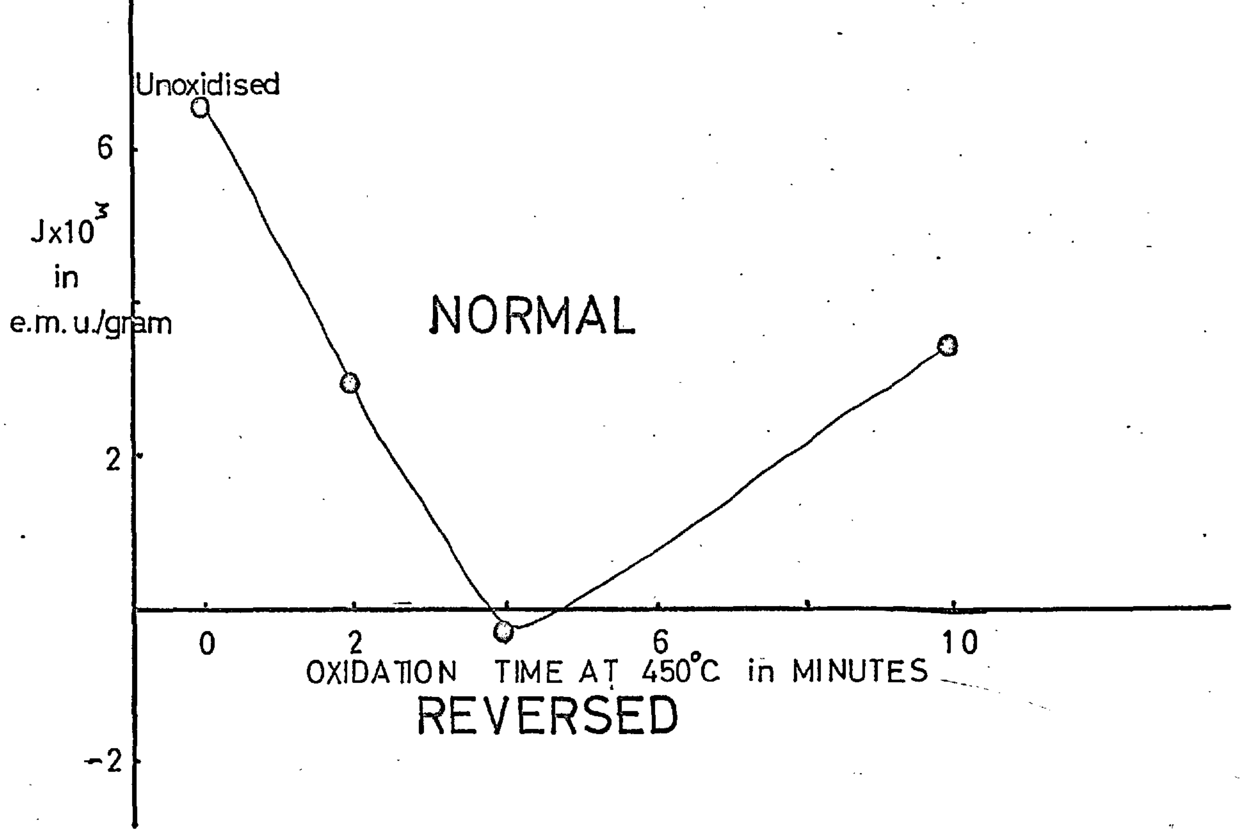


FIG. 17 P.T.R.M. AT 20°C AGAINST OXIDATION TIME AT 450°C FOR SMALL GRAINS



T.R.M. (AT 20°C) against FIELD

FIG. 19a 60% ILMENITE

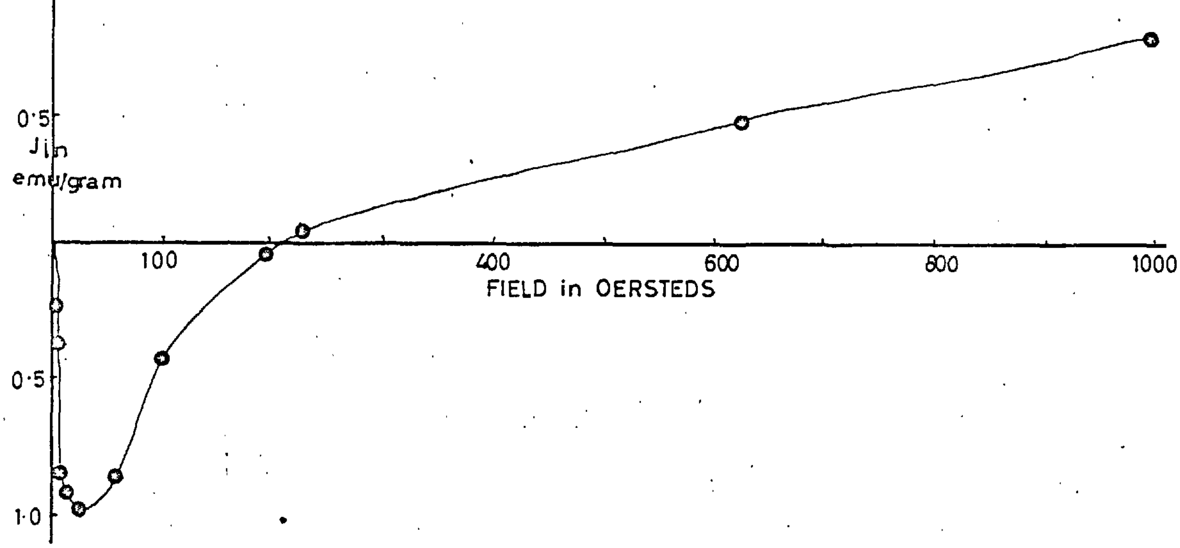
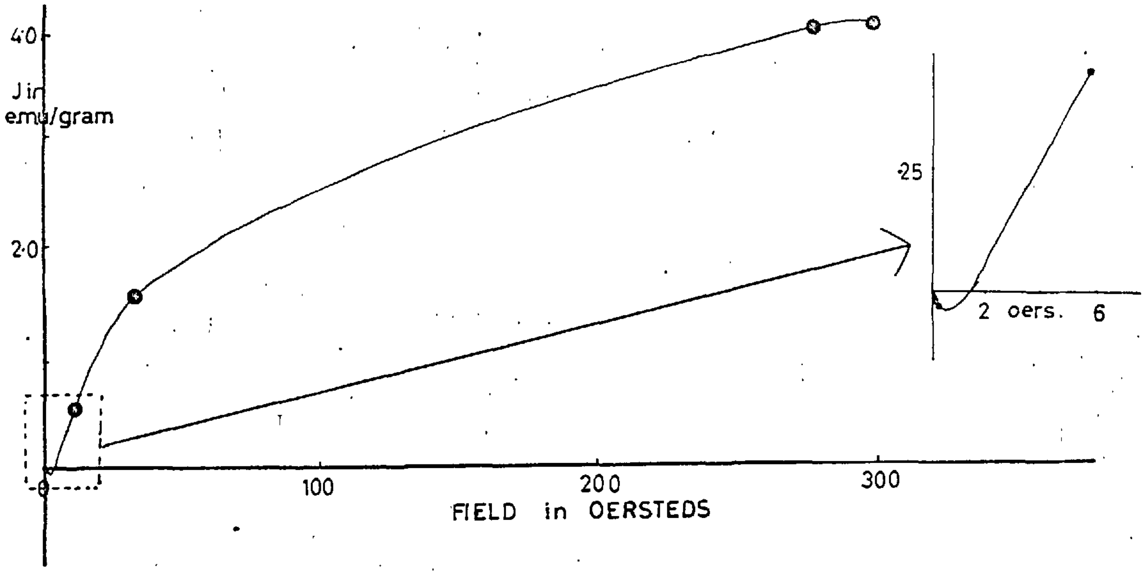


FIG. 19b 70% ILMENITE



T.R.M. FOR ILMENITE-HAEMATITE SERIES

FIG. 18a 60% ILMENITE T.R.M. IN ·4 oersted

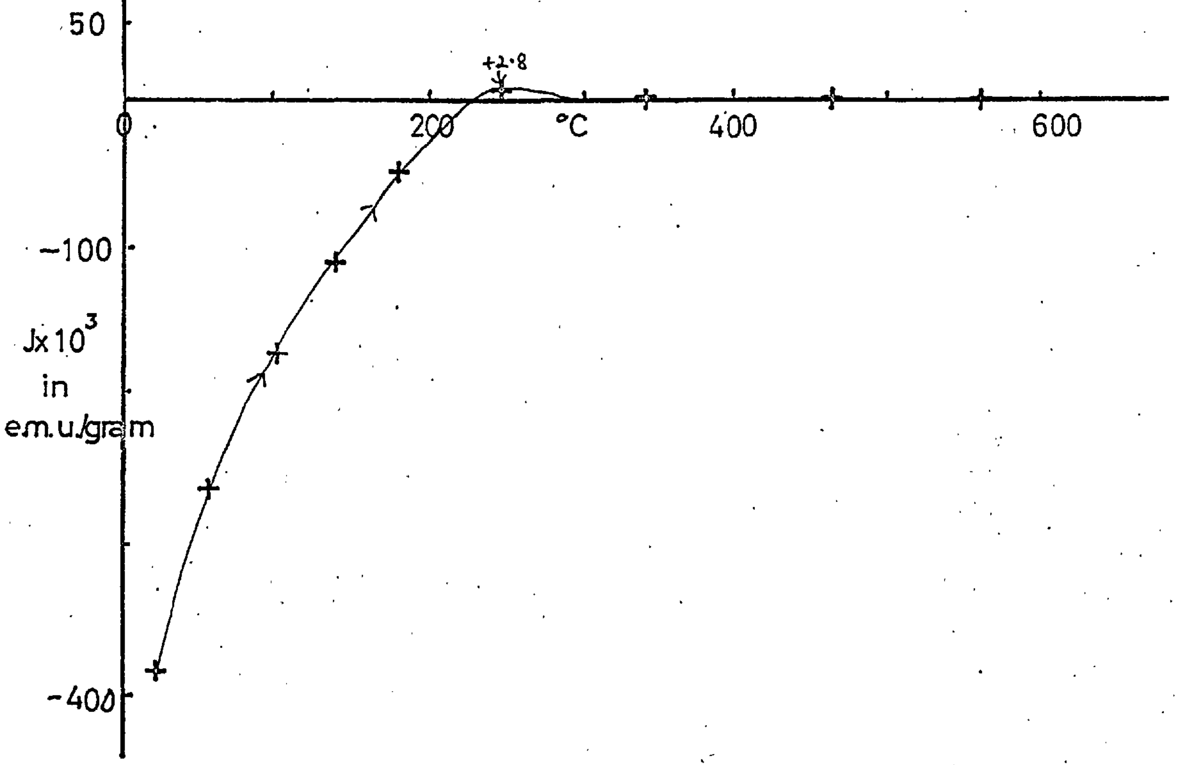
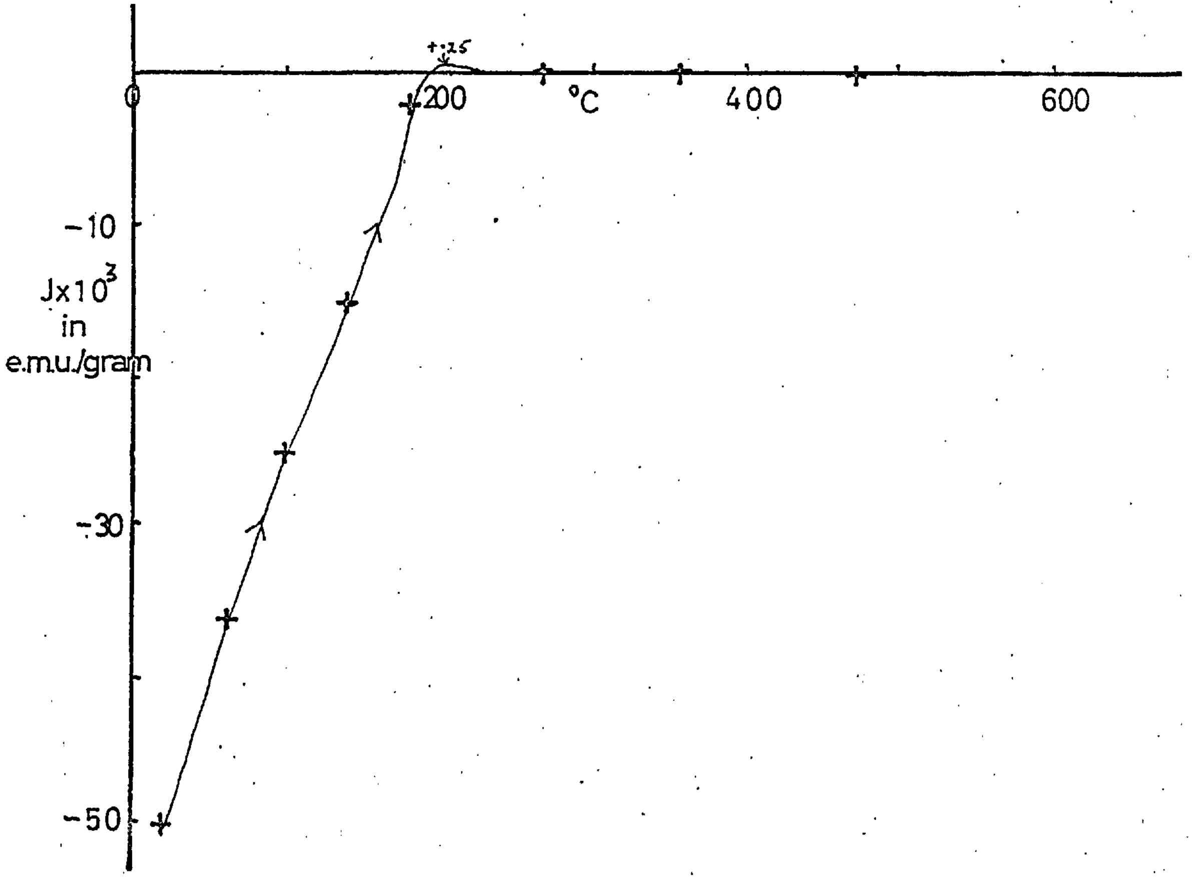


FIG. 18b 70% ILMENITE T.R.M. IN ·4 oersted



CHAPTER 5.

Theories of self-reversal applied to the ulvospinel-magnetite series

5.1. Introduction.

Now that reversal properties in generalised synthetic titanomagnetites have been found it becomes increasingly important to understand the mechanism of such an effect in order to decide whether the mechanism may be applicable to natural samples. It is very important to rock magnetism to decide whether a rock is self reversed or reversely magnetised by field reversal. The reports by Wilson[54] et al of a correlation between reversed and altered rock emphasises the importance even more.

Many theories have been suggested to account for self reversing rocks and there will now be reviewed and their applicability to the oxidised titanomagnetites discussed.

5.2. Neels two component models.

Neel[9] put forward in 1951 possible mechanisms for a two component system A and B to have a reversed magnetic moment.

1. The two magnetic materials A and B have curie points T_A and T_B with $T_B > T_A$ and are closely attached in layers or some other similar geometrical arrangement. Cooling through T_B in a field H produces a moment in B only and if the two components have a negative interaction a back field is set up on A. At T_A this may exceed the applied field H and A acquires a negative moment. Providing the room temperature value of J_A is greater than J_B the nett result is a reversed T.R.M. Fig. 20 shows the required curves for A and B to produce a reversal.

2. J_A need not exceed J_B but chemical action can remove part of J_B again leaving the nett moment negative.

3. Again J_A is less than J_B but B loses magnetic ions and gains non-magnetic ones.

4. After formation of J_A chemical action produces another magnetic mineral J_B which becomes magnetised in a nett negative field due to A and the applied field. When A has disappeared B remains reversely magnetised and no trace of a reversal mechanism remains.

All except number 3 have been found to exist. A theory based on a mixture of number 1 and 4 seems to lend itself in many respects to the case of oxidised titanomagnetites and a model on these lines will be discussed later.

5.3. Neels N type.

The interaction due to two sublattices of the same material can cause reversal of the thermal remanence under the right conditions. Physically the theory can be described as two lattices with the same curie point but different thermal demagnetising curves, one rising sharply and levelling out at room temperature and one rising steadily to room temperature as in Fig. 21. The sum gives a negative room temperature moment. To find the applicability a closer look at the theory is needed. Neel found a family of curves critically dependant on the ratio $\frac{x_A}{x_B}$ where x_A and x_B are the amounts of ions on each lattice. Defining α as the ratio of the interaction between AA and AB sites and β the ratio between BB and AB sites the family of curves and their dependance on β and α were found. The reversing region shown in Fig. 22 lies between $\frac{x_A}{x_B} = 1$ and $\frac{x_A}{x_B} = \frac{1+\beta}{1+\alpha}$. It is possible for a change in the ratio of $\frac{x_A}{x_B}$ to cause a self reversal but in practice α and β are small and so only a very limited region, the N region shows reversals. Although this mechanism has been found in ferrites it does not seem applicable to the results of Chapter 4.

5.4. Reversal by exsolution.

Neel[55] also considered the effect of slow exsolution of a second magnetic phase B from a magnetic phase A. B will become magnetised under the influence of A with A's demagnetising field probably having greatest effect. Thus given suitable conditions a reversed moment can be produced. But if exsolution takes place in particular planes other forces such as Weiss-Heisenburg forces can have a great influence and for small intergrowths the local demagnetising field can be large.

Exsolution does occur in the magnetite ulvospinel series and the ilmenite-haematite series but only very slowly below 600°C. In the oxidised region exsolution has been suggested by Phillips and Ponillard but little is known about exsolution in this area. The oxidation curves of Chapter 4 do not however seem to indicate any exsolution pheomena and as the temperature of exsolution is much higher than the oxidation temperatures used this mechanism is again unlikely to explain the R.P.T.R.M.

5.5. Ionic ordering.

Verhoogen[10] has discussed the possibility of reversal due to ionic ordering. Verwey[56] et al have shown that certain ions have preference for certain sites. The reason for this is not understood but the results show there is increasing affinity of B sites in the series

Fe^{3+} Fe^{2+} Mg^{2+} Al^{3+} Ti^{4+} Ni^{2+}

prefer A sites   prefer B sites

At high temperatures a random distribution is obtained and by quenching to room temperature this is preserved. If ionic ordering takes place reversal of the magnetic moment can take place in samples having a mixture of iron and nonmagnetic ions. Ionic ordering is complete at 0°K and at intermediate temperatures the distribution for a molecule of the type MFe_2O_4 is given by

$$\frac{x(1+x)}{(1-x)^2} = e^{-E/kT}$$ where x is the °/o of one

component and E the energy required to interchange two ions. A proof is given in Appendix 3. Also the rate of ordering has to be considered and it was found that for most ions the rate was given by the diffusion equation

$$D(\text{cms./sec}) = D_o e^{-E/kT}$$

D_o 10^2cms./sec. and E is about 80 cals./mol. This means ordering takes place in 2 days at 500°C and

3×10^4 years at 300°C. The exception is the ordering of Fe^{2+} with Fe^{3+} which only needs an electron transfer.

The generalised formula for a cubic magnetic mineral is $Fe_a^{2+}\ Fe_b^{3+}\ M_c^q\ O_4$ where M is either a nonmagnetic ion~~s~~ or a ~~and~~ vacanc~~ies~~y.

Also $a+b+c = 3$

and $2a+3b+qc = 8$ (charge conservation).

Take $\mu(Fe^{3+})=5$, $\mu(Fe^{2+})=4$

In disordered state

A sites	B sites
$Fe^{2+}_{a/3}\ Fe^{3+}_{b/3}\ M^q_{c/3}$	$[Fe^{2+}_{(2/3)a}\ Fe^{3+}_{(2/3)b}\ M^q_{(2/3)c}]\ O_4$

Nett moment $\mu = \dfrac{4a+5b}{3}$

In the ordered state at 0°K there are two cases to consider

1. $b \geq 1$		2. $b \leq 1$	
A	B	A	B
Fe^{3+}_1	$[Fe^{2+}_a Fe^{3+}_{b-1} M^q_c]O_4$	$Fe^{3+}_b F^{2+}_{1-b}$	$[Fe^{2+}_{a-1+b} M^q_c]O_4$
Moment $\mu = 4a+5b-10$		$\mu = 4a+3b-8$	
μ is negative if $10>4a+5b$		μ is negative if $8>4a+3b$	
Restriction on c $c > \dfrac{2+b}{4}$		Restriction on c $c > \dfrac{4-b}{4}$	
But $b > 1$ $\therefore$ $c \geq .75$		But $b \leq 1$ $\therefore$ $c \geq .75$	

Thus c must be $\geq .75$ for a reversal to take place.

Restriction q

$$2a+3b+qc = 8$$

$$a+b+c = 3$$

$$\therefore \quad c = \frac{2-b}{q-2}$$

Upper limit

$b \geq 1$	$b \leq 1$
$c \geq \frac{2+b}{4}$	$c \geq \frac{4-b}{4}$
$\therefore\ q \leq \frac{12-2b}{b+2}$	$q \leq \frac{16-6b}{4-b}$
But $b > 1$ $\quad q \leq 10/3$ for $b=1$	$b \leq 1\ \therefore q \leq 10/3$ for $b=1$
≤ 2 for $b \to 2$	≤ 4 for $b = 0$

The lower limit is $q \geq 2$

Thus for example $Mg^{2+}Fe^{3+}_{2}O_4$ $(Li^{1+}_{.5}\ Fe^{3+}_{2.5}O_4)$ cannot self reverse but $Fe^{2+}Fe^{3+}Al^{3+}O_4$ can self reverse.

Fig. 23 shows a diagram of q against c and the reversing region is clearly shown and also some of the main series known. Curves of constant μ for ordered and disordered states have been drawn. It is seen that oxidised titanomagnetites fall into the reversing region for $x > .5$. This is seen more clearly in Fig. 24 where x is plotted against the total ordered moment for different degrees of oxidation. (Proof is given in appendix 2). With $x > .5$ reversal due to ionic ordering can occur in an oxidised titanomagnetite. Another interesting possibility is the oxidation of a titanomagnetite with $x > .5$ at a temperature where ionic ordering proceeds at the same rate as the oxidation. This is following the line AB in Fig. 24 in the diagram. Under these conditions a reversal of the moment can occur.

Since ionic ordering takes days even at 500° the process does not seem to explain the mechanism in Chapter 4 as the reversals can be produced at much lower temperatures. Gorter has shown that this phenomena occurs in $\mathrm{NiFeA\ell O_4}$ and this mechanism may be of considerable importance in reversal of igneous rocks where they have been cooled fairly rapidly to temperatures around 300°C and cooled over thousands of years to room temperature.

5.6. Order and Disorder.

Two ordering parameters can be defined

Long range order parameter s

$$s = \frac{(\text{No. A's on A site in state } s) - (\text{A's on A sites when randomly ordered})}{(\text{No. A's on A sites when perfectly ordered}) - (\text{A's on A sites when randomly ordered})}$$

$s \rightarrow 1$ for perfect order and $s \rightarrow 0$ for random (disordered) state.

Short range order parameter

$$= \frac{q(\text{in state } s) - q(\text{random})}{q(\text{ordered}) - q(\text{random})}$$

where q is the fraction of nearest neighbours of opposite type.

During oxidation it seems probable (from x-ray photographs) that the crystal lattice undergoes a great deal of disordering. Interactions between ordered and disordered states cannot be ruled out when considering the interaction in Chapter 4.

5.7. Magnetostatic interaction.

Stacey[57] has put forward arguements to show that magnetostatic interactions between multidomains and single domains with two different minerals A and B cannot produce a reversed T.R.M. But in many cases the two components A and B have a large spread of curie points and other properties due to oxidation or compositional differences and mean values must be used.

Let A have the low curie point. In a field H at the mean blocking temperature of B the moment is $\frac{H}{\overline{N}_B}$

where $\overline{N}_B$ is the mean demagnetising factor. At A's blocking temperature the moment of B has increased by a factor $\overline{R_{AB}}$ and exerts a reversed field on A due to the mean negative interaction coefficient $\overline{N_{AB}}$, equal to

$$\frac{-f_B}{} \frac{H\,\overline{R_{AB}}\;\overline{N_{AB}}}{\overline{N}_B}$$ where f_B is the fraction of constituent B and f_A is similarly the fraction of A.

The moment at room temperature is

$$Hf_B\left\{\underbrace{\frac{\overline{R}_B}{\overline{N}_B}}_{1.} - \underbrace{\frac{f_A\overline{R}_{AB}\overline{N}_{AB}}{\overline{N}_A\;\overline{N}_B}}_{2.} + \underbrace{\frac{f_A\overline{R}_A}{f_B\overline{N}_A}}_{3.}\right\}$$

1. is due to H on B
2. is due to the reversed field of B on A
3. is due to H on A.

The following assumptions can be made

$\overline{R}_B \sim \overline{R}_{AB} \sim \overline{R}_A$ and $\overline{N}_A \sim \overline{N}_B$ and $f_A \sim 2f_B$

Then the moment is $Hf_B\left\{\underbrace{1}_{1.} - \underbrace{\frac{2}{3}\frac{\overline{N_{AB}}}{\overline{N}_B}}_{2.} + \underbrace{2}_{3.}\right\}$

With $\overline{N}_{AB}$ just greater than $\overline{N}_B$ then the P.T.R.M. can reverse but the T.R.M. will not do so, needing an interaction three times as strong to cause reversal of the T.R.M.

This mechanism seems to be applicable to the case of the oxidised titanomagnetite grain but the interaction may be due to some effect other than magnetostatic interaction.

5.8. Exchange anisotropy.

Another form of coupling between two adjacent components which can cause reversal is exchange anisotropy. Here one of the components is antiferromagnetic and one ferro- or ferrimagnetic. The large anisotropy field of the antiferromagnetic can influence the ferrimagnetic and fix its spin directions and hence its direction of magnetisation. This type of interaction can be recognised by a sin θ term appearing in the torque curve and a shift along the H axis of the B-H hysterisis loop. Jacobs[58] et al give an account of the effect first discovered in a Cobalt - cobalt oxide system and Banerjee[35] claims to have found this effect in some Irish rocks. It seems unlikely to produce results similar to those in Chapter 4.

5.9. Other interactions.

Due to the fact that both iron and titanium lie in a transition series in the periodic table the crystal chemistry of their compounds and changes with oxidation is extremely complex. Under certain conditions quantum exchange interactions can be set up and these are almost certainly the cause of the reversals in the ilmenite-haematite series near 60°/o ilmenite. Local demagnetising fields can be set up and can be very large and crystal fields can influence the direction of spins of neighbouring ions. Little information is available on this complex subject however.

5.10. Probable mechanism causing the R.P.T.R.M.

Now that the different reversal mechanisms and interactions have been reviewed it is possible to discuss the most probable mechanism causing the R.P.T.R.M. of synthetic titanomagnetite. The results of Chapter 4 showed that two magnetic components were present in the partially oxidised sample showing a R.P.T.R.M. but only one in the initially unoxidised and final highly oxidised samples. This suggests some transitional state of partial oxidation is probably the origin of the interacting components providing the R.P.T.R.M. Since small grains do not show this effect as markedly as large grains the mechanism of oxidation most likely depends on grain size.

Different chemical mechanisms of oxidation of magnetite depending on grain size have been found by Egger[59] but the maximum grain size investigated was only a few microns and here the grain sizes are of the order of 100 microns. Fig. 25 shows a possible model of the magnetic moments in a large grain and shows five hypothetical stages of initial oxidation. Variation of curie point across the grain, blocking temperatures, T.R.M., P.T.R.M., and P.T.R.M. spectra are also shown for the five stages.

Stage 1. The grain is uniform in composition and its P.T.R.M. is uniformly magnetised in the direction of the applied field H. There is only a slight range of blocking temperatures, (due to different grain sizes and composition) and a corresponding narrow and low P.T.R.M. spectrum.

Stage 2. Oxidation, causing vacancies in the lattice has taken place slightly on the periphery of the grain and a higher curie point is seen on the edge of the grain. Near the edge there is a back field set up by the oxidised region B as shown in Fig. 25b. Thus the moment is reversed in the region near the oxidation boundary but still only influenced by H in the interior. Thus the T.R.M. is normal but has a maximum in the heating curve because of the negative interaction between the oxidised region B and its neighbouring unoxidised region A. The P.T.R.M. is also normal because the oxidised periphery has a larger moment than reversed region which experiences a back field.

Stage 3. Further oxidation has taken place and has given a curie point distribution as shown in Fig. 25c. The interaction has increased and the region affected by the back field increased. The T.R.M. is still positive because the reversed region (in a reversed field of $H_{back} - H_{applied}$) has a moment less than that from the oxidised region in the field H. As the curie temperature of the oxidised region B has risen and is spread out the maximum now tends to appear as an inflexion in the heating curve at intermediate temperatures. The P.T.R.M. is now reversed because the moment of A region in the back field of B is greater than the moment of B in $H_{applied}$. The P.T.R.M. spectrum shows this and also that below a certain temperature only a normal component is seen because the oxidising region causing the back field now has no moment, the field being applied below its curie point.

Stage 4. The majority of the grain is now oxidised but there is still a low curie point in the centre of the grain and this region experiences a back field. The T.R.M. is normal with little sign of the inflexion at intermediate temperatures and the P.T.R.M. no longer reverses but still falls on cooling below T_1, showing a slight negative interaction between A and B still exists.

Stage 5. The grain is now completely oxidised and a fairly uniform high curie point exists throughout. Only one component B is now present and the T.R.M. decreases regularly with temperature. The P.T.R.M. is similar to the T.R.M.

The mechanism is very similar to a combination of Neel's first and fourth mechanism, which have an A.B. negative interaction and oxidised samples in the field of the unoxidised region. Here the unoxidised region is in the field of the oxidised region. The interaction is of the order of 0.2 oersteds for Hext <0.5 oersteds. The mechanism is not very dependent on composition and an extreme limit of quantum exchange, similar to that found in the ilmenite haematite series seems unlikely. Magnetostatic interaction between regions of varying curie points due to varying degrees of oxidation or between a metastable oxidised state and a highly oxidised state is the most probably explanation.

The latter introduces a two stage oxidation process, but the mechanism causing reversals is identical to that described. It was noticed during experiments on the oxidation of synthetic materials that as well as a component with a curie point of 500 to 550°C, a low temperature component with a curie point between 220 and 300° was formed. It is possible that instead of the process previously described, a metastable state of oxidation exists which gives rise to a curie point near 300°C for nearly all titanomagnetites with an original curie point below 300°C. A little additional energy is required to leave this metastable state and move on to a state of high oxidation and when it does acquire this addition energy the curie point quickly rises to 500-550°C, the highly oxidised level. It was noteworthy that only on very few occasions did a curie temperature between 350° and 500°C occur in the oxidation process which seems to indicate it is a little difficult to oxidise past the metastable state, but once past, it easily oxidises to a 500°C curie point.

The evidence for a metastable state of oxidation giving rise to a 300°C curie point in natural specimens is discussed in Chapter 11 together with a possible cause for the metastable state after the thermal demagnetisation of natural samples has been considered.

It is concluded that the reversal mechanism is a combination of Neel's first and fourth mechanisms between two components A and B. B the high temperature curie point component arises from the fact that all highly oxidised titanomagnetites have a 500-550° curie point, and the A component is either due to a range of curie points in grains, parts of which are oxidised to a different degree or to a metastable state of oxidation having a curie point between 220° and 300°C.

5.11. Interaction between oxidised and unoxidised regions.

The following experiment was performed in order to try and investigate the possibility of a negative interaction between oxidised and unoxidised regions. A sample with a curie point of 380°C was given a T.R.M. in a field of .4 oersted in vacuum and reheated in air, in zero field to 340° and held at this temperature. The change of moment with time was then observed and Fig. 26 shows that at first the moment increased but then fell almost to zero. The initial rise was confirmed on another sample. The new curie point was found to be 540°C.

The apparatus used was not ideally suited to this experiment as it was difficult to change the atmosphere without disturbing the sample. Interpretation of this result was also difficult but it did show that oxidising below the curie point in zero field produced some type of thermochemical magnetisation due to the internal field of the unoxidised regions. Similar more controlled experiments may prove a very useful tool in elucidating the problem of low field interactions in partially oxidised titanomagnetites.

5.12. Inference of R.P.T.R.M.

One of the main problems in rock magnetism is the problem of reversely magnetised rocks and the possibility of this mechanism existing in nature must be considered.

The important feature of this mechanism is that a single magnetic material on oxidation produces negative interactions between regions oxidised to a different degree which can cause reversals of the P.T.R.M. A rock with a magnetic constituent in the magnetite-ulvospinel series and a composition giving it a low or intermediate curie point, may be reheated in air or oxidised during formation by magmatic gases (which are shown to be important in this respect in Chapters 10 and 11). During this process the oxidised material can be influenced by the back field of the unoxidised or partially oxidised material and become reversely magnetised. The nett effect is a reversely magnetised rock, which does not show any reversal tendencies in the laboratory. This is an important fact to be considered.

The time scale for oxidation at 100°C in order to produce the reversing region can only be crudely estimated from the extrapolation of the curve of oxidising time against oxidising temperature, Fig. 27, but it appears from such an extrapolation it takes between 10 and 100 years at temperatures between 100° and 150°C. An additional factor is the reduced oxygen pressure and this can increase the time by orders of magnitudes. These figures are conceivable in nature and this reversal mechanism may be extremely important in deciding which reversed altered (oxidised) rocks are self reversed.

FIG. 20 NEELS NO.1 MECHANISM

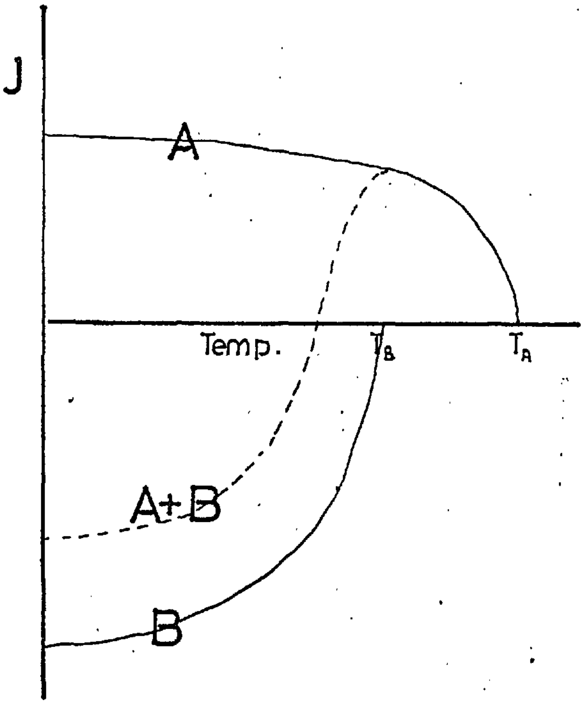


FIG. 21 NEELS N TYPE

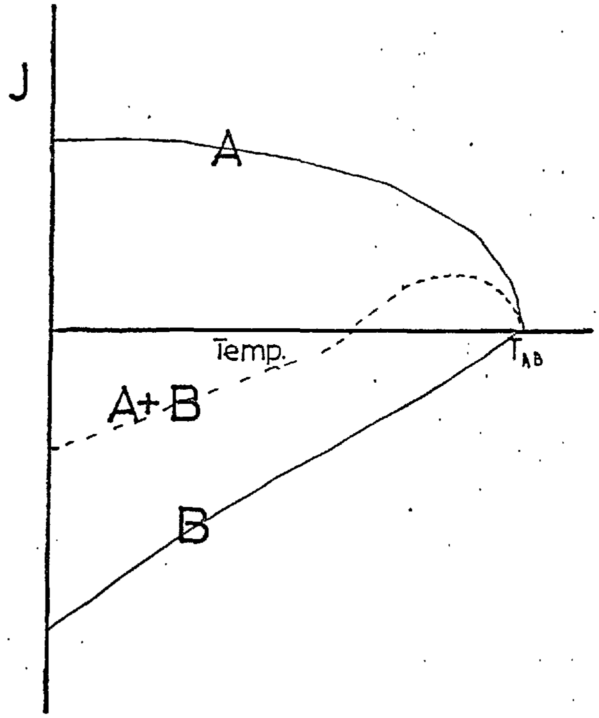


FIG. 22 REGIONS OF N AND P TYPE

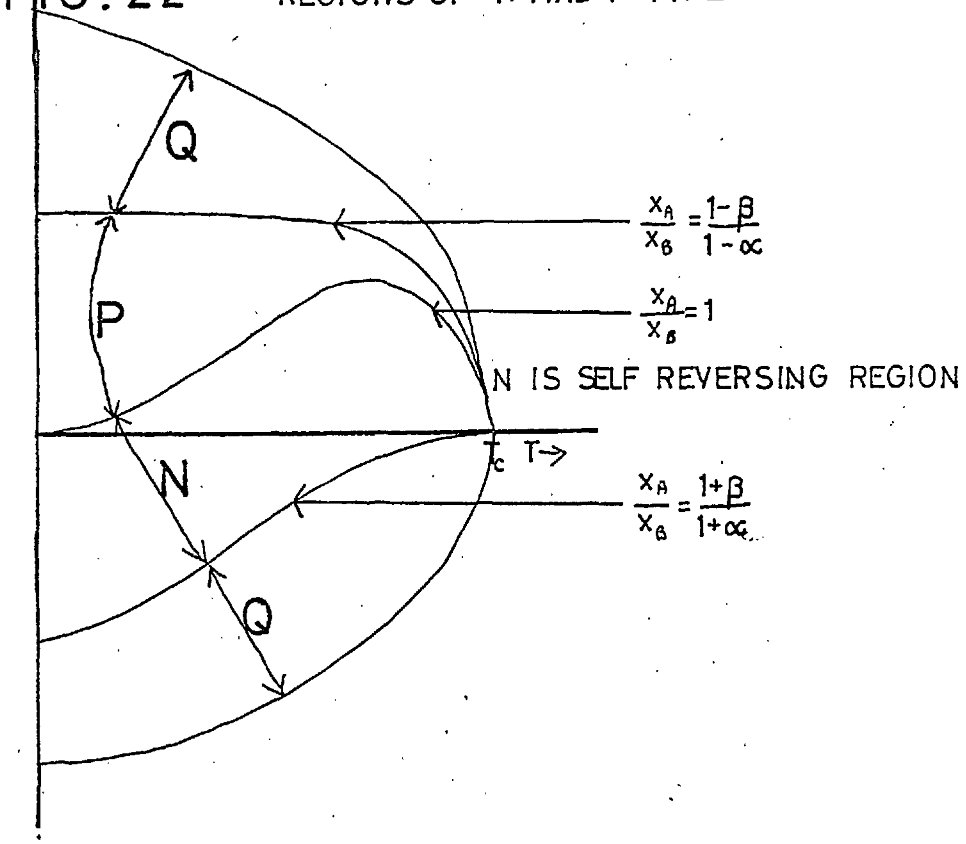
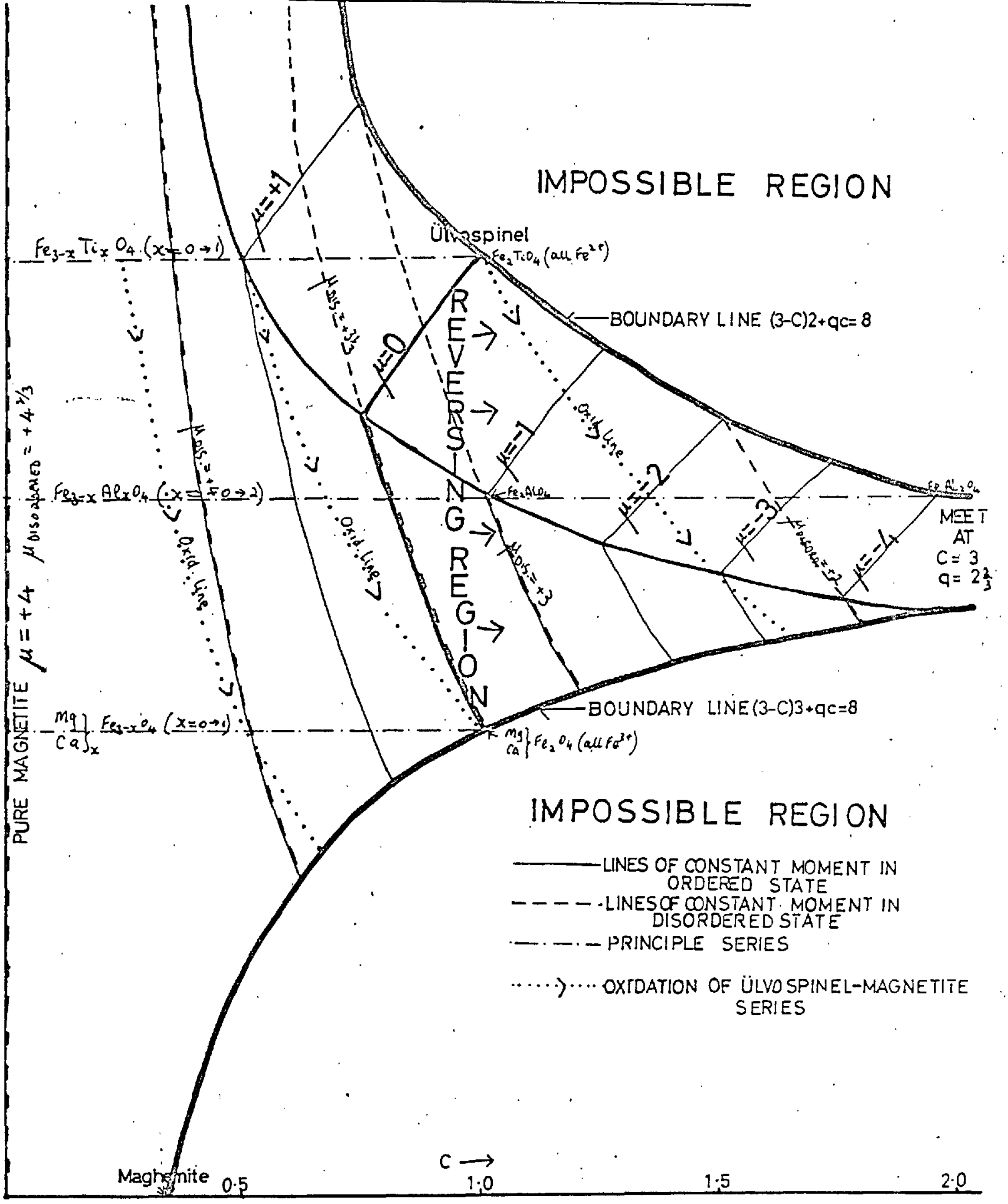


FIG. 23 q AGAINST c FOR MOLECULE $Fe_{3-c}M_cO_4$



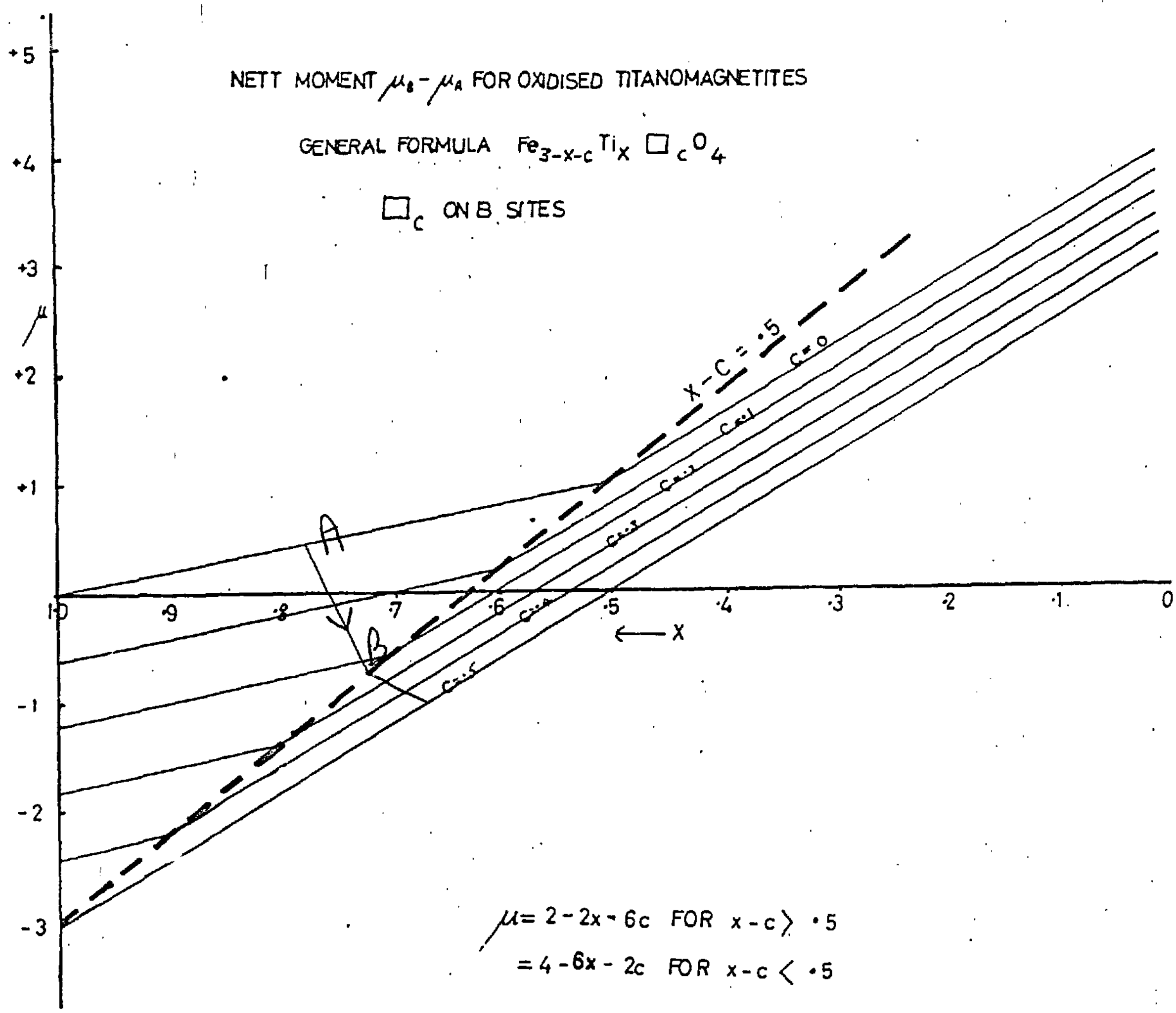

NETT MOMENT $\mu_B - \mu_A$ FOR OXIDISED TITANOMAGNETITES
GENERAL FORMULA $Fe_{3-x-c}Ti_x \square_c O_4$
$\square_c$ ON B SITES
X − C = ·5
C = 0
C = ·1
C = ·2
C = ·3
C = ·4
C = ·5
A
B
μ
+5
+4
+3
+2
+1
-1
-2
-3
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
← X
$\mu = 2 - 2x - 6c$ FOR $x - c > \cdot 5$
$= 4 - 6x - 2c$ FOR $x - c < \cdot 5$

FIG. 24

MECHANISM OF R. P.T.R.M.

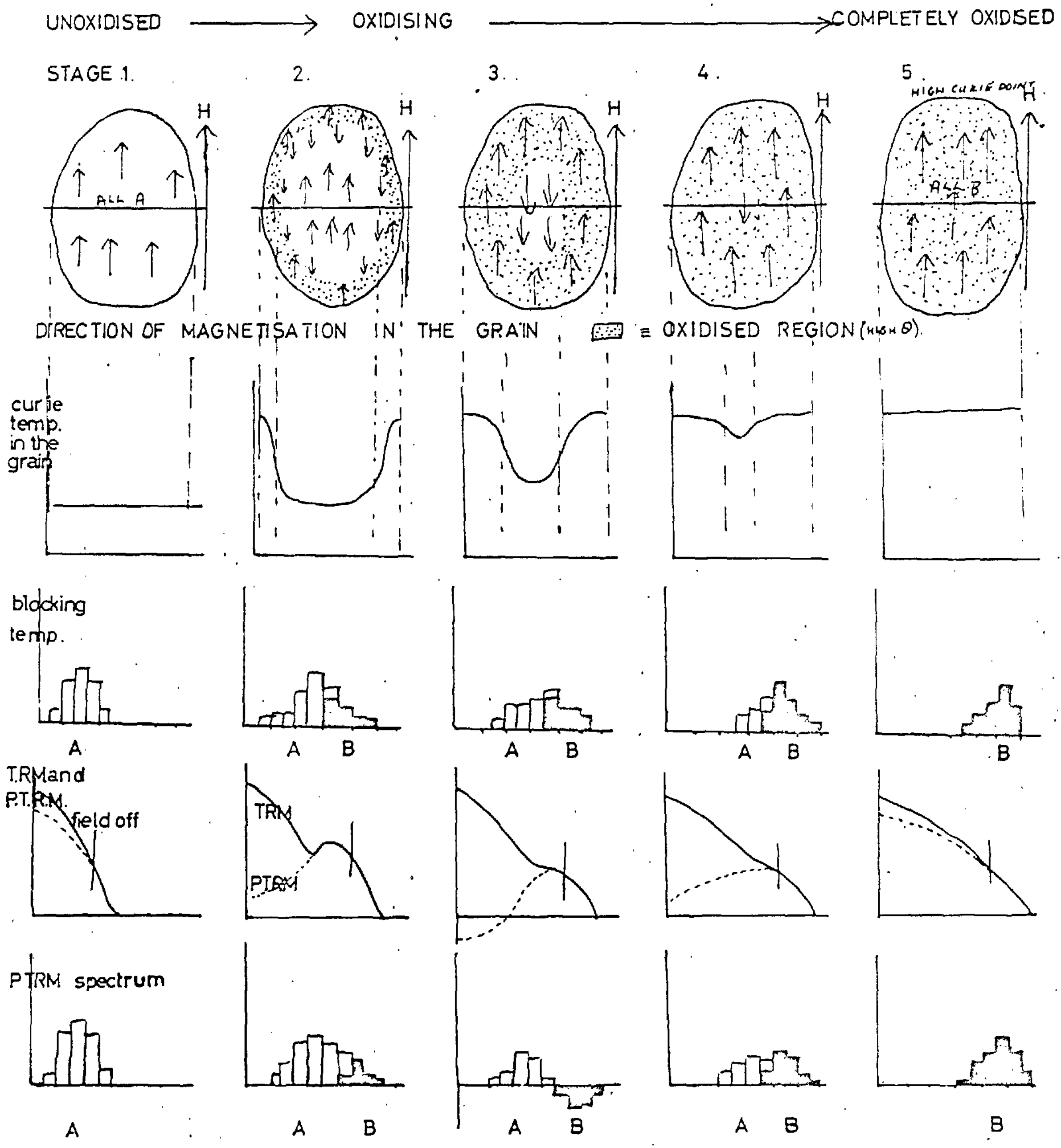
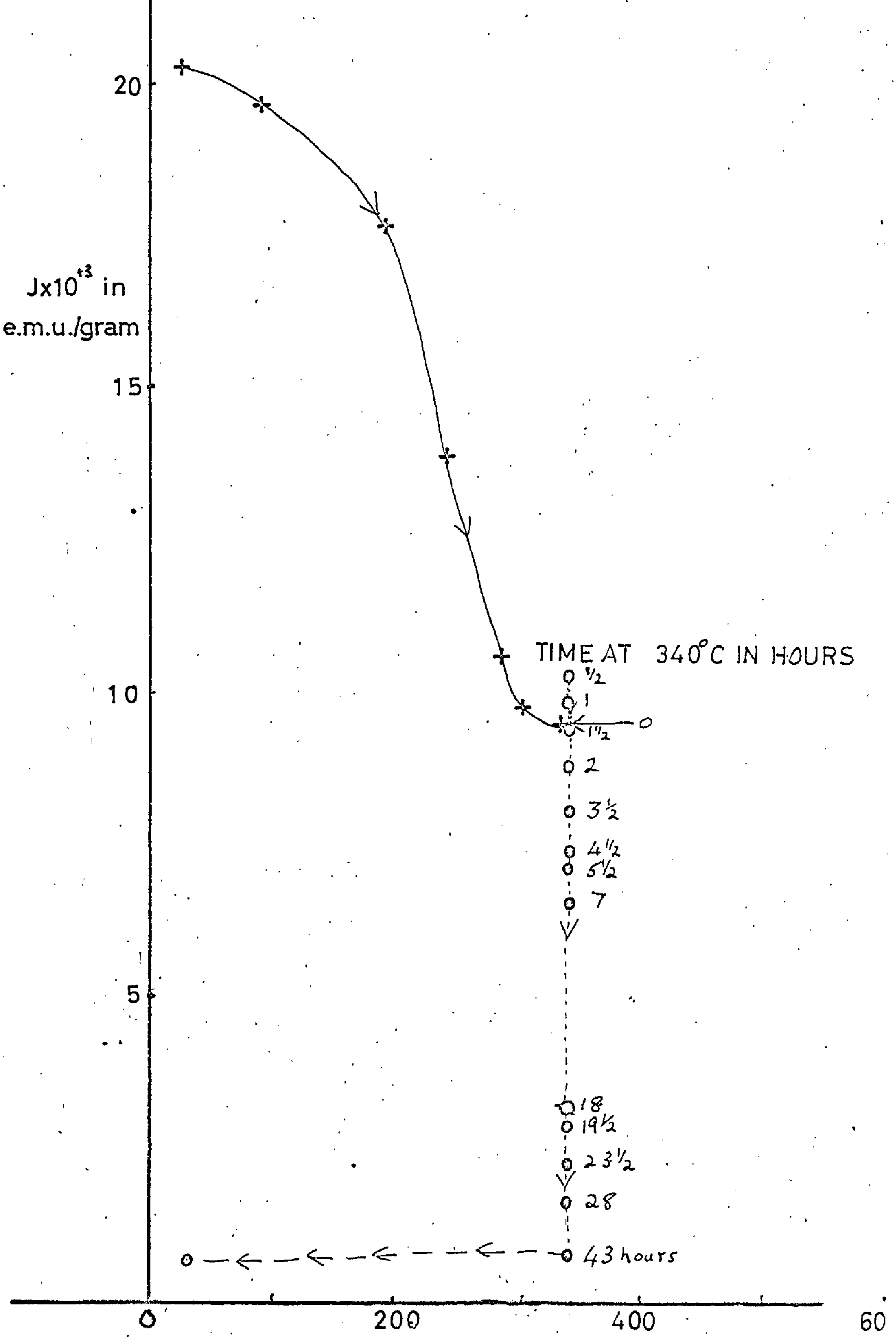


FIG. 25.

FIG. 26 OXIDATION BELOW THE CURIE POINT

X= •47



OXIDISING TIME against OXIDISING TEMPERATURE

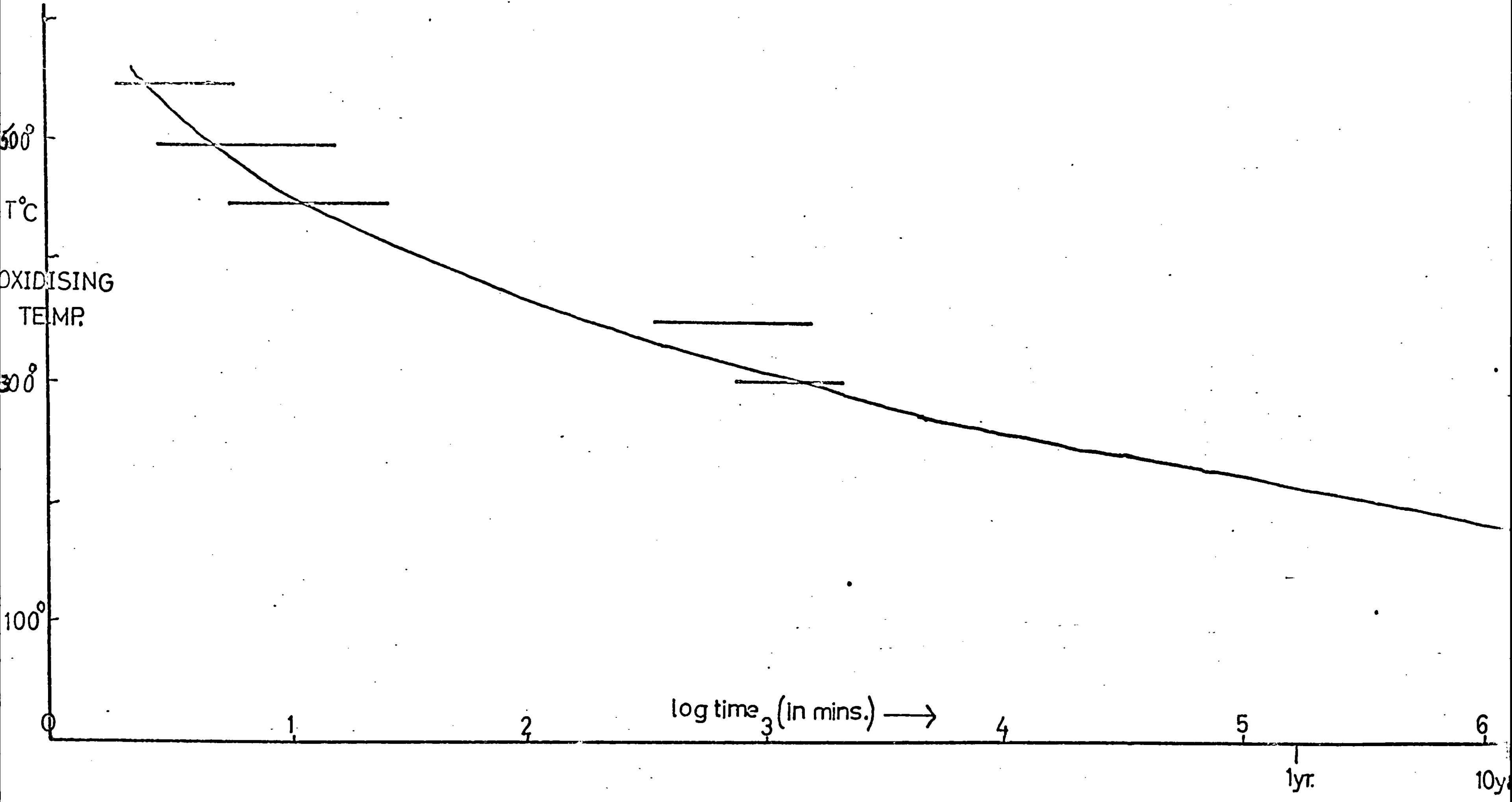


FIG. 27.

CHAPTER 6.

Reduction of synthetic samples

6.1. Introduction.

Uyeda[60] obtained some information about the oxidising and reducing properties of the ilmenite haematite series but very little has been reported on the reduction of the ulvospinel magnetite series. Pouillard[49] successfully used a reduction method to prepare his series of titanomagnetites. It is a natural development to know to what extent the oxidation process is reversible in an attempt to understand the change of magnetic properties due to oxidation.

6.2. Methods used for reduction.

The first method used in an attempt to reduce synthetic samples was to heat an oxidised synthetic specimen (with an original low curie point) in a reducing atmosphere supplied by a stream of coal gas. This was carried out at 650° and the sample heated for 5 hours. On remeasuring the curie point, two curie points were found, 260° and 770°C compared with 560° for the oxidised sample. X-ray photographs confirmed that the 770° curie point was free iron. Clearly the reduction had taken place but had gone too far in some regions of the sample.

It had been found during the preparation of samples that subsequent heatings at high temperature in an evacuated quartz tube reduced the curie point slightly, and brought the curie points throughout the series closer to the accepted values given by Akimoto[28]. It was suspected the discrepancy between the accepted values and the observed values of the curie point was due to the slight oxidation of the sponge iron used in the preparation, this seemed to indicate reduction could take place by heating in an evacuated tube at a suitable temperature. In order to investigate this, samples with x ranging from .295 tc .97 and so originally having a wide range of curie temperatures, were heated to 600°C in air and in all cases the curie temperature rose to between 500° and 600°C and the new cell size was determined. The samples were then sealed in evacuated tubes and heated to 850° for 20 hours. The curie temperature was redetermined and in every case it had fallen. The cell size was again determined for one sample and the remainder reheated to 900° for 48 hours. Again the curie points and cell sizes were determined. Table 3 shows the changes of curie point and cell size for this series of heatings.

Table 3.

X	ORIGINAL CURIE POINT. IN °C	CELL SIZE °A	← OXIDISED → CONDITIONS	NEW CURIE POINT	NEW CELL SIZE	← REDUCED → CONDITIONS	CURIE POINT	CONDITIONS	CURIE POINT	CELL SIZE
·20	540	8·40	HEATED TO 600°C IN AIR	580	8·37	ALL HEATED TO 850°C FOR 20 HRS. IN VACUUM	520	900° 48hr	450	8·43
·295	500			580	8·38		550	900° 22hr	450	
·48	425	8·43		570	8·38		400			
·57	375			570			500	900° 48hr	480	
·67	325	8·45		560	8·39		300			8·44
·77	280			560	8·40		200	900° 48hr	60	8·50
·97	-30	8·51		560	8·42		260	900° 22hr	260	8·44

It was clear the curie point had decreased in all cases and further heating decreased it still further. Also the cell sizes had increased again after the heat treatment, but the new curie points and cell sizes were still different from the original ones. In four samples the new curie points were lower than the original ones and very close to the accepted unoxidised values but in two cases the curie points were still above the accepted value and it appeared that reduction was incomplete in these two cases. The reason was unknown but it probably depended on the position of the excess oxygen atoms in the oxidised sample and it was difficult to explain in great detail.

Another interesting point of information was obtained from a close study of the X-ray photographs. Both the original and the reduced samples gave rise to a photograph which had sharp back lines, indicating the crystal structure was highly ordered. The oxidised sample however had blurred back lines indicating the crystal structure was more disordered. The oxidation process succeeded in increasing the amount of oxygen in the lattice, by changing Fe^{2+} to Fe^{3+} and vacancies are set up to maintain the valency equilibrium. During reduction the temperature (850° or 900°) was sufficiently high for the crystal structure to become perfect and sharp lines appeared again. Fig. 28 shows typical films obtained in each case.

6.3. Effect of reduction on P.T.R.M.

Four samples that had been partially oxidised and whose P.T.R.M. fell on cooling below T_1 were heated in evacuated tubes to 800° for 92 hours and T.R.M. and P.T.R.M. heating curves remeasured. In all cases the curie temperature had dropped considerably and the P.T.R.M. in three cases was identical to that of the T.R.M.

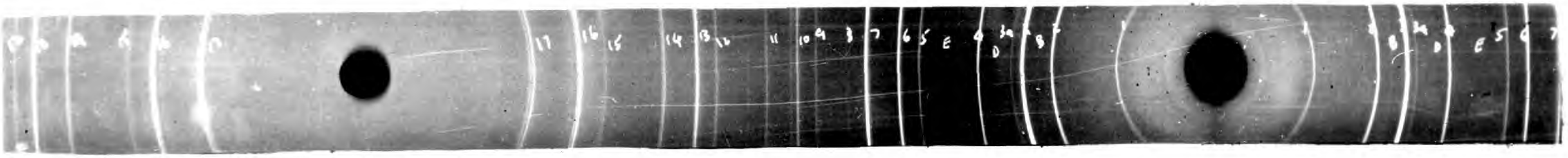
Reduction in this process took place at fairly high temperatures, above 800^{o}C and clearly at this temperature the cations had ordered themselves and the crystal structure was perfect again. This gave a single phase and little spread of curie points and hence the P.T.R.M. acquired was identical to the T.R.M.

Reduction by this method did not produce similar effects on the P.T.R.M. as oxidation which was discussed in Chapter 4 and adds further evidence that the R.P.T.R.M. in Chapter 4 was due to order and disorder produced in the crystal lattice by oxidation and the corresponding production of a spread of curie points or the setting up of a metastable oxidised state.

FIG. 28

X-RAY PHOTOGRAPHS OF SYNTHETIC TITANOMAGNETITES

1. UNOXIDISED X=·20 a_c= 8·39(6)°A LINES 1 to 17 ARE CUBIC TITANOMAGNETITE LINES, B to E ARE ILMENITE LINES



2. OXIDISED X=·29 a_c=8·38(5)°A LINES 1 to 17 ARE CUBIC TITANOMAGNETITE LINES, A to I ARE ILMENITE LINES

3. OXIDISED then REDUCED X=·67 a_c=8·43(8)°A LINES 1 to 17 ARE CUBIC TITANOMAGNETITE LINES, A to I ARE ILMENITE LINES

CHAPTER 7.

Homogenisation and exsolution

7.1. Introduction.

The exsolution into two magnetic phases and homogenisation of two phases forms a very interesting part of rock magnetism but very little precise information is available. Kawai[24] first suggested a hooped shape curve to give a solubility gap in the magnetite ulvospinel series after studying the distribution of double curie points in natural rocks. He concluded that the two maxima obtained were the room temperature points on such a solvus curve. More complicated solvus diagrams have been suggested[22] with an eutectic type curve but this does not seem to have found any experimental support. Vincent et al[23] supported a hooped solvus curve but their curve rose sharply near the magnetite end. In recent work by Kawai[45] on synthetic material he claimed to have observed exsolution into two phases at temperatures as low as 300°C and possible effects of magnetic phases being produced below their curie point were discussed. The different solvus curves are shown in Fig. 29a,b and c.

Many people considered the ilmenite intergrowths found in natural titanomagnetites to be a result of oxidation of original ulvospinel intergrowths caused by exsolution, or alternatively by direct exsolution from a possible ilmenite solid solution.

The question of solid solution series in the generalised titanomagnetite region also gave rise to some interesting ideas and possibilities. The homogenisation and exsolution of the different series had been discussed by Haigh[4].

Thus it seemed to be advantagous to carry out some heating experiments on the synthetic samples to try and elucidate some of the problems.

7.2. Exsolution.

Synthetic samples from throughout the magnetite-ulvospinel series which had been prepared at 900°C were heated at successively lower temperatures for long times and the curie points measured to see when signs of double curie points appeared and to find the upper limit of the proposed hooped solvus curve. The temperatures used were 750°C for 7 days when all the samples showed one curie point, 650°C for 24 days when again only one curie point was seen and 575° for 19 days. At the last temperature the samples in the middle of the series showed two curie points as shown in Fig. 29e. In all cases the samples were quenched from the exsolution temperature. The upper curie point was higher and the lower curie point lower than the original one. The top of the solvus curve can be considered near 600°C. However each sample did not go to the same double curie point and this showed that even after 19 hours at 575° the exsolution was very sluggish and proceeded very slowly. The results agreed with a hoop shape solvus curve rising sharply at the magnetite end as shown in Fig. 29d but the rate of exsolution was much slower than that reported by Kawai.

7.3. Homogenisation.

It had been found possible[23] to homogenise the ulvospinel and magnetite phases in natural rocks and so it was decided to mix two very finely ground magnetic materials with $x = .2$ and $.77$ respectively and heat the mixture in a evacuated tube at a given temperature to obtain some idea of the time taken to produce one magnetic phase. This was observed by measurement of the curie point.

It was found that 4 hours at 800°C produces a single phase and at 750°C after 17 hours only a small fraction of the upper curie point phase remains and this completely disappears after 90 hours at 750°.

It is questionable whether this experiment is very analogous to conditions in nature where the phases are very finely divided because here they were just well mixed but homogenization did seem to be able to take place at a finite rate down to 650°C.

7.4. Conclusions.

The results show that the top of the solvus curve is at 600° and is very flat in this region. It also rises sharply at the magnetite end. This is in agreement with other peoples results but the rate of exsolution is much slower than reported by Kawai. Homogenization can take place at a finite rate between two magnetic phases down to the solvus region. These results suggest that exsolution and homogenization are not important factors in laboratory experiments below 500° and only have marked effects on a geological time scale.

G. 29 SUGGESTED SOLVUS CURVES

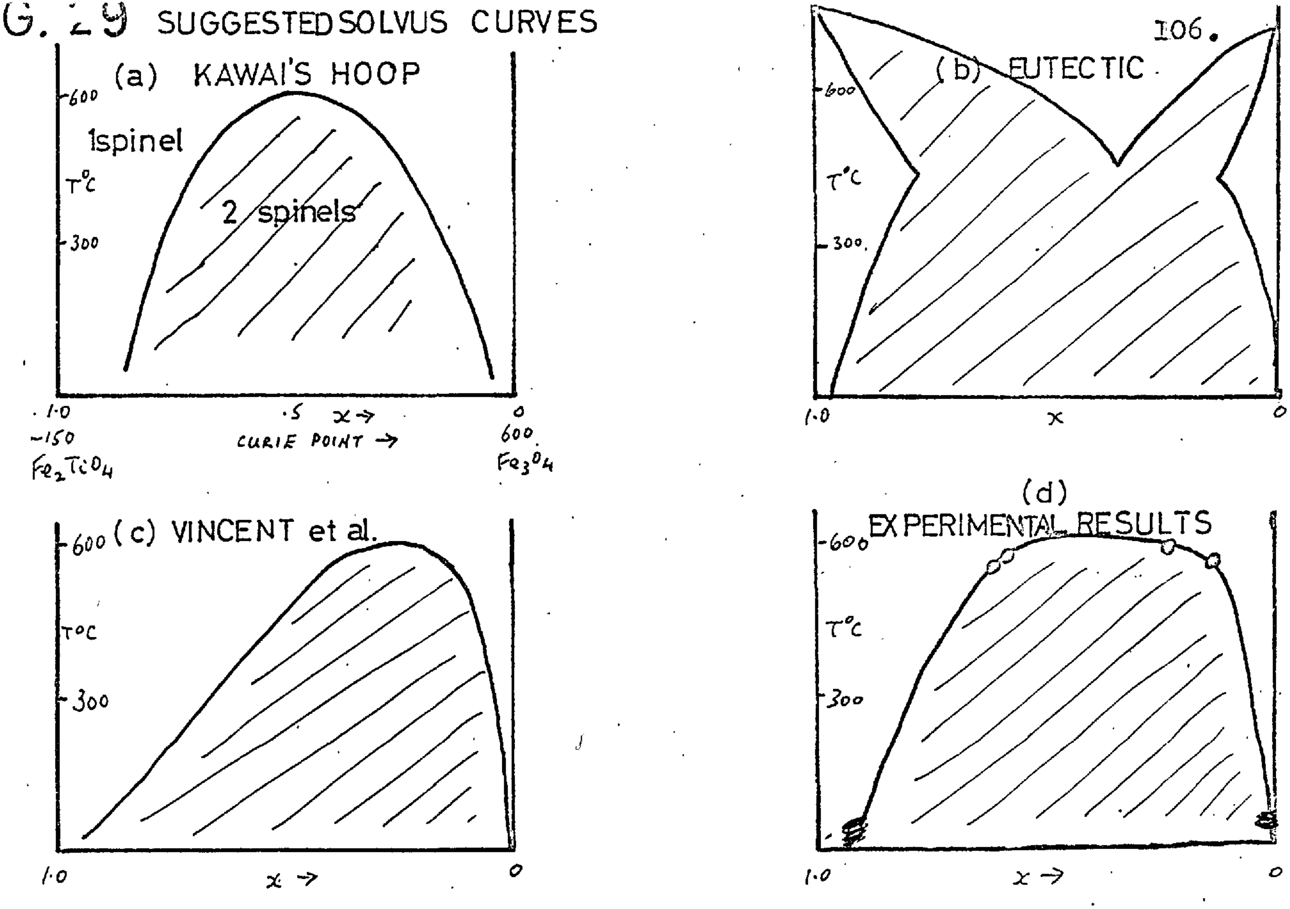
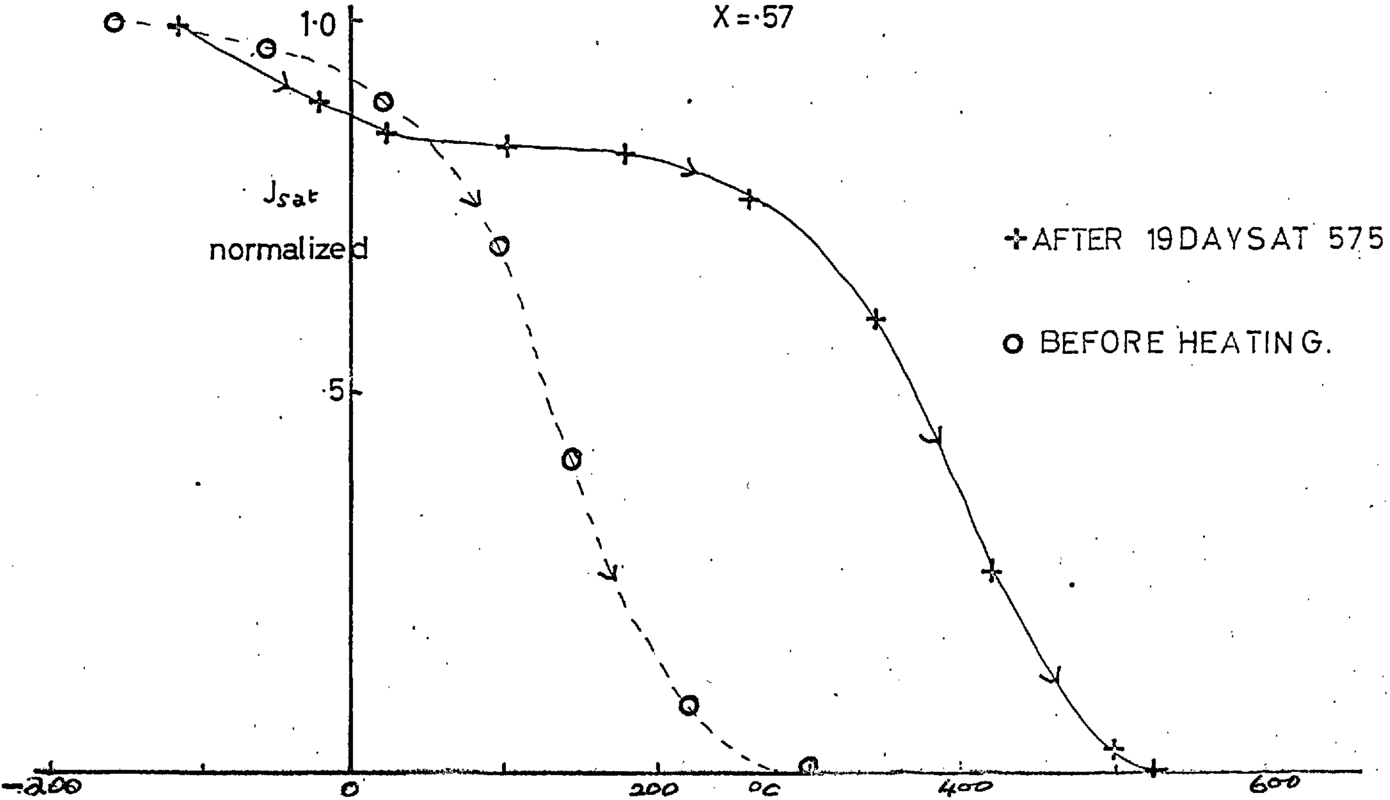


FIG. 29e EXSOLUTION AT 575°C



PART TWO

NATURAL SAMPLES

CHAPTER 8.

Thermal treatment of the Rashiehill Bore

8.1. Introduction.

The remaining chapters deal with the thermal properties of natural samples and the first series of experiments are concerned with the magnetic behaviour of rocks after being heated to temperatures in excess of their curie point in the absence of air. Vincent et al[23] have carried out heating experiments on rocks containing titanomagnetites and have also studied the corresponding petrological changes. They found a reduction of the curie point after heating at a high temperature for a long time and explained this occurrence ~~as~~ by homogenisation of the magnetite-ulvospinel intergrowths.

It was decided therefore to heat-treat rocks in which the principle magnetic constituent was known to be titanomagnetite and investigate the changes in magnetic properties, supported by techniques such as petrology, X-ray analysis and the electron probe analysis of the minerals.

8.2. The Rashiehill Bore.

The first set of samples investigated was from a sill at Rashiehill, Stirlingshire which had been previously investigated magnetically by Everitt[61,62]. The sill was of Carboniferous age and had intruded into limestone coal beds. In the boring taken at Rashiehill, the sill lay between depths of 1354 feet and 1742 feet and samples were available from 15 different places throughout the sill.

Everitt measured the natural intensity of magnetisation and the dips throughout the sill and found the intensity lowest near the upper edge (1.8×10^{-6} e.m.u. per gram), fairly constant in the centre (1800×10^{-6} e.m.u. per gram) and a region with greatest intensity (5330×10^{-6} e.m.u. per gram) 30 to 50 feet from the uppermost edge. A similar distribution was obtained for the saturation moment (Fig. 30). The dips were found to be shallow upwards or downwards, apparently randomly distributed throughout the sill. After many tests he concluded that this was due to some complex reversal mechanism. He also measured the curie points throughout the sill and found a curie point of 550°C throughout the sill, except near the very edge where there were signs of an additional curie point at 330°C. The total iron and titanium content was fairly constant throughout the sill and X-ray pictures of the magnetic fraction showed magnetite and ilmenite lines.

These rocks seemed suitable for investigating the changes in magnetic properties on heat treatment at high temperatures.

8.3. Experimental Procedure.

The following technique was used in the heat treatment of samples. Pieces of rock weighing up to 0.2 grams were placed inside quartz tubes (5 m.m. internal diameter, 2 m.m. wall thickness) and packed with quartz wool. Generally a single piece of rock was used. The tubes were then sealed under a vacuum of 10^{-3} cms. of mercury. Larger samples were made up but it was found that these exploded on heating, generally exploding between 600° and 800°C. The fact that these explosions took place shows the extent to which gas was evolved by the rock on heating, because it would require considerable pressure to break a quartz tube which had 2 m.m. walls. With 0.2 grams of rock a space equal to about three or four times the volume of the rock was left in the tube. This prevented such a great pressure building up and also ensured the sample did not get heated when the tube was being sealed off.

It was found difficult to determine the nature of the gases evolved but a strong smell of sulphur was present on breaking open a capsule. The virgin rock was maintained in a dessicator and a piece weighing 100 grams was found to lose .05°/o in weight over a period of a few months.

Thus the heat treatment can be considered to take place in an atmosphere of the rock gases rather than in a vacuum.

The heat treatment above 700°C was carried out in a large non-magnetic furnace in which the samples were attached to the twin-bored rod holding the thermocouple. After being held at the required temperature for the required time the samples were cooled in air after removing them quickly from the furnace. It was estimated that they cooled to 200°C in a matter of seconds and reached room temperature in a few minutes. This was considered fast enough to preserve the magnetic state at high temperature. The furnace used in the preparation of synthetic samples was not then available. For very long heatings below 650° small vertically elongated furnaces were used and the samples quenched by dropping them into water.

The measurement of the curie points was carried out in a curie balance designed by Kawai and previously described in Chapter 3, and heating curves of the strong field moment from -180° to 600° were taken with the sample still in the sealed tube.

8.4. Results of heat treatment.

The heat treatment produced two very significant changes in magnetic properties. The curie point was considerably lower and the value of the saturation moment J_s was also reduced for the heat treated samples compared with the values for the unheated virgin samples.

Figs. 31a,b and c show typical heating curves for samples from three different places in the sill after heat treatment at 800°C for the times shown and Figs. 32a,b,c and d show the lowering of the curie point for samples heated to various temperatures for various times. Clearly the lowering of curie point was greater at high temperature and after long times. All the curves were normalised because it was not possible to measure J_{sat} absolutely. However the deflection per gram obtained at 20°C gives an approximate indication of the value of J_{sat} and Figs. 33a,b,c and d show plots of deflection per gram at 20°C against curie point for samples from four different positions in the sill. The correlation between curie point and the deflection was very clear and it was concluded that J_{sat} decreased as a result of heat treatment.

It was found that two samples from the same level, even the same hand sample gave different deflections per gram before heat treatment. This was because samples of 0.2 gram were used and in the centre of the sill, where the cooling of the magma was slowest, the magnetite grains were up to 1 mm. in diameter. Thus it was not surprising to find large fluctuations in intensity per gram for samples of 0.2 gram. Thus the graphs of deflection per gram against curie point had an expected scatter but the general trend was unmistakeable.

Before discussing possible mechanisms the dependance on the temperature and time of heating and also the position of the samples in the sill will be discussed.

8.5. Temperature, time and position dependance.

It is difficult to see the dependence of curie point on all three variables in one diagram so Fig. 34a,b and c have been drawn, plotting curie point against time of heating for different ranges of quenching temperature. The dependance in position in the sill is shown by combining samples within 10 feet of the edge in group A, those near the intensity peak 30 to 50 feet from the upper edge in group B and the ones from the centre in group C. Fig, 35a,b, and c show the family of curves obtained by plotting curie point against time of heating for the different regions of the sill. Here the quenching temperatures 900°, 800°, 700°C are differentiated.

Although a fair amount of scatter takes place (which is not surprising as the whole sill has been divided into just three catagories) the following points are clear.

1. The higher the temperature and the longer the time of heating the greater is the lowering of curie point.
2. The samples B from the intensity peak have curie temperatures falling more quickly than those from the centre which in turn fall more quickly than the samples from the edge at all quenching temperatures.
3. The curie point falls to a limiting value for all regions but this limit varies with different regions, the peak being lower than the centre which is in turn lower than the edge.
4. The curie point tends to a limiting value at each temperature but it is a different value depending on temperature, being lower for heat treatment at 900°C than 800° which is in turn lower than that for 700°C.
5. The range of temperature used was 950° to 540°C. After heating at 950° for 2 hours the curie point was lowered to 210°C for a rock from the B region and after

heating for 39 days at 540°C the curie point was lowered to 475°C for a rock from the same area. Between these temperatures at 800°, for example, the time taken is about 20 hours to lower the curie point to 250°C.

Thus this effect could be observed for all temperatures down to 540° but at this temperature the time taken was very long and the limiting values of curie point could only be estimated for the case of 900°, 800° and 700°C.

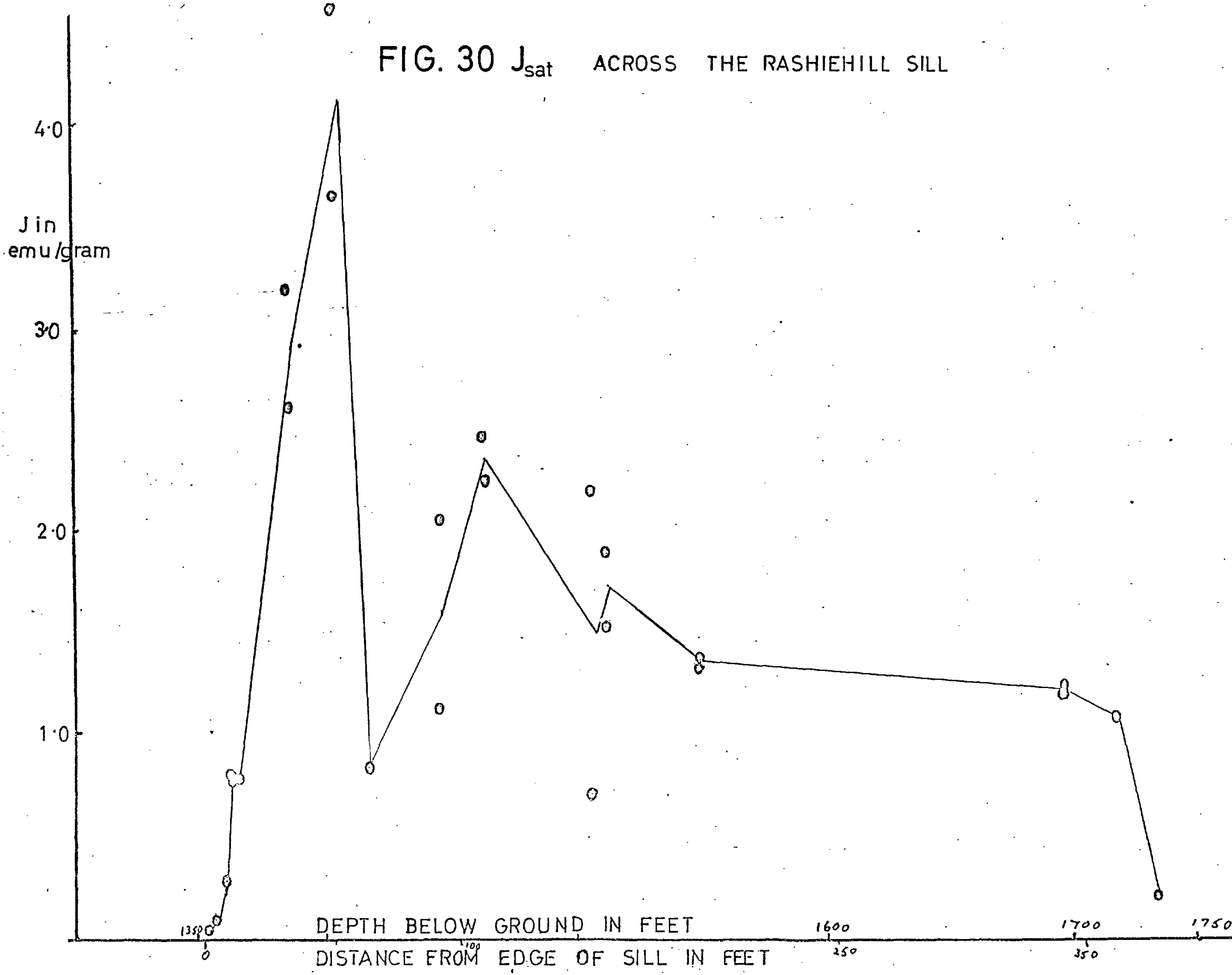
8.6. Other observations.

One important feature of the heating curves is that no double curie points were observed although heatings were made from -180° to 600°C. At ~~very~~ low temperatures (-170°C) a sharp rise was sometimes observed as in Fig. 32c but on comparison with the heating curve of a piece of ilmenite it seemed to be due to the ilmenite in the rock.

All the heating curves were repoducable and a repeat of the heating curve gave identical results. Two pieces from the same region in the sill after heating to the same temperature for the same time gave identical heating curves and curie points and so the effect is quite reproducable and unaffected by heating to 600° during the measurement of the curie point.

Before describing further experiments to elucidate the mechanism causing the reduction of the curie point the petrological changes caused by heat treatment and X-ray and electron probe data will be discussed.

FIG. 30 J_{sat} ACROSS THE RASHIEHILL SILL



J sat. AFTER HEAT TREATMENT AT 800°C

FIG. 31a 32FEET FROM THE EDGE

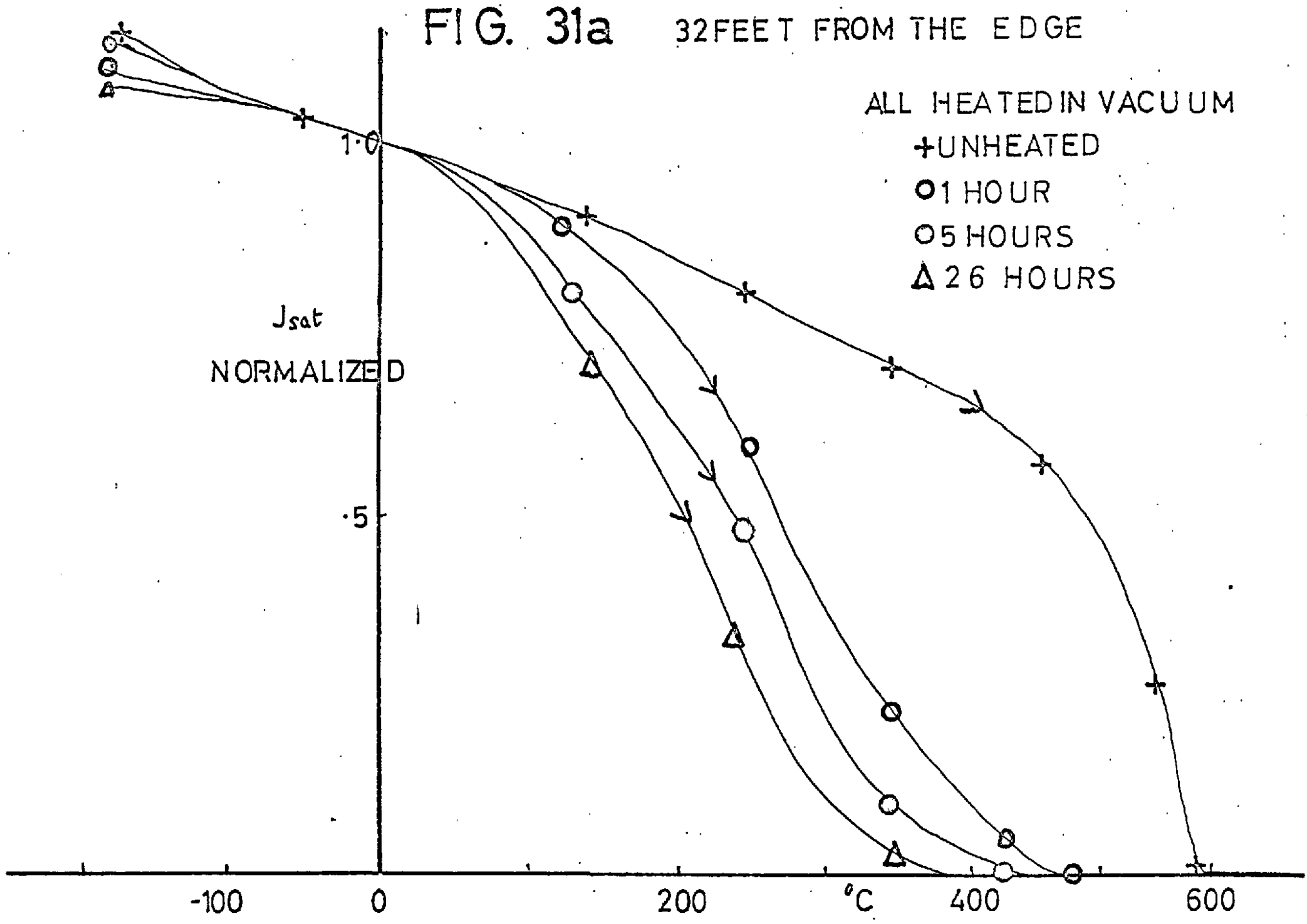


FIG. 31b 50 FEET FROM THE EDGE

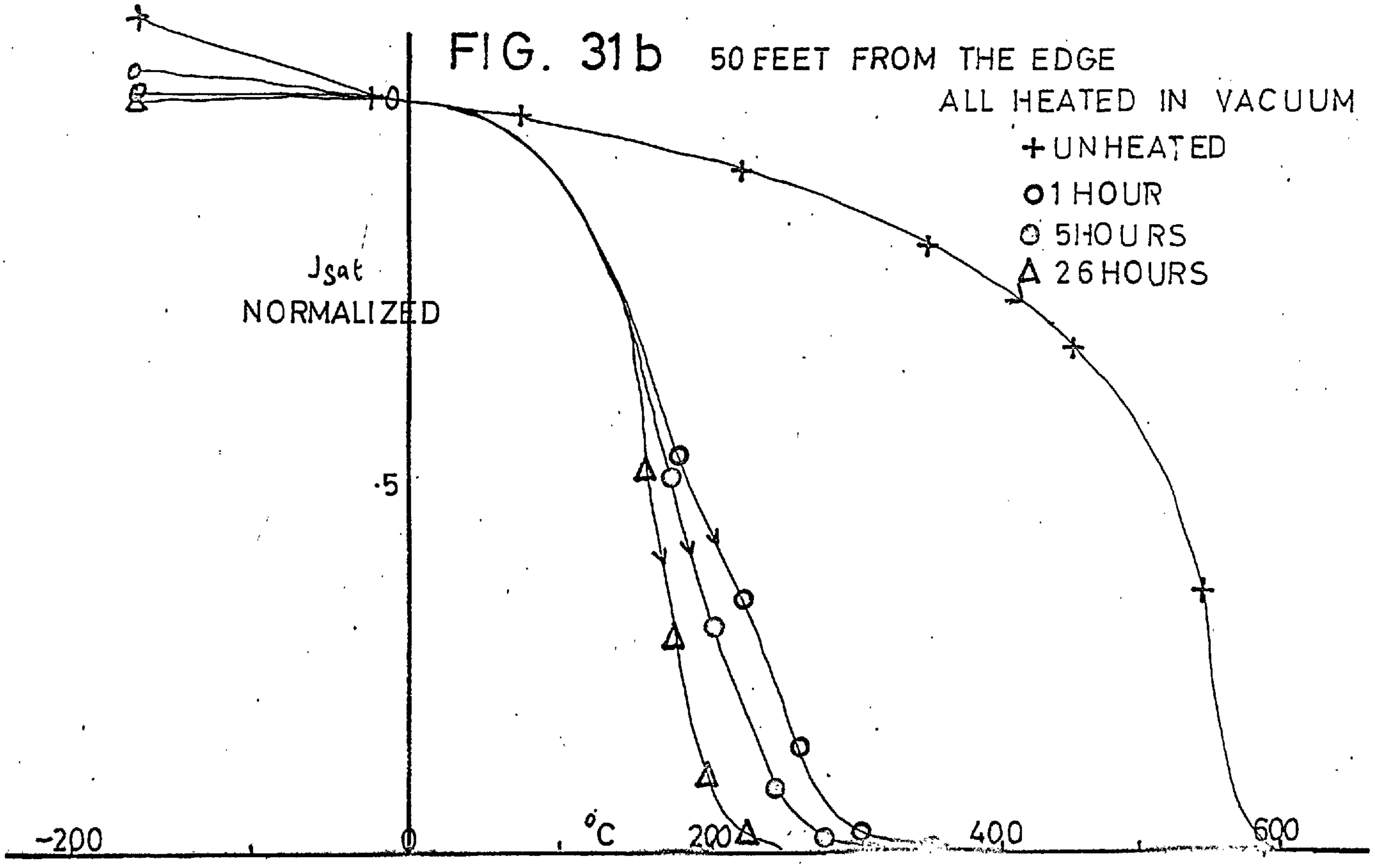
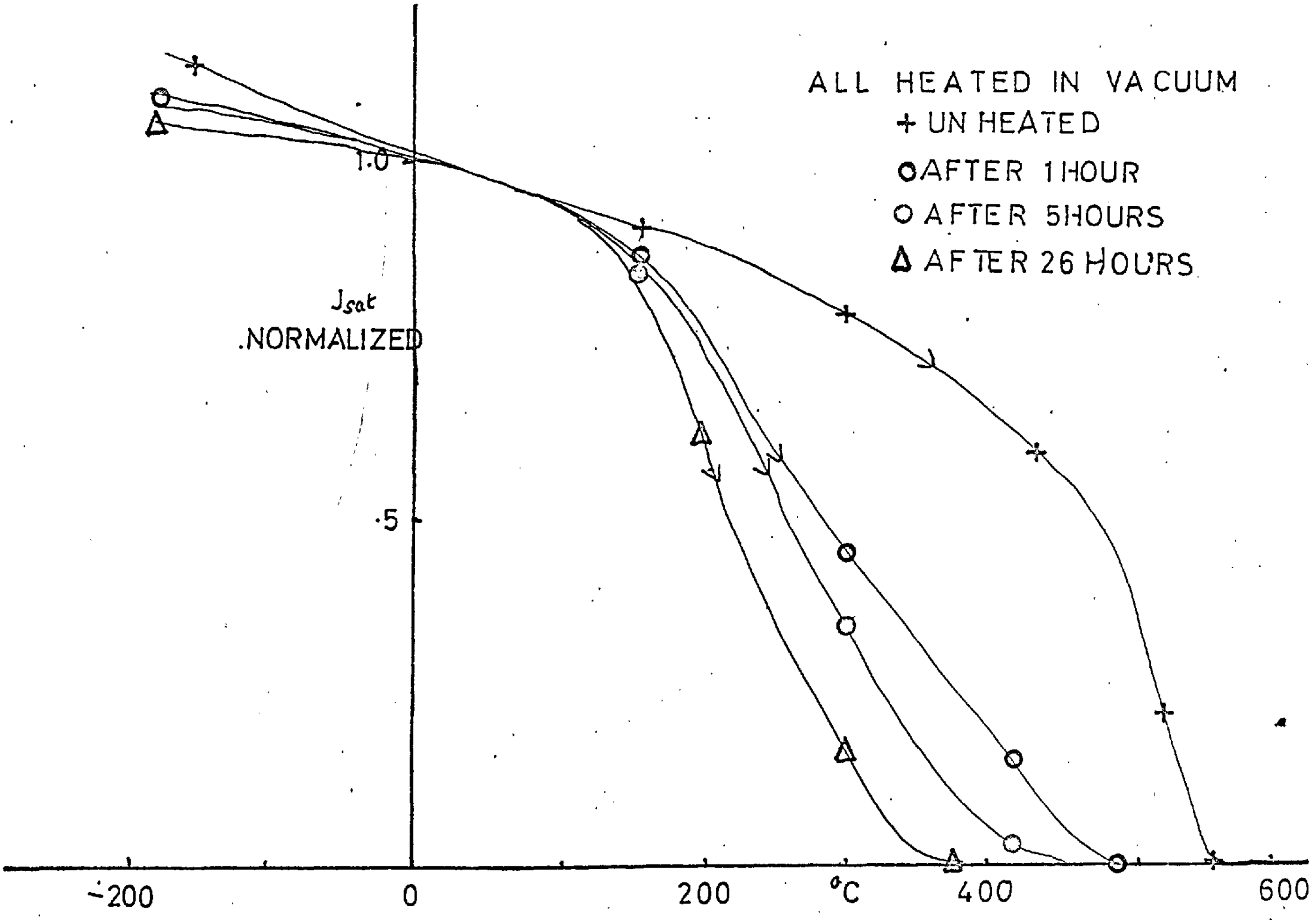


FIG. 31c 201 FEET FROM THE EDGE



AFTER HEAT TREATMENT AT DIFFERENT TEMPERATURES

FIG 32a 93 FEET FROM THE EDGE

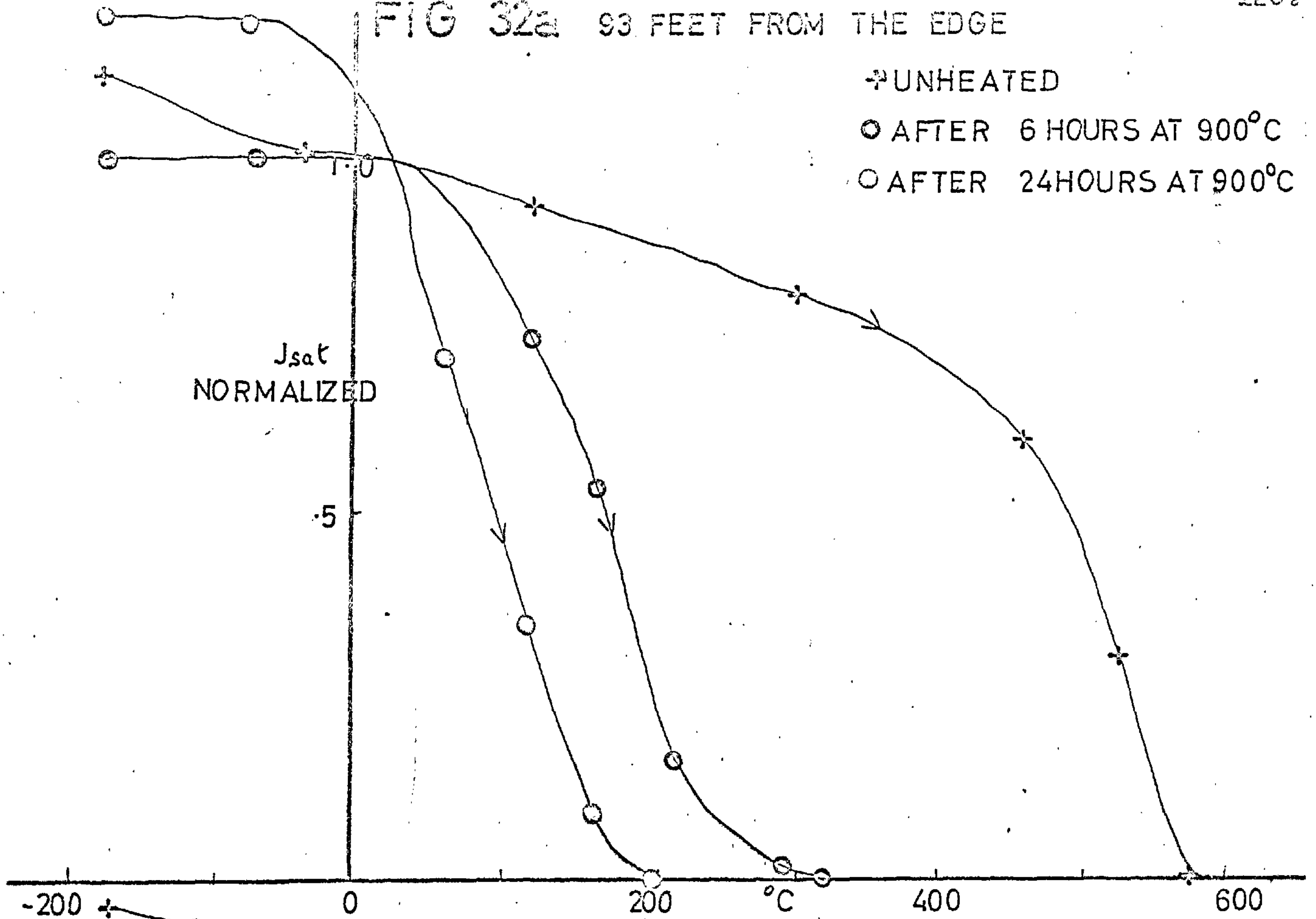


FIG 32b 345 FEET FROM THE EDGE

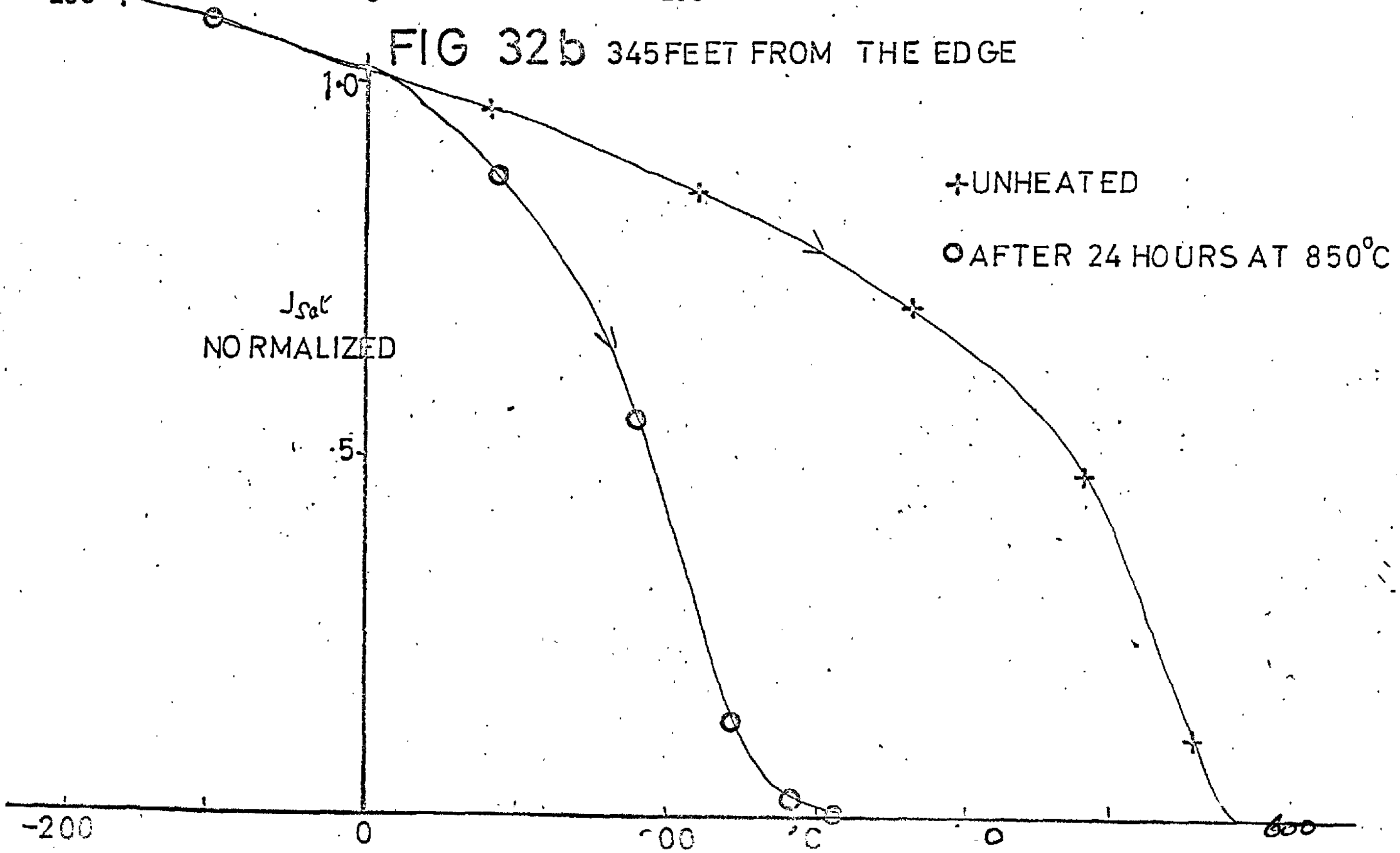


FIG 32c 50FEET FROM THE EDGE

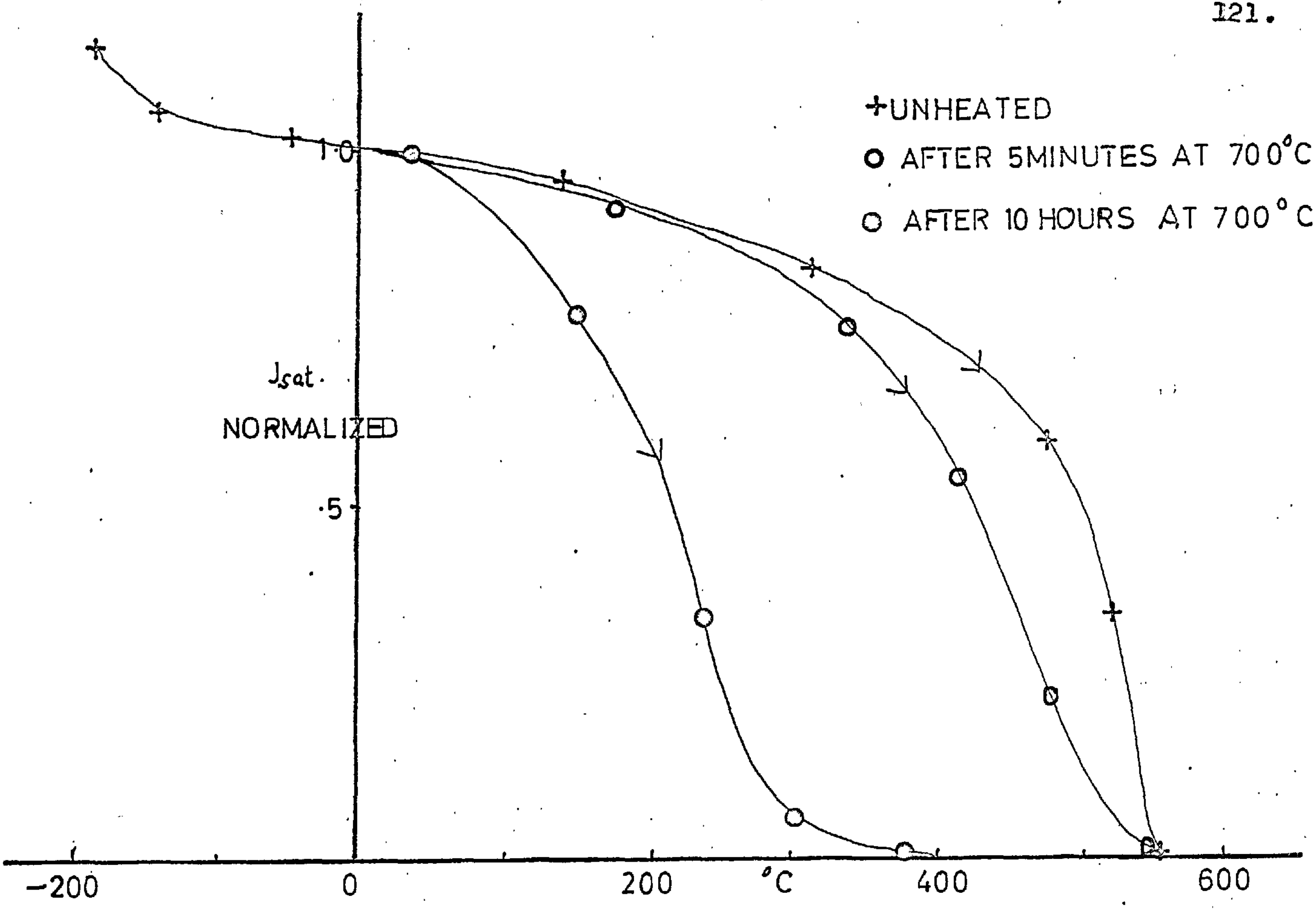
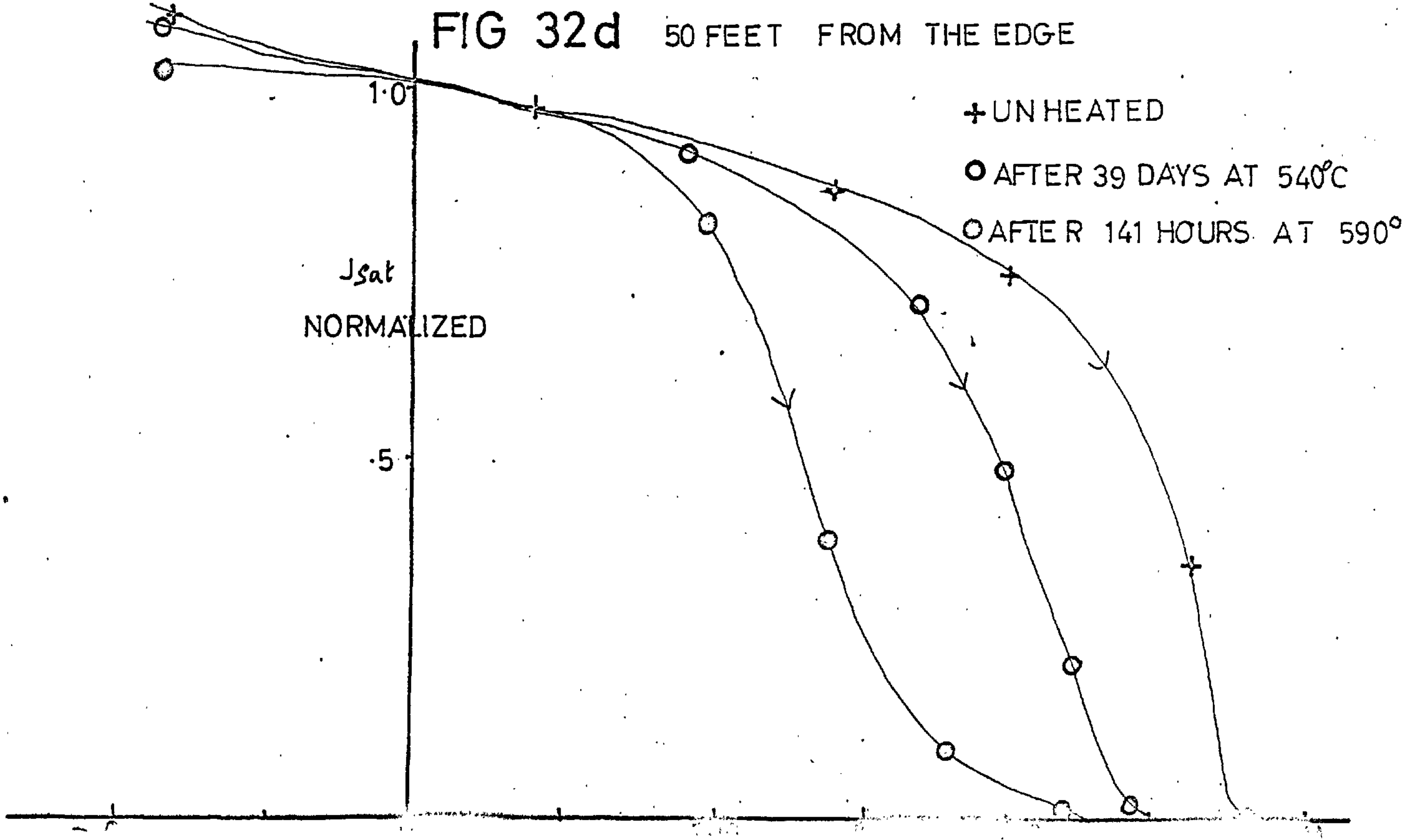


FIG 32d 50 FEET FROM THE EDGE



DEFLECTION/ GRAM against CURIE POINT

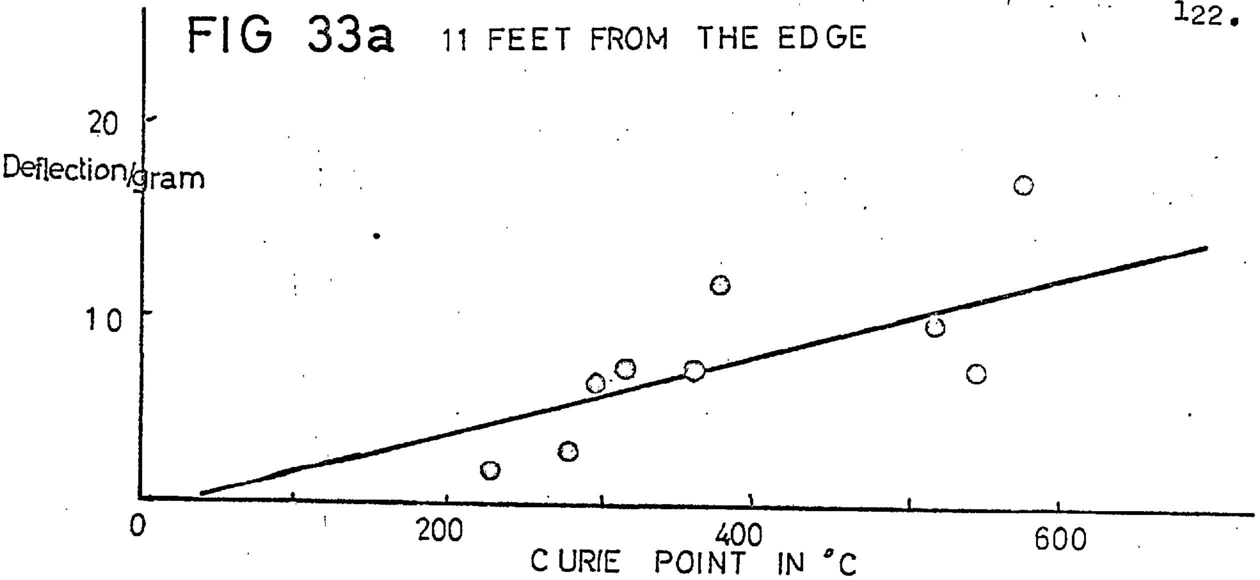


FIG 33a 11 FEET FROM THE EDGE

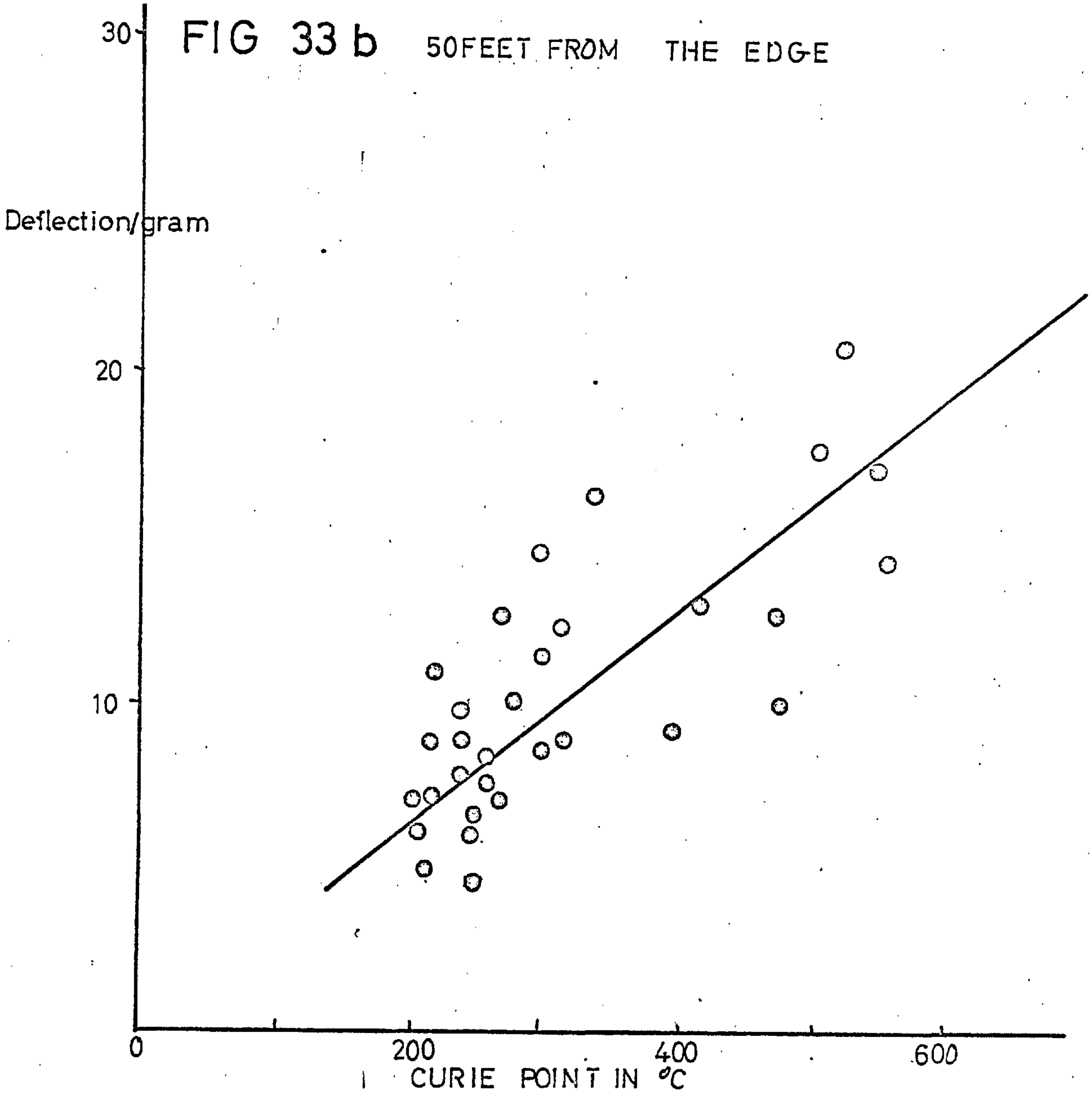


FIG 33 b 50FEET FROM THE EDGE

FIG. 33c 32 FEET FROM THE EDGE

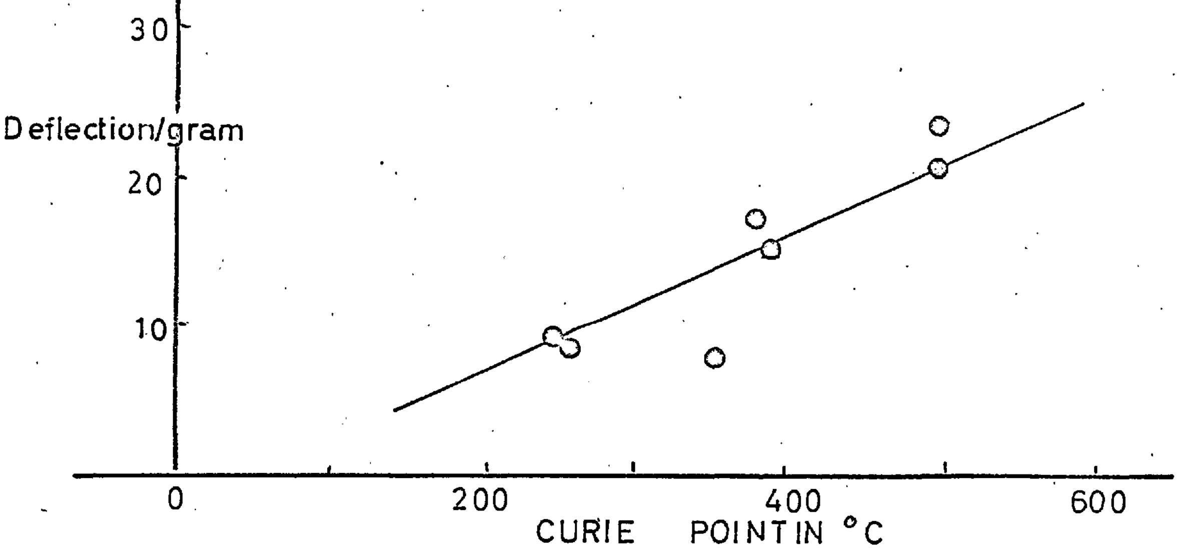
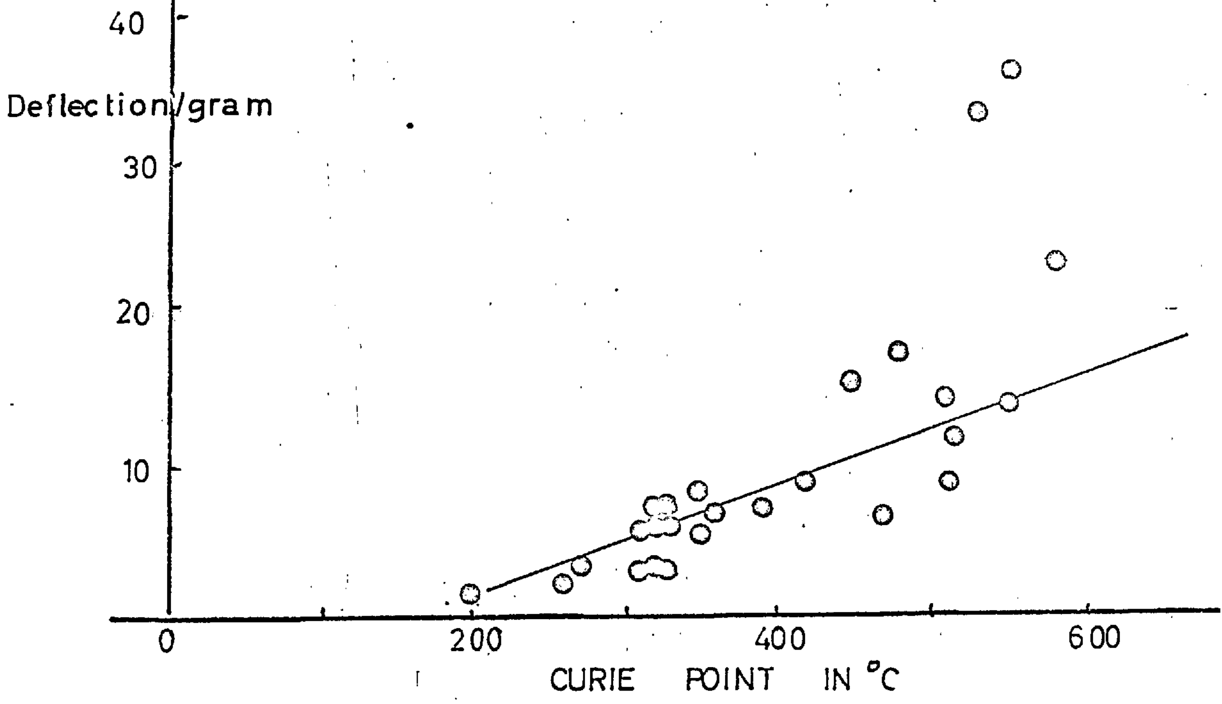


FIG 33d 201 FEET FROM THE EDGE



CURIE POINT against HEATING TIME FOR DIFFERENT QUENCHING TEMPERATURES

FIG. 34a TEMPERATURE = 900°C

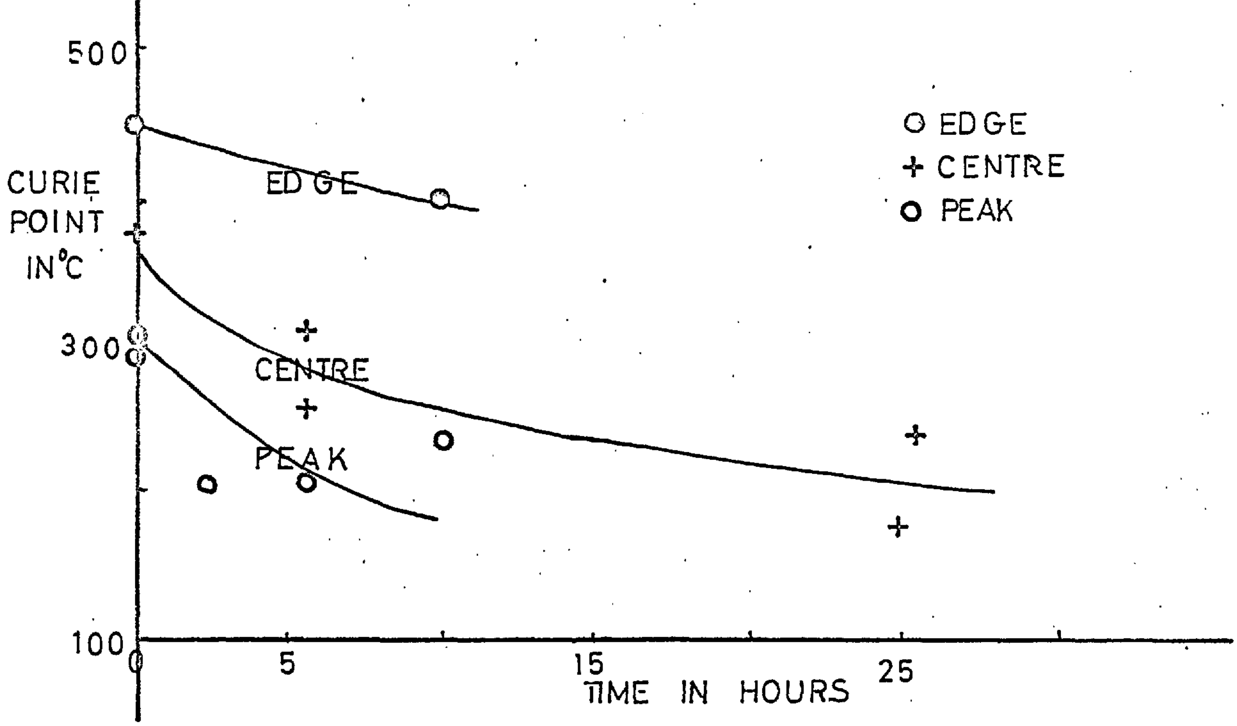


FIG 34b TEMPERATURE = 800°C

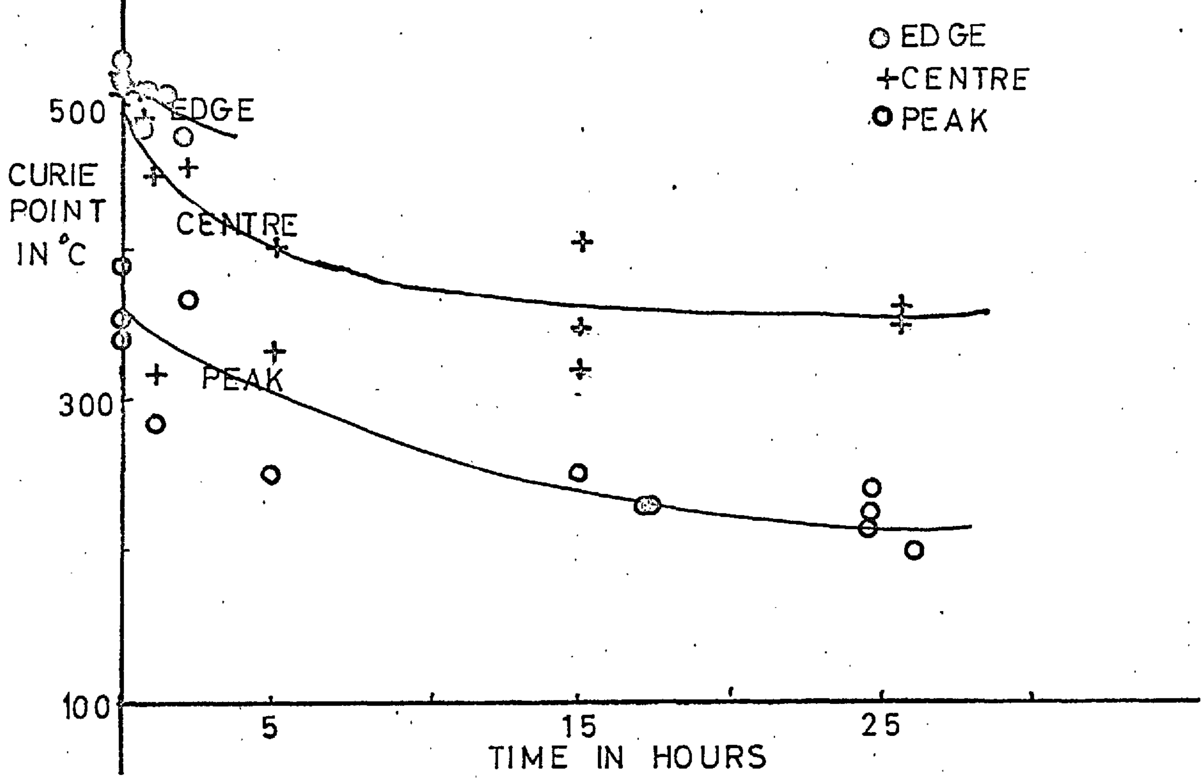
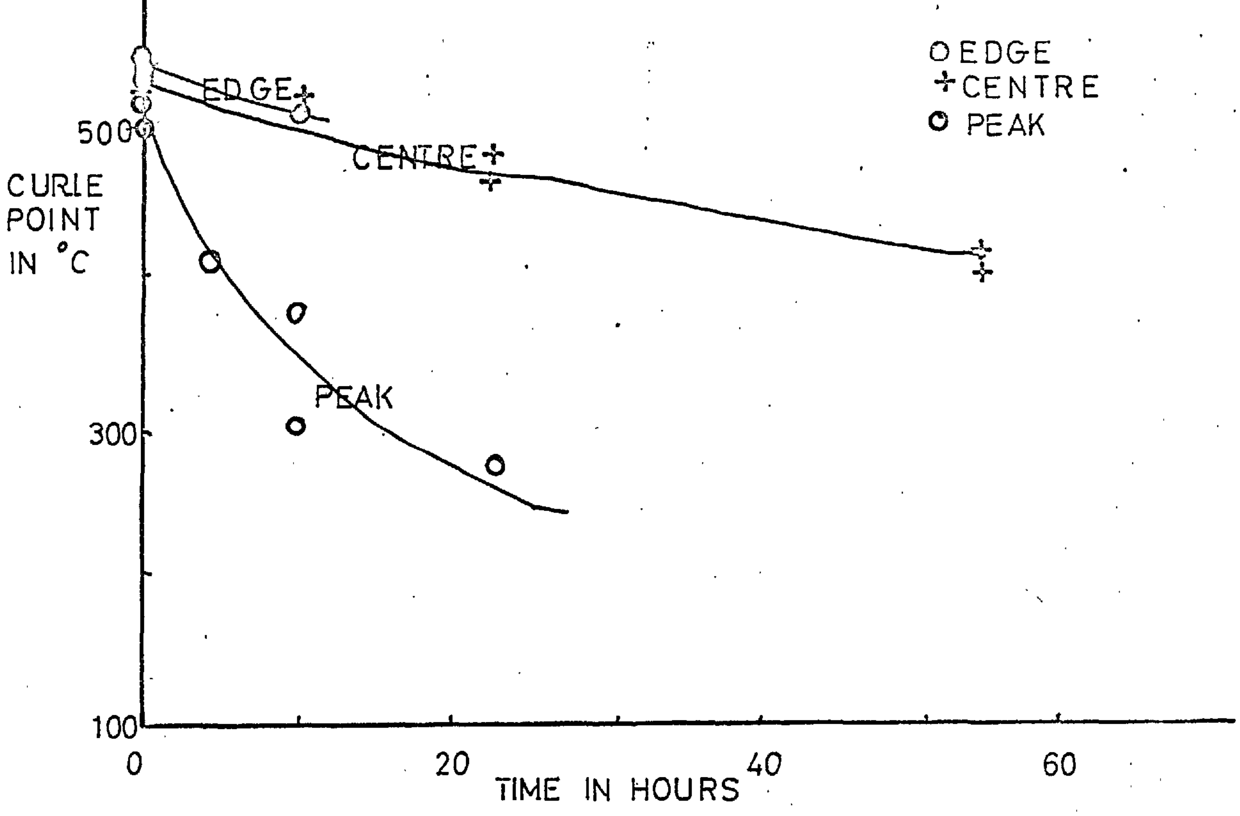


FIG 34c TEMPERATURE = 700° C



CURIE POINT against HEATING TIME FOR DIFFERENT POSITIONS IN THE SILL.

FIG. 35a EDGE

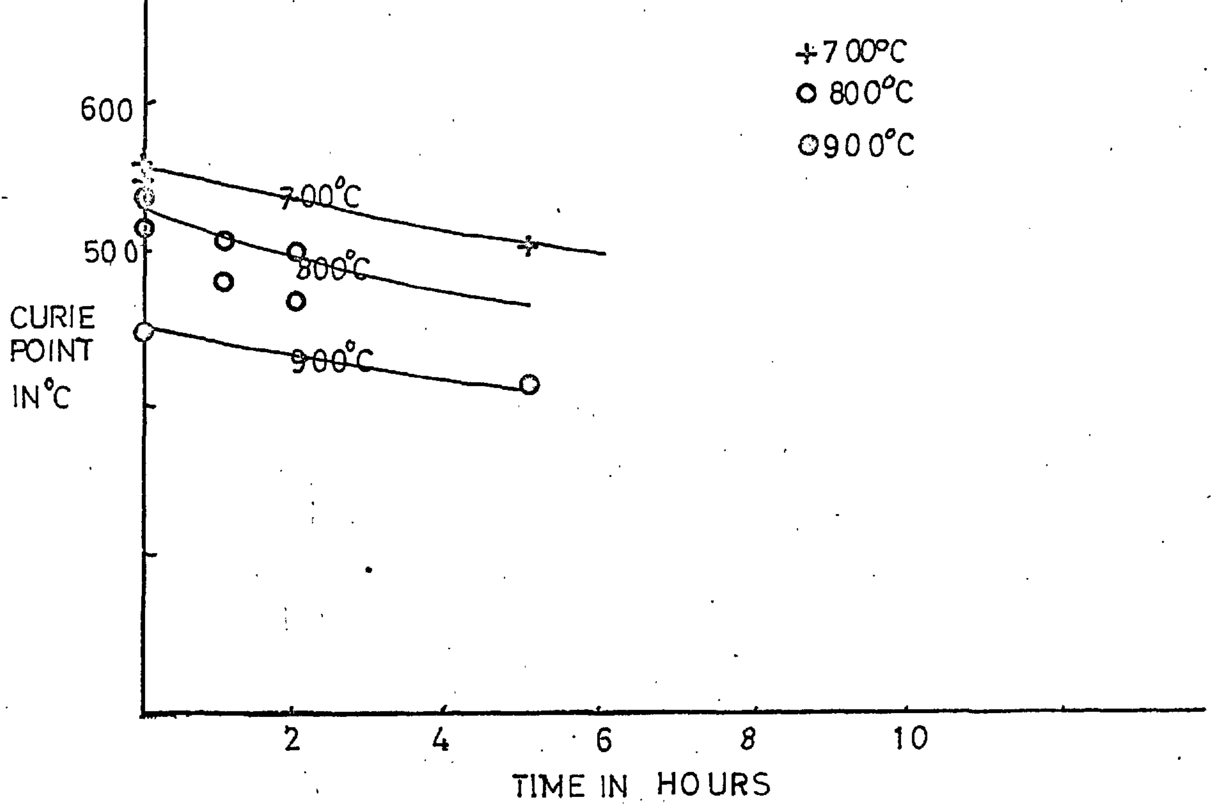


FIG. 35b CENTRE

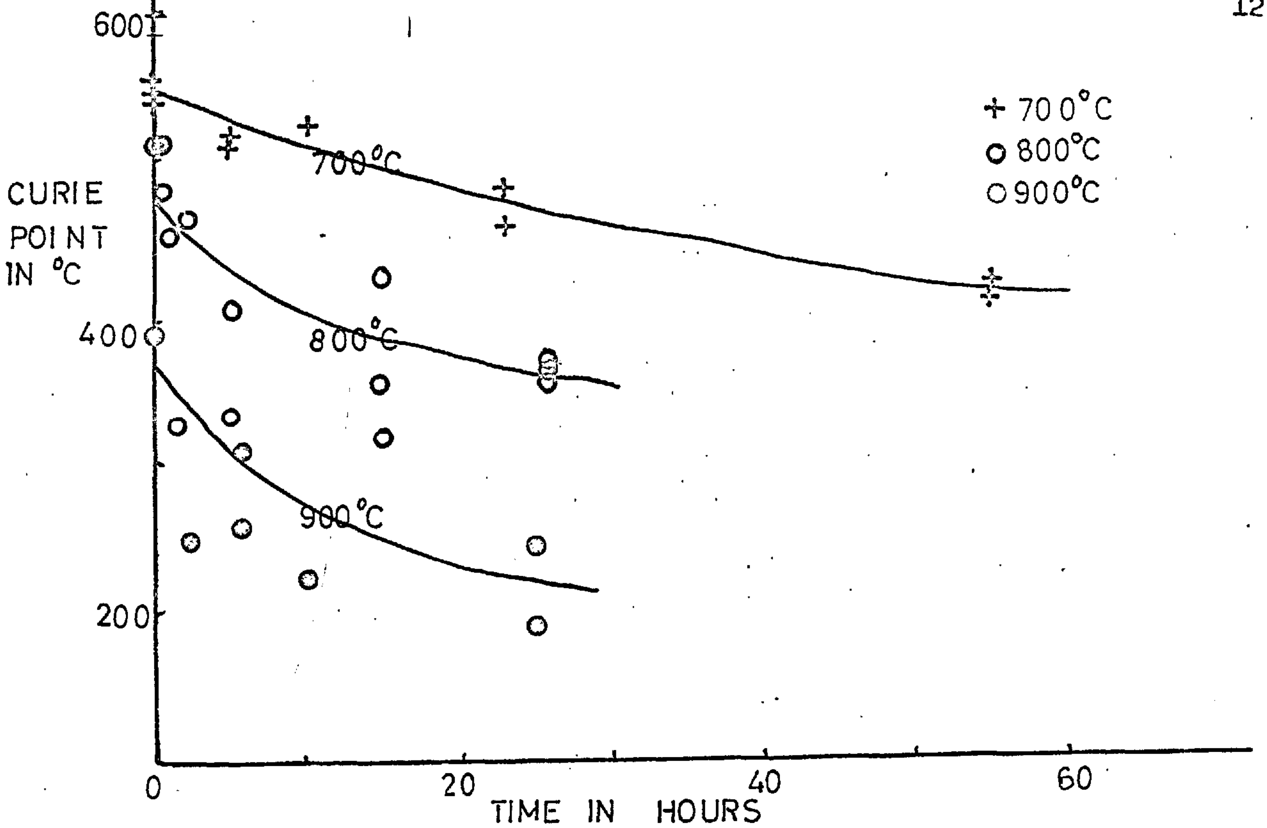
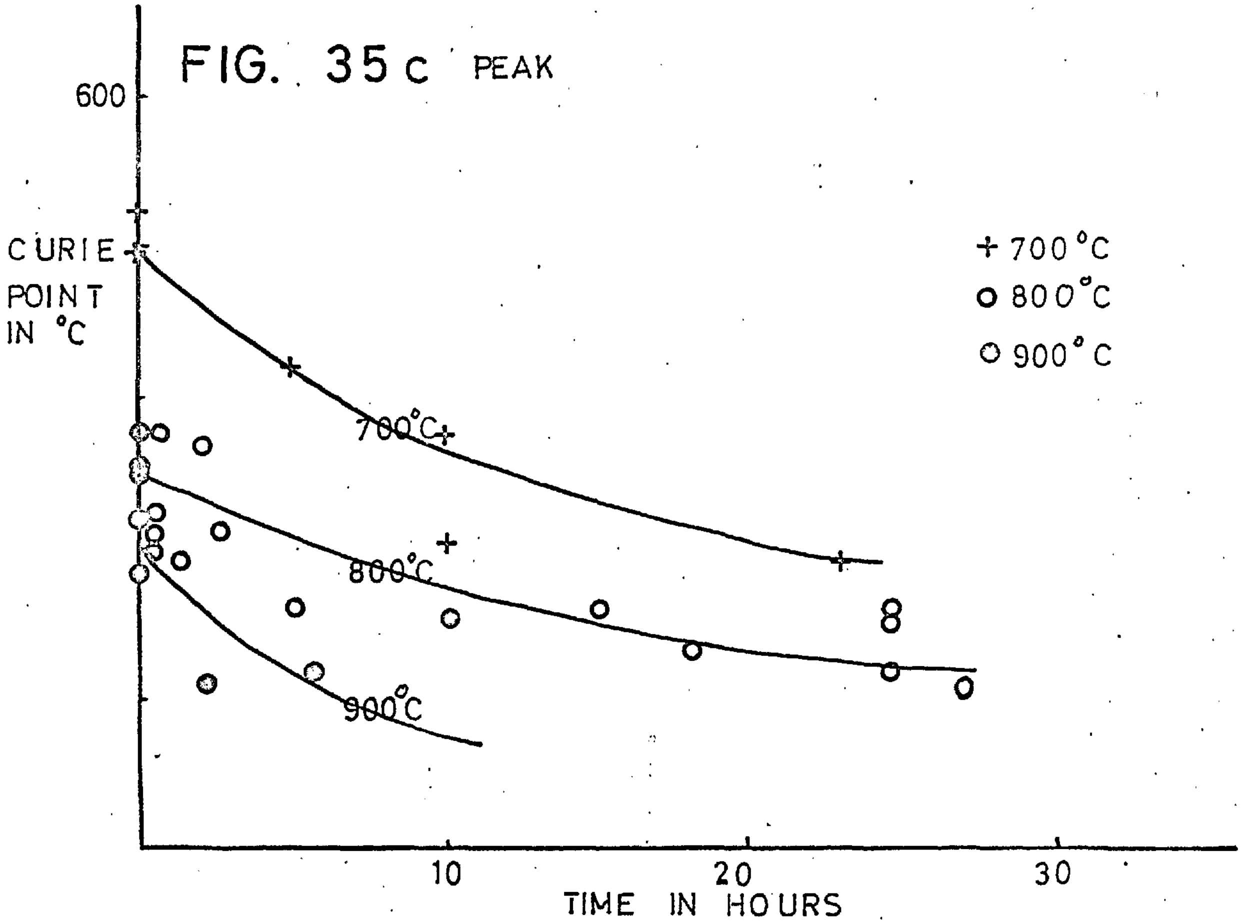


FIG. 35c PEAK



CHAPTER 9.

Petrology of the Rashiehill bore and X-ray and election probe analysis.

9.1. Introduction.

From a study of the polished surface of a rock in reflected light it is possible to identify the different magnetic minerals present. Magnetites appear as bright isotropic areas, ilmenite as bright anisotropic areas and pyrrhotite as ~~a~~ bright more yellow areas. It was decided to make a study of the magnetic grains before and after heat treatment to discover changes that visibily take place during heat treatment. It was possible to use magnifications of up to 1200 on the microscope available.

9.2. Unheated samples.

Samples from 10 positions in the sill were examined. It was found that the grain size varied from .01 mm. on the upper edge to .05 mm. ten feet away up to 1.0 mm. in the centre of the sill. The area of opaque material present varied from 1 to 2^{o}/o ten feet from the edge to 5 to 6^{o}/o in the centre of the sill. In region B where the natural intensity is a maximum the amount of opaque was about 8^{o}/o.

The total area investigated was about 100 square mm. in each case, comprising of 5 samples of approximately 20 square mm., and quite large fluctuations in the percentages were found in different specimens from the same level.

The sample nearest the upper edge had too small a grain size for close study. Ten feet away the magnetic grains were still very small and tended to gather in clusters as shown in Fig. 36. Magnetite and ilmenite grains were observed separately and some grains contained both isotropic and anisotropic areas. A small percentage of pyrrhotite was seen.

The samples from the centre of the sill were very suitable for study because of the large grain size. They all seemed to fall into a similar pattern and the main points are listed below and illustrated in Figs. 36 to 40.

1. Although some small isotropic pieces and some large anisotropic ilmenite pieces were seen separately, most of the large grains consisted of areas of isotropic and anisotropic material. The different anisotropic areas in a grain were generally out of phase as shown in Fig. 39 and crystalline registry existed in many places between the isotropic and anisotropic regions.
2. Crystalline registry also existed between opaque

and non-opaque regions as in Fig. 38 and 39.

3. Generally the ilmenite had a better polish than the magnetite.

4. About 2 to 4°/o pyrite or pyrrhotite was seen, generally as small separate pieces.

5. At very high magnification (x 1200) traces of a fine structure were seen in the magnetite, the size being approximately 1 micron but it was too small to say if this texture was isotropic or anisotropic.

6. The large grains were generally cracked and Fig. 38 shows a typical grain. All the grains are observed in the centre of the sill, 30 feet to 385 feet from the upper edge appeared very similar to this.

7. Very often the grains were very broken and Fig. 37 shows typical broken up grains which were anisotropic. It could not be decided if these were being eaten away or growing.

8. No oriented lamallae of ilmenite were visible except the possible very fine texture seen. The ilmenite always appeared as a large free piece or lathes or bars of ilmenite. This probably means the ilmenite was formed at a later stage than the magnetite.

9. Thin polished sections were examined and showed the

very fine texture, when viewed at 1200 magnification, to be probably ilmenite suggesting oxidation processes have taken place in the rock. But it could not be definately stated that this was the case.

10. Fig. 41 shows the effect of etching with HF. The small anisotropic piece was unaltered but some of the magnetite became very pebbly while some remained rather unattacked.

9.3. Heat treated samples.

After heat treatment the whole rock appeared much lighter and on breaking the capsules a strong smell of sulphur was obtained. The polished sections showed the following differences.

1. The isotropic material appeared to be very pitted even after repolishing and the anisotropic pieces comparitively unaffected. Fig. 39 shows a grain before and after heating (which had not been repolished) and it was clear that the magnetite has been altered much more than the ilmenite and the pyrrhotite had disappeared after heating.

2. In all heated samples examined no pyrite or pyrrhotite was ever seen.

3. The non-opaques appeared much lighter and with crossed niichols are almost transparent and gave a glossy appearance

as though the rock had melted and flowed. This seemed very prominent in the samples heated above 800°C.

4. Dark green areas of non-opaque now seemed to be associated with the opaques.

5. The amount of opaque seemed to have reduced. A measurement of the percentage area of opaque present in all the heated samples compared with the amount in virgin samples confirmed this but in order to be quite sure the following experiment was performed. The percentage of opaques, both isotropic and anisotropic were measured for four pieces of rock from each of six different positions in the sill. The rocks were then heat treated at 850°C for 24 hours, the new curie points measured and the percentage of opaques remeasured. An estimate of the accuracy with which the areas could be measured was that the discrepencies between the total areas before and after heating was 5 per cent. Fig. 42 shows the percentage isotropic and anisotropic material before and after heating for the different positions in the sill. Very clearly the amount of isotropic material had reduced and the anisotropic had not changed significantly.

9.4. Petrological Differences.

1. The isotropic material became pitted and altered by

the heat treatment while the anisotropic material seemed unaltered.

2. The iron sulphides disappeared on heating.

3. The non-opaque minerals had been altered and were much lighter and almost transparent except near the opaque grains where dark green areas were seen. The latter might be due to transfer of metallic ions to the surrounds.

9.5. X-ray analysis.

X-ray diffraction photographs were taken of six magnetic separates from different parts of the sill on a Phil~~l~~ips 8.5 cm. X-ray camera. The magnetic fractions were obtained by grinding the rock to a fine powder and then making a suspension in water. The magnetic fraction was removed by means of a hand magnet inside a test-tube. The process was repeated six times before a suitable X-ray sample was obtained.

The cubic cell-size obtained is shown in Fig. 43 plotted against position in the sill. For all the samples the cell size was almost that of magnetite. Also present was an ilmenite phase and cell sizes measured show that it has a cell size of almost pure ilmenite. It was noteworthy that no second cubic phase was detected. The cell sizes measured were subject to a large error because the back lines which are the most important ones for accurate measurement were very blurred as seen from the films in Fig. 44. The back lines arise from high order reflections and this shows that the crystal structure was not perfect for more than 10 or 12 layers of atoms. Dislocations, strains the effect of oxidation or impurities then enter to complicate the position. This always seemed to be the case for materials in rocks.

It was not possible to extract the magnetic fraction from the heat-treated material and no comparison of cell size after heat-treatment could be made.

The important conclusions that can be drawn from the X-ray rock was that one cubic phase only exists and that ilmenite although non-magnetic still appears in the magnetic fraction because it coexisted so closely with the magnetite in the large grains. The cell sizes were approximately correct for the curie points found.

9.6. Electron probe microanalysis.

A limited time was available on the instrument[63], which can measure the percentage Fe, Ti and other elements above Al in the atomic table, over an area of 1 square micron.

From the iron to titanium ratio the value of x in the series $(1-x)\ Fe_3O_4 . x\ Fe_2TiO_4$ and y in $(1-y)Fe_2O_3 . y\ FeTiO_3$ can be determined.

An unheated sample from the centre of the sill gave x = .44 on a single spot reading. On taking readings along a line scan of 15 microns variations of x from .42 to .51 were obtained. In the ilmenite phase y was found to be .90. In the grain measured calcium was the only other element present with up to 2°/o in places. This adds an error to x as the position of the Ca atoms in the lattice is unknown, i.e. does Ca occupy Fe^{2+} sites or not. The error in x is about .02 to .04.

For the heat treated sample (after 850°C for 24 hours and now having a curie point of 360°C) x was found to vary between .41 to .43 in three spot tests. The value of y was .94.

For the position in the sill where the maximum intensity was observed only a spot reading of x after heating could be observed and it gave x = .60.

The conclusion to be drawn from these readings are that the titanium content appears fairly constant to within 10°/o for a line span of 15 microns and as the area of a spot reading was 1 square micron it can be concluded that the titanomagnetite was fairly homogeneous. Any fine texture which would give rise to large titanium variations, i.e. ulvospinel exsolved from magnetite must be ~~an order of magnitude~~ less than 1 micron if they exist at all.

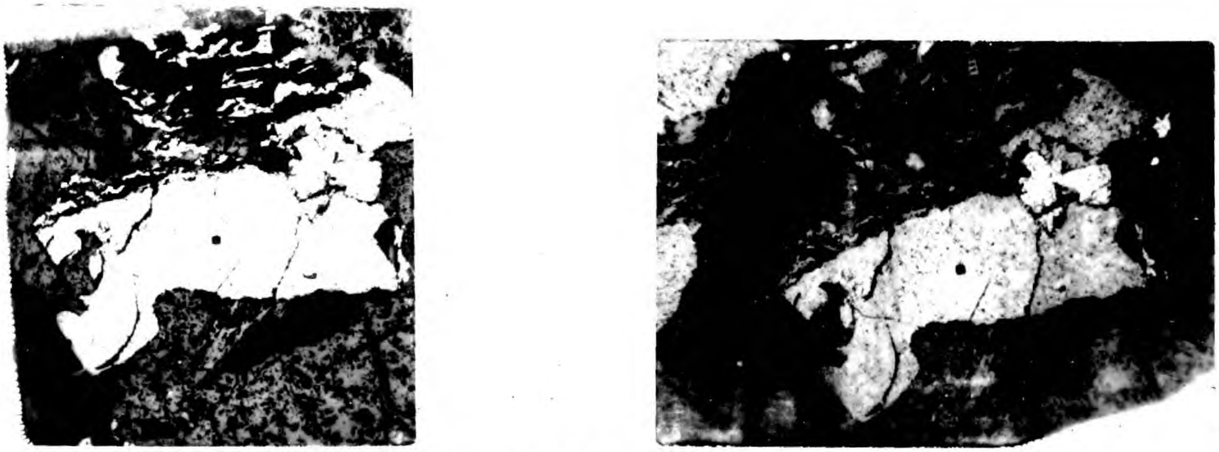
FIG. 36 13 FEET FROM THE EDGE

MAGNIFIED x 55
IN ORDINARY LIGHT

A LARGE NUMBER OF SMALL GRAINS ARE PRESENT

FIG. 37 32 FEET FROM THE EDGE

MAGNIFIED x 55 IN ORDINARY LIGHT NICHOLS 6° OFF CROSSED



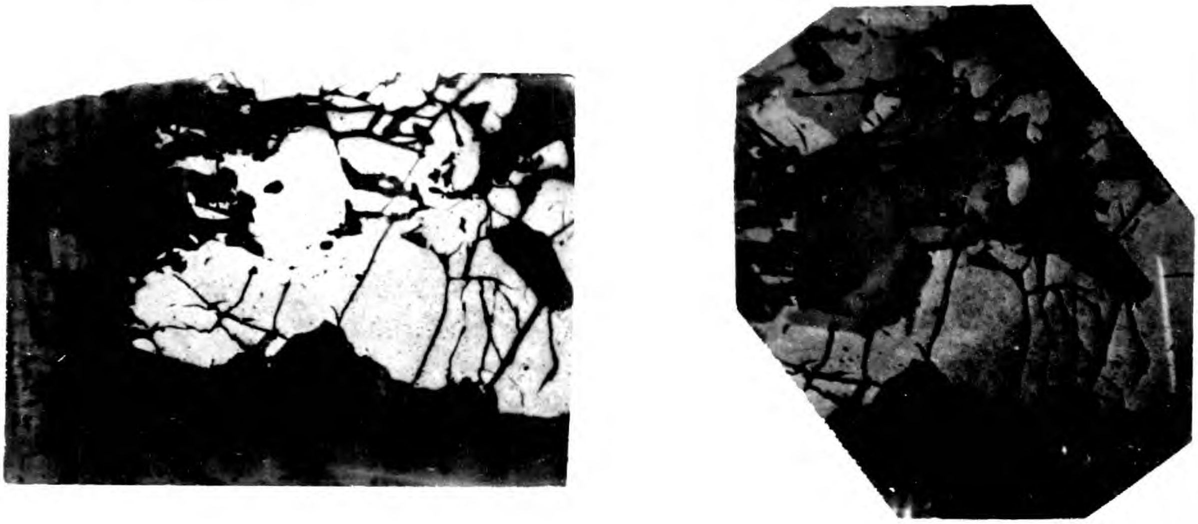
LARGE ISOTROPIC AND SMALL ANISOTROPIC AREAS ARE PRESENT

FIG. 38 CENTRE OF SILL

MAGNIFIED x 55

IN ORDINARY LIGHT

NICOLS 6° OFF CROSSED



LARGE ISOTROPIC AND ANISOTROPIC AREAS ARE PRESENT

MAGNIFIED x 220

CRYSTALLINE REGISTRY BETWEEN OPAQUES AND NON-OPAQUES IS SEEN

FIG. 39 CENTRE OF THE SILL


MAGNIFIED x 55 IN ORDINARY LIGHT

NICOLS 6° OFF CROSSED

ISOTROPIC AND ANISOTROPIC AREAS ARE PRESENT

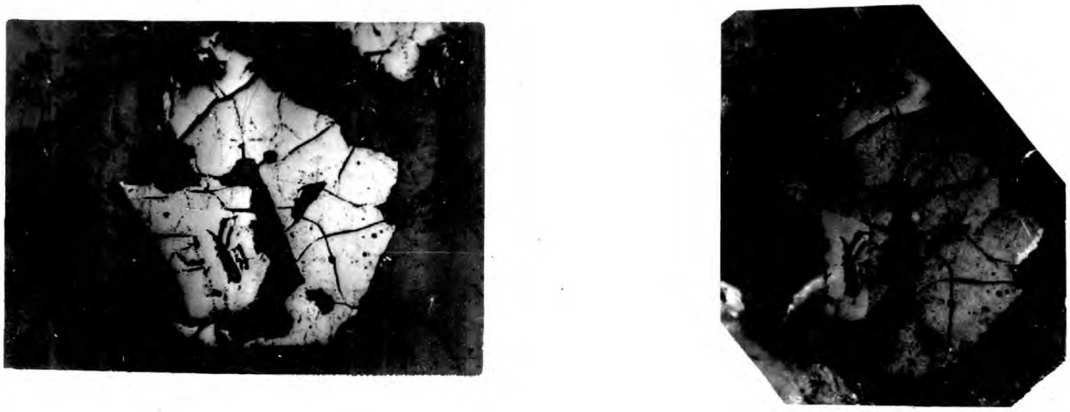
MAGNIFIED x 220


CRYSTALLINE REGISTRY BETWEEN OPAQUES AND NON-OPAQUES

MAGNIFIED x 55


AFTER HEAT TREATMENT
THE ISOTROPIC AREA IS MORE ALTERED THAN THE ANISOTROPIC REGION

FIG 40 345 FEET FROM THE UPPER EDGE



MAGNIFIED x 55 IN ORDINARY LIGHT

NICOLS 6° OFF CROSSED

ISOTROPIC AND ANISOTROPIC AREAS ARE PRESENT

FIG. 41 32 FEET FROM THE EDGE

ETCHED FOR ½ MINUTE WITH H.F.

MAGNIFIED x220 IN ORDINARY LIGHT

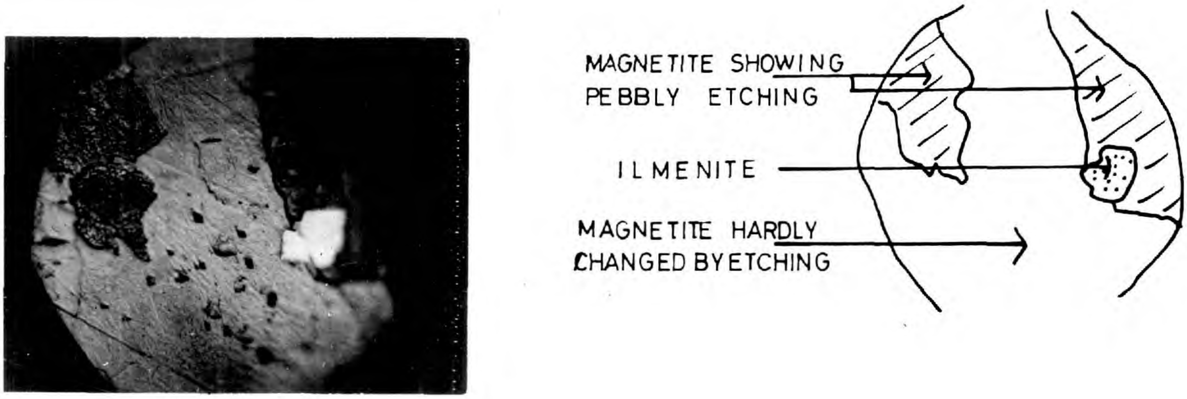


FIG. 42 % AREA OF OPAQUE MINERALS BEFORE AND AFTER HEAT TREATMENT

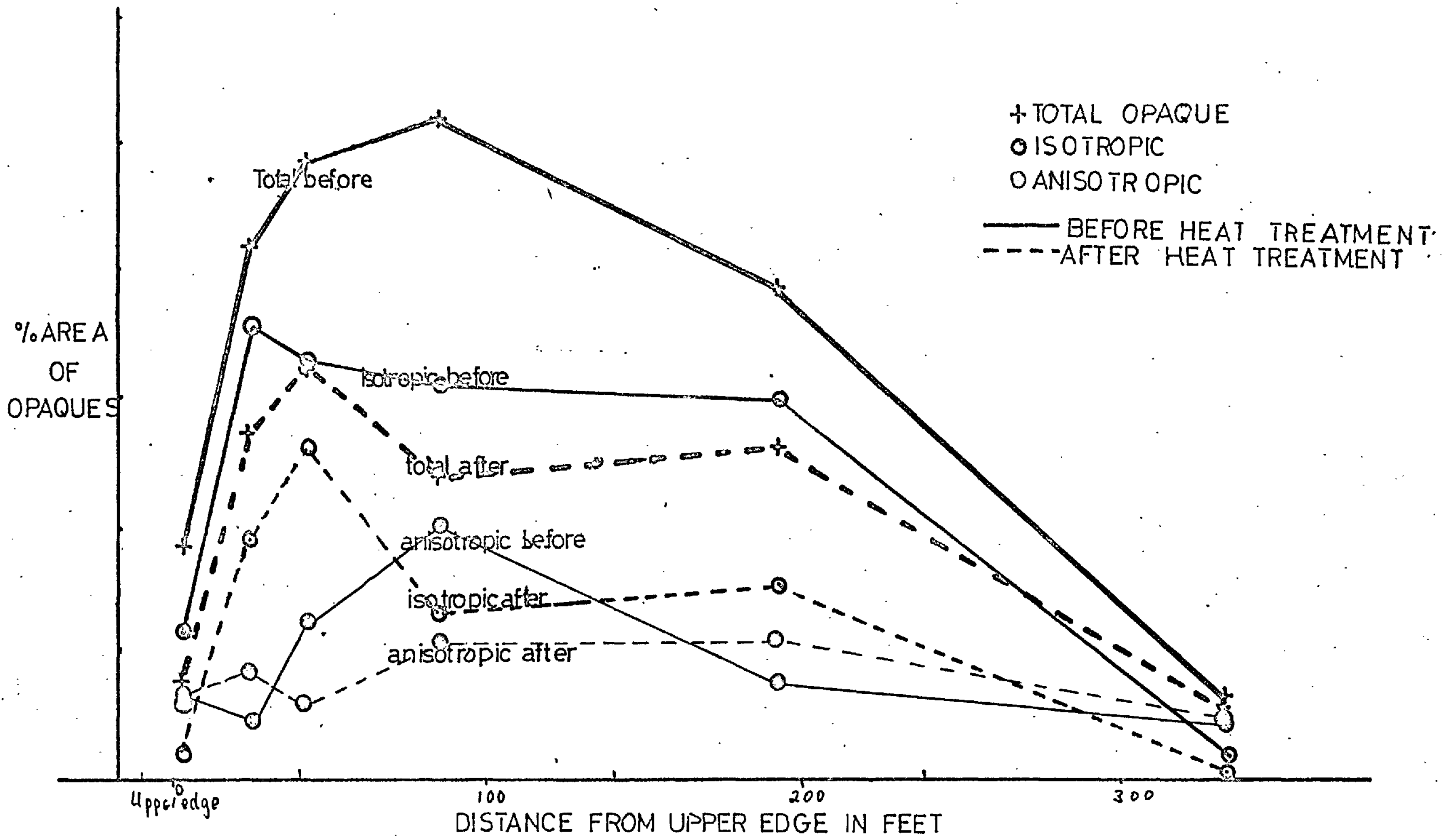


FIG. 43 CUBIC CELL SIZE for different positions in sill

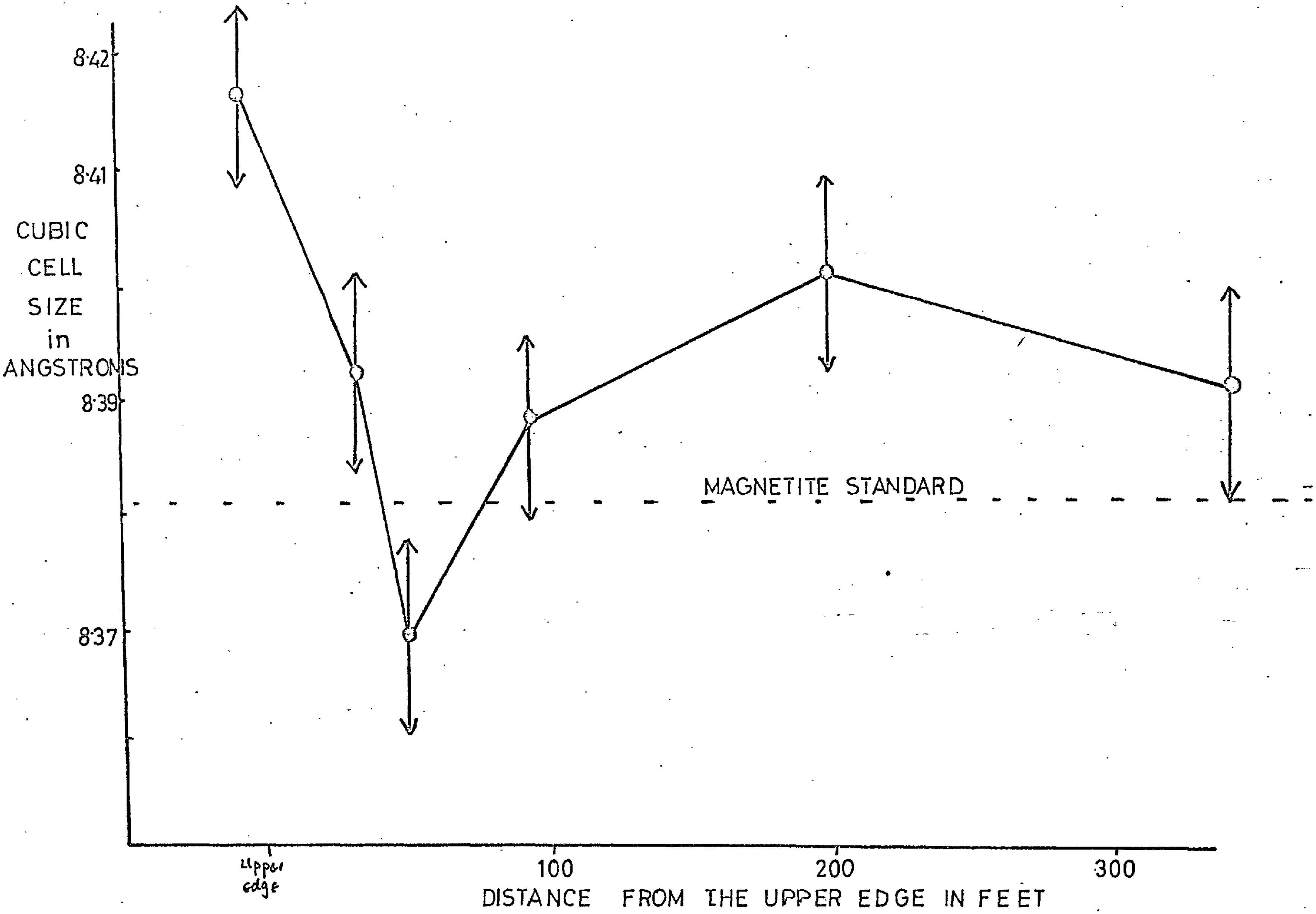


FIG. 44

X-RAY PHOTOGRAPHS OF MAGNETIC SEPARATES FROM THE RASHIEHILL BORE

1. 30 feet FROM THE UPPER EDGE a_t= 8·39 Å LINES 1 to 17 ARE TITANOMAGNETITE LINES, A to V ARE ILMENITE LINES

2. CENTER OF THE SILL a_c=8·40 LINES 1 to 17 ARE TITANOMAGNETITE LINES, 18 to 25 ARE ILMENITE LINES

CHAPTER 10.

Further heating experiments and extension to other igneous rocks.

10.1. Heat treatment of oxidised samples.

In Chapter 8 the dependence on temperature, time, and position in the sill of the thermal properties of the sill was discussed. The next series of experiments describe the effects of heat treating oxidised samples. The following procedure was adopted. The samples were heat treated at high temperatures and their new low curie points remeasured with the samples still in evacuated tubes. The rock was now heated to 600° in air and cooled slowly. Due to oxidation the curie point had risen again. A further heat treatment in an evacuated tube was carried out and the new curie point again measured. Fig. 45a,b and c show the set of curves obtained for three samples, two near the intensity peak and one in the centre. The same pattern was repeated in all three cases. The sample acquired a low curie point after the first heat treatment. Then the curie point rose to almost 550°C after oxidation although traces of a low curie point were still seen. After the second heat treatment the curie point fell again and a very similar curie point to that found after the first heat treatment was obtained and also a similar heating curve. Thus an oxidised sample behaved in a very similar way to a virgin sample during heat treatment at high temperature.

For one set the changes were followed petrologically by having three samples and polishing one after every stage in order to make a comparison. The virgin sample and the first heated sample appeared very similar to the samples described in Chapter 9. After heating in air however many new features appeared. The background of non-opaques appeared red in colour in many places when viewed under crossed nichols and the magnetite grains although still pitted were very light blue on the edge and slightly more brown in the centre. Alteration was seen near the cracks and the rocks were clearly oxidised. After the second heat treatment the redness in the background had disappeared and the magnetite was still pitted and appeared similar to the rock after the first heat treatment.

These observations agreed with the observed magnetic changes.

10.2. Magnetic separates.

The magnetic separates from four levels were heat treated and their curie points fell in a similar way to that of the whole rock.

10.3. Loadstones.

Before discussing possible explanations of this phenomena it was decided to see if similar effects occured in other igneous rocks.

Two loadstone samples from Sweden were heat-treated but no change was found in the curie point as shown in Fig. 46. It was known from chemical analysis[64] that the magnetic fraction consisted of pure magnetite.

10.4. Other sills.

Samples were available from three other sills, the Whinsill in North East England, the Outmain sill in Ayrshire, and the Spitzberg sill from Northern Sweden. All three sills appeared slightly altered petrologically, especially the Outmain sill and they all had high initial curie points of 550°C.

After a similar heat treatment to that given to samples from the Rashiehill bore, the curie points were remeasured and Fig. 47a,b and c show the curves for one sample from each sill. In all cases the curie points had fallen a great deal to values even lower than those obtained from the Rashiehill sill.

10.5. Discussion and explanation.

There are three possible explanations of these results, homogenisation, reduction or a combination of both.

1. Homogenisation.

Homogenisation in the ulvospinel-magnetite series has been repeated[23] and does cause a fall in the curie point. Homogenisation requires two phases to be present and thus two curie points, which become one phase with an intermediate curie point. Two curie points moving together can be expected. Also because the intensity of magnetisation increases approximately linearly with curie point, no change in intensity will be observed, one phase decreasing in intensity as the other increases in intensity. In the rocks measured there was possibly a very fine structure but it was less than 1µ in size. However ulvospinel had only been reported as a fine cloth-like texture. The lower curie point may have been masked by the greater intensity of the upper curie point and the X-ray pattern explained by the fact that the blurring of the lines was due to a spread of compositions, or the ulvospinel being too finely divided to be observed. Thus the second phase may be present but was undectable even by the electron probe.

The intensity values and the results from the oxidised samples cannot be explained by a homogenisation process and the limiting value of curie point should be the same for all quenching temperatures but this was not found to be the case.

If the process were homogenisation then at temperatures below 600° where the solvus region exists exsolution ~~may~~ would be found in samples with a 200 to 300°C curie point. This was ~~attempted~~ investigated with four such samples, heating one at 400° for 39 days and the others at 525, 575° and 590°C for 13 days, but the curie temperatures remained practically unaltered, rising by 10° in three cases but showing no sign of a second curie point. It is possible that exsolution takes place on a much longer time scale than can be achieved in the laboratory. Wright et al[28] obtained homogenisation but failed to produce exsolution.

Thus homogenisation is not a satisfactory explanation of all the facts.

2. Reduction.

The results can be explained by reduction effects. These require one phase and one curie point, with the titanomagnetite initially in an oxidised state. After reduction the curie point would be lower, the intensity decreased but the same iron to titanium ratio as in the original sample. All these were found to be associated with the process.

A limit would be reached with heating time and for different heating temperatures different limits would be observed because reduction is a chemical change due to a chemical reaction and the equilibrium states are temperatue dependent. This is another striking difference from homogenisation.

The behaviour of the oxidised rock was clearly a repeat of the process and the X-ray pattern due to disorder in the crystal lattice similar to that found in oxidised synthetic titanomagnetites.

The reduction process demands that the rock is in an oxidised state initially. Wilson et al[54] and Ade-Hall[65] have already shown that the behaviour and properties of many igneous rocks can only be explained by assuming they are in an oxidised state so that the requirement that sills are in oxidised state is plausible.

The cause of reduction has to be discussed. It is known from the fact that explosions occurred on heating too much rock in a sealed evacuated quartz tube that a great deal of rock gas can be emitted. Sulphurous material and water vapour have been found and there were probable other gases as well. Chapter 11 shows the different effects rock gas can have and it is possible that the rock gas has reducing properties in some cases. The question whether the rock gas is oxidising or reducing is difficult to answer as it depends on the prevailing conditions when the minerals were formed. However even in an inert atmosphere reduction of an oxidised synthetic titanomagnetite can take place at the temperatures used for these heat treatment. This was shown in Chapter 6 Uyeda[32] found in a study of the ilmenite-haematite series, heating in an evacuated tube had reducing effects.

There is a strong case for reduction being the cause of this phenomena

3. Homogenisation and reduction.

If the very fine texture is ilmenite caused by oxidation of exsolved ulvospinel then a combination of both above methods may be the explanation. The ilmenite may homogenise directly into the host magnetite but this seems unlikely or get reduced before homogenisation takes place.

This has many similar arguements against it as in the homogenisation case and an additional one is that the large ilmenite grains appear to be unaffected. Reduction of proposed ilmenite intergrowths would surely affect all the ilmenite present.

10.6. Conclusions.

A critical review of the suggested mechanisms in the light of all the experimental facts shows that reduction is the cause of this phenomena. This explains all the results and the work on synthetic material shows it is possible to reduce oxidised titanomagnetites in an inert atmosphere simply by heat treatment.

This immediately leads to the conclusion that the original sills must have been in an oxidised state and this is supported by petrological evidence.

In rock magnetism many people do not like to work with surface rocks because they fear weathering (~~oxidation~~) effects may influence the direction of remenent magnetisatio Everitt[62] has shown that measurements from sills buried deep underground still can give unreliable results and the fact that these sills have been shown to be in an oxidised state makes the choice of material very selective. The sills and lavas may be oxidised any time in their history and so samples with high curie points which appear to be oxidised, should be avoided for reliable palaeomagnetic data to be obtained.

J_{sat} FOR HEAT TREATED OXIDISED SAMPLES

FIG. 45a SAMPLE 32 FEET FROM THE EDGE

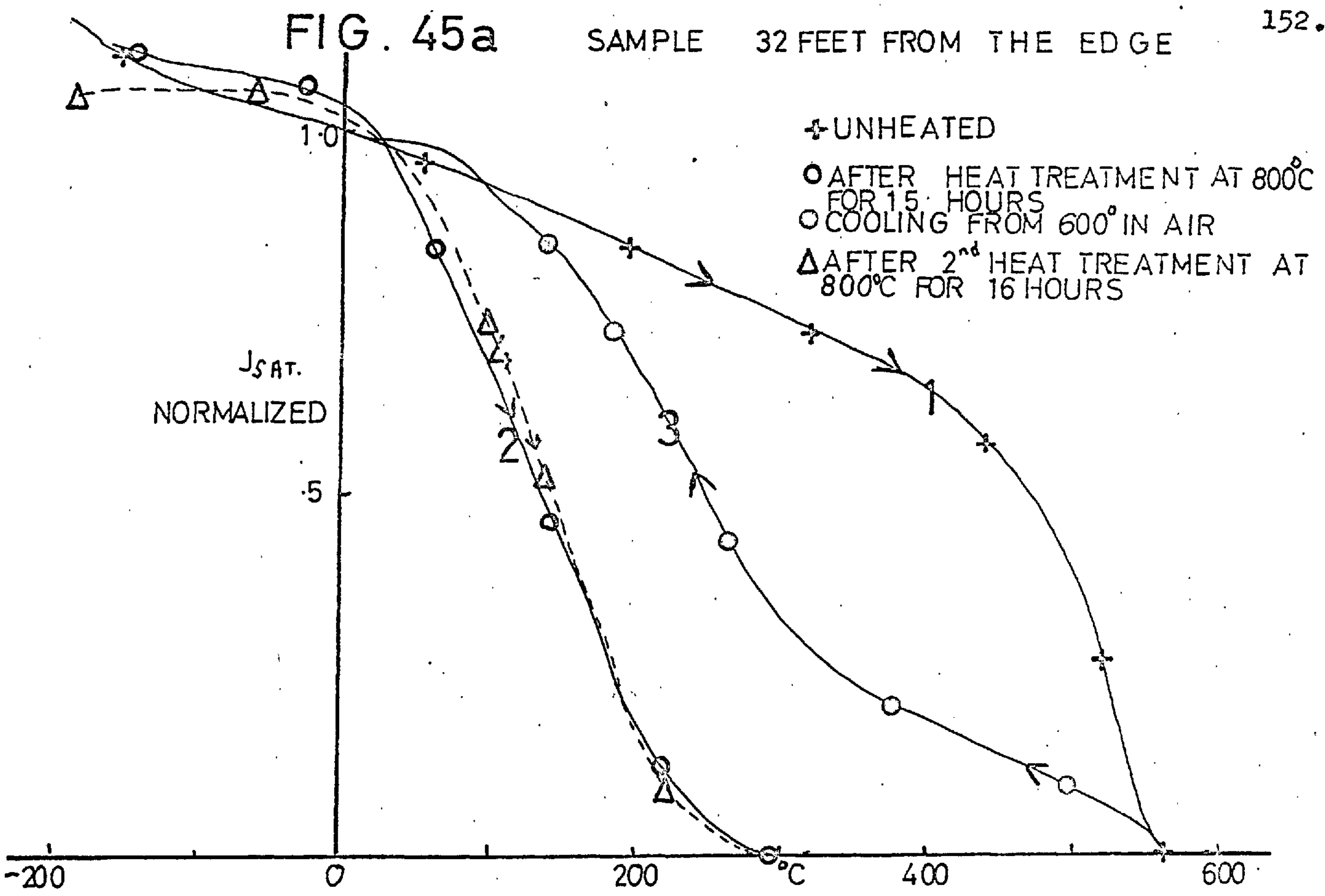


FIG. 45b SAMPLE 50 FEET FROM THE EDGE

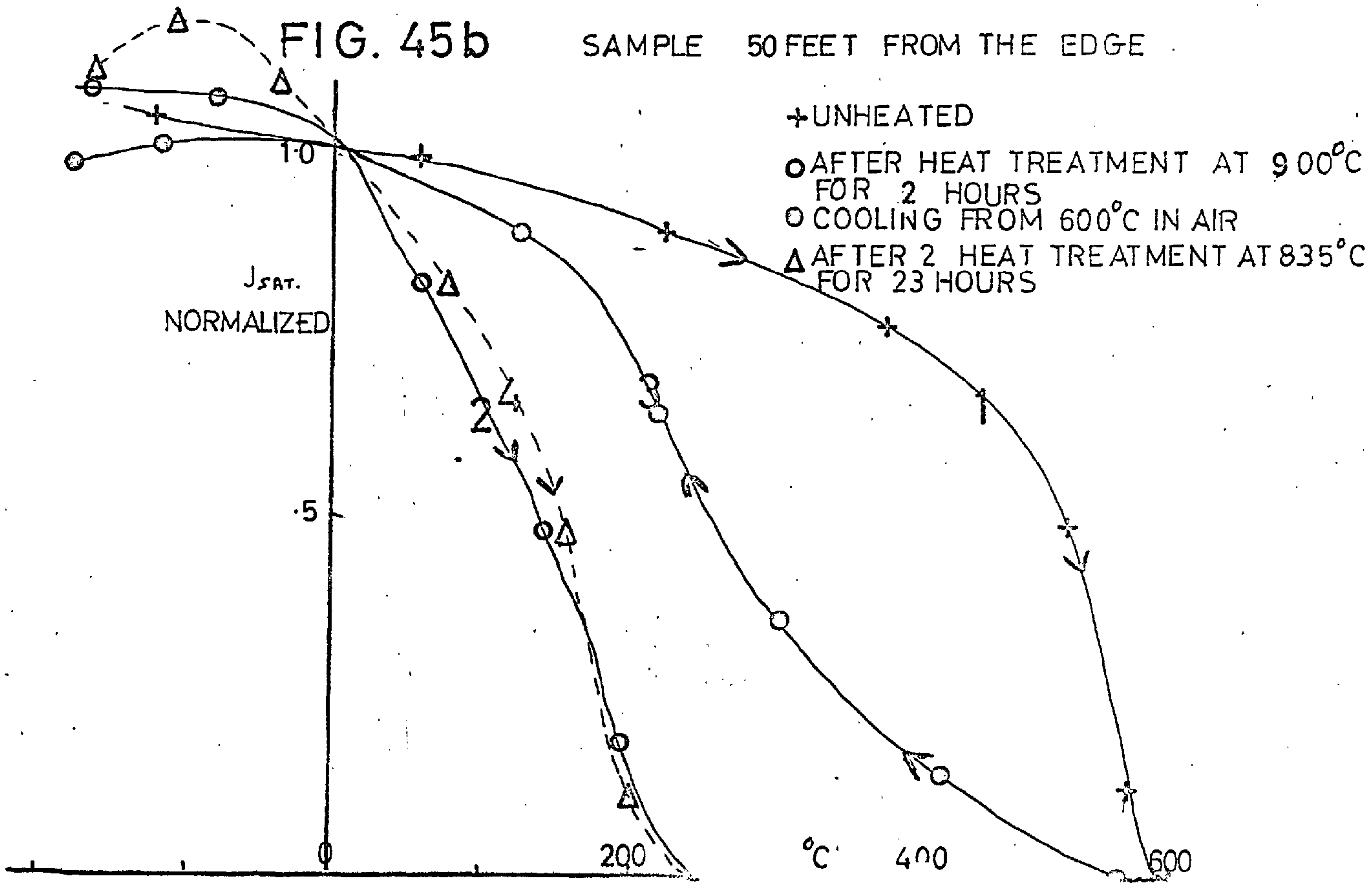


FIG. 45c SAMPLE 201 FEET FROM THE EDGE

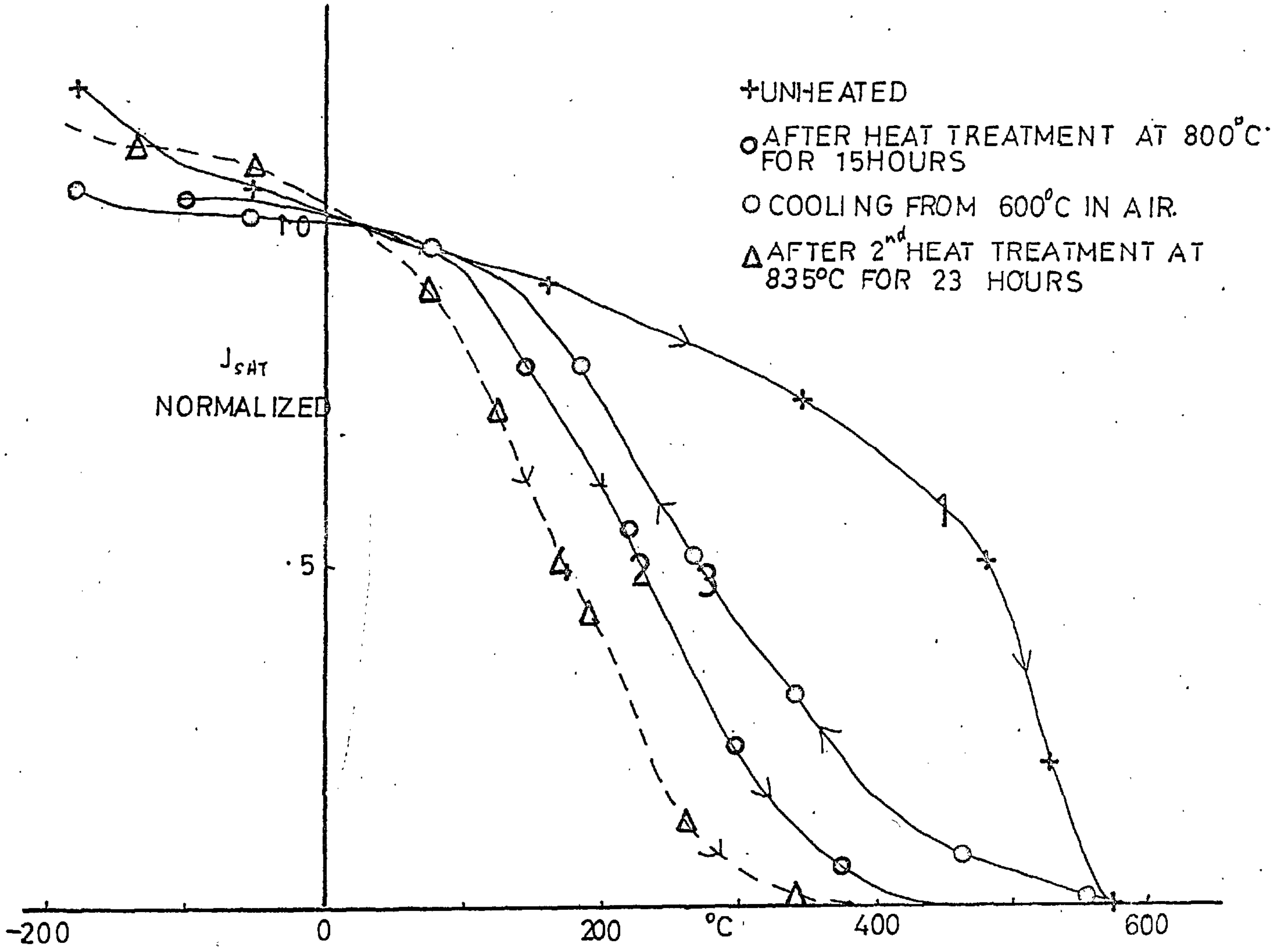
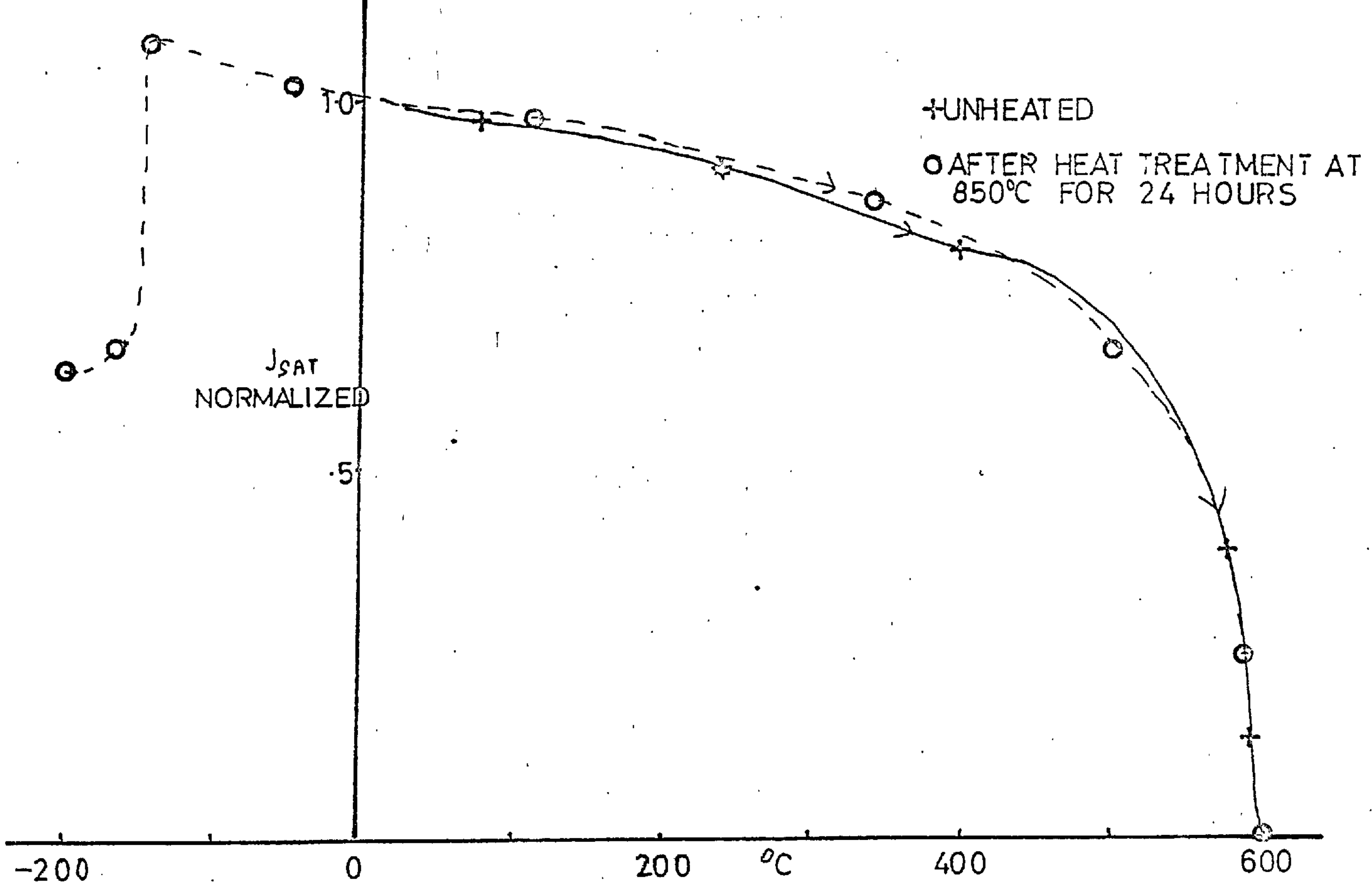


FIG. 4.6 J_{SAT} FOR HEAT TREATED LOADSTONES



HEAT TREATED SILLS

FIG 47a $J_{SAT.}$ FOR OUTMAIN SILL

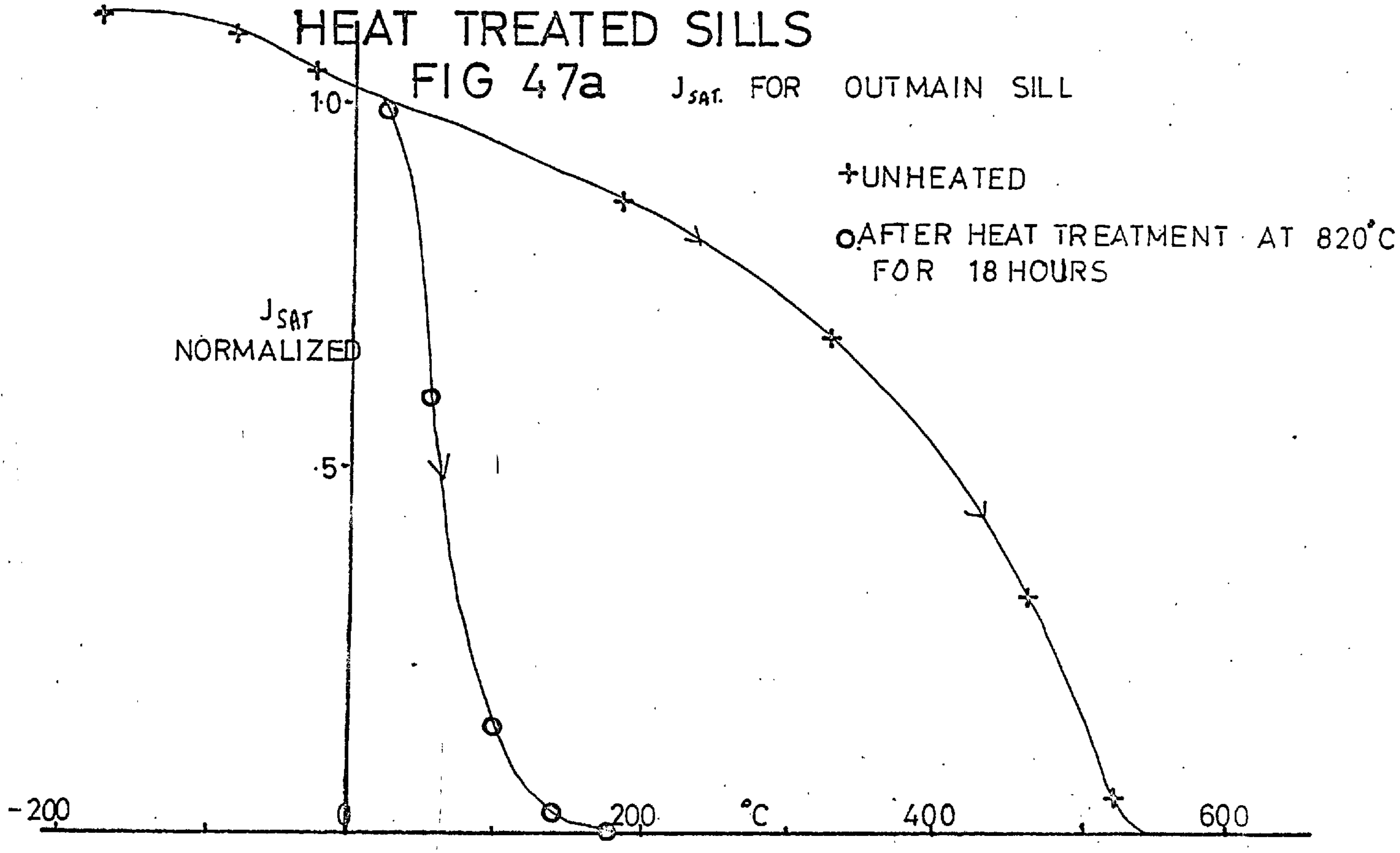


FIG. 47b J_{SAT} FOR SPITZBERG SILL

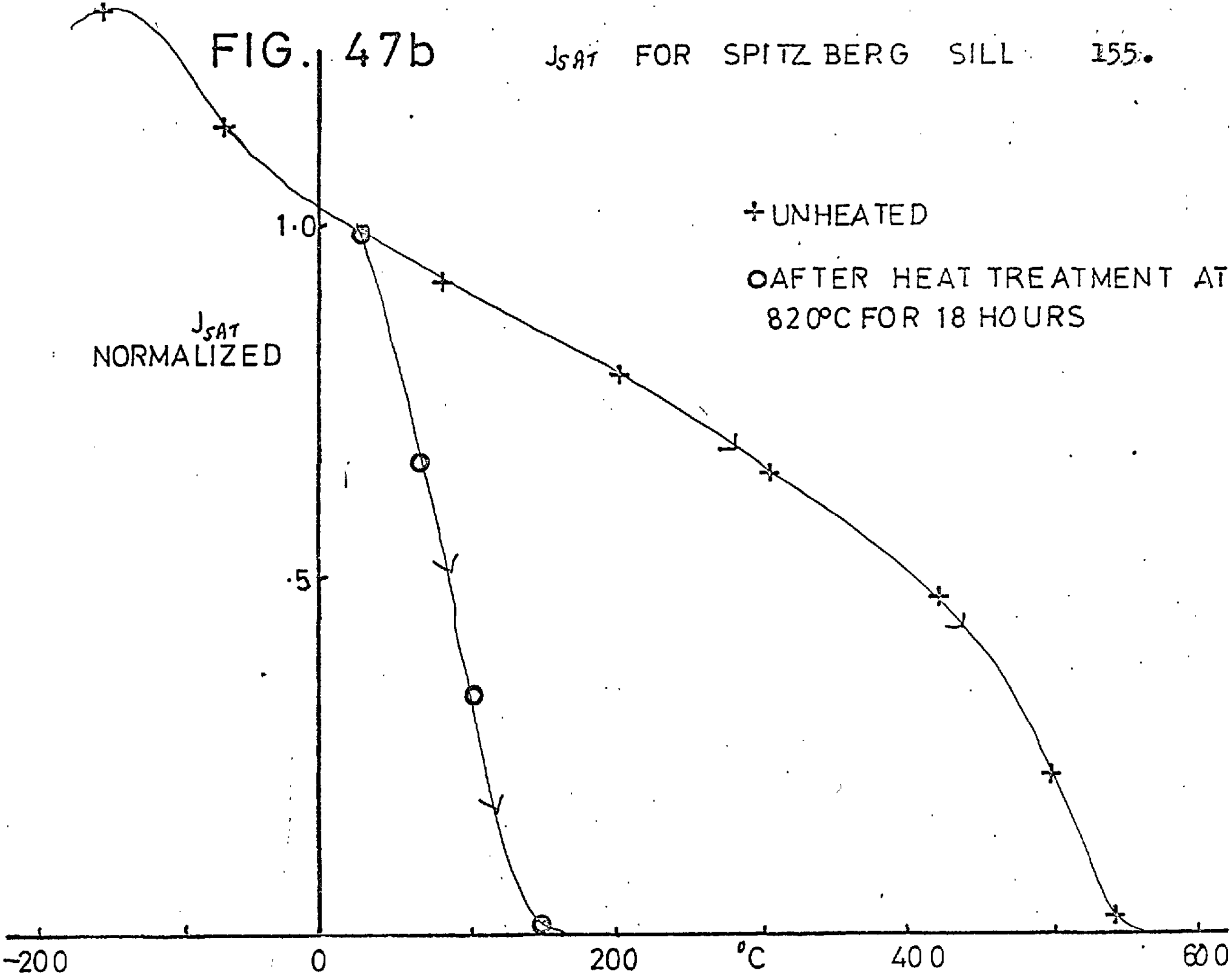
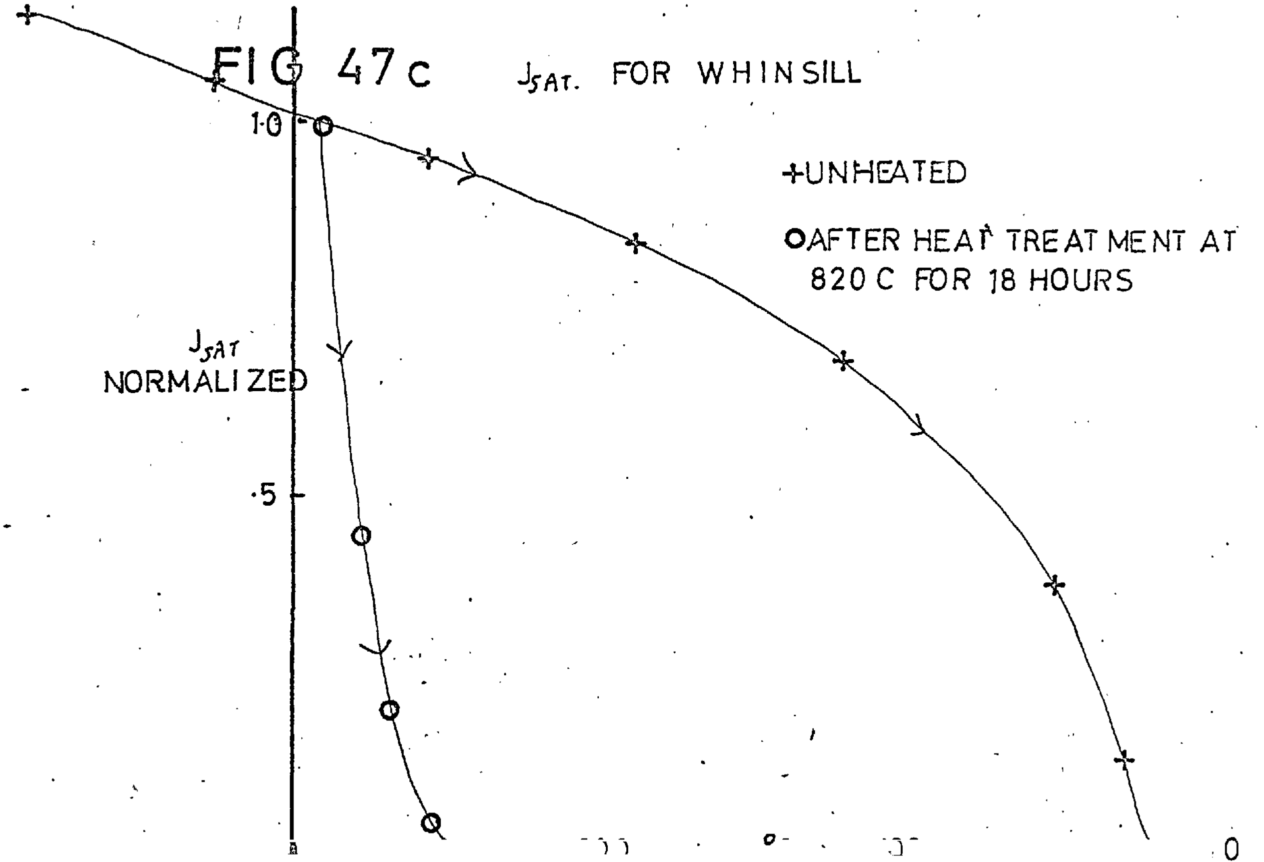


FIG 47c $J_{SAT.}$ FOR WHINSILL



CHAPTER 11.

Thermal demagnetisation of rocks.

11.1. Experimental procedure.

In the last chapter the importance of the gases evolved on heating rocks in an evacuated space was shown. It was decided to thermally demagnetise different igneous rocks in air and in evacuated tubes and to compare the heating and cooling curves obtained. Rocks used were from sills, irish lavas, recent Hawaiian lavas and submarine lavas. The curves were measured on the instrument built by Wilson and Smith described in Chapter 3. The samples weighed approximately 0.2 grams and again variations of the saturation moment J_{sat} at 20°C were observed due to inhomogenity.

Polished thin sections of all the rocks investigated were studied to see if there were any striking petrological features which may be used to elucidate the differences in the thermal demagnetisation curves.

11.2. Sills.

Samples were available from four sills.

1. Whinsill.

Fig. 48a and b show the results obtained from two of the three samples measured. The curves in air and in an evacuated tube are very similar except on Fig. 48b, which was for a sample from the centre of the sill. Here further oxidation takes place and the curie point rises to 600° from 550°C. Cooling curves follow the heating curves very closely with slight thermal hystersis present.

Petrologically the magnetic grains were similar to the Rashiehill sill in general features, being up to 1mm. in size. Some pieces of isotropic material and a few large pieces of free ilmenite were present. The large grains had large isotropic and anisotropic areas and away from the ilmenite boundary some clothlike texture was seen. It suggested the Ti ions may be drained into the ilmenite.

2. Rashiehill sill.

All samples measured had high curie points (560°) and cooling curves followed the heating curves fairly closel as shown in Fig. 49a and b. This has been discussed petrologically in detail in Chapter 9.

3. Spitzberg sill.

The heating and cooling curves all were very similar to each other and to those from the Rashiehill sill.

Again free and skeletal ilmenite were seen and the magnetite in the large grains appeared altered.

4. Outmain sill.

Fig. 50a shows the set of curves for a sample 20 feet from the top edge. There is slight oxidation in air and the cooling curves are just significantly lower than the heating curves, comparing with the thermal hysteresis from other sills. This piece again had free ilmenite present but the magnetite appeared more blue in colour and clearly had been maghematised. Altered magnetite was a common feature. The other two samples from the centre of the sill had more interesting curves and the curves for one sample are shown in Fig. 50b. The third is very simila On cooling the intensity was below the heating curve and a ne component appears with a 250° curie point. This happens in air and in an evacuated tube. Petrologically two features stood out. The magnetite in the large grains was altered especially at the edge and along cracks and up to 10^{o}/o pyrrhotite and much free ilmenite were present.

11.3. Irish lavas.

The Irish samples were from lavas, dykes and lavas baked by dykes. They fall magnetically into two groups.

The baked and badly weathered rocks which petrologically appear altered have high curie points and gave similar curves when in air and in evacuated tubes as shown in Figure 51a. The remainder had low curie points and gave an interesting effect on heating. In air above 300° the moment increases with temperature and gives a similar curve to that for synthetic specimens with a similar curie point heated in air (Figs. 4d and 4e). The interesting feature was that even in the evacuated tubes a similar effect was observed. Fig. 51b shows the heating and cooling curves and also the heating and cooling curves (which were identical) for a sample preheated to 600° in a continuous vacuum before sealing and a heating curve taken. Even this does not suppress the oxidation which must have taken place inside the rock as the gas escaped. Oxidation was carried further in air as shown by the higher curie point on cooling in air. Four samples showed this effect. Petrologically these samples contained many small titanomagnetite grains up to 20 microns in size, showed no exsolution and possessed no free ilmenite.

11.4. Hawaiian lavas.

Two recent lavas (formed in 1750 and 1950) were measured. The older lava showed two curie points and little difference in air or in vacuum. Both exsolved and unexsolved ilmenite was present and magnetites growing together with non-opaques were also seen. The 1950 lava had curves similar to the Outman sill. One curie point was seen on heating but on cooling gave a lower intensity and a trace of a lower curie point. This rock consisted of very small (1 to 10 microns) well shaped magnetite grains.

11.5. Submarine lavas.

A lava flow from the Crozet Isles containing no ilmenite and small homogeneous magnetite grains with a curie point of 100°C repeated perfectly in an evacuated tube but in air on cooling from 600° had a curie point of 400° with traces of the original one at 100°C.

Six submarine lavas from the ocean floor were measured and fell into two groups. Three behaved as in Fig. 52a, and oxidised in air to a 590° curie point and in an evacuated tube oxidised to a 510° curie point. All three had original curie points at 300°C. No exsolution was found in these samples which consisted of predominently skeletal magnetite and small discrete ilmenite grains. Three other samples of submarine lavas gave curves similar to Fig. 52b. These all had curie points near 100°

(with quite a large spread) and curves repeated in an evacuated tube but oxidation occured in air. These samples had very little ilmenite and the magnetite appeared in two grain sizes 5 to 20 microns and 1 to 2 microns suggesting that there is two generations of magnetite present.

11.6. Discussion.

The above experiments show that all igneous rocks do not behave in the same way and that the rock gases evolved have far reaching effects on the shape of the thermal demagnetisation curve and the corresponding cooling curve.

Sills, with a high curie point, are in general comparatively unchanged after heating in air or in an evacuated tube, probably because they are already in a state of oxidation. The exception was the highly altered Outmain sill, where a low temperature curie point appeared on cooling.

The recent Hawaiian lava gave a similar effect but the 200 year old one did not do so.

The Irish lava flows and dykes fell into two groups. The baked and weathered rocks with high curie points presumably already oxidised showed little change but the lava flows with curie points near 300°C all showed an increase in moment above this temperature, a typical sign of oxidation. A great deal of rock gas was evolved (the Irish rocks were the most likely to explode) and as the oxidation could not be prevented even by continuous pumping off of the gas it must be concluded that somehow all the rocks of this type from Northern Ireland evolve a strongly oxidising atmosphere on initial heating to above 300°C.

The submarine basalts from the ocean floor with curie points near 300°C showed a similar effect, partially supressed in an evacuated tube but definitely oxidising even then. These rocks were cooled quickly on formation, the petrology confirms this, and have not been exposed to the air since. Yet they still evolve oxidising gases on heating and the conclusion must be drawn that the gases are trapped when the rock is first formed. However, the submarine basalts with a 100°C curie point do not show this behaviour. The heating and cooling curves are identica and repeatable when in an evacuated tube, although the rocks oxidised in air of course.

Thus in this series of experiments on igneous rocks, some remain unchanged when heated in an evacuated tube, some have a low curie point component formed and some still are oxidised by the rock gas. It is noteworthy that all the last grouping have original curie points of 300°C which is something of a mystery temperature in rock magnetism. For plateau basalts Ade-Hall[65] found that the majority have a composition corresponding to a curie point of 50-100°C in an unoxidised state, but were found to have curie points near 300° and 550°C. These are also the two temperatures at which the maxima occur when the frequency of occurrance of curie point is plotted against curie point for all rocks ever measured, Fig. 53a. With the 550° curie point maxima accounted for by complete oxidation the 300°C curie point may conceivably correspond to a metastable partially oxidised state so that oxidation takes place in two stages.

In the case of synthetic samples 300°C again appears as an important temperature, being the curie point of the low temperature phase causing the R.P.T.R.M. In some cases the original curie point was near 300°C but for the sample containing 97°/o ulvospinel reversal of the P.T.R.M. was found and the low curie point component had its curie point at 350°C. A metastable state in the oxidation process may prove to be a very important idea.

11.7. Production of a metastable oxidised state.

In all rock magnetic work two ranges of temperature appear to be especially significant, 500-550°C and 250-320°C. The former range is the curie temperature of the end product in the oxidation of a titanomagnetite irrespective of composition but the 250-320° range of curie point has not yet been explained. It has been mentioned in 11.6 that the Irish rocks with a 300°C curie point have an unusual behaviour and Wilson[54] et al in a study of basalts found a curie point distribution with maxima at 550 and 300°C, Fig. 53b. These should have curie points near 100°C according to composition from electron probe measurements if they were homogeneous and unoxidised. Fig. 53a shows the curie point data for all rocks measured from a survey of the literature and the results of this chapter added. The Japanese results do not indicate which were double curie points so to avoid the complication of double curie points. Fig. 53c has been drawn omitting the Japanese results. The broad maximum at 300°C which extends at one side to 100°C is very clear and pronounced.

Fig. 24 in chapter 4 showed the moment of an oxidised ordered titanomagnetite and the variation with increasing number of vacancies 'C'. It undergoes a discontinuous change of slope along the line x-c = 0.5. This physically corresponds to Fe^{3+} ions now appearing on B sites due to oxidation with the A sites full of Fe^{3+}.

Now Fe^{3+} ions prefer A sites (due to the size of the ion) and so it was assumed that the product of Fe^{3+} on B sites would need more energy than on A sites, and so the energy required to cause oxidation would undergo a finite discontinuity at this point. On this basis the following curves were computed. By direct calculation (given in Appendix 2) the line corresponding to $x-c = 0.5$ was drawn on a ternary diagram in the generalised titanomagnetite region Fig. 54. This corresponds to Fe^{3+} appearing on B sites provided all vacancies occur in B sites. The vacancies have been shown to prefer B sites.

Also on the diagram of moment against x (for x between 1 and .5) lines of constant curie points and oxidation have been added to the contours of c. Fig. 55. The former were calculated from data taken from the ternary diagram Fig. 6 where the dotted lines represent the author's extrapolation of the Japanese results. The oxidation lines and contours of c were theoretically calculated. Also drawn was a diagram of x against c and lines of oxidation and curie point contours again drawn Fig. 56.

All these diagrams clearly show that the stage where the proposed energy of oxidation discontinuity occurs corresponds to a curie point range of 220-320° for x lying between 0.5 and 0.78 which is the range in which most natural samples occur and the range where the basalts of Ade-Hall lie. These calculations were made assuming the vacancies represented by □ in the molecular formula occur in B sites. For oxidation with no ordering a random arrangement of vacancies may occur. The critical line is now $x - \frac{7}{6}c = 0.5$ (Proof is given in Appendix) and is shown in Fig. 54. Fig. 57 shows the plot of moment μ against x for different c values and it is seen that the self reversing region has considerably decreased. The new critical line however is even better because in the range x between 0.5 and 0.8 all compositions meet the line with curie points between 220° and 300°C.

Thus a metastable state of oxidation can exist in titanomagnetites with x between 0.5 and 0.8 and corresponds to a curie point distribution between 220° and 300°C as found in natural samples.

The theory assumes that

1. The energy required to begin oxidation of Fe^{2+} to Fe^{3+} on B sites is greater than on A sites.
2. A large degree of preferential ordering exists in

natural titanomagnetites. If it is not quite ordered originally the effect will be to reduce the energy required (as some Fe^{3+} are already on B sites) and not change the curie temperature range. In this case the metastable oxidation state is less stable than in the ordered state. The distribution of vacancies if not ordered only enhances the effect.

Thus in nature the following scheme can be devised to account for the curie point distribution. The titanomagnetite has a composition corresponding to a 100°C curie point initially. The surface lavas and submarine lavas cool quickly to 100-200°C. Here they are influenced by magnetic gases and undergo oxidation. The curie point rises to 300°C that is to the metastable oxidised state but since the rocks are only at 100°C the thermal energy of the lattice is not sufficient to overcome the energy barrier causing the metastable state, and oxidation ceases and the rock finishes cooling. When heated to above 300°C in the laboratory, there is sufficient energy to cause oxidation. This makes the energy gap required about 7×10^{-14} ergs (k T). Other rocks cooled more slowly can oxidise to a 550° curie point during cooling, having sufficient thermal energy to pass the metastable state.

Some rocks will have cooled too quickly or will not have been subjected to oxidising conditions and remain with a low curie point. Thus a histogram similar to the one shown in Fig. 53d would be expected and compares quite well with the experimental results Fig. 53c. An important conclusion arising from this theory is that most rocks appear to be in a fairly ordered state.

This scheme explains the world survey of curie points obtained and the behaviour of the rocks measured in the laboratory.

11.8. Low field T.R.M. and P.T.R.M.

Some of the samples previously measured in a strong field and described in this chapter were given T.R.M. and P.T.R.M. in a similar way to the synthetic samples in chapter 4 and the thermal demagnetisation curves in zero field measured. All samples were sealed in evacuated tubes.

Three types of curve were obtained. The Whinsill, the Rashiehill sill and the baked Irish rock showed a continuous fall in the T.R.M, with temperature and the P.T.R.M. was similar to the T.R.M. as shown in Fig. 58a. The Outmain sill gave more interesting results. One sample 15 feet from the upper edge behaved as above but two samples from the centre of the sill behaved as shown in Fig. 58b. The T.R.M. had a maximum at 250° and the P.T.R.M. fell on cooling below T_1 and almost reversed. Clearly a negative interaction was present between two components in these two cases in a similar way to the partially oxidised synthetics. These were the samples that acquired a lower curie point after heating to 600°C in an evacuated tube as described in section 11.2. The presence of two components is difficult to explain but it might be that reduction of parts of the material was responsible.

A weathered dyke from Ireland showed a similar effect and again the P.T.R.M. just failed to reverse as shown in Fig. 58c. This rock has been oxidised by weathering and the existence of a metastable state of oxidation or simply some unoxidised grains seemed to be the cause of the low temperature component.

The third type of curve produced is shown in Fig. 58d. The sample from Sudan had not previously been measured in strong fields but was of interest in that it was found[66] that the natural remanence reversed on heating. The T.R.M. fell steadily with temperature but the P.T.R.M. decreased on cooling below T_1 and just failed to reverse. A similar set of curves was found for one of the Hawaiian lavas. Again a metastable oxidised state may be a partner in the negative interaction.

Lewis[52] has shown a similar effect to occur in Indian lavas and finds a R.P.T.R.M. is obtained by using the magnetic separates only.

In these experiments 5 out of 12 samples showed some form of negative interaction which appeared very similar to the R.P.T.R.M. of partially oxidised synthetic titanomagnetites and so this phenomena is by no means a rare occurance. This supports the inferences in chapter 4 when a R.P.T.R.M. in synthetic samples was discussed and this type of mechanism can leave far reaching effects on rock magnetism.

11.9. Conclusions.

Three main conclusions arise from this chapter.

1. Heating rocks in evacuated tubes does not always prevent alteration taking place and the rock gases can have important thermal effects.

2. There is support for the idea of a metastable oxidised state due to the additional energy required to cause oxidation of Fe^{2+} to Fe^{3+} on B sites [illegible] than on A sites. This may cause a component with a 300° curie

point to be formed on oxidation of a titanium rich titanomagnetite.

3. Negative interaction which can cause reversal of the P.T.R.M., exists in many rocks, between a high curie temperature component (500-550°C) and a low temperature component (220-300°C) and may be important in rock magnetism.

sat FOR THE WHINSILL HEATED IN AIR AND IN THE ABSENCE OF AIR

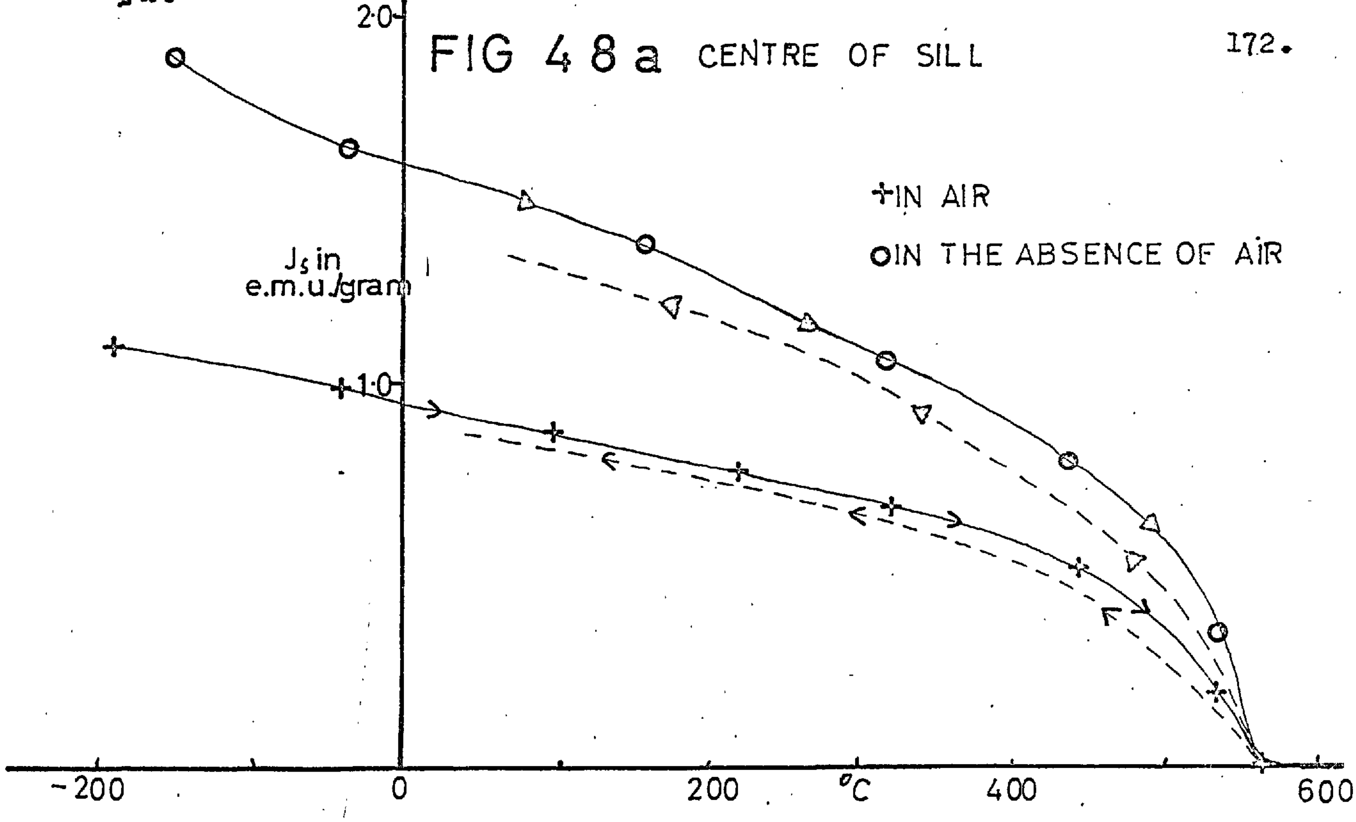


FIG 48 a CENTRE OF SILL

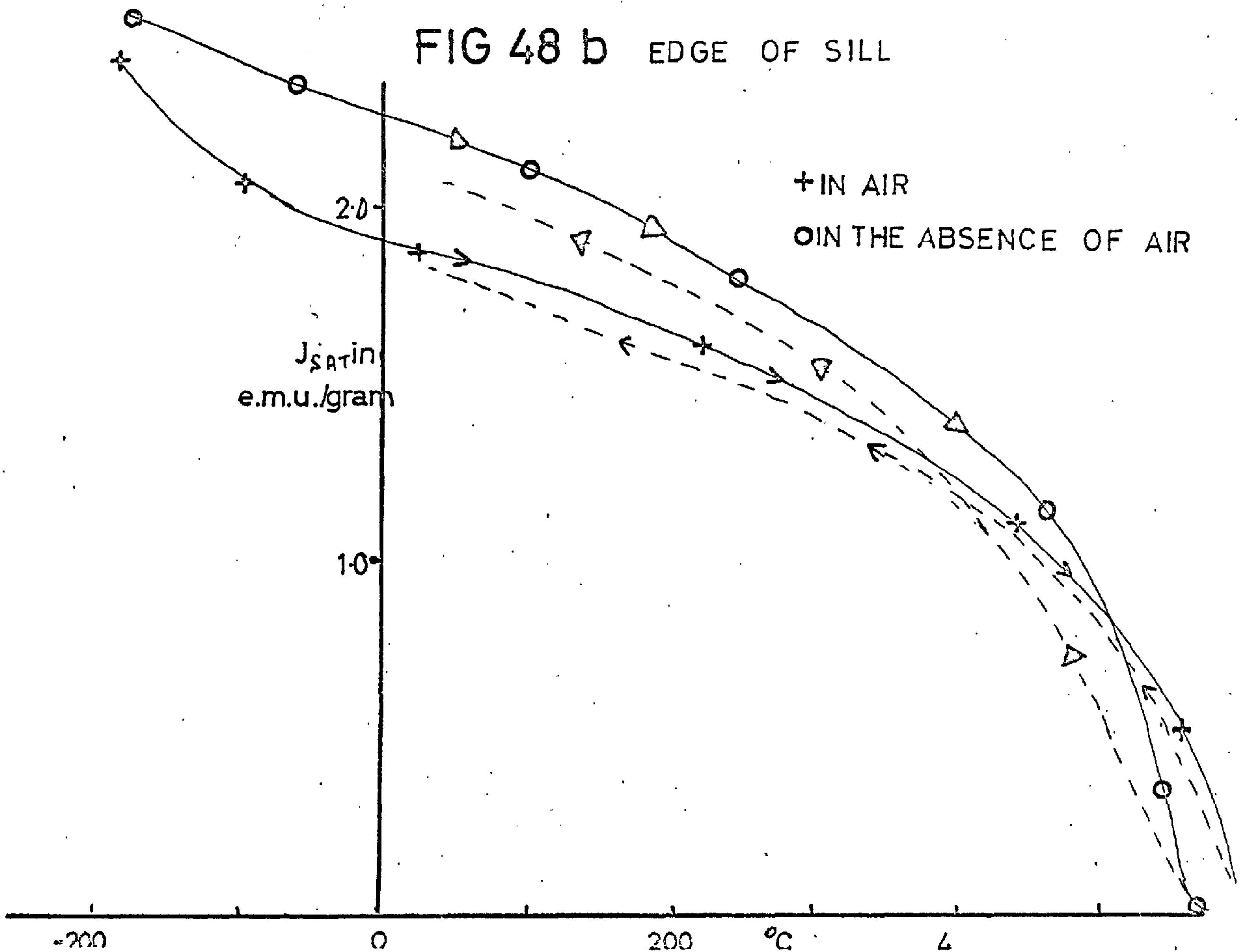


FIG 48 b EDGE OF SILL

J_{sat} FOR THE RASHIEHILL SILL

FIG. 49a 32 FEET FROM THE EDGE

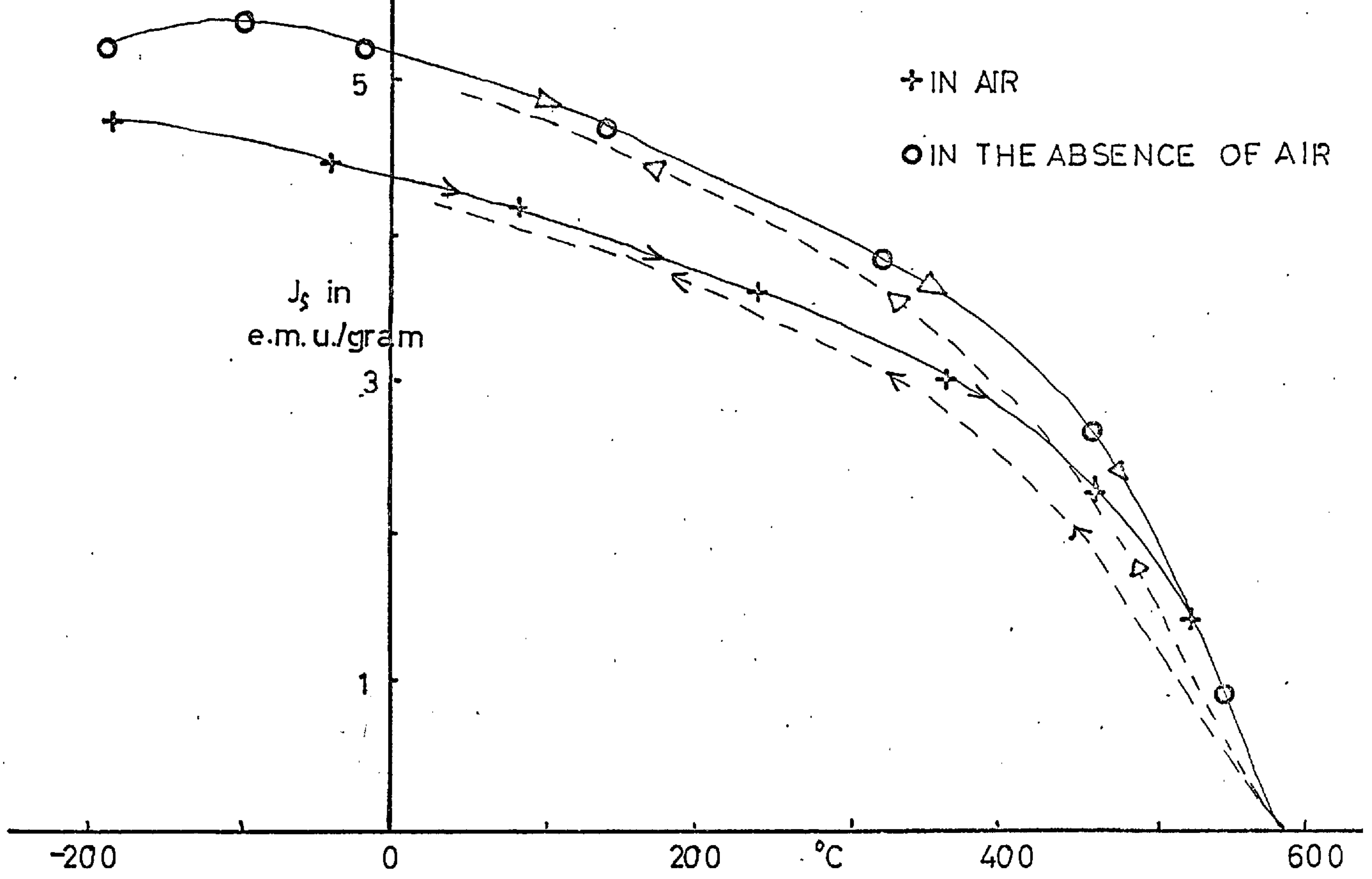
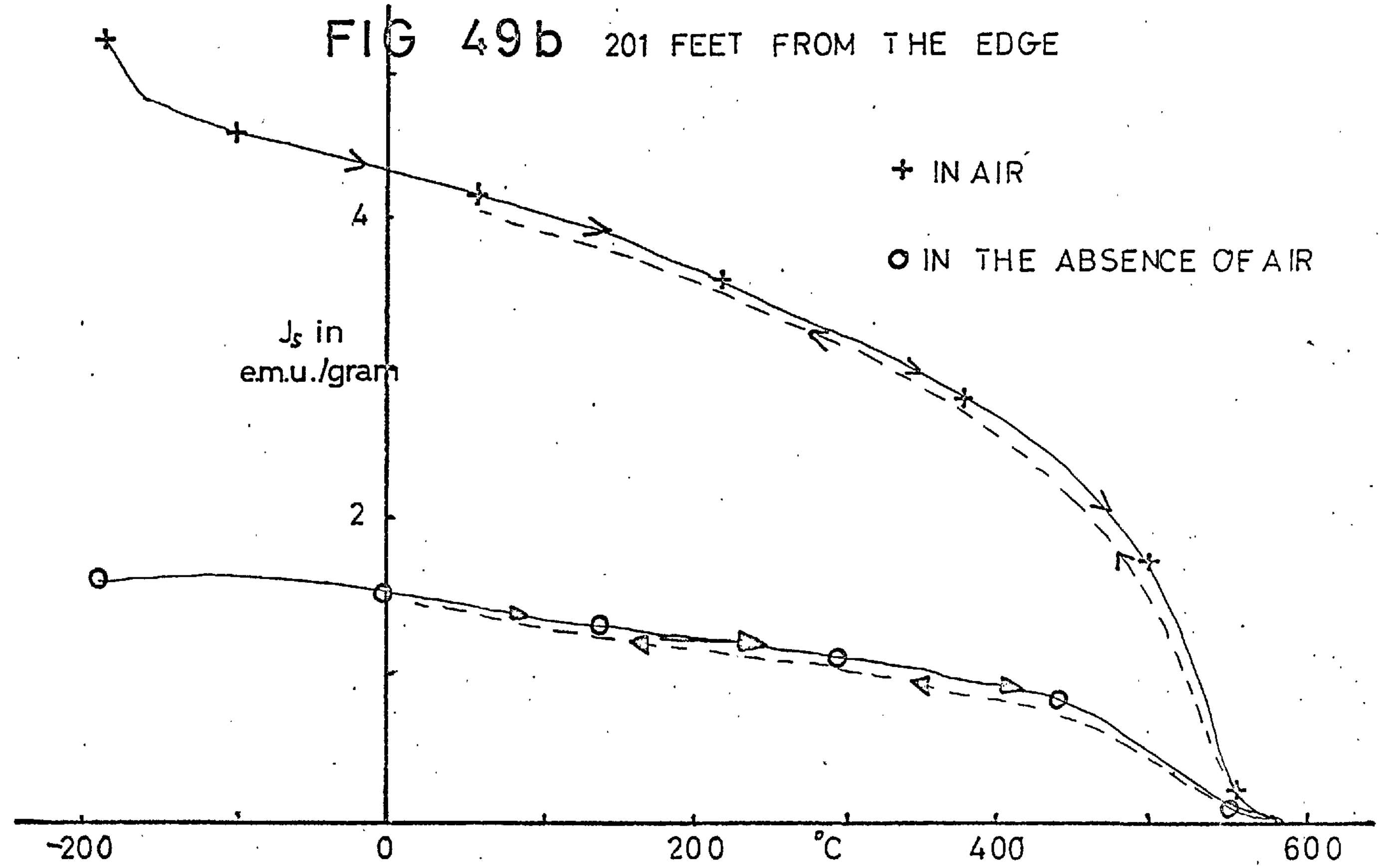


FIG 49b 201 FEET FROM THE EDGE



J_{sat} FOR THE OUTMAIN SILL

FIG. 50a 23 FEET FROM THE EDGE

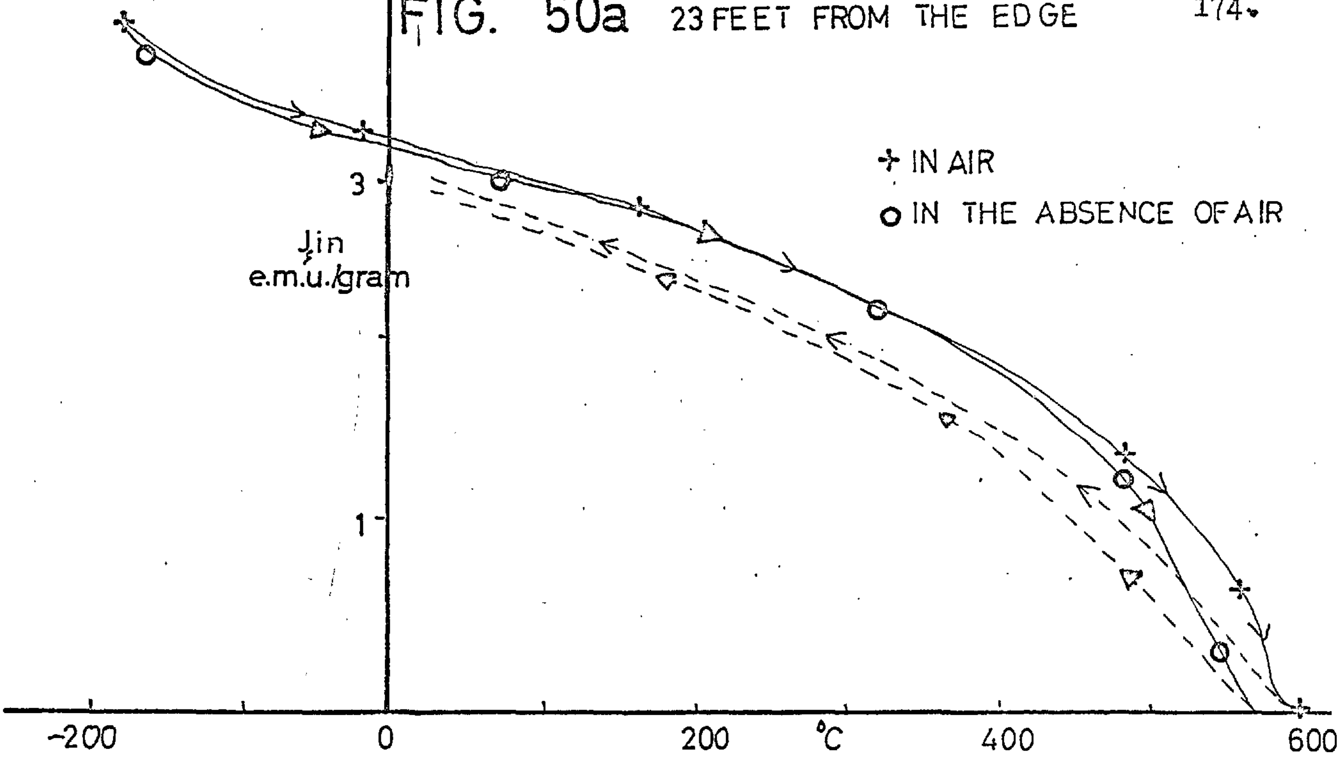
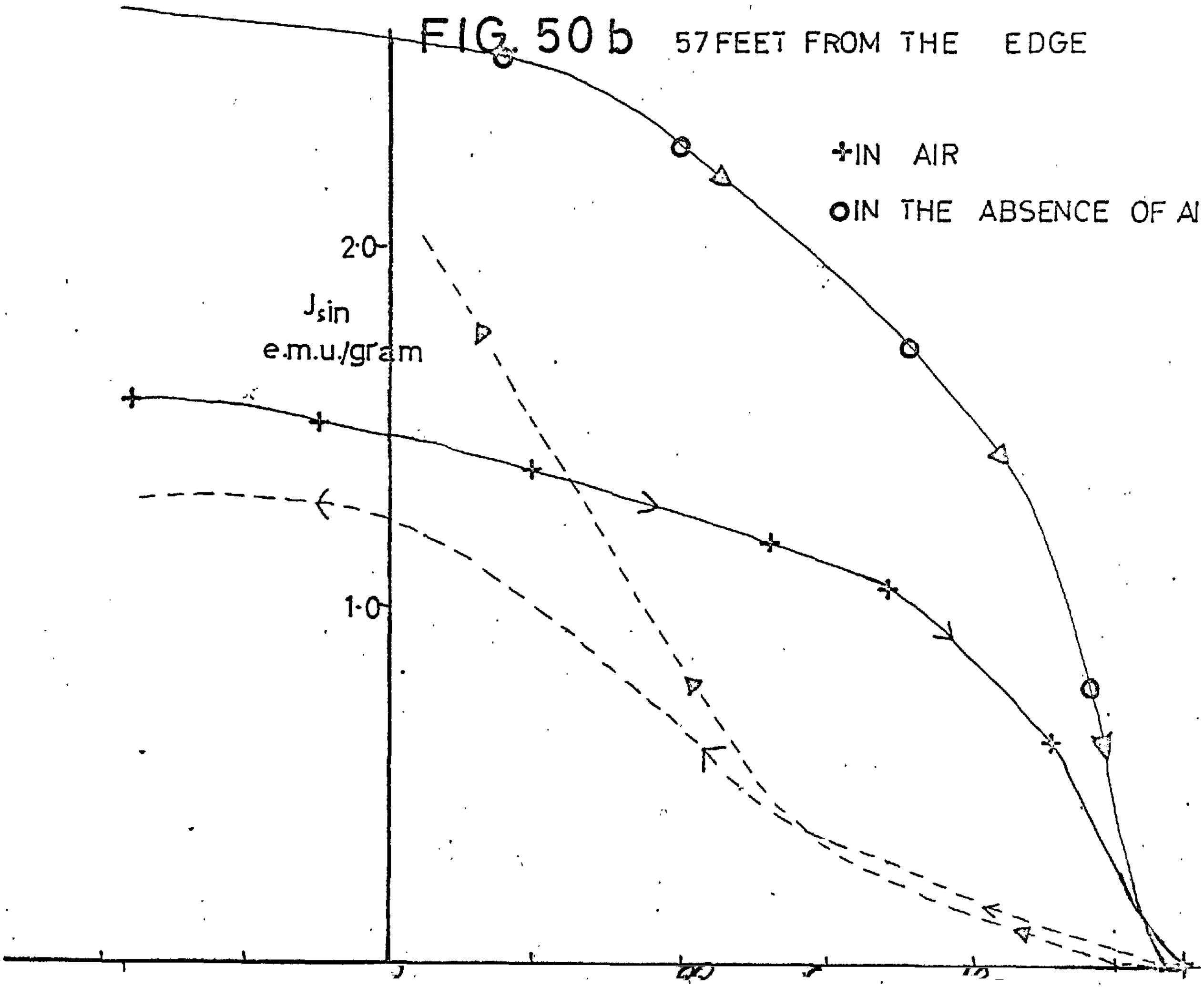


FIG. 50 b 57 FEET FROM THE EDGE



J_{sat} FOR IRISH LAVAS

FIG 51a A BAKED CONTACT

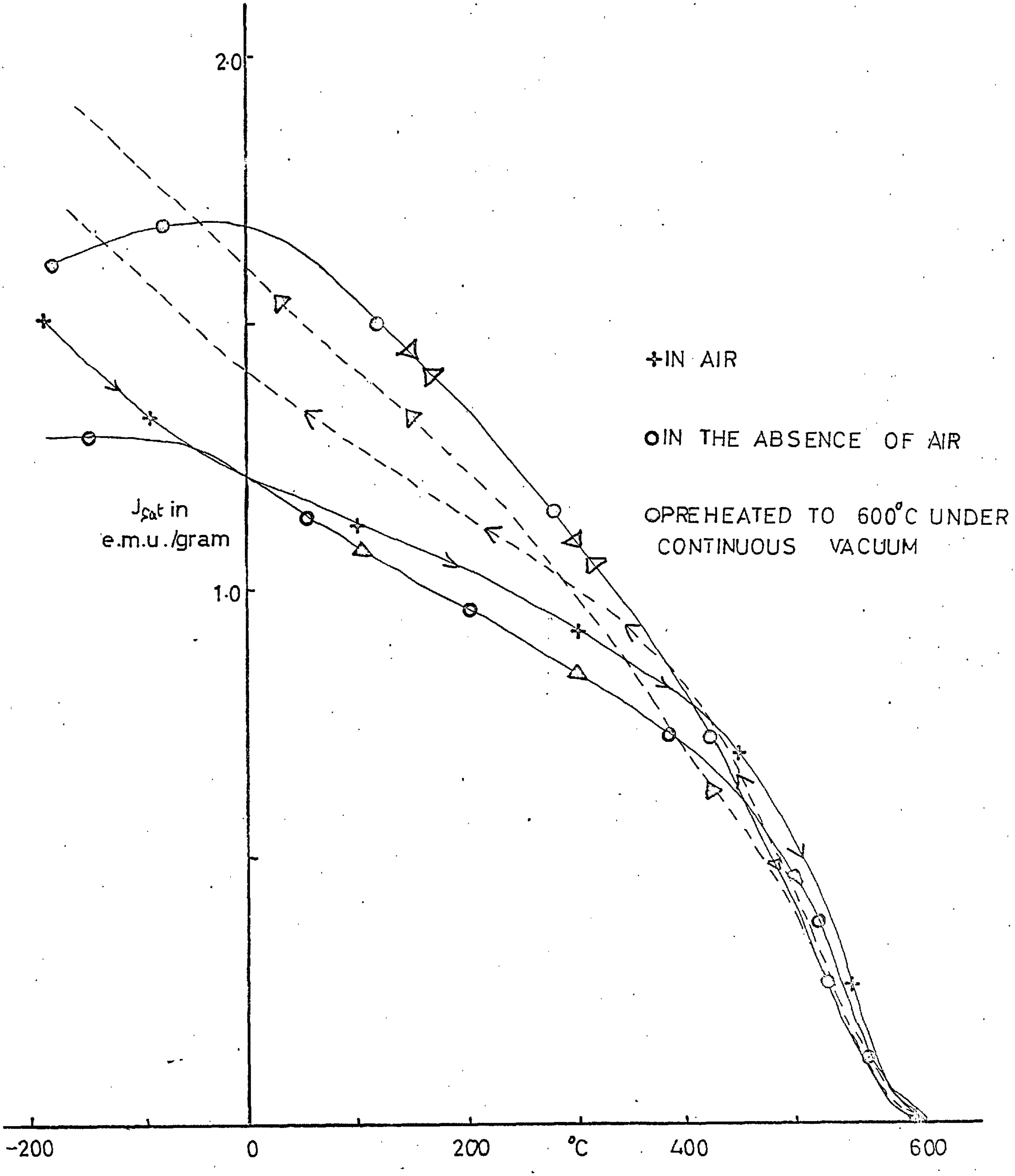
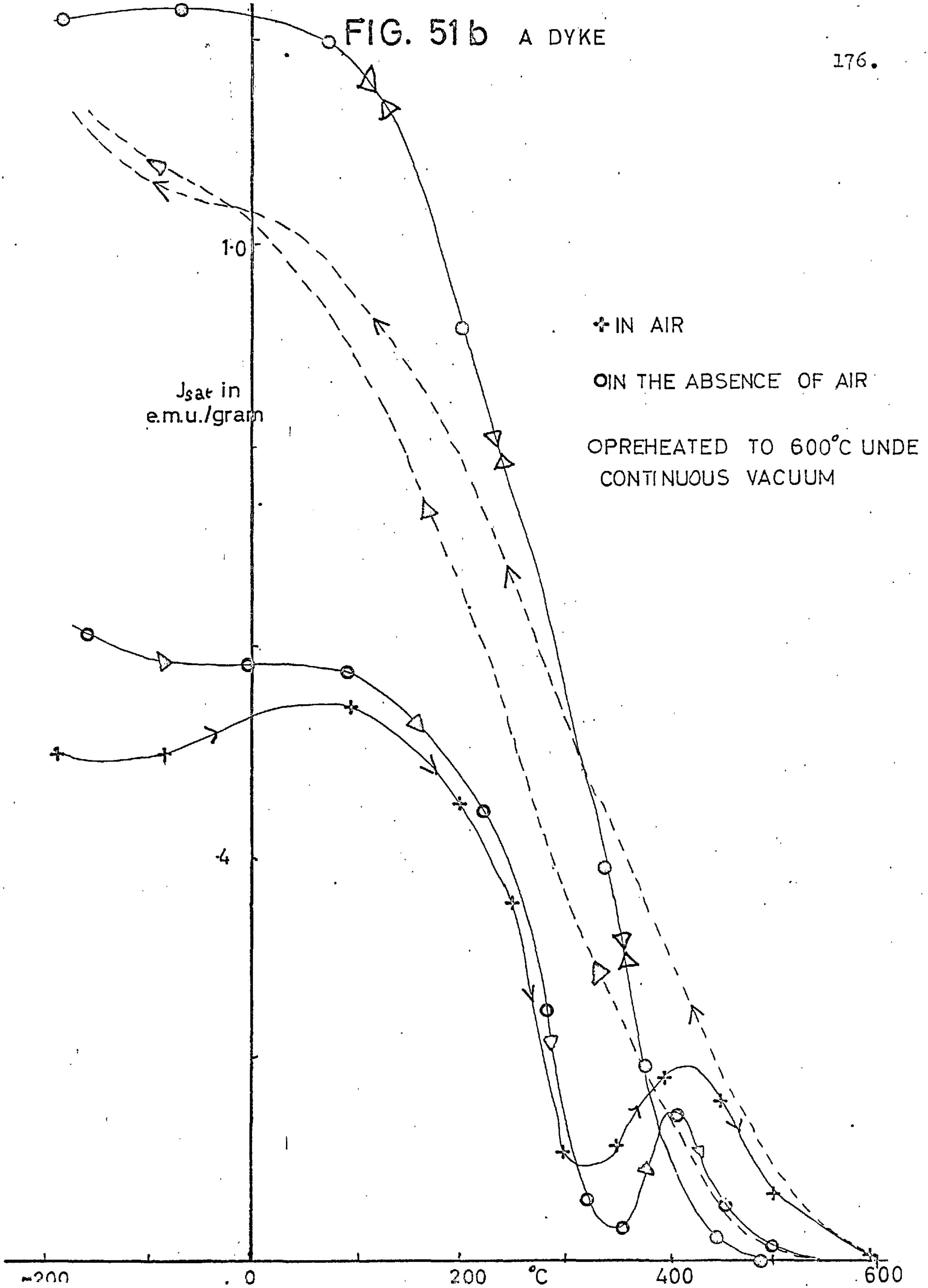


FIG. 51b A DYKE



J_{sat} FOR SUBMARINE LAVAS

FIG 52a

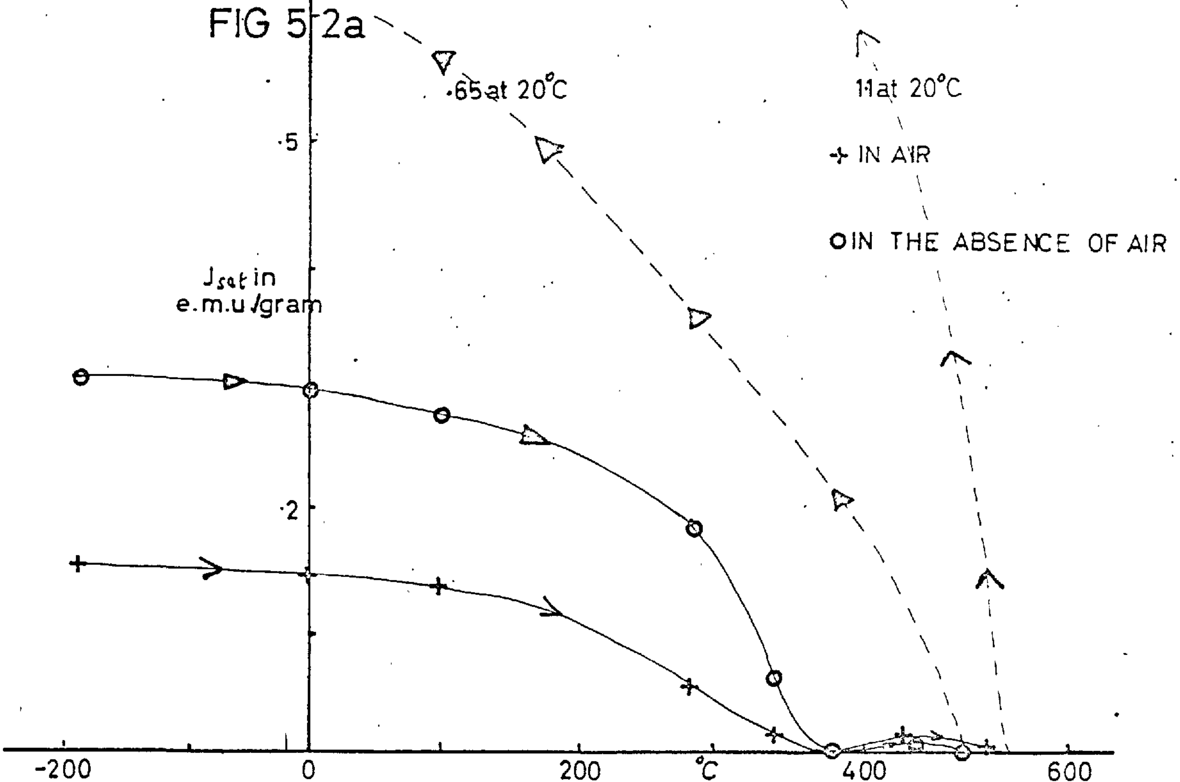


FIG 52b

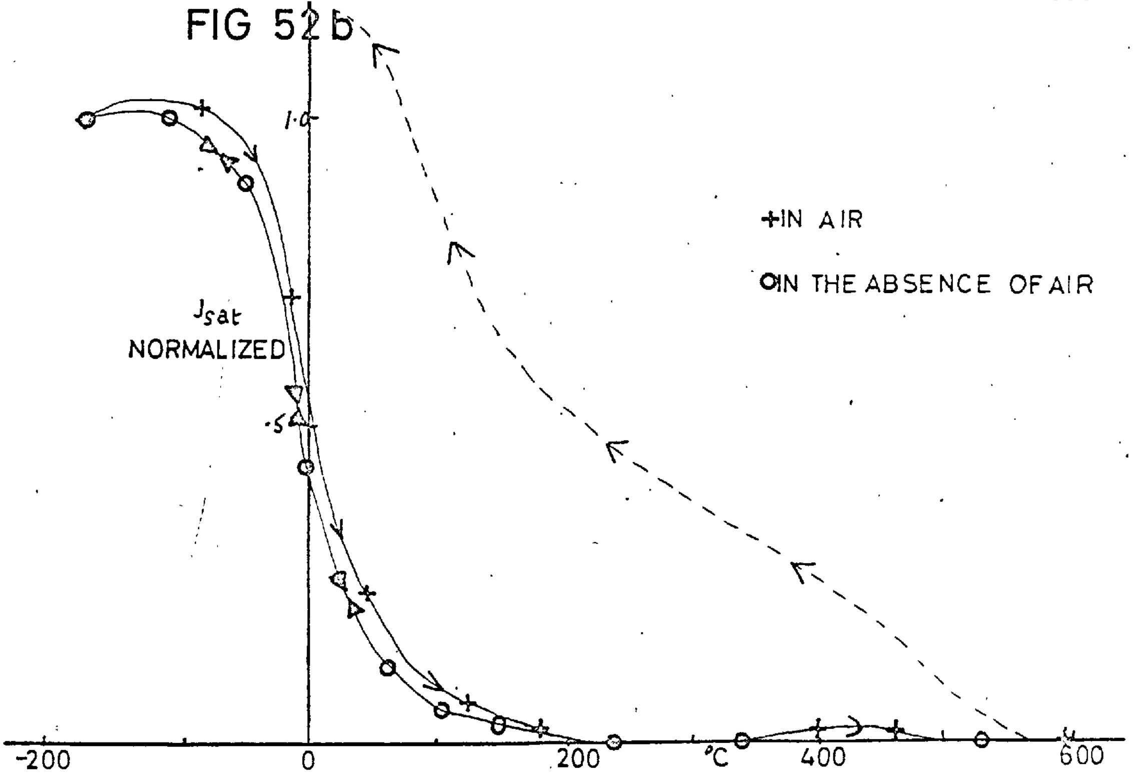


FIG. 53a

HISTOGRAM OF ALL PUBLISHED CURIE POINTS

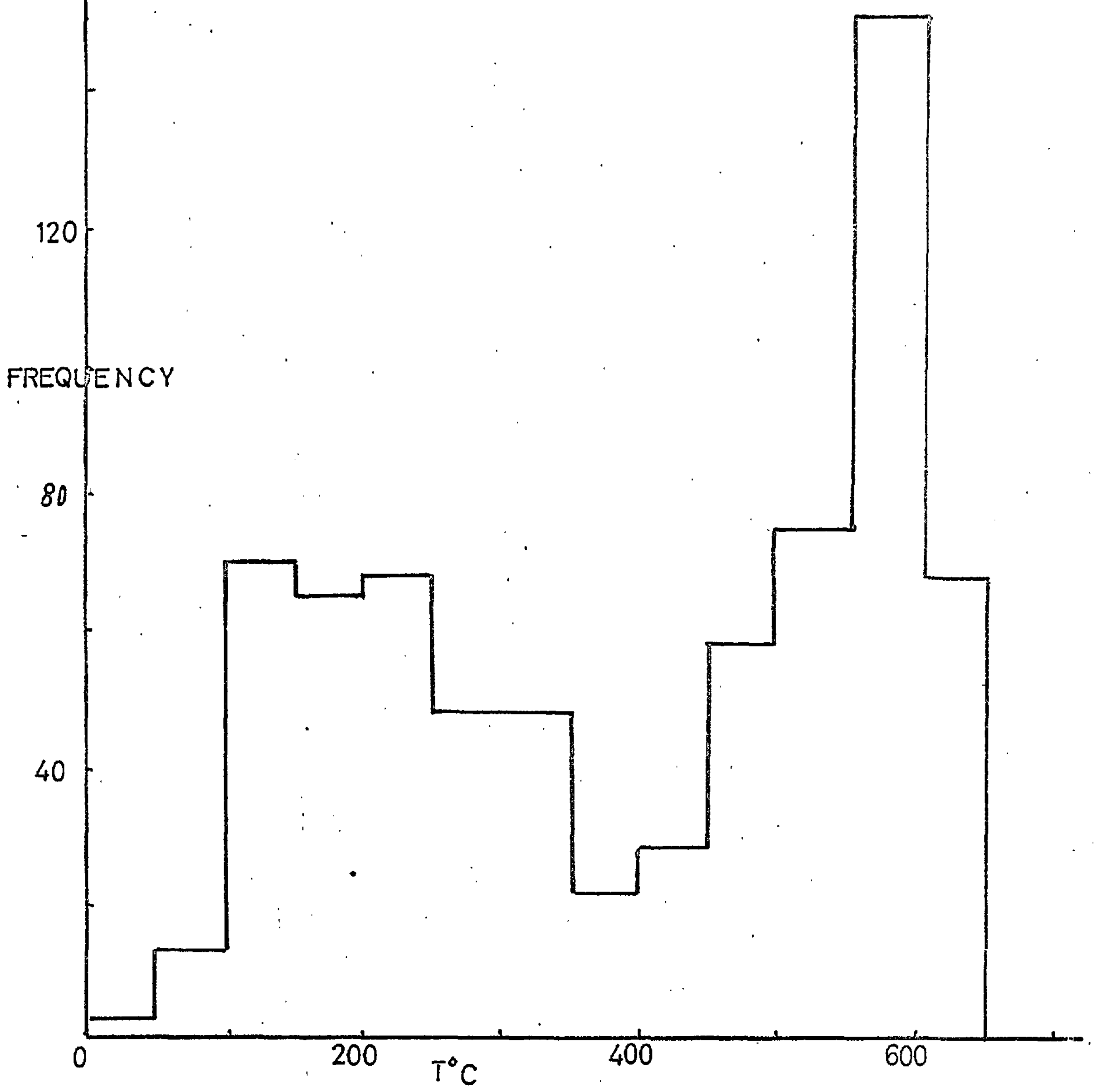


FIG. 53 b

DISTRIBUTION OF CURIE POINTS FOR BASALTIC LAVAS (WITH SINGLE CURIE POINTS)

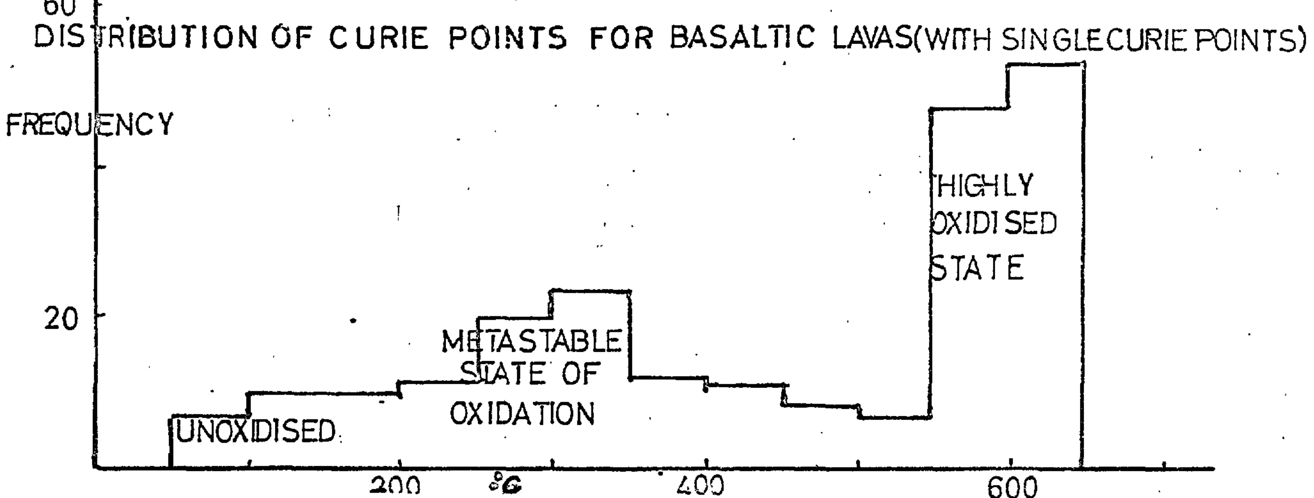


FIG 53c

ALL PUBLISHED CURIE POINTS EXCEPT THE JAPANESE RESULTS

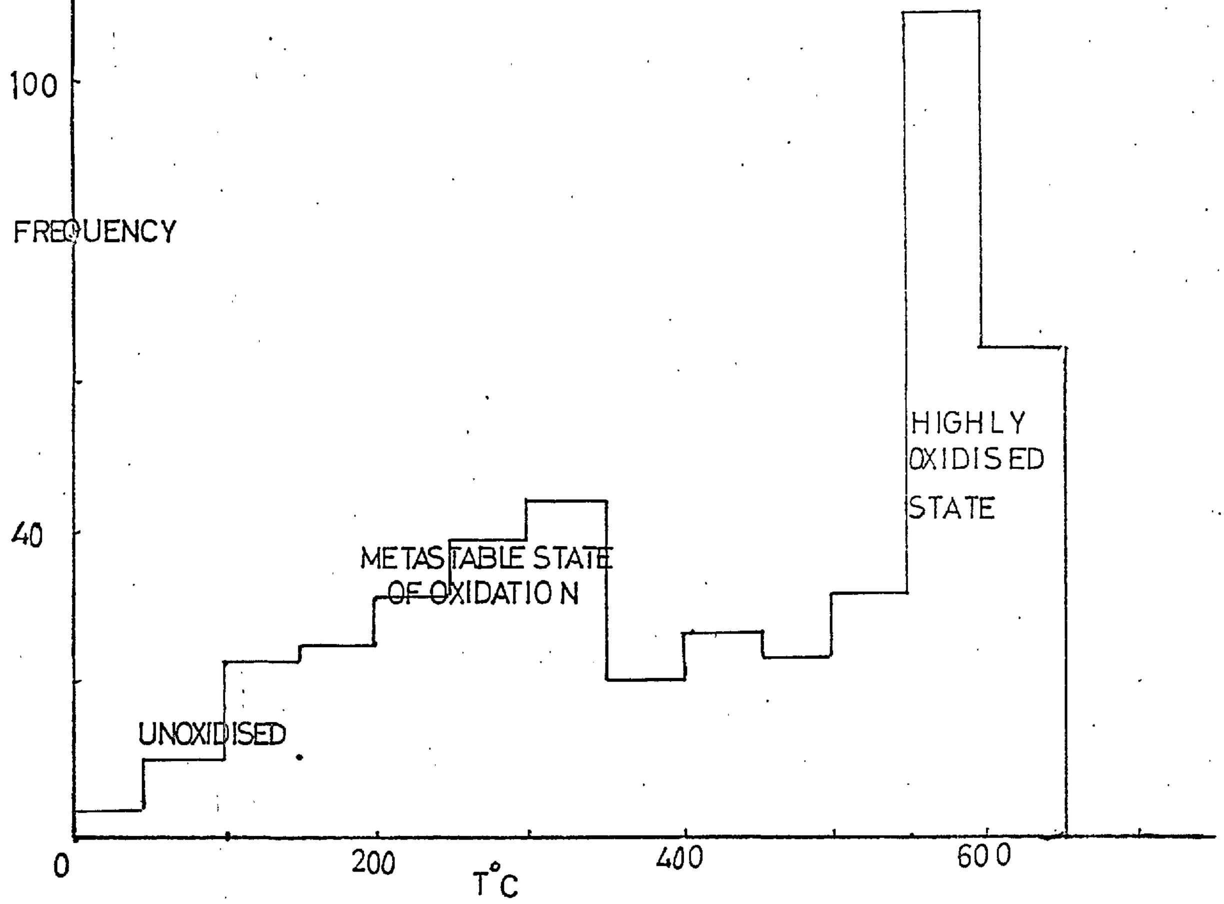


FIG. 53d

THEORETICAL DISTRIBUTION OF CURIE POINTS

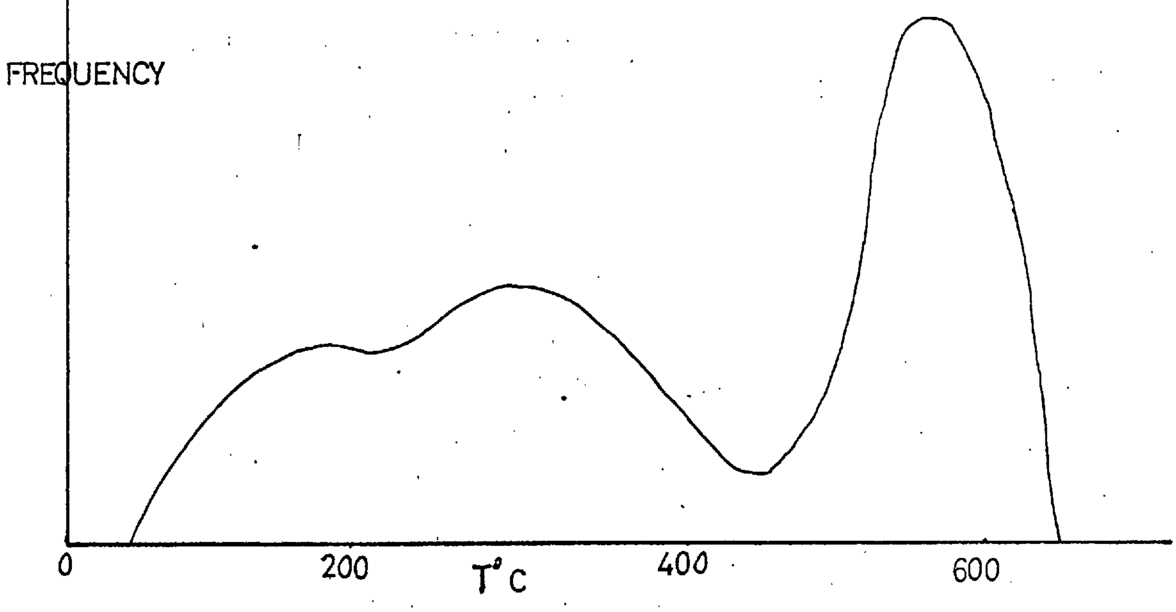
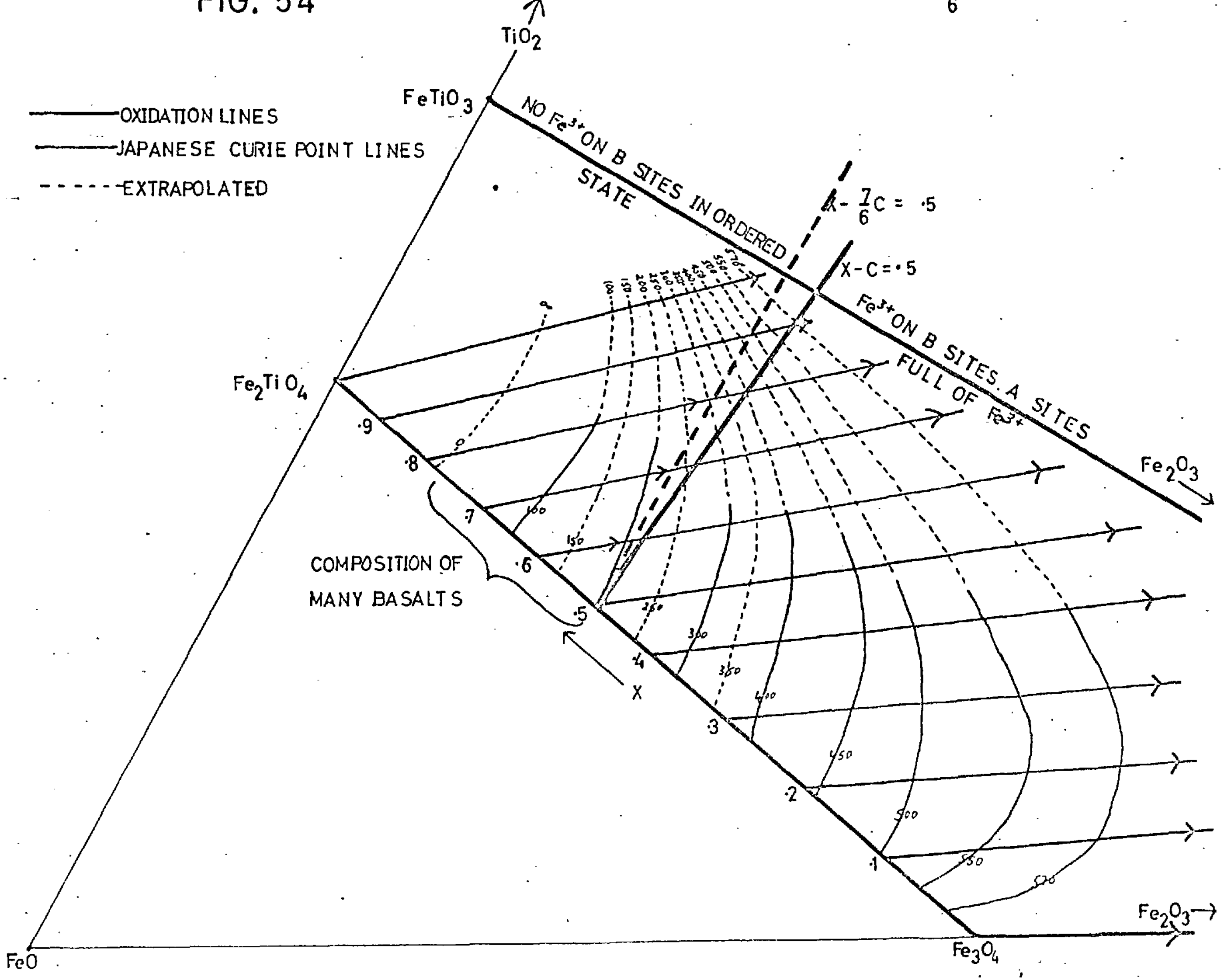


FIG. 54 TERNARY DIAGRAM SHOWING THE LINES $X-C=\cdot5$ AND $X-\frac{7}{6}C=\cdot5$



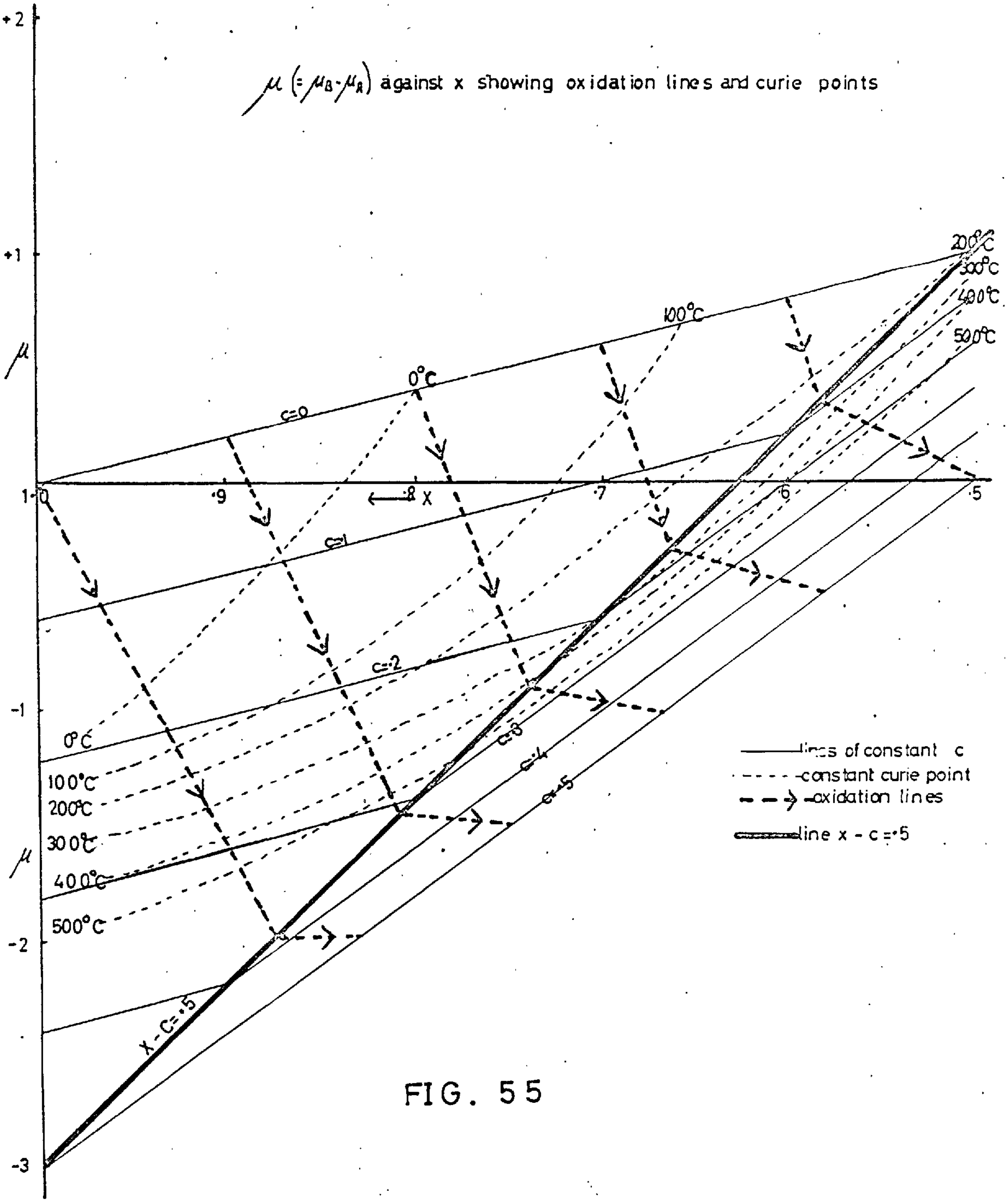
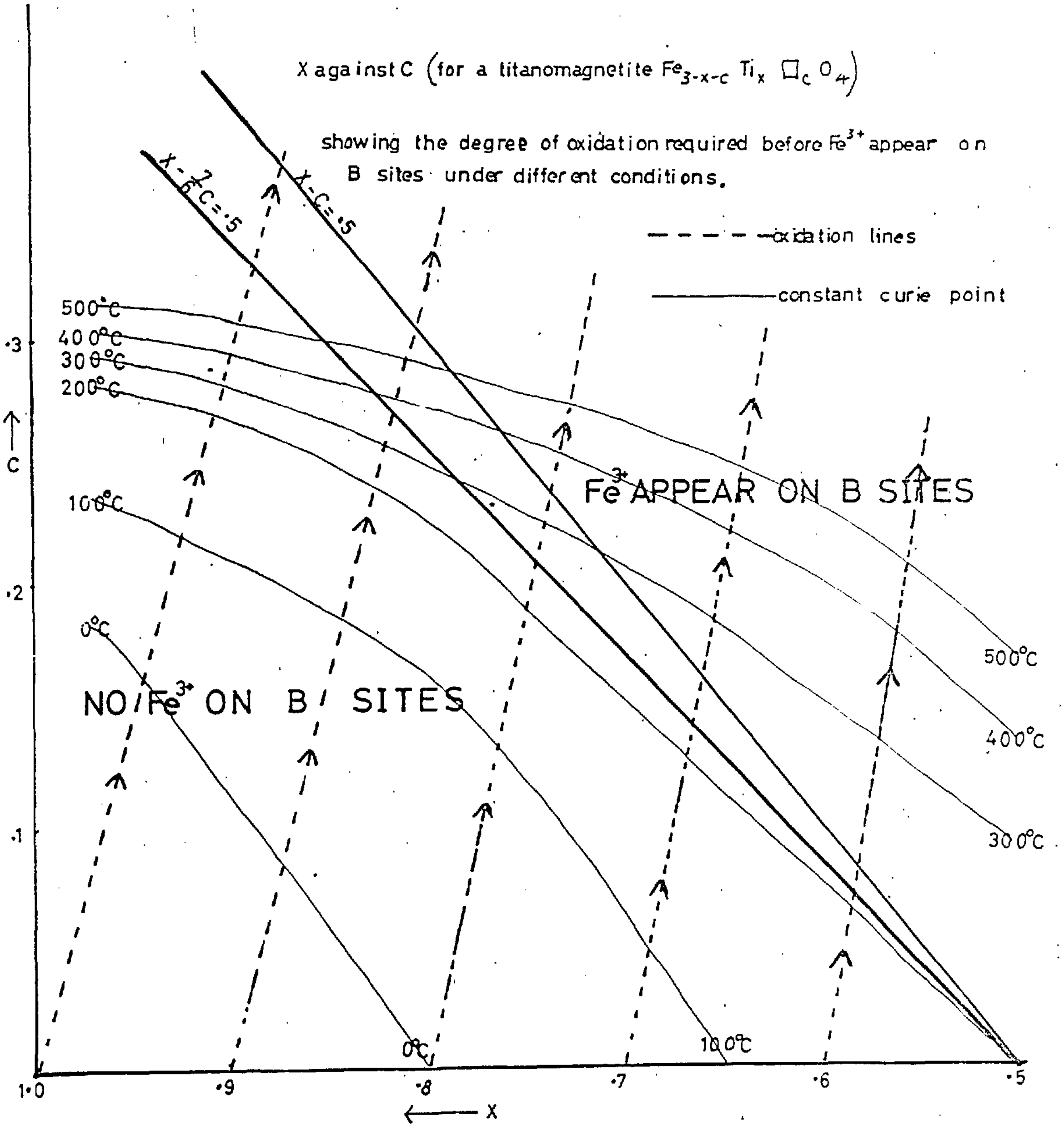

μ (= μ_B - μ_A) against x showing oxidation lines and curie points
+2
+1
-1
-2
-3
μ
μ
1·0
·9
·8 X
·7
·6
·5
c=0
c=1
c=2
c=3
c=4
c=5
0°C
100°C
200°C
300°C
400°C
500°C
x - c = ·5
lines of constant c
constant curie point
oxidation lines
line x - c = ·5

FIG. 55



X against C (for a titanomagnetite $Fe_{3-x-c}Ti_x\square_cO_4$)

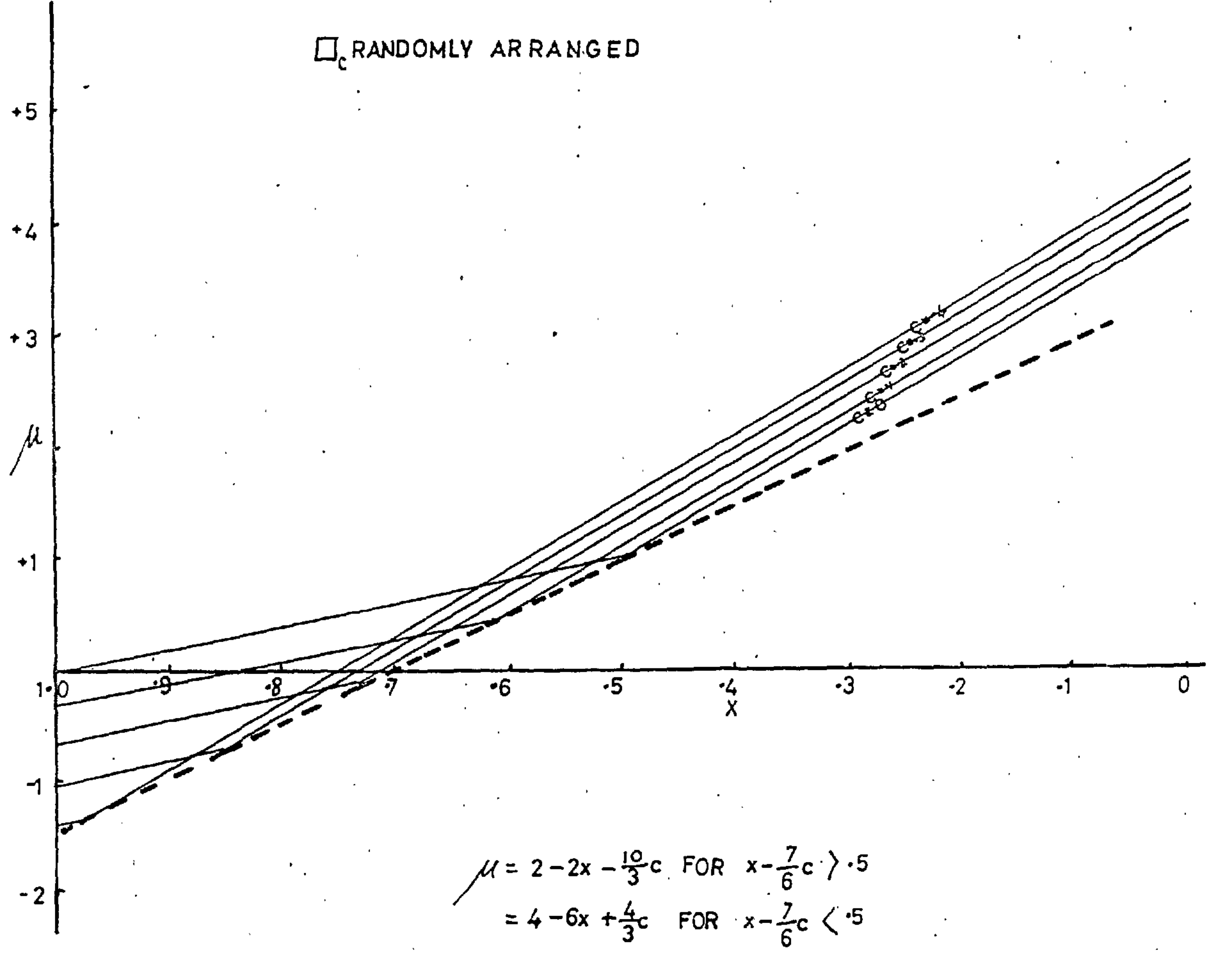
showing the degree of oxidation required before Fe^{3+} appear on B sites under different conditions.

FIG. 56

NETT MOMENT $\mu_B - \mu_A$ FOR OXIDISED TITANOMAGNETITES

GENERAL FORMULA $Fe_{3-x-c}Ti_x\square_cO_4$

$\square_c$ RANDOMLY ARRANGED



$$\mu = 2 - 2x - \frac{10}{3}c \quad \text{FOR} \quad x - \frac{7}{6}c > \cdot 5$$
$$= 4 - 6x + \frac{4}{3}c \quad \text{FOR} \quad x - \frac{7}{6}c < \cdot 5$$

FIG. 57

THERMAL DEMAGNETISATION OF T.R.M. AND P.T.R.M. FOR NATURAL SAMPLES

FIG. 58 a RASHIEHILL SILL

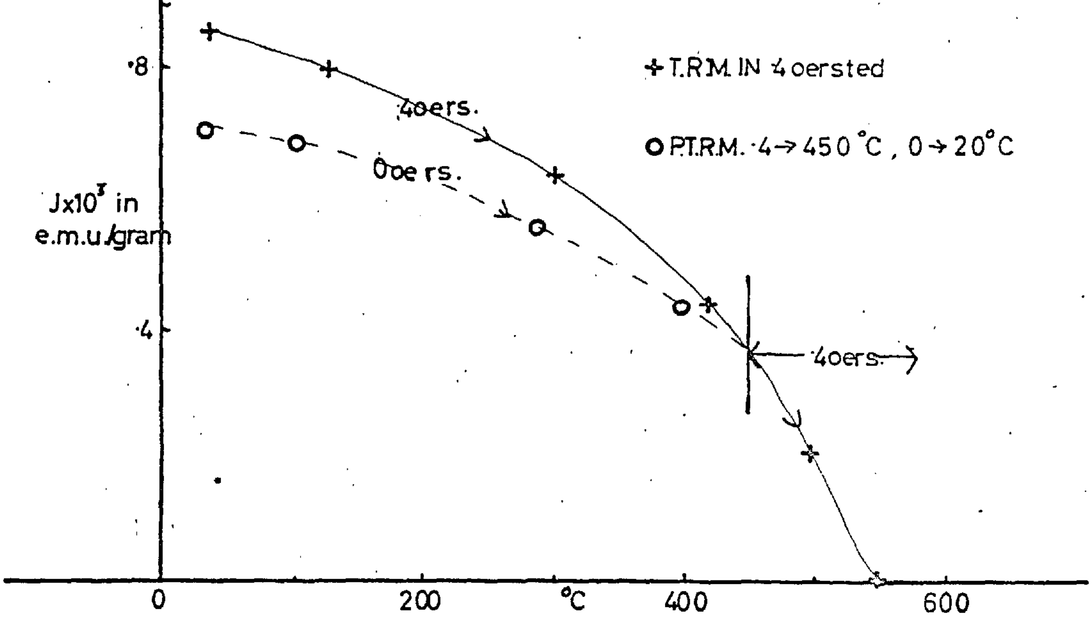


FIG. 58 b OUTMAIN SILL

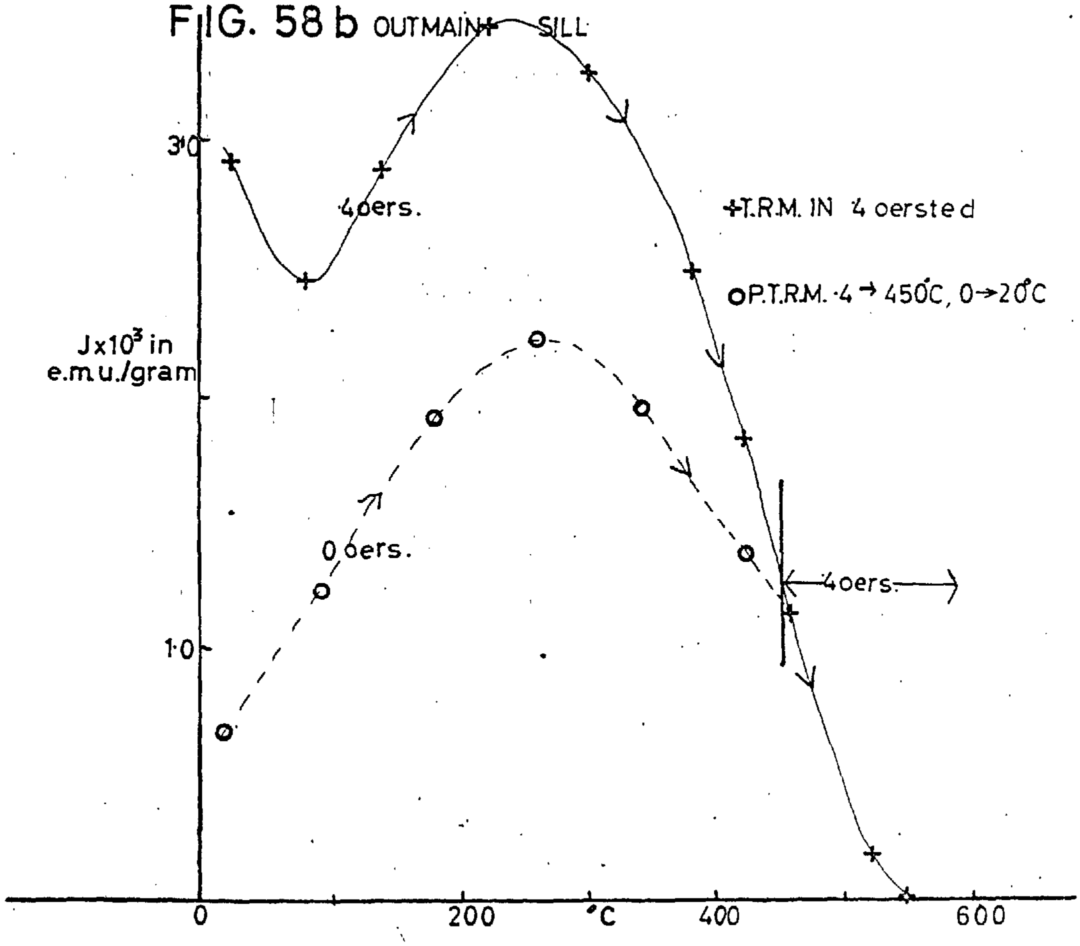


FIG. 58c IRISH LAVA (WEATHERED DYKE)

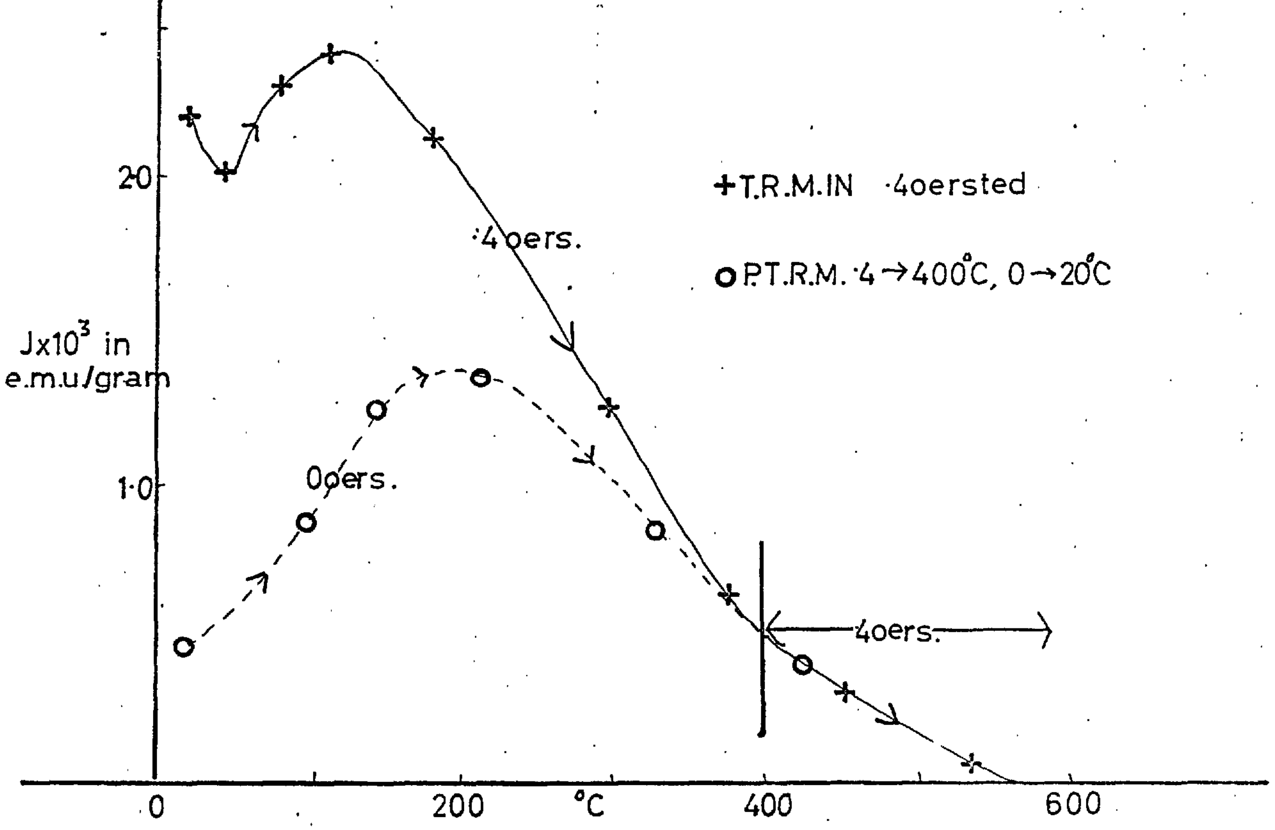
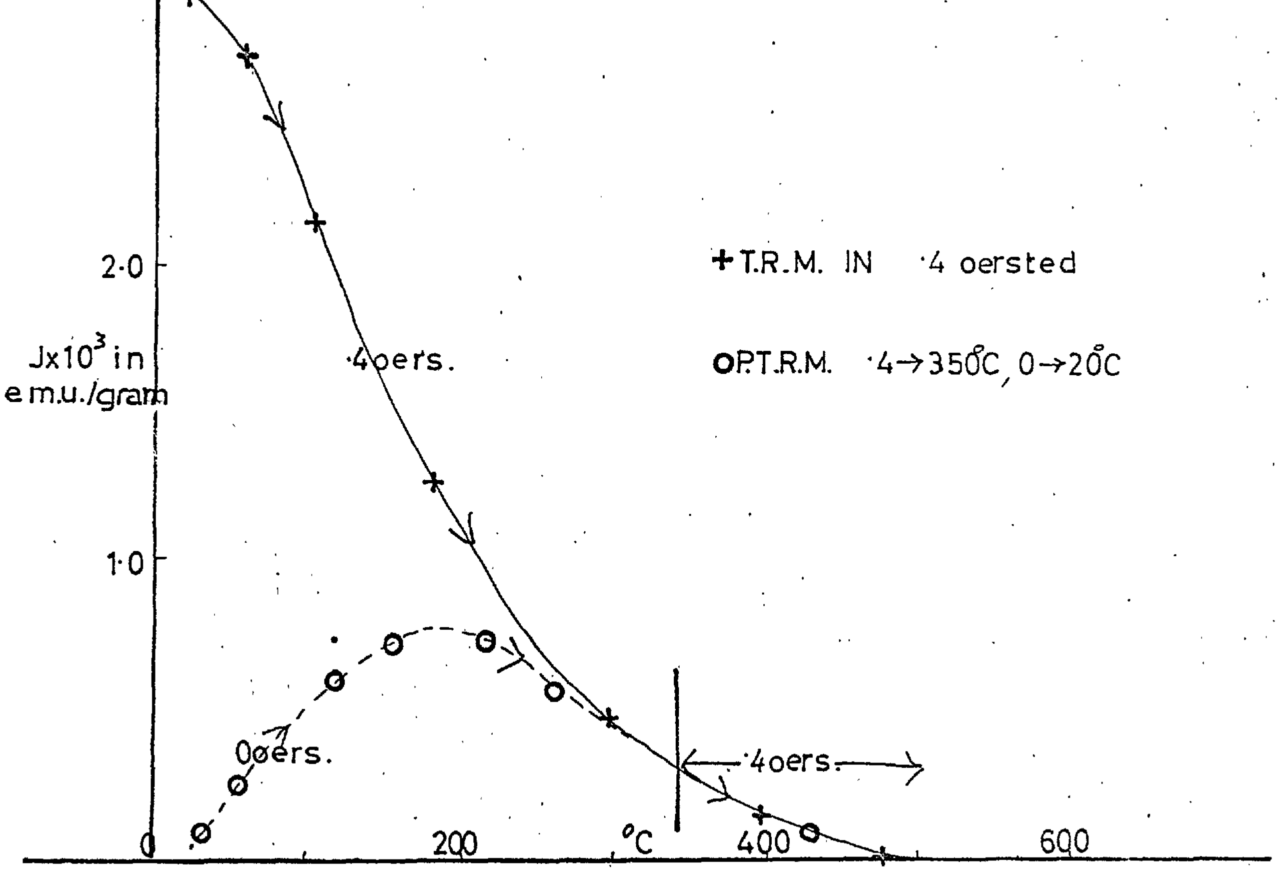


FIG 58d SUDAN LAVA



CHAPTER 12.

Comparison of natural and synthetic titanomagnetites and conclusions.

12.1. Oxidation.

Both synthetic and natural samples show similar properties when heated in air and after heating to 600°C the curie point rises irrespective of composition. Samples with an original 300°C curie point acquire on heating a moment due to thermochemical magnetisation which corresponds to the formation of a high curie point material. Oxidisation does take place more slowly in natural samples which is not surprising considering the synthetic samples are fine powders and the natural samples pieces of rock.

When heated in an evacuated tube however major differences appear. The synthetic samples are unaltered but the natural samples can still oxidise with a corresponding increase in curie point, produce a low temperature component or remain unaltered, depending on the rock gases evolved.

12.2. Reduction.

It was found possible to reduce oxidised synthetic titanomagnetites by heating in an evacuated tube at high temperatures, (800° to 900°) for a few hours. This type of process is the most probable explanation of the results of heat treating, under similar conditions to the synthetic samples, rocks from four different sills. The curie point and intensity decreased and the evidence points to a reduction process. Thus both natural and synthetic samples can be reduced by heating in evacuated tubes at high temperatures.

One important inference from this is that the sills measured, must have been originally in an oxidised state and this is an important conclusion.

12.3. Homogenization and exsolution.

Experiments on synthetic samples support a skew shaped hooped solvus curve for the magnetite-ulvospinel series with a maximum at 600°C but the processes were found to take place so slowly that they do not appear to have a major influence on laboratory experiments. Below 500°C a time scale of tens of thousands of years is required.

12.4. T.R.M. and P.T.R.M.

The important discovery of a reversed P.T.R.M. was made in partial oxidised synthetic titanomagnetites. It only occurs in a limited region of oxidation and is not present in unoxidised or highly oxidised samples. A mechanism depending on two components with a negative interaction was found.

In some natural samples a similar behaviour was found but the P.T.R.M. did not quite reverse. However a negative interaction between two components was sometimes present and the conditions for reversal by this mechanism were satisfied.

Previously reversed T.R.M. or P.T.R.M. has been reported for the haematite-ilmenite series and for pyrrhotite and now titanomagnetites which form the most important magnetic series in rock magnetism have been found to possess reversal properties in the range where many naturally occurring titanomagnetites fall.

The conclusion to be drawn is that self reversal in oxidised rocks may be much more common than at first imagined.

An interesting follow up to this work is the production of a thermochemical remanent magnetisation by heating the thermal remanence to a temperature below the curie point in zero field, allowing oxidation to take place and to observe the moment of the oxidised sample develop in the internal field of the original component.

It is conceivable that a rock will reverse its direction of magnetisation during oxidation in a laboratory experiment in the near future.

12.5. Theories of reversal.

Theories have been examined for the ulvospinel-magnetite series and oxidation effects considered. The reversal of the P.T.R.M. seems to be explained by a combination of Neels mechanisms. The two components have a negative interaction and arise either from a curie point distribution in a partially oxidised grain or from a metastable oxidised state giving rise to a 300°C curie point. The existance of a metastable oxidised state is supported by the results obtained from synthetic and natural samples and one possible cause of such a metastable state may be the difficulty in producing Fe^{3+} on B sites in the oxidation process.

ACKNOWLEDGEMENTS

I wish to express my appreciation and thanks to Professor P.M.S. Blackett for his stimulating interest and encouragement throughout this work. I am grateful to Dr. R.L. Wilson, who supervised the first two years work, for his many helpful suggestions and for assisting with much of the petrological work.

Mr. T. Kelly and Dr. J. Ade-Hall carried out the electron probe analysis and the X-ray equipment belonging to the teaching laboratory was made freely available by Dr. C.E. Wyn-Williams.

My thanks must be expressed to the other members of the Rock Magnetism Group for their help, especially Mr. M. Lewis with whom many hours of fruitful discussion was spent and Miss J.E. Langbein who was of great assistance in preparing the synthetic materials.

I would like to thank Mrs. S. MacGarry for typing the thesis.

APPENDIX 1.

Instruments built for these studies.

1. High temperature furnace.

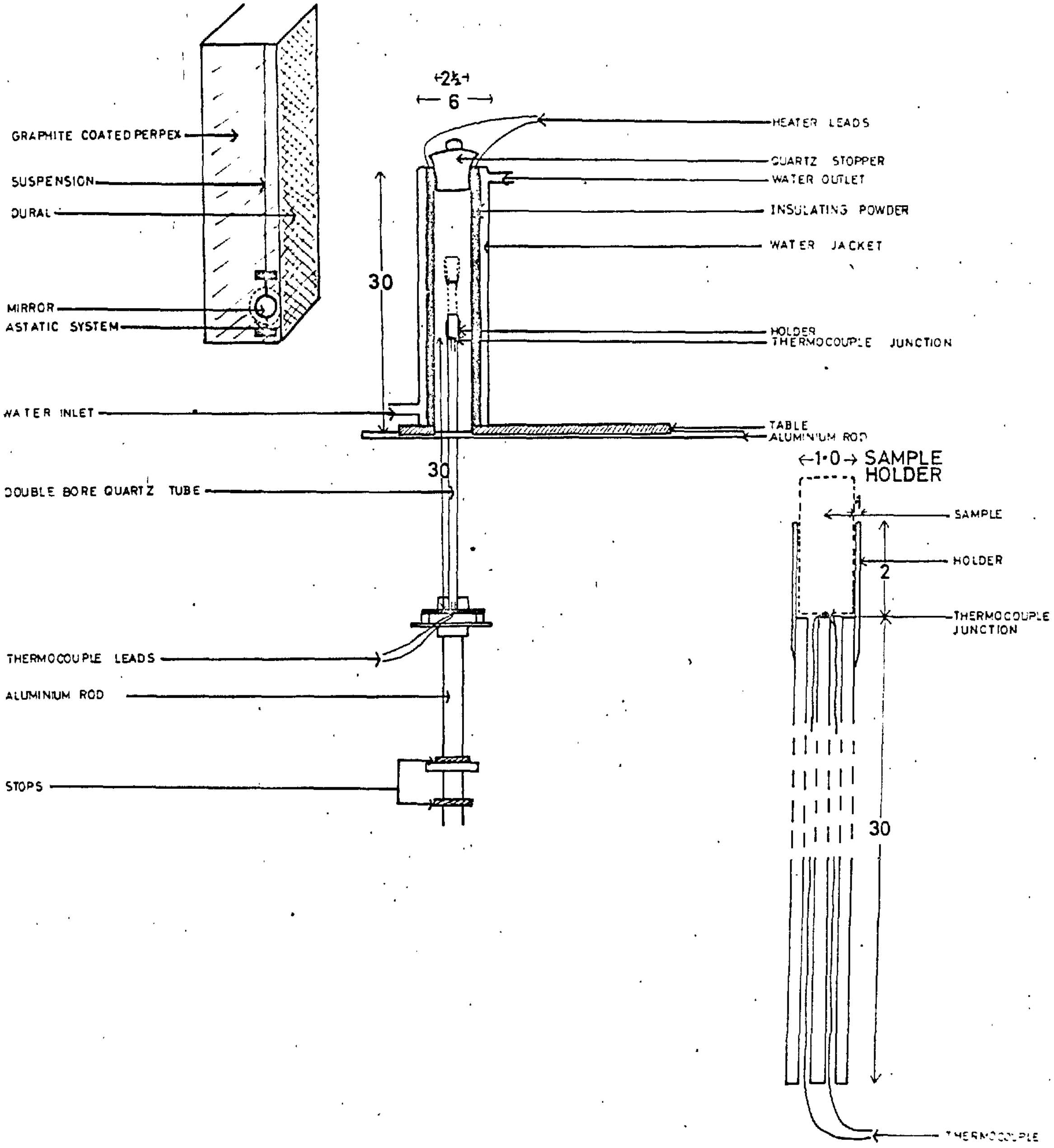
The furnace consists of thick constantan were wound onto a 1 inch diameter, 2 feet long quartz tube and this is mounted vertically in a block of insulating material (commercially sold as capsulin). The sample and the thermocouple are suspended from the top of the tube and the sample removed by releasing a clip. It falls into a copper beaker filled with sand and water and can be cooled in known fields. The temperature is automatically controlled. The furnace can be used up to 925°C and has the advantage enabling samples to be quenched very quickly.

2. Low field thermal demagnetising instrument.

This instrument consists of a specially designed furnace and an astatic magnetometer. The furnace is non-inductively wound, water cooled and can reach temperatures of 625°C and is mounted vertically. The sample moves vertically at the side of the astatic system and stops are set to give maximum deflection with the sample and the furnace at a given distance from the astatic system. The sample sits in a quartz holder which has a double bore stem to allow the platinium-pallador thermocouple to be situated close to the sample. The sensitivity is adjusted by moving the furnace and holder nearer the astatic system and the maximum sensitivity that can be obtained is 5×10^{-5} e.m.u. per cm. deflection. To prevent heat reaching the astatic system one side of the housing was made of dural, the rest being graphite coated perpex but the water cooled jacket and air gap proved to be sufficient thermal insulation. The dural also acted as the damping plate. Fig. 59 shows a diagram of the system. Helmholtz coils were used to give a zero field to better than 1°/o and the sample can be cooled in fields up to 2 oersteds. The instrument has the advantage that the sample can be measured on cooling without having to be rotated to oppose the applied field as happens when the specimen is placed underneath the astatic system.

FIG 59 LOW FIELD INSTRUMENT (NOT TO SCALE)

ALL DIMENSIONS ARE IN CENTIMETRES



APPENDIX 2.

Theoretical calculations in the TiO_2, FeO, Fe_2O_3 system.

Calculation of the percentage Fe, Fe_2O_3, TiO_2 by weight. On the usual terniary diagram (Fig. 6) for FeO, Fe_2O_3, TiO_2 any point P can be represented by

P $A FeO : B Fe_2O_3 : C TiO_2$ by molecular parts (1)

and $A+B+C = 1$

But P $\bar{x} Fe : \bar{y} Fe_2O_3 : \bar{z} TiO_2$ by molecular parts (2)

$X Fe : Y Fe_2O_3 : Z TiO_2$ by weight (3)

It is required to find X, Y, Z from A, B, C.

Comparing (1) and (2) for Fe, Ti, O content.

$$\bar{z} = C$$

$$\bar{x} + 2\bar{y} = A + 2B$$

$$3\bar{y} = A + 3B$$

$$\therefore \ \bar{z} = C : \ \bar{y} = \frac{A+3B}{3} : \ \bar{x} = \frac{A}{3}$$

X, Y and Z follow from $\bar{x}$, $\bar{y}$ and $\bar{z}$ by multiplying by the respective molecular weights.

Magnetite-ulvospinel.

General formula is $Fe_{3-x}Ti_xO_4$ $(1+x)FeO(1-x)Fe_2O_3xTiO_2$ and molecular $^o/o$ O is 4/7.

Ilmenite-haematite.

General formula is $Fe_{2-x}Ti_xO_3$ $xFeO(1-x)Fe_2O_3xTiO_2$ and molecular °/o O is 3/5.

But generalised titanomagnetites lie between these limits and cannot be so easily expressed.

General formula.

$Fe_{b-a}\ Ti_aO$ per oxygen atom.

$\therefore$ $Fe_{b-a}Ti_aO$ $AFeO: BFe_2O_3: CTiO_2$

and molecular °/o O is $\frac{1}{1+b}$

$\therefore$ $C = a$

$B = 1-b-a$

$A = 3b+a-2$ on comparing Fe, Ti and O.

Series limits are given by $C = a = 0$ (no Ti)

and $B = 0$ (no Fe_2O_3)

Thus from a knowledge of a and b only the position on the terniary diagram and the percentage by weight of Fe, Fe_2O_3 and TiO_2 required to give the empirical mixture can easily be calculated.

Also many lines of interest can be computed and plotted by writing the various conditions as algebraic expressions for a and b.

Lines of constant Ti content.

Here a is constant and lines are obtained by varying b.

Constant Fe lines.

Here b-a is constant and using different constants a family of lines can be drawn.

Oxidation lines.

These correspond to the ratio Fe/Ti=constant. Therefore $\frac{b-a}{a}$ is a constant and the lines can be drawn.

Constant Fe^{2+}.

The general formula can be written as

$$Fe^{3+}_{y}\ Fe^{2+}_{3-y-x-c} Ti_{x}\ \square_{c}\ O_{4}$$

$$\left[\text{N.B. } \frac{3-c}{4} = b,\ \frac{x}{4} = a\right]$$

Also for charge conservation $y = 2-2x+2c$

∴ Rewrite molecule as $Fe^{3+}_{2-2x+2c}\ Fe^{2+}_{1+x-3c}\ Ti_{x}\ \square_{c}\ O_{4}$

per oxygen atom $Fe^{3+}_{\frac{1}{2}-2a+2c'}\ Fe^{2+}_{\frac{1}{4}+a-3c'}\ Ti_{a}\square_{c'}\ O$

where $c' = c/4$.

Lines of constant Fe^{2+} are lines $1/4+a-3c' =$ constant.

Also in titanomagnetites $4b+c = 3$ i.e. $b+c' = 3/4$

Eliminating c' $3b-2-a =$ constant .

Thus a family of lines for different constants can be drawn.

Lines of degree of oxidation can similarly be found

Oxidising equation is $Fe^{2+} \Rightarrow \frac{2}{3} Fe^{3+} + \frac{1}{3} \square$

Let q °/o Fe^{2+} be oxidised.

Molecular expression is

$$Fe^{2+}_{(1-q)(1+x)}\ Fe^{3+}_{2-2x+\frac{2}{3}q(1+x)}\ Ti_x\ \square_{q/3(1+x)}\ O_4$$

or per oxygen atom

$$Fe_{\underbrace{3/4 - q/3(1/4 + a)}_{b}-a}\ \ Ti_a\ \square_{q/3(1/4+a)}\ O$$

$\therefore$ $b = 3/4 - q/3(1/4+a)$ and family of lines for different values of q can be drawn.

Line $x-c = .5$

This corresponds to Fe^{3+} beginning to appear on B sites during oxidation assuming all vacancies are on B sites.

Here $a-c' = .125$

But $b+c' = .75$ for titanomagnetites.

$\therefore$ $a+b = .875$ gives the required line.

Line $x - \frac{7}{6} c = .5$

This corresponds to Fe^{3+} beginning to appear on B sites during oxidation assuming $\square$ are randomly distributed.

$$\text{Here } a - \tfrac{7}{6}c' = .125$$

$$b + c' = .75$$

$$\therefore \quad a + \tfrac{7}{6}b = 1 \text{ gives the required line.}$$

Thus the parameters a and b allow easy calculation of all the interesting lines.

<u>Calculation of</u> $\mu_B - \mu_A$ for ordered oxidised titanomagnetites

1. Assume $\square$ are all on B sites (Experimentally so if oxidation is slow)

Starting with $Fe^{3+}_{y}\ Fe^{2+}_{3-y-x-c}\ Ti_x \square_c O_4$.

There are two cases

$y \le 1$		$y \ge 1$	
A site	B site	A site	B site
$Fe^{3+}_{y} Fe^{2+}_{1-y}$	$[Fe^{2+}_{2-x-c} Ti_x \square_c]$	Fe^{3+}_{1}	$[Fe^{3+}_{y-1} Fe^{2+}_{3-y-x-c} Ti_x \square_c]$
$\mu_A = 5y+4(1-y)$		$\mu_A = 5$	
$\mu_B = 4(2-x-c)$		$\mu_B = 5(y-1)+4(3-y-x-c)$	
$\mu_B - \mu_A = 4-4x-4c-y$		$\mu_B - \mu_A = 2+y-4x-4c$	

But $y = 2-2x+2c$ from charge conservation

$\therefore$ $\underline{\mu_B - \mu_A = 2-2x-6c}$ $\qquad$ $\underline{\mu_\beta - \mu_A = 4-6c-2c}$

At the boundary when Fe^{3+} are just about to appear on B sites x-c = 1/2 (Equating moments)

2. Assume $\square$ are randomly distributed, i.e. 1/3 on A sites and 2/3 on B sites.

Again there are two cases.

$y \leq 1 - c/3$	$y \geq 1 - c/3$
A sites B sites	A sites B sites
$Fe^{3+}_y Fe^{2+}_{1-y-\frac{c}{3}} \square_{c/3} \left[Fe^{2+}_{2-x-\frac{2}{3}c} Ti_x \square_{\frac{2}{3}c}\right]$	$Fe_{1-c/3} \square_{c/3} \left[Fe^{3+}_{y-1+\frac{c}{3}} Fe^{2+}_{3-y-x-c} Ti_x \square_{\frac{2}{3}c}\right]$
$\mu_A = 5y+4(1-y-c/3)$	$\mu_A = 5-5c/3$
$\mu_B = 4(2-x-2/3c)$	$\mu_B = 5(y-1+c/3)+4(3-y-x-c)$
$\mu_B-\mu_A = 4-4x-\frac{4c}{3}-y$	$\mu_B-\mu_A = y+2-\frac{2}{3}c-4x$

Again charge is conserved y = 2-2x - 6c

$\therefore$ $\underline{\mu_B-\mu_A = 2-2x-\frac{10c}{3}}$ $\qquad$ $\underline{\mu_B-\mu_A = 4-6c+\frac{4}{3}c}$

At the point where Fe^{3+} begin to appear on B sites

$$x - \frac{7}{6}c = \frac{1}{2}.$$

APPENDIX 3.

Ionic ordering at T^o Absolute

Consider a general molecule of the type MFe_2O_4 where M is divalent.

This can be written as $M_xFe_{1-x}[Fe_{1+x}M_{1-x}]\ O_4$

For a general thermodynamical system the probability of finding n_i in state i is

$$W = \frac{n_i!}{{}_{i}n_i!}$$

$$\text{i.e. } \delta \log W = \sum \delta n_i(\log n_i + 1) .$$

Let the energy required to interchange M to Fe site be ΔU.

From thermodynamics $\Delta U - TdS = 0$

$$\therefore \Delta U + Tk \log W = 0$$

For N atoms in the lattice let X of M be on A site

$$\therefore \quad n_1 = X$$

$n_2 = N-X$ and for one M change

$n_3 = N+X$ $\delta n_1 = +1 = \delta n_3$

$n_4 = N-X$ $\delta n_2 = -1 = \delta n_4$

$$\therefore \Delta U + Tk \log \frac{X(N+X)}{(N-X)^2} = 0 \quad \text{and } x = \frac{X}{N}$$

$$\therefore \frac{x(1+x)}{(1-x)^2} = e^{-\Delta U/kT}$$ which is the ionic ordering at T^o Absolute for MFe_2O_4 .

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