(A) Magnetic Materials in Oxidized Olivine and their contribution to the natural remanent magnetization of rocks.

(B) The Natural Remanent Magnetization of some Triassic Red Sandstone

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ABSTRACT

The main section of this thesis is concerned with the alteration of olivine, and its importance to rock magnetism. The work started, when the extraction of the magnetic mineral from certain rocks extracted altered olivine, not the expected iron-titanium oxide minerals. The initial aim of the work was to duplicate this natural alteration in the laboratory as simply as possible. It was found that heating olivine in air produced visually similar alteration.

The work continued by investigating further this alteration. The aim was to investigate the heating in air of olivine to various temperatures, between 650 - 1100°C. The heating lasted for periods between five minutes and forty days. The experiments were repeated for five olivines of different compositions. The results were obtained by measuring the changes in magnetic parameters, and viewing the optical changes in a polished section. Identification of the alteration products was by magnetic evidence and X-ray powder patterns.

The results showed the alteration to be a two stage process. The first stage produced from the olivine a very strongly magnetic material, identified as magnesioferrite. This material appeared as a sub-microscopic opaque material within a green pseudomorph of olivine. The second stage of the alteration oxidized this mineral forming hematite; visually the pseudomorph was reddened in colour.

The magnesioferrite was found to acquire a very high thermoremanent magnetization. It was so high that if 5% of a rock was composed of altered olivine, the natural remanent magnetization could be due entirely to the altered olivine. Due to the ease of ionic reordering within the magnesioferrite, its magnetic properties depend on its thermal equilibrium temperature; so depend on the thermal history of the altered olivine.

The final chapter is concerned with the determination of a Triassic paleomagnetic field direction for Britain. The aim was to determine a more accurate field direction using rapid rock sampling techniques. By using a large number of samples a Triassic paleomagnetic field direction was obtained from a New Red sandstone, with a smaller circle of confidence than previously determined. The paleomagnetic field direction was declination 5° E. of N; inclination 34° downwards and α_{95}, the semi-cone angle of 95% confidence, 6.5°.

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CONTENTS

CHAPTER 1

INTRODUCTION

Paleomagnetism is the study of the ancient magnetic field of the earth as determined from the present magnetic remanence of rock samples. The magnetic remanence of rocks arises from small amounts of iron-bearing minerals, comprising about 5% of the rock. Manifestly, the interpretation of paleomagnetic results depends on the identification and understanding of these minerals and their magnetic properties.

The magnetic remanence of a rock can be acquired by several known processes. The more important methods are thermoremanence, chemical remanence and depositional remanence. On cooling in a magnetic field, from above the Curie points of the magnetic minerals present, a rock will acquire a thermoremanence (TRM). TRM is responsible for the magnetization of igneous rocks, which are a major paleomagnetic research material, and for the magnetization of the surrounding rocks, which have been baked by the igneous rocks. When minerals are altered by a chemical or phase change chemical remanence (CRM) is the resultant magnetization, if the change takes place in a magnetic field below the Curie point of the minerals formed. Magnetic minerals, which settle out from water, tend to align with the ambient magnetic field, and so acquire depositional remanence (DRM). DRM is a weak form of remanence being affected by the shape of the mineral and motion of the water, as the mineral settles. Sedimentary rocks possess a remanence which can be CRM or DRM or a combination of both.

The natural magnetic moment of a rock specimen has both direction and intensity. In the use in paleomagnetism of the direction of the magnetization, two basic assumptions are made. Firstly, the moment of the minerals was aligned with the ambient magnetic field, when the rock was formed or altered. The justification of this assumption lies in the archeomagnetic measurements and in the research on magnetic minerals, synthetic and natural. Secondly, the moment has not been changed irretrievably after the remanence was acquired. Some secondary magnetization can be erased in the laboratory by either alternating magnetic field demagnetization or by thermal demagnetization. This latter assumption has been justified by the agreement of the results from different rocks and different workers from the same geographic location.

The results of the measurement of the directions of magnetization were found to support an elderly hypothesis and introduce an unexpected phenomenon. The direction of the ancient magnetic field of the earth as found from the remanent magnetization of rocks from one continent, of the same age show good agreement but differ from the present earths magnetic field. The results are best interpreted as showing the variation in the position of the continent, the old idea of continental drift. This paleomagnetic evidence shows excellent correlation with paleoclimatic evidence (Blackett 1961, Opdyke 1962) supporting continental drift.

The unexpected phenomenon is that groups of results of the direction of the magnetization of the rocks from one location sometimes divide into two distinct directions, differing by 180°. The set of results, in closest agreement with the present earths magnetic field, are called normally magnetized. The other set are termed reversely magnetized. This difference can be explained either by the dipole field of the earth having been inverted when the reversed rocks were magnetized or by the self reversal of the minerals. Several theoretical models for obtaining a moment in a reversed direction to the applied magnetic field have been proposed (Stacey 1963). At present, the evidence is more readily interpreted in terms of field reversal (Wilson 1962, Irving 1964).

Cox et al have correlated absolute age determinations with the polarity of the natural magnetic remanence on a world wide basis, finding that rocks of the same age have the same polarity (Cox et al 1968).

The intensity of the ancient magnetic field of the earth is a more difficult quantity to determine. By a comparison of the intensity acquired by a specimen, when cooled in a known field, with the natural remanent magnetization, the ancient field strength is, in principle, determined. Two assumptions are made in this work. Firstly, the intensity of magnetization is proportional to the magnetic field applied during the acquisition of the magnetization. Secondly, the production of the thermoremanence in the laboratory has not altered the magnetic minerals present. The assumption has led to careful selection of suitable samples and rigorous testing before and after the laboratory heatings. The results of different workers correlate and indicate, the magnetic dipole field of the earth has averaged in the Tertiary time period to 30% below the present value (Smith 1967).

The petrological study of magnetic minerals has recently led to the correlation between the oxidation state of the minerals and the magnetic properties of the rocks. The iron-titanium oxide minerals are viewed at high (x 1200) magnification using an oil immersion objective on the microscope, in a polished section of a rock sample. The minerals are classified by the degree of oxidation on a progressive oxidation scale. By averaging over a large number of iron-titanium oxide grains, an overall oxidation state is assigned as a number to the rock specimen. Correlations are sometimes found between these oxidation states and the direction, normal or reversed, of the natural magnetization. The reversely magnetized samples exhibit higher degrees of oxidation that the normally magnetized specimens (Wilson, Watkins 1967). These correlations are always of a statistical nature, and are as yet unexplained.

As the magnetic minerals progress in degree of oxidation, olivine (a magnesium - iron silicate) can likewise show progressive oxidation. Olivine alteration products can be shown to be highly magnetic, in the natural rocks. This thesis is concerned with this oxidation of olivine. The work described deals with a series of experiments, which examined the alteration in a selection of natural olivines of known composition. The correlation between magnetic and optical properties of the alteration products is examined. The alteration products are identified from magnetic and X-ray powder pattern evidence. The results of these oxidations are discussed with regard to their significance to paleomagnetism. The importance of the results is due to the possible identification of a magnetic material not before identified in paleomagnetic rock samples.

CHAPTER 2

THE MAGNETIC MINERALS

2.1 Introduction

The magnetic minerals, which are of interest to paleomagnetism, have in the majority of examples been fully investigated. It is convenient here to review the relevant magnetic properties together with the properties of the magnesium ferrites.

The majority of rock forming minerals are either diamagnetic or paramagnetic. These two classes of minerals have only been of secondary interest to rock magnetism, which is mostly concerned with ferrimagnetic and ferromagnetic minerals. The importance of the chemical composition of the less magnetic minerals is now being realized, with its insight into the condition of formation of the rocks. A petrographic study of these minerals can indicate the state of oxidation, which together with their size and abundance can indicate the physical and chemical conditions present when the rock was formed. This information can indicate when the natural remanence of the magnetic minerals was acquired.

The ferromagnetic and ferrimagnetic minerals, which can be separated out from the crushed basaltic rock sample with a bar magnet, are found to be oxides of iron and titanium or sulphides of iron, with little impurity. Chemical analysis has shown these minerals to lie within the $FeO - Fe_2O_3 - TiO_2$ system (Fig2.1) or to be an iron sulphide.

The magnetization of a mineral is due to the magnetic moments of its individual ions. If the moments of the ions are aligned parallel, the resultant magnetism is termed ferromagnetism. If the moments of the ions are split into two sub-lattices in the crystal, then there are two possibilities. If the moments of the two sub-lattices are equal and antiparallel, the magnetism is termed antiferromagnetism. If the moments of the two sub-lattices are unequal and antiparallel, the magnetism is termed ferrimagnetism. The magnetization of the rock samples is due to the ferrimagnetism of the iron-titanium oxides. An exception is hematite, which is antiferromagnetic with weak parasitic ferromagnetism.

The magnetic properties of these magnetic minerals are dependent on division of the ions between the two sub-lattices. The magnetic properties will depend on the state of oxidation of these minerals, which changes the ferric : ferrous ion ratio, as well as the iron : titanium ion ratio. The magnetic properties can be affected by the order and disorder of the ions in the mineral. Carmichael (1961) has suggested that the ordering of the ferrous ions can be responsible for the reversal of the natural remanence of some special rocks. In this situation the ordering is altered by the movement of an electron only, between ferrous and ferric ions, but ordering can be altered by the movement of the non-magnetic titanium ions or by impurities.

2.2 The Magnetite - Ulvospinel Series

There is a complete solid solution series between magnetite Fe_3O_4 and ulvospinel Fe_2TiO_4. Magnetite is a cubic crystal of the inverse spinel structure. The general spinel unit cell is of the form $X_8Y_{16}O_{32}$ where X and Y represent cations with 2 and 3 electrons missing respectively. The lattice is defined as normal or inverse according to the distribution of the cations, X and Y. The oxygen anions form a cubic close packed structure. The cations occupy some of the tetrahedral and octahedral interstices, termed A and B sites respectively.

A NORMAL spinel has 8 X ions on A sites
16 Y ions on B sites
and is written $8(X[Y_2]O_4)$
an INVERSE spinel has 8 Y ions on A sites
8Y and 8X ions on B sites
and is written $8(Y[X_1Y]O_4)$

Hence, the unit cell of magnetite contains 8 molecules of magnetite and is written

$$8(Fe^{3+}[Fe^{2+}, Fe^{3+}]O_4)$$

The magnetic moments of the ions on the A and B sites are aligned antiparallel, so that magnetite is ferrimagnetic.

The accepted relevant constants for magnetite are a cubic cell dimension of 8.375Å, a Curie point of 578°C, saturation magnetization of 92-93 emu/gm at room temperature or 98.2 emu/gm at 0°K, with a direction of easy magnetization (111).

Ulvospinel has an inverse spinel structure $Fe^{2+}[Fe^{2+}Ti^{4+}]O_4^{2-}$. The magnetic moments of the two sub-lattices are antiparallel and equal, so ulvospinel is antiferromagnetic. The Neel point is below room temperature and ulvospinel is paramagnetic at room temperature. This mineral occurs naturally only as intergrowths in titanomagnetites, and has so far only been detected in intrusive rocks.

There is a complete solid solution series between magnetite and ulvospinel at high temperatures. The variation of the relevant parameters is shown in Fig. 2.2.

2.3 Maghemite ($\gamma\ Fe_2O_3$)

Maghemite has an inverse spinel structure but is deficient in cations. The structure is formed with cation vacancies on the octahedral sites. The usual unit cell given is as $Fe_8^{3+}[Fe_{13.33}^{3+} \square_{2.67}]O_{32}^{2+}$. The mineral inverts to hematite ($\alpha\ Fe_2O_3$) when heated. The inversion temperature is variable from 275°C to 800°C. This inversion means that the Curie point of maghemite cannot be directly measured. The accepted value is about 675°C, determined by extrapolation and the saturated magnetization is 83.5 emu/gm at room temperature.

Titanomagnetites found in rocks are often partially oxidized. They do not fit into the magnetite-ulvospinel series but have cation deficiencies similar to maghemite. These minerals are called titanomaghemites and on the ternary diagram lie between the magnetite-ulvospinel and the hematite-ilmenite series but with the cation deficient spinel structure.

2.4 The Hematite-Ilmenite Series

Hematite has a rhombohedral unit cell, which is nearly hexagonal. It is antiferromagnetic with weak parasitic ferromagnetism. The cause of this ferromagnetism is unexplained. Hematite is the main magnetic mineral in red sedimentary rocks (Collinson 1965). The Curie point of hematite is 675°C and it has a saturation magnetization of 0.1-0.5 emu/gm.

Ilmenite is similarly rhombohedral and is paramagnetic at room temperature.

The solid solution series between hematite and ilmenite is restricted at room temperature. It is limited to within 10% at either end of the series (Charmichael 1961). The properties of the series are shown in Fig. 2.3.

2.5 Pyrrhotite

Pyrrhotite is the only iron sulphide which is ferrimagnetic. It has usually a composition of the form FeS_{1+x} where $0 \leq x \leq 0.14$. It can be either antiferromagnetic or ferrimagnetic depending on the value of x.

2.6 The Magnesium Ferrite Series

The magnesium ferrites are of importance in this work because of their occurrence in altered olivines. Magnetite is an end member of the series. The series is formed by the exchange of magnesium ions for the ferrous ions in magnetite. There is a complete solid solution series between the two end members. The complement of magnetite is magnesioferrite $MgFe_2O_4$. The series is best written as $Fe_2^{3+}\{(1-x)Fe^{2+}\ x\,Mg^{2+}\}\,O_4^{2-}$.

The crystal structure for the series is a mixed spinel structure. The magnesium ions have more freedom of position than the titanium ions in the similar magnetite-ulvospinel series. The magnesium ions can be found occupying either A or B sites, depending on the temperature at which the crystal structure is at equilibrium. The magnesium ions prefer to occupy the B sites with decreasing equilibrium temperature. A magnesium ferrite, produced at a high temperature and then quenched, will maintain the high temperature form of the crystal structure. It will have a high crystal equilibrium temperature. If the same ferrite had been slowly cooled, the crystal equilibrium temperature would be much lower, near to room temperature. This lower equilibrium temperature structure is more inverse. The fully inverse structure is the most ordered structure, and so the more inverse structure has the lower equilibrium temperature (Allen 1966).

The variation of the crystal properties and the magnetic properties is more complicated than for previous series. These properties are affected by the variation of the $Mg^{2+} : Fe^{2+}$ ratio as with other series, but also the crystal properties, for a fixed $Mg^{2+} : Fe^{2+}$ ratio, will vary depending on the ordering of the crystal structure. These crystalographic and magnetic properties will, therefore, depend on both the heat treatment and the oxidation state of the ferrite. The oxidation of the ferrite will effectively produce a higher $Mg^{2+} : Fe^{2+}$ ratio with free hematite.

The effect of the variation of the Mg^{2+} : Fe^{2+} ratio on these crystalographic and magnetic properties has been sparsely studied. The variation of Curie point has been found for magnesium ferrites prepared by heating mixtures of end members of the series to 800°C for several hours (Fig. 2.4, Benard and Chaudron 1937). The method of cooling the samples was not recorded. The series may contain excess of either ferrous or ferric oxide. The ferric oxide is known to be able to cause a rise of the Curie point for a magnesioferrite (Fig. 2.5, Forestier 1928).

The effect of the variation in structure for a fixed ion ratio has been studied for $MgFe_2O_4$ (Fig. 2.6, Allen 1966: Fig. 2.7, Pauthenent and Bochirol 1951, Kriessman and Harrison 1956). Both the cell size and the saturation magnetization decrease as the structure becomes closer to an inverse spinel, that is as the crystal equilibrium temperature becomes lower. The time for thermal equilibrium to be attained in the magnesioferrites varies from 30 minutes at 1200°C to several hours at 600°C (Fig. 2.8, Epstein and Frackiewicz 1958).

For this series, cell sizes give little indication of the Mg^{2+} : Fe^{2+} ratio, due to the effect of ionic ordering. Similarly, differences in the saturation magnetization will only give information about the Mg^{2+} : Fe^{2+} ratio, if the samples, with different ratios, have the same equilibrium temperature. The Curie point can be affected by any excess of ferric oxide, which can be caused by the oxidation of the magnesioferrite. So while the presence of magnesium ferrites, in a sample, may be detected either magnetically due to peculiar magnetic behaviour, which is caused by the ease of ionic reordering or through X-ray powder photography, the compositions of the ferrites can only be found chemically. The chemical analysis of magnesioferrites produced during the alteration of olivine may be virtually impossible due to the extremely fine nature of the intergrowths of the ferrite in the pseudomorph of the olivine.

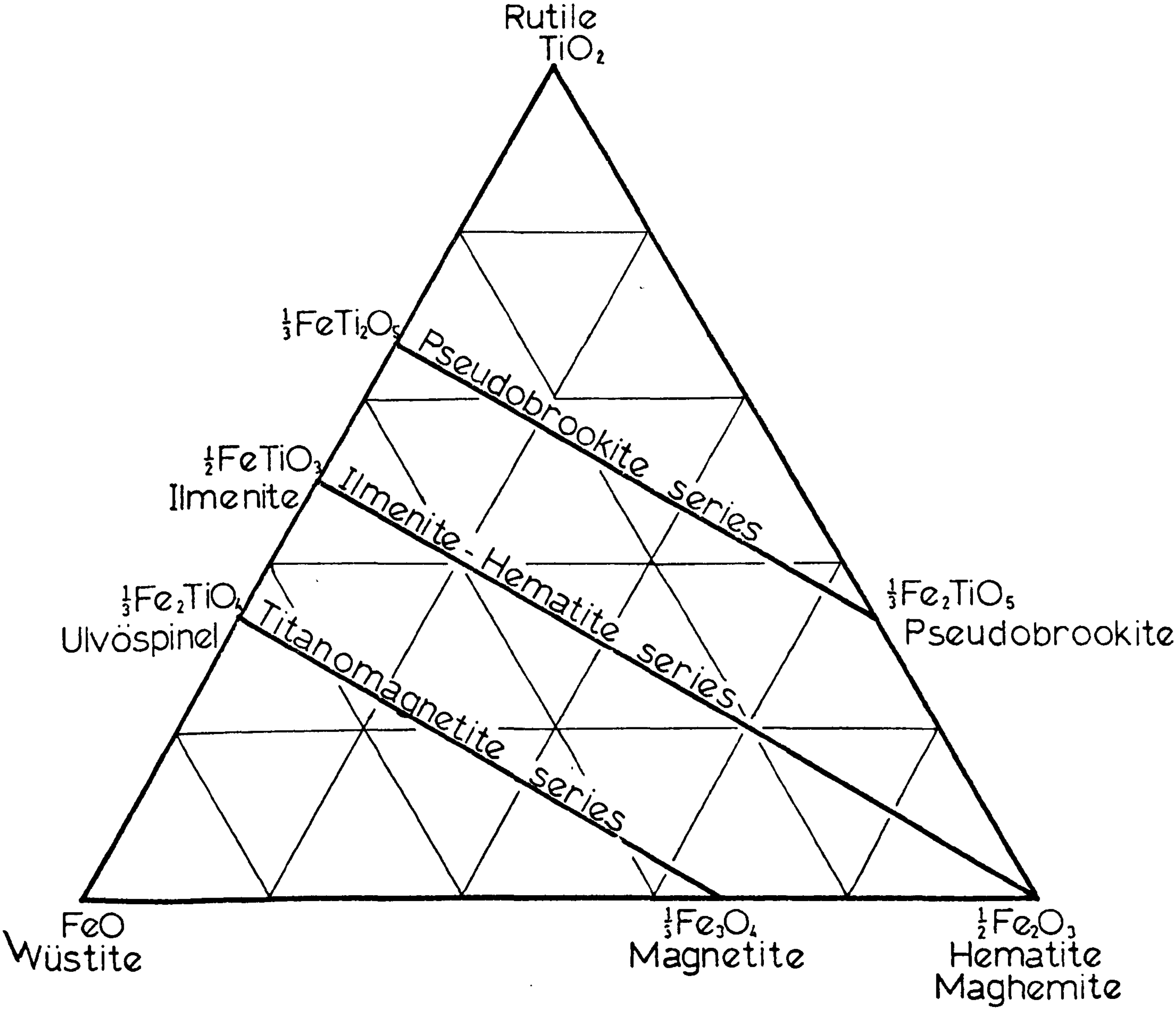


Fig 2.1 The $FeO-TiO_2-Fe_2O_3$ Ternary Diagram

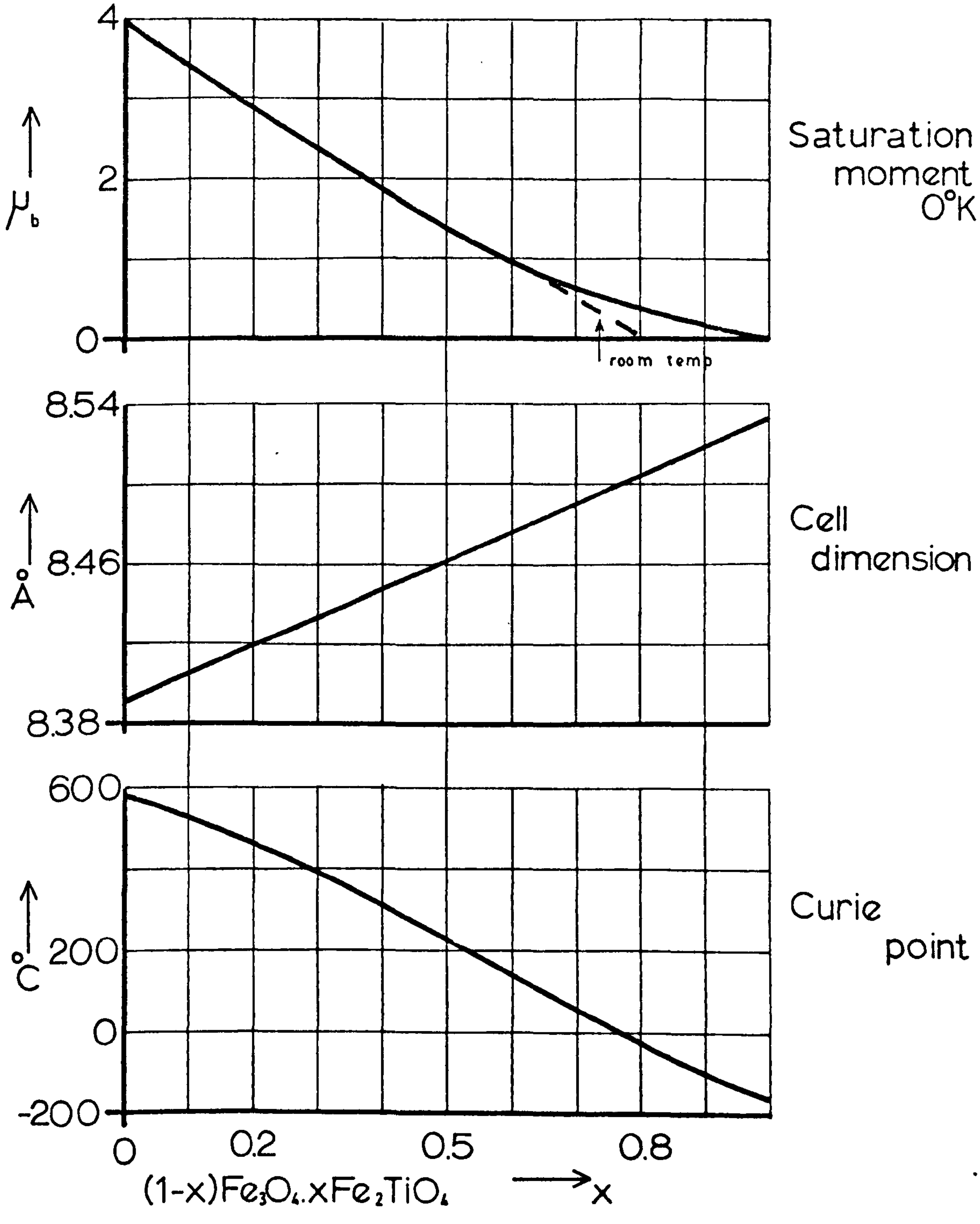


Fig 2.2 Parameter Variations of Titanomagnetites

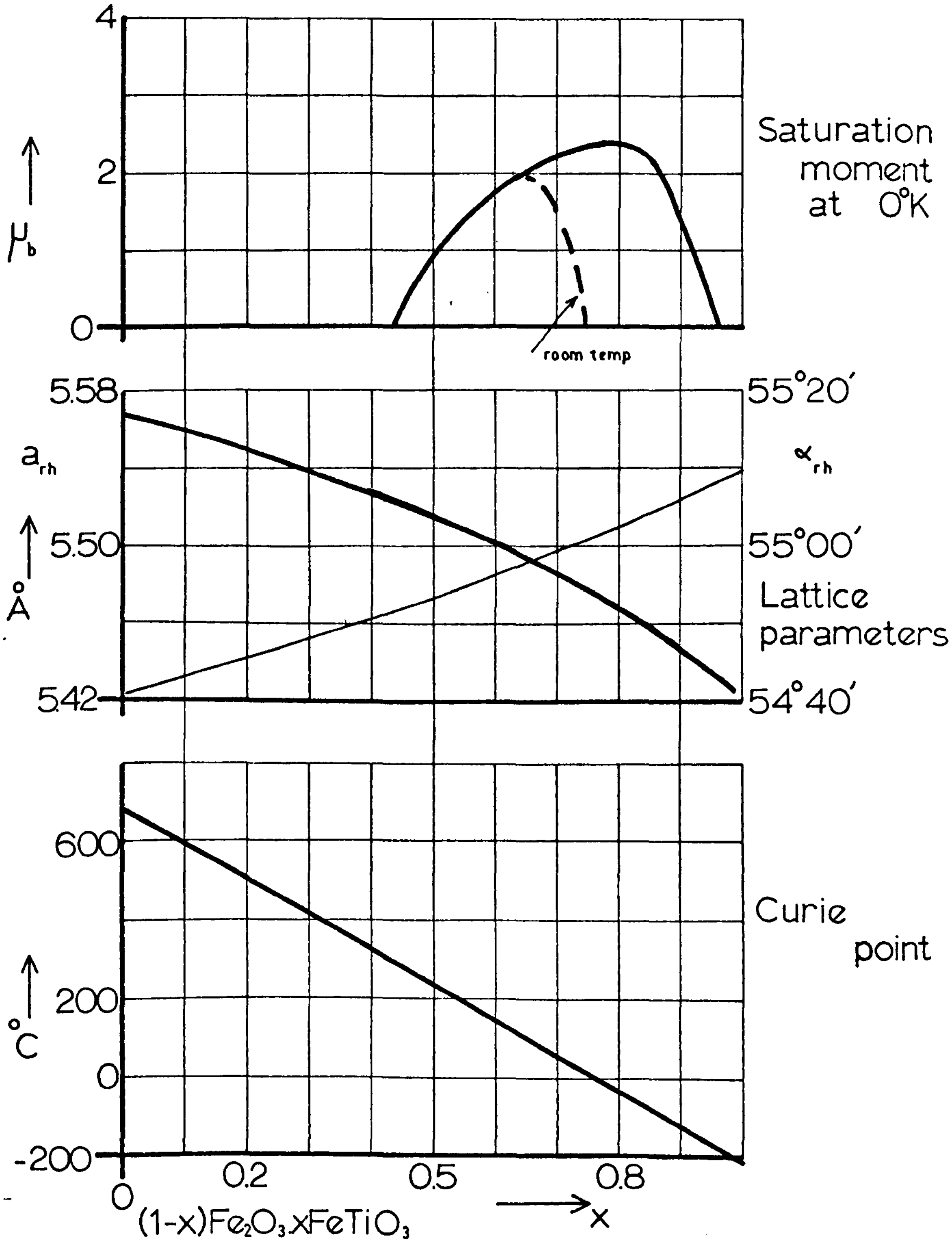


Fig 2.3 Parameter Variations of Ilmenite - Hematite series

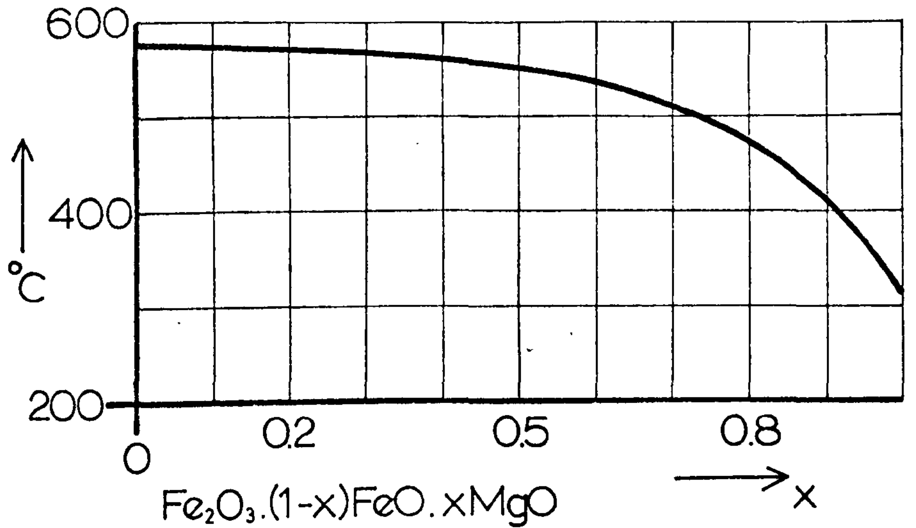
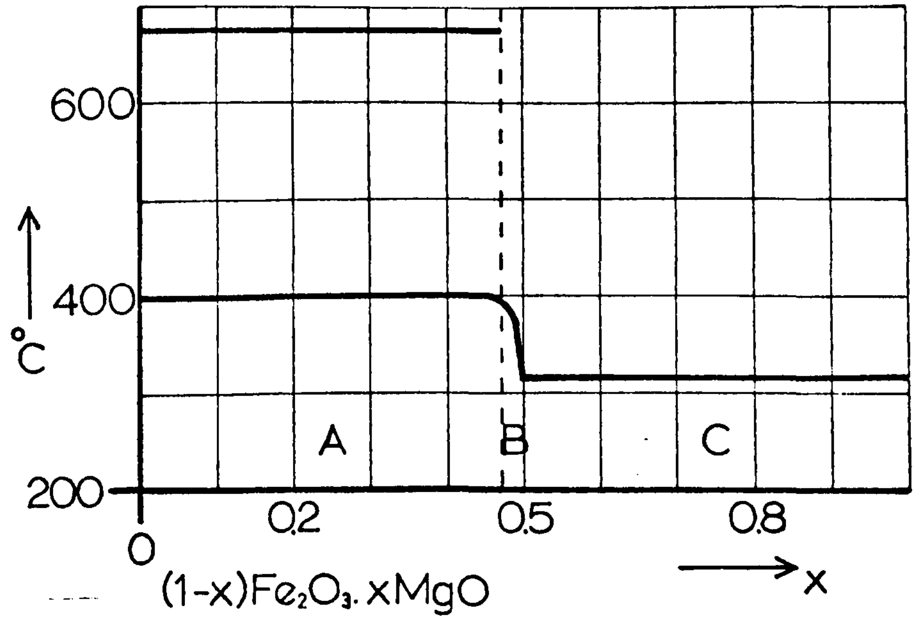


Fig 2.4 Curie Point of the Magnetite - Magnesium ferrite series



Region A - Fe_2O_3 + Solid Solution
B - Solid Solution of Fe_2O_3 in Fe_2MgO_4
C - Fe_2MgO_4 + MgO

Fig 2.5 Curie Point of the Hematite - Magnesium ferrite series

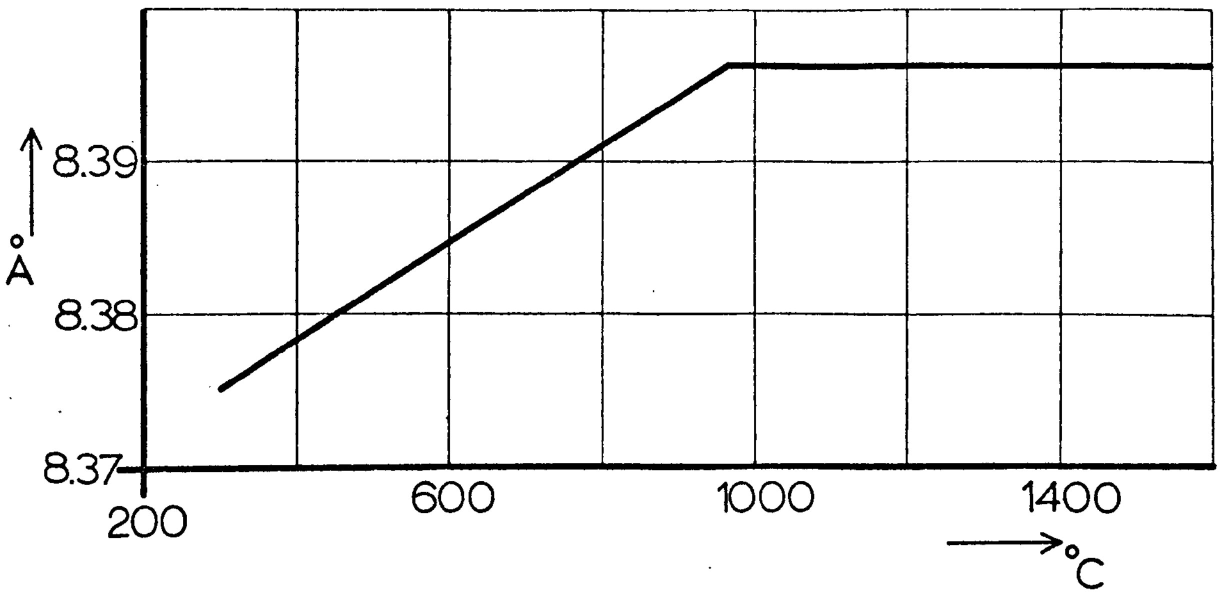


Fig 2.6 Cell Size of Magnesium ferrite as a function of Quenching Temperature

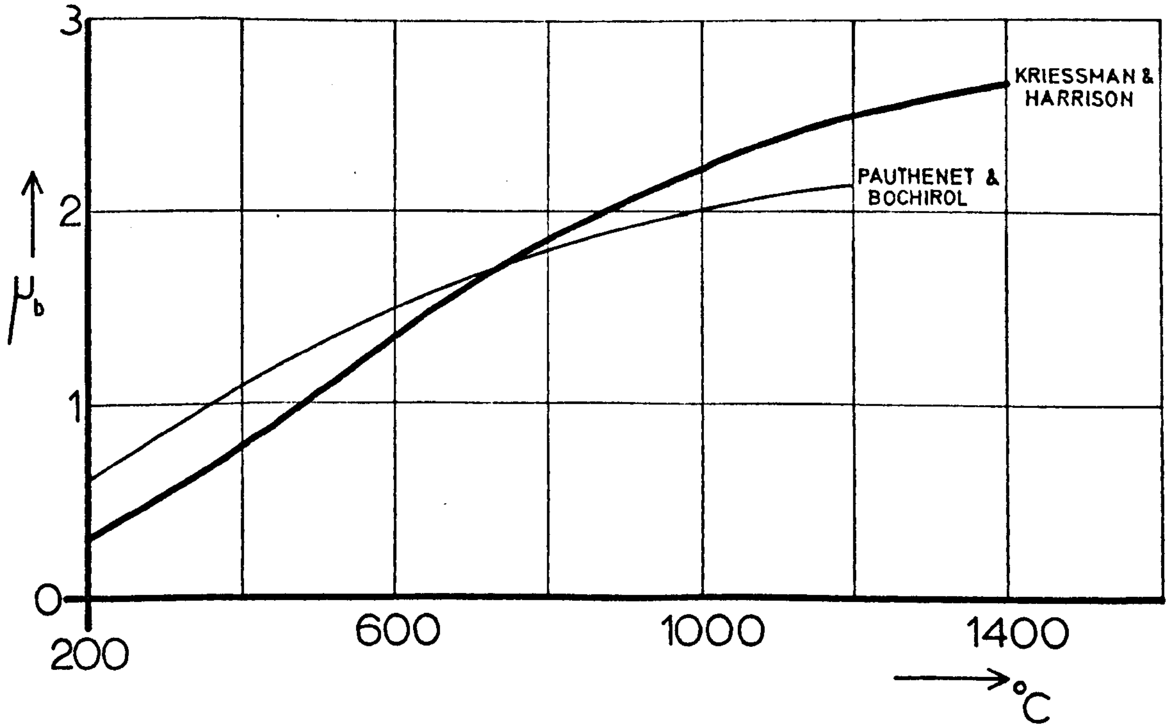


Fig 2.7 Saturation Moment of Magnesium ferrite as a function of Quenching Temperature

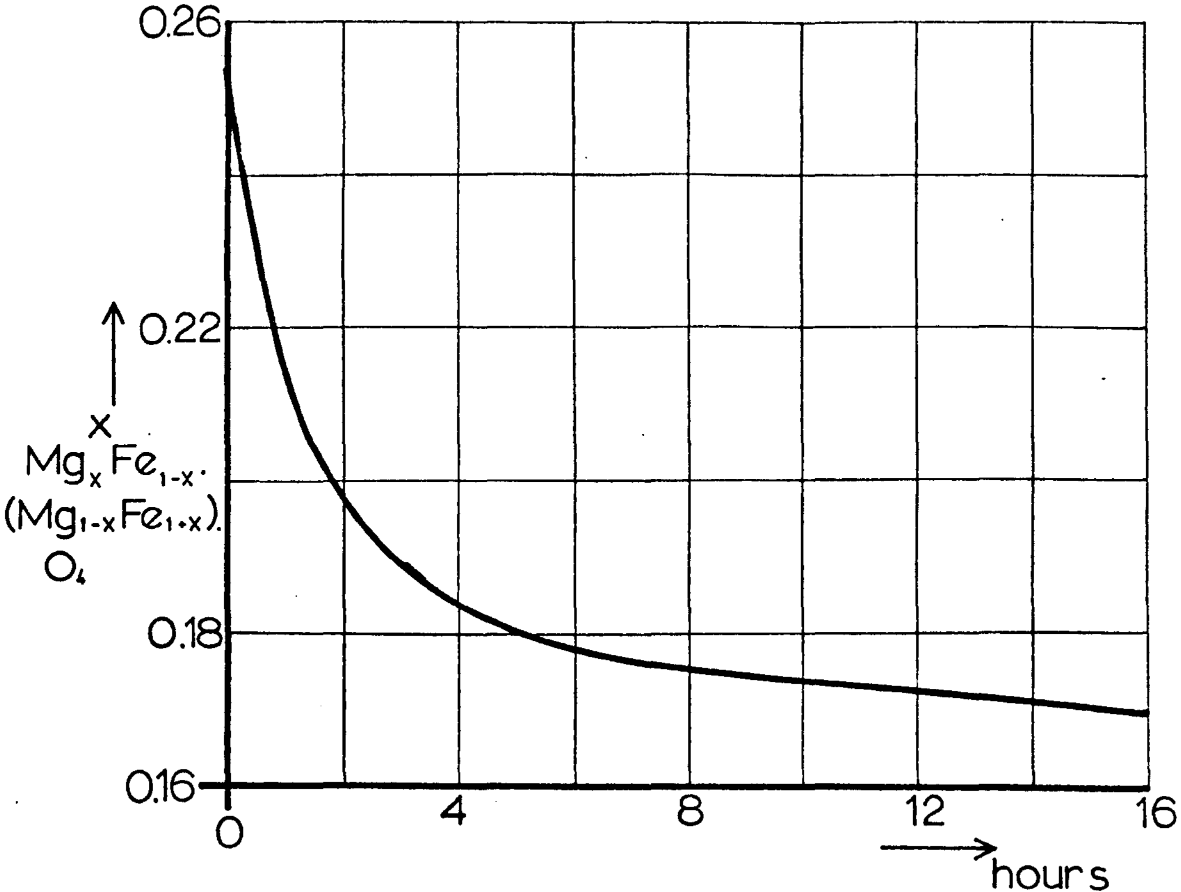


Fig 2.8 Tetrahedral Fraction of Magnesium ions in Magnesium ferrite as a function of tempering Time at 600°C

CHAPTER 3

THE OLIVINE MINERALS

3.1 Introduction

A definition of a mineral is that which is a naturally occurring homogeneous solid, inorganically formed, with definite chemical composition, and ordered atomic arrangement. The crust of the earth is composed of many different minerals. These minerals are formed in three main processes. Minerals are formed by crystallization from the molten magma from the earths interior as it cools at or near the surface of the earth. Secondly, minerals are formed by the physical action of the atmosphere or hydrosphere on existing minerals, this process is called sedimentation. Minerals are also formed below the weathered zone by physical or chemical alteration of pre-existing material, called metamorphism.

3.2 General Mineralogy

The crust of the earth is composed of eight major elements; oxygen, silicon, aluminium, iron, calcium, sodium, potassium and magnesium. No other element is present in more than 1% by weight. Hence, most of the minerals are compounds of oxygen or oxygen and silicon with one or more of the metallic elements. Minerals can be classified into silicates and non-silicates. The silicate minerals compose one third of all species of minerals but constitute over 90% by weight of the minerals in the earths crust. The silicate minerals are conveniently sub-divided with regard to their crystal structure.

The silicon and oxygen atoms join together such that there are four oxygen ions lying at the corners of a tetrahedron with one silicon ion at the centre of the tetrahedron. This silicon-oxygen tetrahedral structure is basic to all silicate minerals which differ in the manner in which they have the tetrahedra linked together. If the tetrahedra do not share any oxygen ions and are linked by metallic ions, these silicates are called orthosilicates and have a silicon-oxygen composition of the form SiO_4. A common example is olivine. The tetrahedra may be linked in pairs, sharing one oxygen ion. These silicates have the silicon-oxygen ratio Si_2O_7, an example is hemimorphite. If each tetrahedron shares two oxygen ions then a ring structure may be formed of either three (Si_3O_9), four (Si_4O_{12}) or six (Si_6O_{18}) tetrahedra. A typical example is tourmaline. Instead of forming a ring, a long chain of tetrahedra may be formed. A similar structure occurs when two parallel chains are linked together. The single chain (SiO_3) occurs in pyroxenes, the double chain (Si_4O_{11}) occurs in amphiboles. If three oxygen ions are shared the tetrahedra can join to form a sheet structure (Si_2O_5). Serpentine and chlorite are examples of sheet silicates. Finally, the framework silicates (SiO_2) are formed when all the oxygen ions are part of two tetrahedra and a three dimensional network is formed. The silica and feldspar groups are framework silicates.

3.3 The Mineralogy of the Olivine Group

3.3.1 Chemistry of the Olivines

Olivines are orthosilicates in which the tetrahedra are joined by either magnesium or ferrous ions. These metallic ions show a complete diadochy and so there is a complete solid solution between forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) (Fig. 3.1). In nature the olivines contain little impurity, due in part to the lack of suitable replacement ions in the magmas from whence they crystallize.

The olivine group has the general form of $(M)_2\ SiO_4$, where M may represent any divalent cation. Normally this ion is magnesium or iron but manganese-ferrous olivines have been found. Chromium, nickel and calcium have been reported as minor impurities in some olivines. Ferric iron is found in analyses of olivines. This ion is thought to be an alteration product and not of primary origin. This impurity may often be seen inside the crystal as orientated wedges and does not simply replace the ferrous iron in the olivine structure.

The magnesium-ferrous olivine solid solution series is considered to be an ideal solid solution series. Sahama and Torgeson (1949) have shown that the replacement of one cation by the other is thermochemically perfect. This conclusion means that substitution of magnesium for ferrous iron and v.v. occurs without causing any structural strain. However, the effects of the larger ferrous iron can be seen in the variation of the melting points of the olivines, fayalite 1205°C and forsterite 1890°C. The larger ferrous ion has the efect of reducing the cation-oxygen bonds and hence reducing the melting temperature. This consequence is of importance in the crystallization of olivines from a magma.

3.3.2 Physics of the Olivines

The structure of the olivines is that of the orthosilicates. The oxygen ions form sheets in the (100) plane and are in approximately the hexagonal close packed arrangement. These oxygen sheets form the stable ionic arrangement during the alteration of olivines. The cations lie between the oxygen ion sheets and have six nearest oxygen ions. The dimensions of the crystal structure vary directly with the magnesium : iron ratio due to the larger size of the ferrous ion. The unit cell size can be used to determine the Mg : Fe ratio. However, it is more convenient to use the separation of the (130) planes as determined from X-ray diffraction, as developed by Yoder and Sahama (1957) (Fig. 3.2). They have fitted a determination curve as below:-

$$F_0 = 4233.91 - 1494.59 \; d_{130}$$

where F_0 is the molecular percentage of forsterite in the olivine and d_{130} is the determined (130) plane spacing.

Many of the physical properties of the olivine series show variation, often linear, with composition. This dependence on composition allows the approximate composition of an olivine to be easily determined. Both refractive indices and optic axial angles vary linearly with composition (Henriques 1958, Bowen and Shairer 1935) although optic axial angles also depend on crystallization environment. The density of the mineral shows a non-linear variation with composition. Bloss (1952) fitted a determinative curve as below:-

$$Fa = -207.754 + 47.68521 \rho + 5.25529 \rho^2$$

where Fa is molecular percentage of fayalite and ρ is the density of the material.

3.3.3 The Genesis of Olivines

Olivines are formed in igneous and metamorphic conditions. In the formation of igneous rocks, olivines are the first ferromagnesian silicates to form. They crystallize together with the calcic soda feldspars. The opaque minerals are thought to precede the olivines in crystallizing. The early crystallization of the olivines implies that they are present when the magma is at high temperatures. This situation may be the reason for their frequent alteration. The magnesium rich olivines, because of their higher melting point, crystallize first. If any fractional crystallization occurs due to, for example gravity settling, the residual liquid will become iron enriched. This enrichment will mean the ground mass olivines will be richer in iron then the phenocrysts. If cooling is too fast for equilibrium to be obtained zoning of the crystals will occur, the outer zones of the crystals being iron enriched. If the magma becomes more silicious, for any reason, the early forsteritic olivines will react with the silica to form pyroxene. This reaction is often seen as a reaction or corrosion rim around an olivine.

Metamorphic formation of olivine can be by either contact or regional metamorphism. Forsterite is formed from dolomitic limestones and fayalite is formed from iron rich sediments. Olivine can be formed by folding or shear stress on rocks when the pressure converts pyroxenes into olivines.

3.4 The Natural Alteration of Olivine

The natural alteration of olivine is both abundant and varied. The different alteration products and processes are not yet fully understood. Work on the alteration of olivine is extensive but as yet there is considerable variation in the results. The alteration products of olivine can be divided in different ways, high and low temperature alterations, deuteric and postdeuteric alterations. However, due to the uncertainty over the alterations, the most useful classification is by optical properties.

The alteration of olivines can be optically divided into four groups, the alteration termed serpentinization type A, that producing red alteration products called iddingsitation type B, that producing green alteration products type C, and that producing alteration with opaques throughout the pseudomorph of olivine, type D. A few general points can be made for all of these alterations. The alteration products have a higher iron : magnesium ratio than the altered olivine. This difference implies the leaching of iron from the olivine. The ferrous ions are oxidized to ferric ions in the alterations. The oxygen ion lattice of the original olivine is stable throughout the alteration. The alteration products accept this layer structure with little or no change. The alteration of the silicate structure is mainly achieved by the movement of silicon ions, (Gay and Lemaitre 1961). The metallic ions also diffuse through the oxygen structure to form local concentrations forming goethite, magnetite or hematite alteration products. The workers agree that the alterations start along cracks in the olivines and proceed from the outside towards the centre.

Serpentinization, type A alteration, affects minerals other than olivine, often pyroxenes will be altered. Serpentinization is the result of low or medium grade metamorphism, that is at temperatures below 500°C (Turner and Vergoogen 1960). It can be formed by low pressure folding or shearing. When olivine is formed where the folding pressure is high, pressure regions are more conducive to volume changes and serpentine may be formed. During serpentinization olivine is converted into serpentine ($Mg_6Si_4O_{10}$ $(OH)_8$) which has two forms chrysotile and antigorite. This process often involves the formation of iron oxides either as discrete material or as a submicroscopic mineral throughout the serpentine. The occurrence of these oxides greatly affects the magnetic properties of the rock (Shapoval 1963, Shteynberg and Malakhov 1964, Gaucher 1965).

When the alteration results in red-brown alteration products, type B alteration then the practice is to call the alteration iddingsitation. The more recent work has shown it to be a complex alteration process. The group name iddingsite has been found to be a complex grouping of several minerals. Authors using different samples have obtained differing results. Iddingsite has been found to consist of a sheet silicate structured mineral and goethite ($FeO(OH)$). The exact nature of the sheet silicate has not yet been determined. Sun (1957) found it to be amorphous, Brown and Stephens (1959) determined it to be near to chlorite or smectite. Wilshire (1958) determined it as a mixture of chlorite and smectite or a chlorophaeite with a chlorite structure, Smith (1969) found it to be a chlorite, Gay and Lemaitre (1961) thought that it was not positively definable and suggested that the variation of previous results was due to the different degrees of iddingsitation in the specimens. Baker and Haggerty (1967) determined that the alteration is a interstratification of chlorite and smectite and vermiculite, with varying degrees of mixing.

The alteration to a green product, type C, has been generally less well investigated and the product has been called bowlingite, serpentinite, chlorite, nontronite and vermiculite, which are all variations of sheet silicates and chlorophaeite, which is submicroscopically crystalline. Baker and Haggerty concluded that it is a chlorite-smectite-hydromica interstratification in varying degrees of complexity.

The alteration producing iron oxides, type D, without serpentinization, has again not been widely studied. This deficiency may be due to the situation that polished rock sections viewed under reflected light, rather than the more usual thin sections of material viewed with transmitted light, have to be used to examine the iron oxides. Wilshire (1958) noted that iron oxides, opaques, may predominate in a pseudomorph of olivine. Gay and Lemaitre (1961) identified in the alteration of olivine, type B, a spinel structure, which they called either magnetite or magnesioferrite. They suggested this mineral had been formed before the iddingsitation occurred. Muir et al (1957) found in a thermally metamorphosed rock, marginal separation of magnetite and the formation of orthopyroxene. Haggerty and Baker (1967) recently investigated carefully this alteration and identified the products to be magnetite and enstatite (Mg_2SiO_3) as metastable products and hematite and forsterite as stable products.

The conditions of formation of these alteration products are subject, in some types of alteration, to conflicting evidence. The type D alteration is produced at high temperatures (Haggerty and Baker 1967) from the evidence of heating experiments (to be described in 3.5) and the association of high temperature accessory minerals. Serpentinization occurs at the lower temperatures. It is with types B and C that the conditions are not definitely known. Baker and Haggerty concluded a low temperature <400°C of formation for type B, iddingsite. Their conclusion was reached because of the presence of low temperature of formation minerals smectite and goethite and the low temperature associated secondary minerals, and the similarity of the effects of weathering. Wilshire (1958) found that weathering continued alteration rather than caused alteration. He found that iddingsite showed indications of the flow of the lava. The presence of fresh olivine rims around the altered phenocrysts has been reported (Sheppard 1962). This evidence suggests that iddingsitation takes place at high temperatures, in contradiction of Baker and Haggerty's views.

Baker and Haggerty suggest that the type C alteration is a continuous process throughout cooling. The exact alteration mineral depends upon the temperature of formation.

3.5 Heating Experiments on Olivine

Several attempts have been made to reproduce natural alteration of olivine by heating olivines in the laboratory. Gay and Lemaitre (1961) attempted unsuccessfully to produce iddingsitation using iron, acqueous and acid solutions, conditions they deemed necessary, and temperatures to 600°C at 1000 atmospheres. These experiments would indicate that a higher temperature is required. Fawcett (1965) heated olivine, altered to the type C alteration, in air at 600°C. He produced the red-brown alteration, with chlorite rimmed with opaques and other intermediate mixtures.

Haggerty and Baker (1967) have heated 20%Fa olivine in air for varying times at several temperatures. They readily produced material optically alike to the type D natural alteration. The iron oxides produced either spread throughout the olivine or formed a thick rim about the pseudomorph. They identified magnetite and enstatite at higher temperatures (850°C - 1000°C) as a metastable state, which altered to hematite and forsterite after further heating. Between 600 - 850°C hematite and forsterite develop even after a short period of heating.

Champness and Gay (1968) have done similar experiments. Their results are more complex, but they found a spinel-like phase which altered to a hematite-like phase on further heating. They found that the silica produced yielded a stable pyroxene-like structure when it reacted with the olivine.

There are two other reported heating experiments which are of importance to this work. Christie (1959) heated olivine basaltic glass under water pressure. He found that plagioclase was always formed. Magnetite was formed at low temperatures (<300°C) and hematite formed above this temperatures. Weaving (1962) experimented on the heading of chlorophaeite, an alteration product of olivine. His magnetic and X-ray results indicated an impure hematite was formed when the samples were heated to 600°C but petrological measurements were not made (Fig. 3.3).

3.6 Conclusions

Olivines form a complete orthosilicate solid solution series between magnesium orthosilicate, forsterite Mg_2SiO_4 and ferrous orthosilicate, fayalite Fe_2SiO_4. There is a complete diadochy between the magnesium and ferrous ions. The series can be considered to be ideal. The position of an olivine in the series may be determined from X-ray diffraction.

The olivines are formed early in the course of the magma cooling, and so are susceptible to alteration due to changing conditions. They are readily altered into complex products in varied conditions. The appearence of various iron oxides in these alterations is of importance to paleomagnetism, as these oxides may be responsible for the magnetic properties on which some paleomagnetic work is based. The reproduction of some of the natural alterations by heating experiments indicates the possibility of using such experiments to look at the magnetic consequences of these processes.

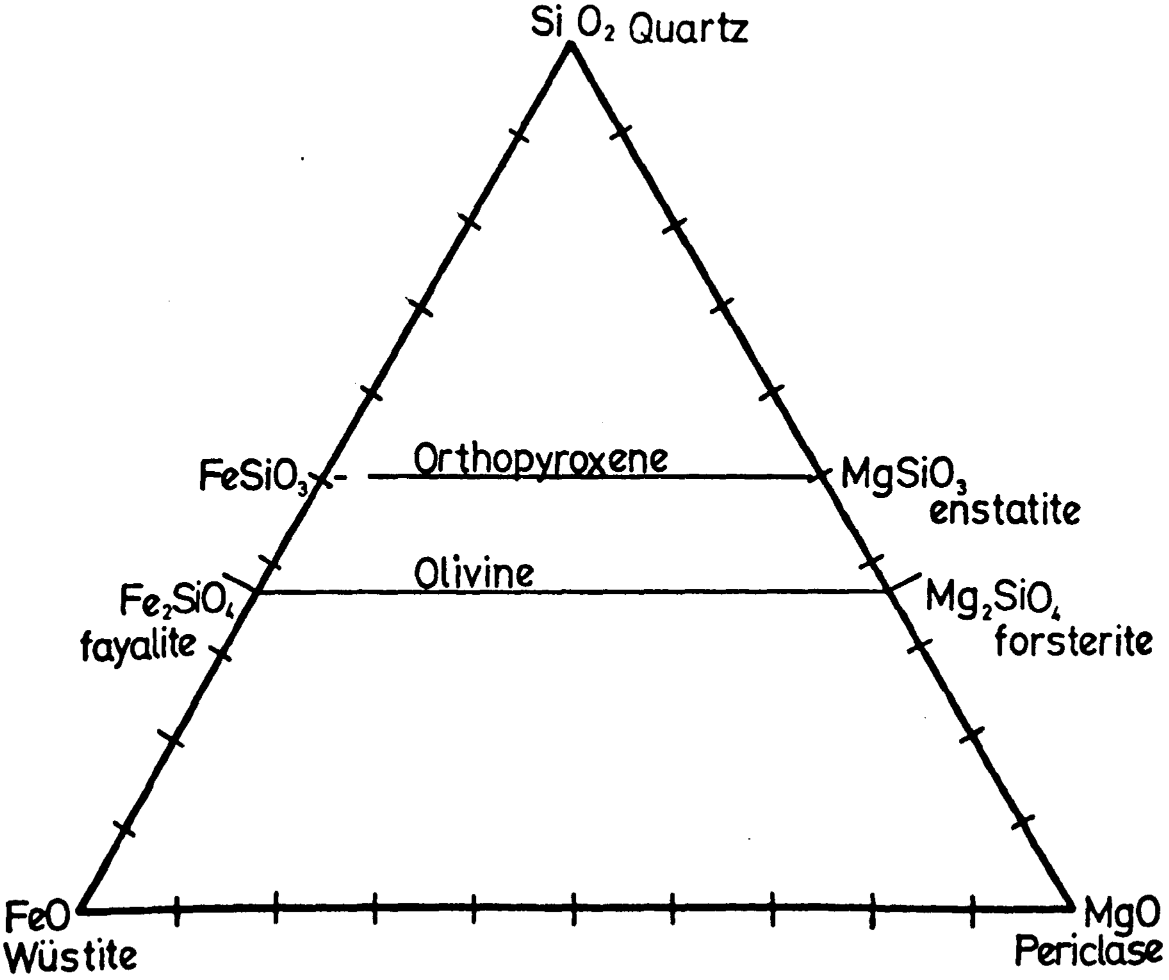


Fig 3.1 The FeO - MgO - SiO_2 Ternary Diagram

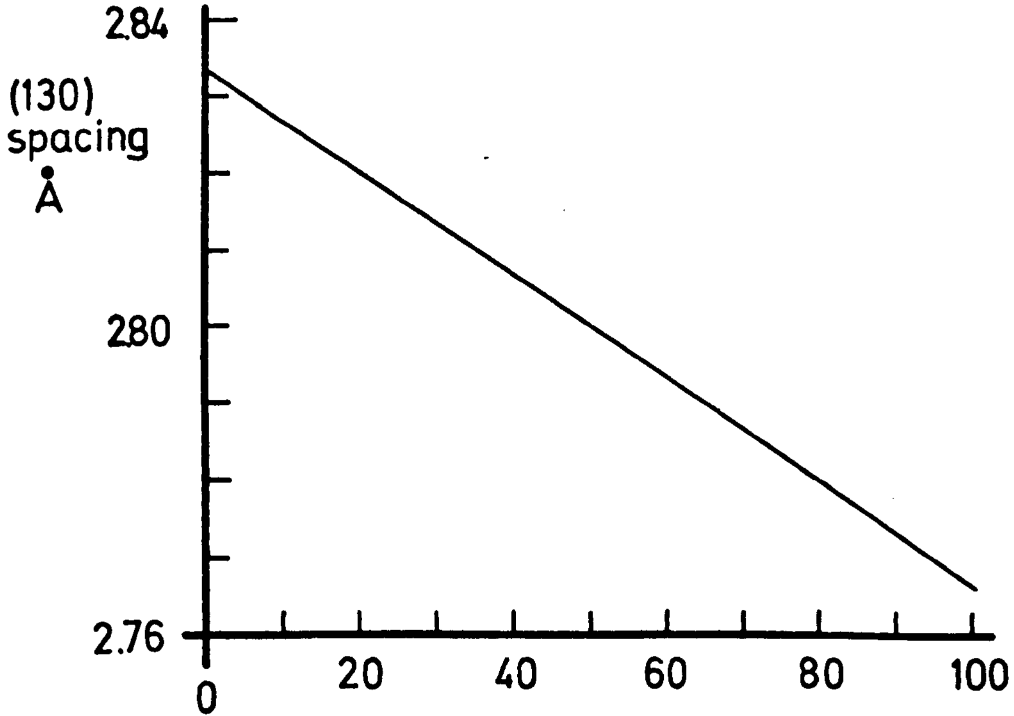


Fig 3.2 The Variation of (130) Spacing with Olivine Composition

Olivine X-Ray Determinative Curve

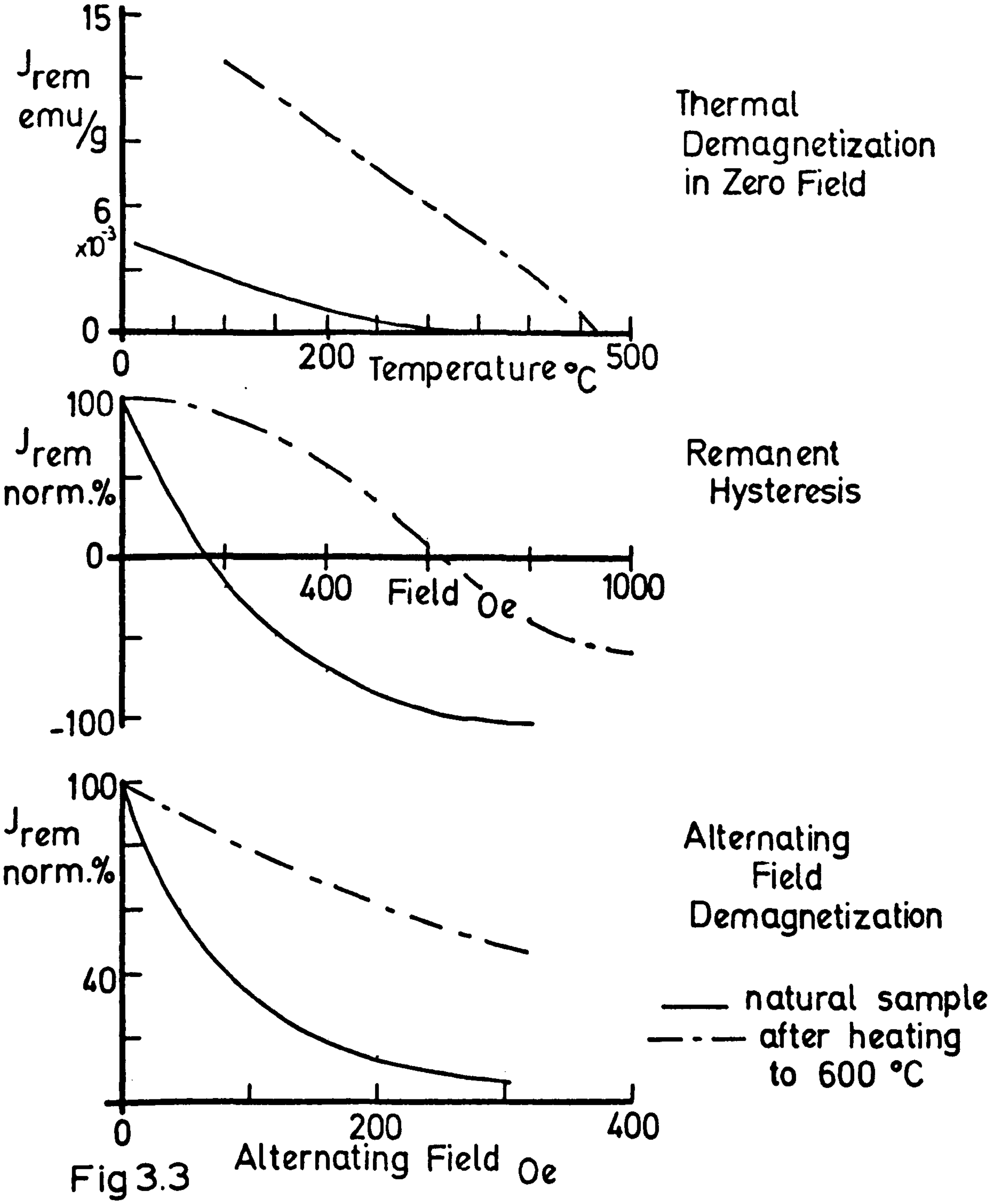


Fig 3.3
The Magnetic Behaviour of the Saturation Remanence of Chlorophaeite before and after being heated.

CHAPTER 4

EXPERIMENTAL TECHNIQUES AND MATERIALS

4.1 Introduction

The extensive use of petrology in rock magnetism is of quite recent origin. The petrographic examination of large numbers of specimens has helped to link mineralogical properties of rocks with their magnetic properties. The occurrence and condition of iron-titanium oxides has been linked with the magnetic properties of igneous rocks (Watkins and Haggerty 1967, Ade Hall 1969) and metamorphised rocks (Moskaleva and Zotova 1965).

In some igneous rocks a correlation between the direction of natural magnetization and the oxidation state of the iron-titanium oxide minerals has been found statistically (Wilson and Watkins 1967). The oxidation state of the minerals is determined by the classification of the iron-titanium oxides in a rock, on an oxidation scale, with homogeneous titanomagnetite being indicative of the lowest oxidation state and intergrowths of pseudobrookite, hematite and rutile indicating the highest oxidation state. This correlation has shown that the more highly oxidized iron-titanium oxides, indicating a more high oxidized rock, were more likely to be present in a rock, that had a reversed direction of natural magnetization, than were the less oxidized minerals. This correlation has yet to be shown on a general basis, but given its validity, the cause is unknown.

A use of petrography to rock magnetism has been to help to identify the magnetic minerals responsible for the natural magnetization of rocks. In the low oxidation state rocks, the iron-titanium minerals visible, have the same magnetic properties as the general magnetic properties of these rocks. In the highly oxidized rocks, the iron-titanium oxides are sometimes less magnetic than would be indicated by the general magnetic properties of the rock. This result would indicate that either the magnetism of these rocks is due to other minerals or the magnetic properties of these iron-titanium oxides are modified by the conditions in the rock.

Together with the oxidation of the iron-titanium oxides, the olivine in the rock is oxidized. This alteration can produce iron oxides as alteration products in various forms. The magnetic properties of these secondary oxides are dependent on their composition and their mode of occurrence. The effect of their presence on the magnetization of the rock may be similar to the effects of the secondary oxides produced during serpentinization (Shteynberg and Malakhov 1964).

4.2 Preliminary Work

The problem of the identification of the magnetic minerals in the oxidized rocks can be readily solved. A magnetic extraction from a crushed oxidized rock will separate the magnetic minerals. The magnetic minerals were so extracted from several highly oxidized rocks and were found to be similar from each of the rocks.

The samples were finely ground in a non-magnetic pestle and mortar. The powder was spread on a clean paper and a bar magnet, on top of a sheet of paper, was passed about 1 cm above the crushed sample. The magnetic material was attracted to the underside of the paper, covering the magnet. To extract the weaker material, the magnet was simply moved closer to the sample. The strongly and weakly magnetic extracts were placed in a mould and set in araldite. These mountings were polished for viewing with a reflection microscope, using oil immersion at x 1200 magnification. The weakly magnetic fraction was a mixture of three main types of material. There was a red sponge-like material (P. 4.1, 4.2). This material made up the majority of the fraction. There were large discrete opaque grains present and some green sponge-like material. The sponge-like material had the appearance of submicroscopic ($< 1\mu$) opaque grains scattered through a coloured semi-transparent material. The strongly magnetic material, consisted of the green sponge-like material, occasionally with small opaque grains attached (P. 4.3, 4.4, 4.5, 4.6). The edges of some of this material were reddened but little entirely red sponge-like material was present. The conclusion drawn was that this sponge-like material, identified by petrologists as altered olivine, was highly magnetic and could be responsible for the natural magnetization of these highly oxidized rocks.

X-ray diffraction patterns of powder samples of the strongly magnetic material were obtained using a Guinier camera. The powder diffraction photographs were of insufficient clarity to give positive identifications of minerals present. A difficulty of the X-ray work with these samples and the difficulty which occurred again later, was that the patterns of the minerals, which were thought to be present, had many of their strongest lines very nearly coincident. This coincidence of the strong lines meant that identification was dependent on minor lines, which required clear photographs for their accurate measurement. The photographs of the strongly magnetic material indicated the presence of magnetite-like and hematite-like structures, together with olivine. The Curie points of the two rock samples were measured to be 540°C and 560°C. These Curie points indicated that hematite was not the major magnetic material present.

4.3 Initial Heating Experiments

As the extraction of the highly magnetic material had produced material other than the discrete iron-titanium oxides, which had tacitly been assumed to be the magnetic minerals bearing the NRM, three problems were raised of importance to paleomagnetism. What was the highly magnetic sponge-like material? Secondly, what were its magnetic properties? Thirdly, when in the history of the rock was the material formed, that is when did the rock acquire its natural remanent magnetization?

A series of experiments was initiated to indicate, if under simple laboratory conditions, these alteration products could be formed. If they were formed, an outline of their magnetic properties could be determined, and so perhaps answers to these question proposed. The immediate purpose of these initial experiments was to determine the pattern for more extensive work, which would give more detailed results.

A variety of sample material was used for this initial series of experiments. The selection of samples was determined by the availability of material containing olivines, as olivine was thought to be the starting mineral for the magnetic sponge-like material. The sample material used was to be as alike as possible to rock specimens used for paleomagnetic work. A rock sample, a dunite containing a large amount of olivine, and two samples of separated material (an olivine of unknown composition and a basaltic glass containing microcrystals of olivine) were used. The experiments linked petrographic and magnetic changes due to simple heating of the samples. The samples were heated at a selection of temperatures between 650 and 1000°C, for periods of time between five minutes and one week. They were heated in a furnace, which was open to the air. At the conclusion of the heating the samples were quenched in air in a known magnetic field. The lowest temperature used, 650°C, was arbitary but as little alteration occurred at this temperature during the laboratory heatings, no lower temperatures were tried. The upper temperature, 1000°C, was limited by the furnace and because a reaction between the quartz sample holder and the sample occurred at higher temperatures (Lewis 1968).

The results have been summarized in Table 4.1. Two samples of olivine and two samples of glass were similarly heated for one day at $1000^{\circ}C$. One sample of each material was in a quartz tube with one end open to the air. The other samples were sealed in an evacuated quartz tube. The pressure in the tube was $< 10^{-2}$ torr. The weight of the samples used were insufficient for accurate magnetic measurements to be made. A piece of each of these four samples were prepared as described previously for microscopic examination.

The olivine heated in the evacuated holder, showed little sign of alteration, except that the sample had an overall lighter colouration. A few lines of opaque material were scattered through the crystal. These lines consisted of small, $\sim 1\mu$, opaque grains arranged in weaving lines. The olivine, which had been heated in the open tube was highly altered (P. 4.7, 4.8). The alteration was greatest at the rim of the crystal, but there were regions throughout the crystal with different densities of alteration. These regions had definite boundaries and may indicate zoning of different compositions within the olivine. The alteration was of the form of submicroscopic opaque grains, $< \frac{1}{2}\mu$, grouped in a green semi-transparent material in the form of striations or irregular shapes. Round the rim of the crystal the alteration produced reddening which penetrated into the crystal, especially along cracks.

The glass sample in the evacuated tube was altered to a light brownish colour with very few opaque grains ($\sim 1\mu$). The included crystals showed no sign of alteration. The glass sample, heated in an open holder, was of similar appearance but the opaque grains were more profuse and larger (2μ). There were areas of larger, 5-10μ , opaque grains. These opaque grains were surrounded by areas devoid of opaque material and appeared to have grown by leaching the surrounding glass of opaque material (P. 4.9). The included feldspar crystals, which were identified by their lath-like shape, were unaltered by the heating. The included olivine crystals were altered, with reddening about the edges and opaque material had started to form at the edges and spread inwards (P. 4.10).

Samples were similarly prepared and heated at 1000°C for seven days. Optically the samples were similar to those samples heated for one day. Generally the opaque grains, which were formed, were larger and more extensive throughout the crystal. The areas of the samples, which had turned red, had extended from the edges into the crystal (P. 4.11, 4.12, 4.13).

Samples were prepared and heated at 850°C for both one and seven days. The samples, both olivine and glass, heated in vacuum were slightly altered in colour but there were no visible opaque grains. After heating in air, small opaque grains were visible in both samples, as with the samples heated at 1000°C. There was no reddening at the edges of these samples and the glass had a bluish-green background colour (P. 4.14, 4.15, 4.16).

All the samples acquired a weak thermoremanence on quenching in the 0.5 oe magnetic field, with the sample, which had been heated in air; having a remanence at least 10 x larger than the sample heated in vacuum. The untreated samples were non-magnetic, within the limits of the magnetometers.

These experiments demonstrated that olivine could be altered to a material visually similar to that magnetically extracted from a highly oxidized rock. The alteration occurred on heating the olivine samples to 850°C and above when in air but to a negligible extent when heated to the same temperatures in vacuum. Glass can also be altered by similar heating but not to a product found in rocks used in paleomagnetic work.

Samples of olivine and dunite were sealed in an evacuated tube at a pressure of $< 10^{-2}$ torr. The samples were heated to 1000°C for 24 hours and then quenched in a magnetic field. The samples were examined to test their magnetic properties and a piece of both samples was removed and prepared for microscopic examination. The remainder of the samples were reheated at 1000°C for progressively longer periods of time. After each heating, magnetic examination of the samples were made and a piece removed for optical work. A further olivine sample was similarly heated to 850°C. The results are shown in Table 4.1.

On heating the olivine to 1000°C in an evacuated sealed tube, as before little alteration was visible except for the general lightening of the colour of the crystal. After heating for five minutes in an open tube, marked alteration was visible. The rim of the sample was reddened and the density of the alteration decreased towards the interior of the crystal. The alteration appeared to be opaque grains, which were submicroscopic, $< 5\mu$, and either in thin wavy lines, or elliptical shapes with their major axes aligned. With further heating, the alteration spread towards the centre of the crystal and became denser at the edge. The alteration became the irregular elliptical shaped type (P. 4.17, 4.18).

The virgin olivine was non-magnetic, within the sensitivity of the magnetometer. The heating, in an evacuated tube, had little effect on the magnetic properties of the sample. After heating the sample in air for even five minutes, the saturation remanence had risen by a factor of five over its initial value. The saturation remanence had risen by a factor of ten over its initial value after heating for one hour. These samples were weakly magnetic and the saturation remanence, measured with an astatic magnetometer, proved the only magnetic parameter which was accurately measurable throughout the series of heating. The Curie point was constant at 550°C after heating in air for 20 to 60 minutes.

The similar heating of the olivine to 850°C produced alteration. After heating for 60 minutes at 850°C the alteration was visually similar to that produced after heating for five minutes to 1000°C. The opaque grains were neither as large or as extensive as after heating to 1000°C. The saturation remanence did not rise as quickly and required 60 minutes heating to give the same remanence as acquired after five minutes at 1000°C. The heating of the sample of olivine to 650°C for periods up to 24 hours did not produce any alteration which could be seen in a polished section or detected magnetically.

The heating of a sample of dunite to 1000°C gave very similar results to those obtained from heating the olivine. After heating in vacuum, the dunite showed little visual alteration. The edge of the sample was a lighter colour. On heating in air for one hour the sample became highly reddened with areas of bright orange containing highly reflecting internal surfaces. There were no visible discrete opaque grains. On further heating the opaque grains formed about the rim of the sample, with striations of opaque grains visible in the interior after four hours heating. The heated sample was highly magnetic. After heating the sample was quenched in a known magnetic field and the thermoremanence acquired was measured with an astatic magnetometer. This TRM for the dunite rose by a factor of 100 over its initial value during the heating in air for four hours.

These experiments demonstrated that olivine could be easily altered into a material, optically similar to that found in oxidized rocks. The altered samples were highly magnetic. The necessity of air, or oxygen during the heating was demonstrated by the rapidity of the reaction, when the sample was open to the air. The dunite experiment showed that olivine could be altered in rock samples as easily as could separated olivine.

4.4 Experimental Procedure

The technique used in the initial experiments was modified to give a standard technique for more detailed experiments. These experiments would examine the variation of the alteration products with changing heat treatments on different known compositions of olivine.

The technique used was that a single sample of an olivine was subjected to a sequence of heatings at a predetermined temperature. After each stage of the sequence the alteration products were examined. A sample of known weight of an olivine was packed with quartz wool into the sealed end of a quartz tube. The quartz wool was used to prevent the sample moving, when magnetic measurements were being made. The quartz tube was evacuated to below 10^{-2} torr and sealed. The sample was heated for a decided period in the furnace at the predetermined temperature.

The furnace was a non-inductively wound coil about a quartz tube. The tube was placed vertically into Caposeal insulating blocks. The temperature of the furnace was measured by a thermocouple introduced through twin bore quartz tubing into the centre of the furnace. The sample was hung by platinum wire adjacent to the thermocouple. The temperature was controlled automatically to $\pm 5^{\circ}$C by a Cambridge Indicating Controller. The temperature was limited to 1000°C to protect the furnace. When used at 1100°C, the furnace burnt out.

The samples were required to be quenched after heating, in order to retain the high temperature form of the alteration. A quartz tube, of diameter such that the small holder would be a close fit into this tube, was introduced into the furnace from below, through an asbestos plug. This tube reached into the furnace just below the centre of the furnace. The lower end of the tube was in a beaker of salt. This beaker was at the centre of a set of Helmholtz coils. These coils gave a known magnetic field, which was aligned with the quartz tube from the furnace. A sample, after it had been heated, was manoeuvered into the top of the quartz tube at the centre of the furnace, and released. The sample dropped out of the furnace into the cool air in the centre of a known magnetic field. The sample thus acquired a thermoremanence along the axis of the sample holder.

The samples were quenched in a field of 0.5 oersted, similar magnitude to the earths magnetic field. The samples cooled to 100°C in ten minutes and were cooled to very near room temperature in about half an hour. When at room temperature the TRM acquired on quenching was measured under an astatic magnetometer, with the sample rotating about the direction of magnetization to be measured. The sample was placed in a rotating A.C. demagnetizing apparatus, without applying a demagnetizing magnetic field. This apparatus has a vigorous action, reversing its direction of motion every two revolutions. If the TRM was remeasured, an easy check whether the sample was loose was made. The heating was often found to loosely cake the sample together. Some loose samples were found and were unsuitable for A.C. demagnetization.

The TRM was A.C. demagnetized in peak fields of up to 500 oersted, using a "tumbling" A.C. demagnetization apparatus (Methods in Paleomagnetism: A.C. demagnetization p 221-254, 1967). The demagnetization curve gave an indication of the hardness of the magnetic material. The saturation magnetization was measured using a magnetic balance in a field of 5000 oe and the saturation remanence measured by the astatic magnetometer. The saturation remanence was A.C. demagnetized as for the TRM and these curves showed the hardness of the magnetic material responsible for the saturation properties.

The sample was resaturated and the saturation remanence was measured during thermal demagnetization in zero magnetic field, using an astatic magnetometer furnace (Wilson 1962). If possible the high field Curie point, using a Curie balance, was also measured. The presence of two or more magnetic minerals could be detected by the measurement of multiple Curie points.

After the sample had been thermally demagnetized in zero field it was cooled in a known magnetic field, 0.62 oe, from 700°C to room temperature over several hours. The TRM acquired in this way was measured and either A.C. demagnetized or thermally demagnetized. The sealed quartz sample holder was then opened and a small piece of the sample extracted. This piece would be mounted and polished for optical examination at the end of the series of heatings.

The sample was packed with quartz wool into the closed end of a short quartz tube. The other end was left open to the air. The sample was heated in the furnace at the same temperature for a determined time. After this time it was quenched in the known magnetic field as before. The sequence of magnetic measurements was repeated except that the sample was sealed in an evacuated quartz tube before any thermal demagnetization. This precaution was to limit any oxidation during the thermal demagnetization. The piece of the sample to be used for optical work was removed before the sample was sealed. At the end of the magnetic measurement the sample was repacked in an open quartz holder and reheated in the furnace at the same temperature for a longer period of time.

Using this technique, the progression of the alteration of the sample, with the duration of heating at a particular temperature was followed magnetically and optically. The technique was used for different compositions of olivines. As the effect of water vapour on the alteration of olivine was thought to be of some importance, the furnace was filled with water vapour. A large head of water was connected to a quartz tube, which was introduced into the centre of the furnace, from the bottom. The water head was adjusted so that it was at the level of the top of the water filled tube in the furnace. The furnace was heated to 1000°C and sealed. The water evaporated in the furnace and the level outside was maintained constant until a steady level was reached. The furnace was then presumed to be full of water vapour. While no attempt could be made to estimate the amount of water present, an amount of water vapour was emitted when the lid of the furnace was removed. However, this system was an easy method for the introduction of quantities of water vapour to the sample during the heating.

A complete list of all the heating experiments carried out using this technique is given in Table 4.2.

4.5 Experimental Materials

Five samples of olivine were used for these experiments. Four samples were obtained from Dr. G.P.L. Walker at the Geology Department of Imperial College and the fifth from Dr. J.D. Bell at the Geology and Mineralogy Department of the University of Oxford.

The olivine samples were separated from the rock material at the Geology Department, Liverpool University. The rock samples were crushed and partially separated in a magnetic separation apparatus. The final separation was by hand picking. The purity of the samples was > 90% olivine and with < 5% included opaque material. The natural, extracted, olivines were non-magnetic within the limits of the magnetometers available, which implies that the opaque material would have no effect on the subsequent results.

The samples provided, were of known approximate fayalite/forsterite composition. These compositions were remeasured using the X-ray technique of Yoder and Sahama (1957). Specimens of the olivine samples were ground with some pure silicon and prepared for X-ray analysis. The specimen was mixed with a little cow gum and the spherical blob stuck to the end of a quartz fibre. Powder photographs were taken with a Philips apparatus using an 11 cm diameter camera, and Cobalt Kα radiation. A mean of the Kα doublet was used in calculation as the lines could not be distinguished on the photograph. The olivine (130) line was measured and corrected with reference to the silicon (111) line, using the 2θ value quoted by Yoder and Sahama. The results are as given in Table 4.3. The composition determined by this method is the average composition of the crushed sample. The X-ray determinations are accurate to about ± 5% FA.

TABLE 4.1

RESULTS OF INITIAL HEATINGS

	Time of Heating	Saturation Remanence	Petrography
Olivine at 1000°C	24 hrs in vacuum	4×10^{-3} emu/gm	no visible opaques : light colour
	5 mins in AIR	20×10^{-3} emu/gm	opaques as lines : lines throughout crystal
	20 mins in AIR	67×10^{-3} emu/gm	reddened at edges : opaques in clusters
	35 mins in AIR	112×10^{-3} emu/gm	opaques showing more lineation with reddened edges
	60 mins in AIR	200×10^{-3} emu/gm	similar to after 35 mins
Olivine at 850°C	24 hrs in vacuum	3×10^{-3} emu/gm	no visible alteration
	5 mins in AIR	8×10^{-3} emu/gm	
	20 mins in AIR	7×10^{-3} emu/gm	
	35 mins in AIR	19×10^{-3} emu/gm	
	60 mins in AIR	22×10^{-3} emu/gm	little alteration : few opaque material "strings" about the crystal rim

TABLE 4.1 (Continued)

	Time of Heating	Saturation Remanence	Petrography
		QUENCHED TRM	
Dunite	24 hrs in vacuum	1×10^{-3} emu/gm	no visible opaque material
at 1000°C	1 hr in AIR	44×10^{-3} emu/gm	highly reddened : high internal reflectivity
	2 hrs in AIR	68×10^{-3} emu/gm	appearance of linear arrangement of opaque material
	3 hrs in AIR	86×10^{-3} emu/gm	striations of opaques spreading from edge
	4 hrs in AIR	96×10^{-3} emu/gm	more opaque material visible but some loss of lineation

TABLE 4.2

EXPERIMENTAL HEAT TREATMENTS

Heat Treatment	Olivine 1	Olivine 2
1000°C	24 hrs in Vacuum 5 mins - 9 days in air 2 - 20 days in air	24 hrs in Vacuum 5 mins - 9 days in air 2 - 20 days in air
850°C	24 hrs in Vacuum 5 mins - 9 days in air	as for 1
650°C	no alteration produced after 24 hrs in air	as for 1
1100°C	24 hrs in Vacuum 5 mins - 9 days in air	as for 1
1000°C in WATER VAPOUR	24 hrs in Vacuum 5 mins - 9 days	as for 1

TABLE 4.2 (Continued)

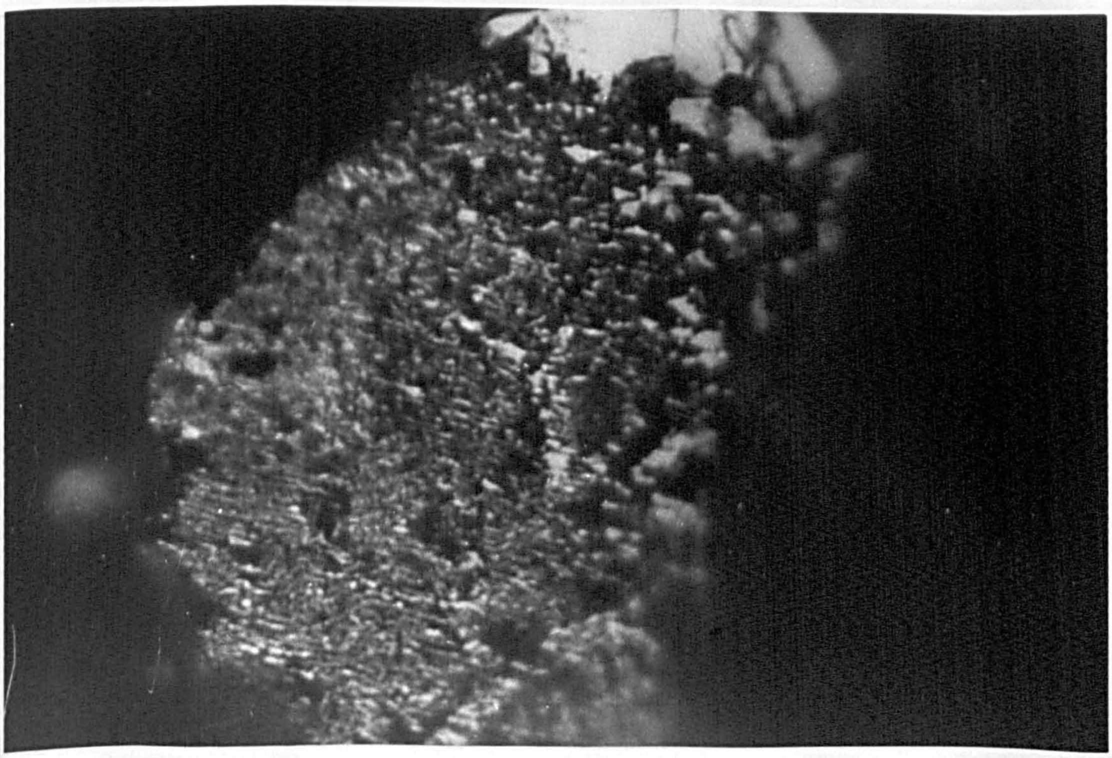
Heat Treatment	Olivine 3	Olivine 4	Olivine 5
1000°C	24 hrs in Vacuum 5 mins - 9 days in air	24 hrs in Vacuum 5 mins - 9 days in air	24 hrs in Vacuum 5 mins - 9 days in air
850°C	as for 1	as for 1	as for 1

TABLE 4.3

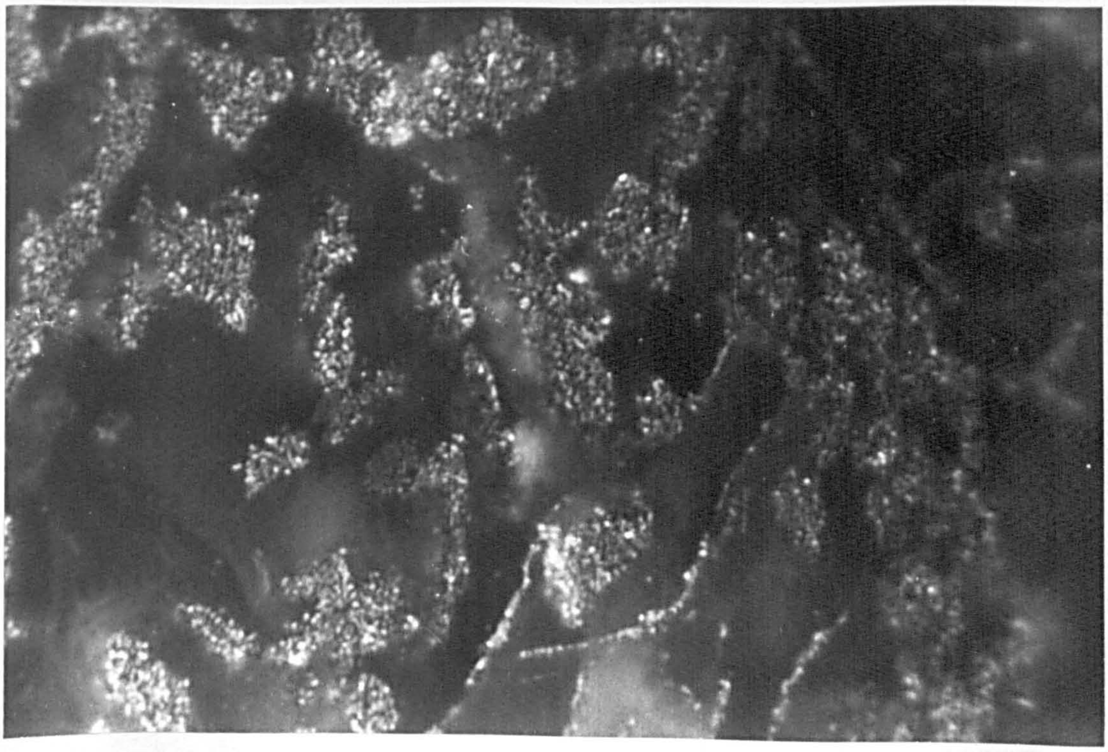
EXPERIMENTAL MATERIAL

	Supplier of Sample	Origin of olivine and suggested composition	X-ray determined compositions
Olivine 1	Dr. Walker Imperial College	Icelandic Basalt 15% FA	5% FA
Olivine 2	Dr. Walker	Azores Basalt 25% FA	(13% FA ((15% FA
Olivine 3	Dr. Bell Oxford University	Skaergaard Intrusion 43.4% FA	(42% FA ((38% FA
Olivine 4	Dr. Walker	Somalia Gabbro 58% FA	47% FA
Olivine 5	Dr. Walker	Aberdeenshire Gabbro 75% FA	82% FA

P. 4.1 Red sponge-like material with attached opaques in weakly magnetic extraction

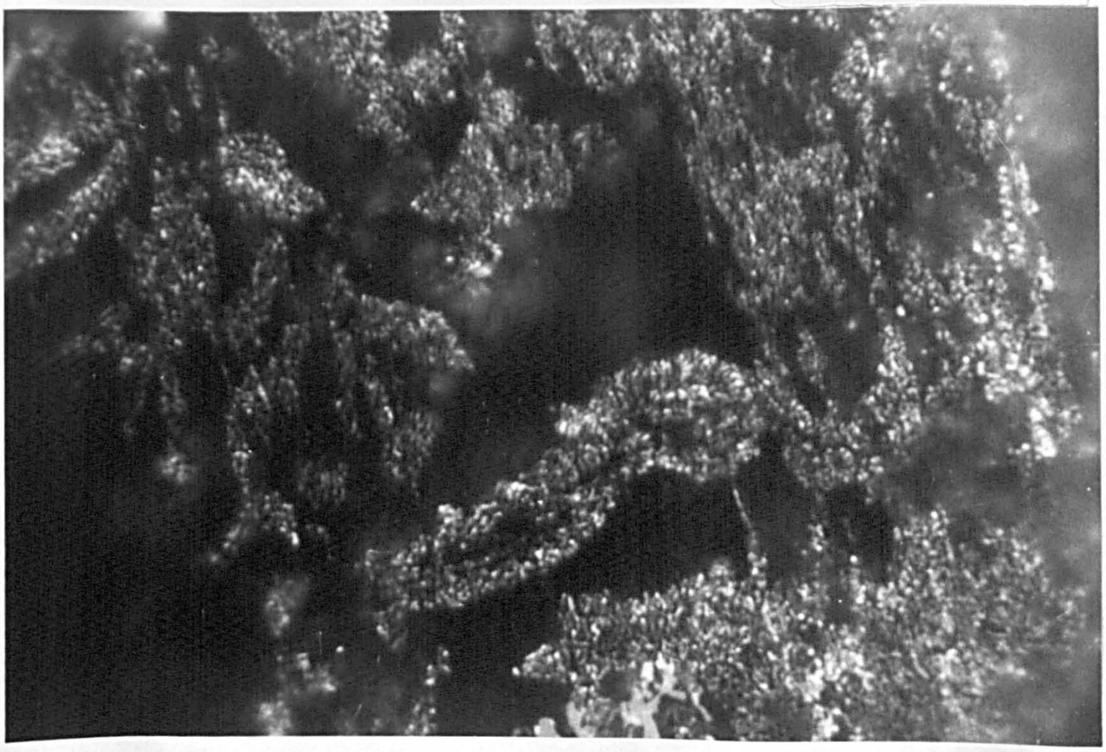


P. 4.2 Red sponge-like material in weakly magnetic extraction

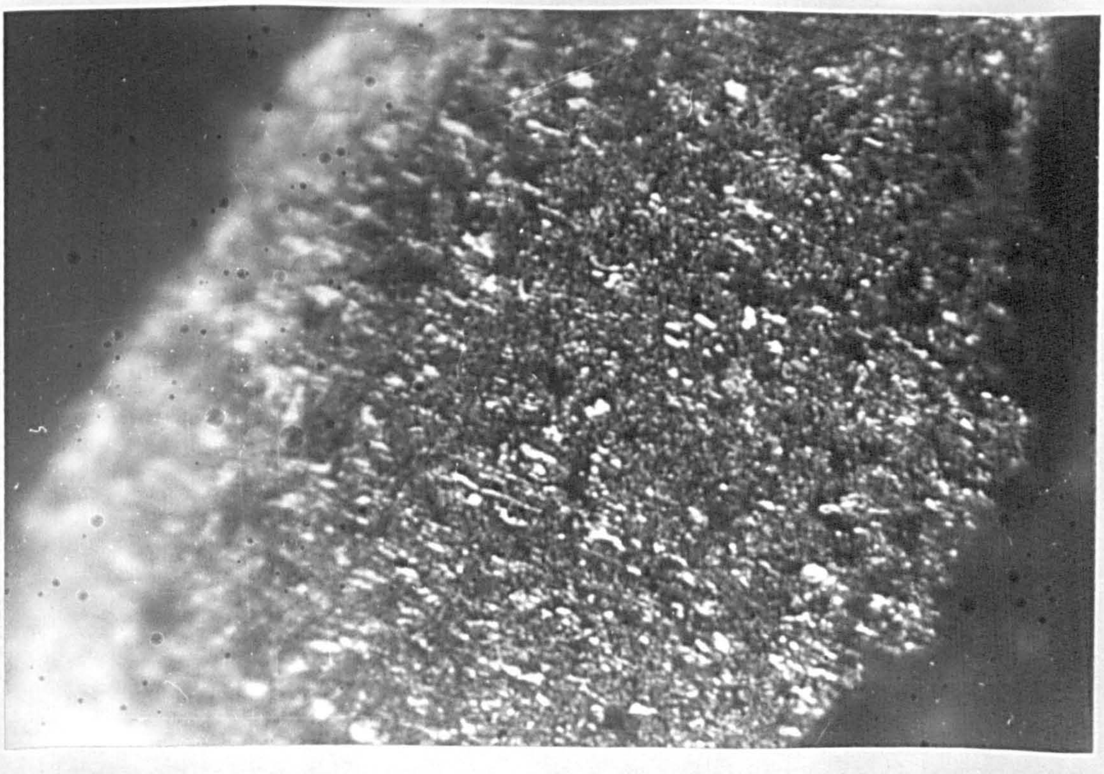


P. 4.3 Green sponge-like material in strongly magnetic extract

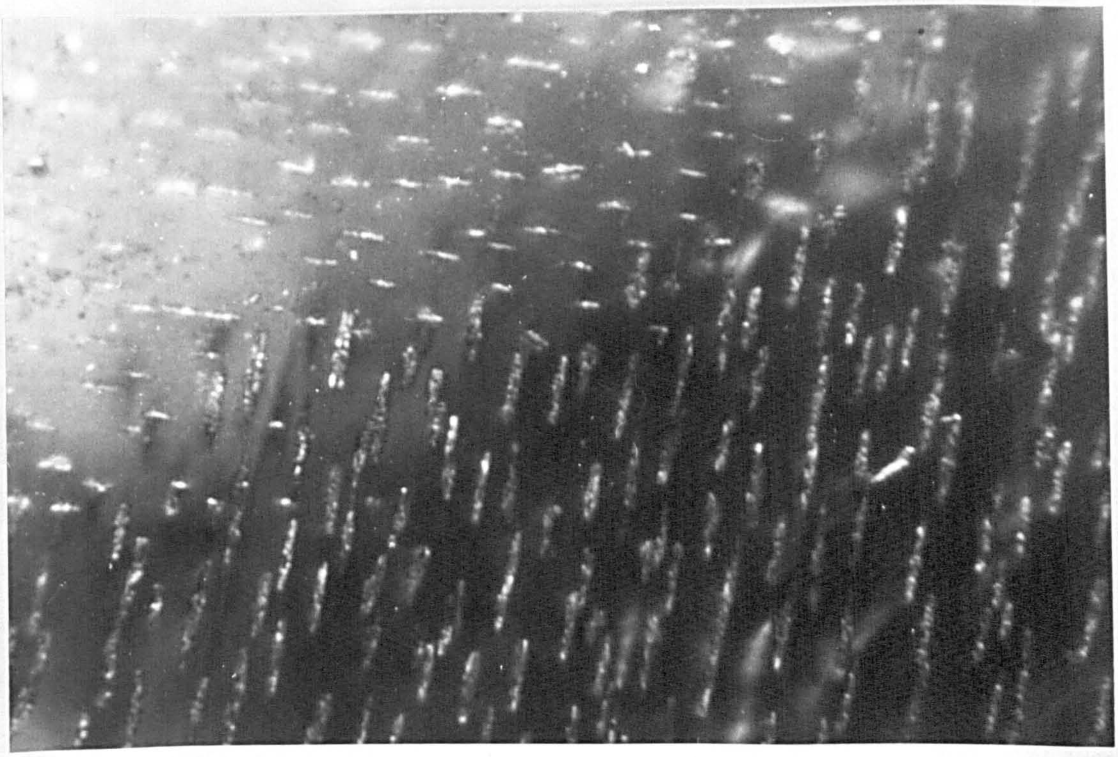
P. 4.4 Green sponge-like material with attached opaque material



P. 4.5 Green sponge-like material with slightly courser material, present in strongly magnetic extract.



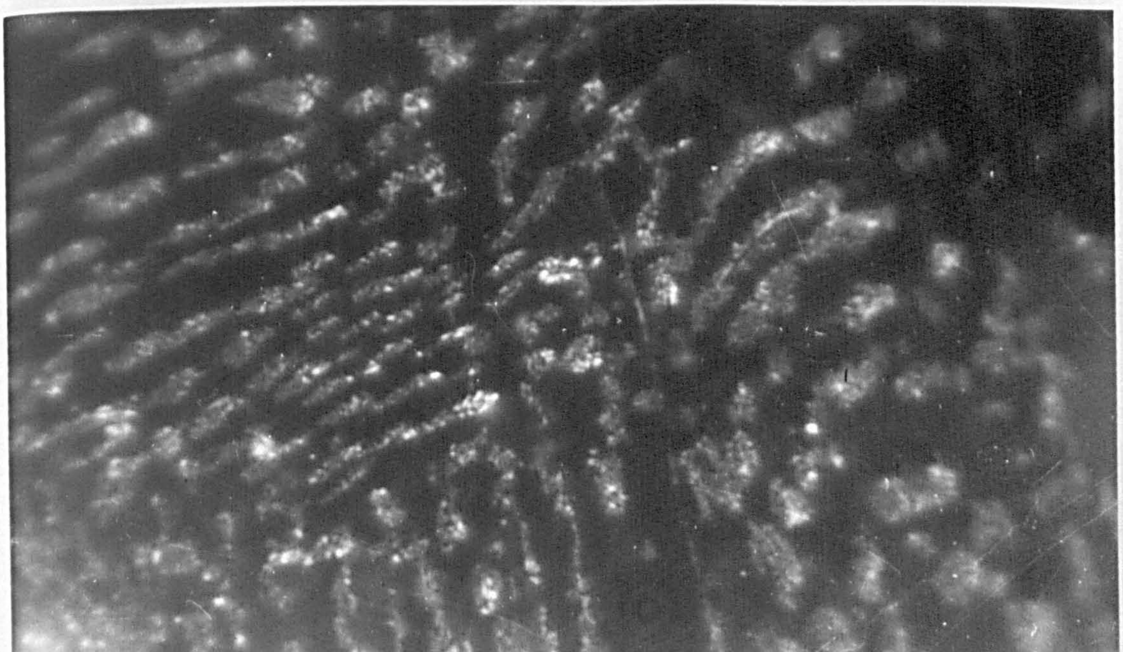
P. 4.6 Green sponge-like material with aggregation of internal opaques to form microscopic opaque material, present in strongly magnetic extract



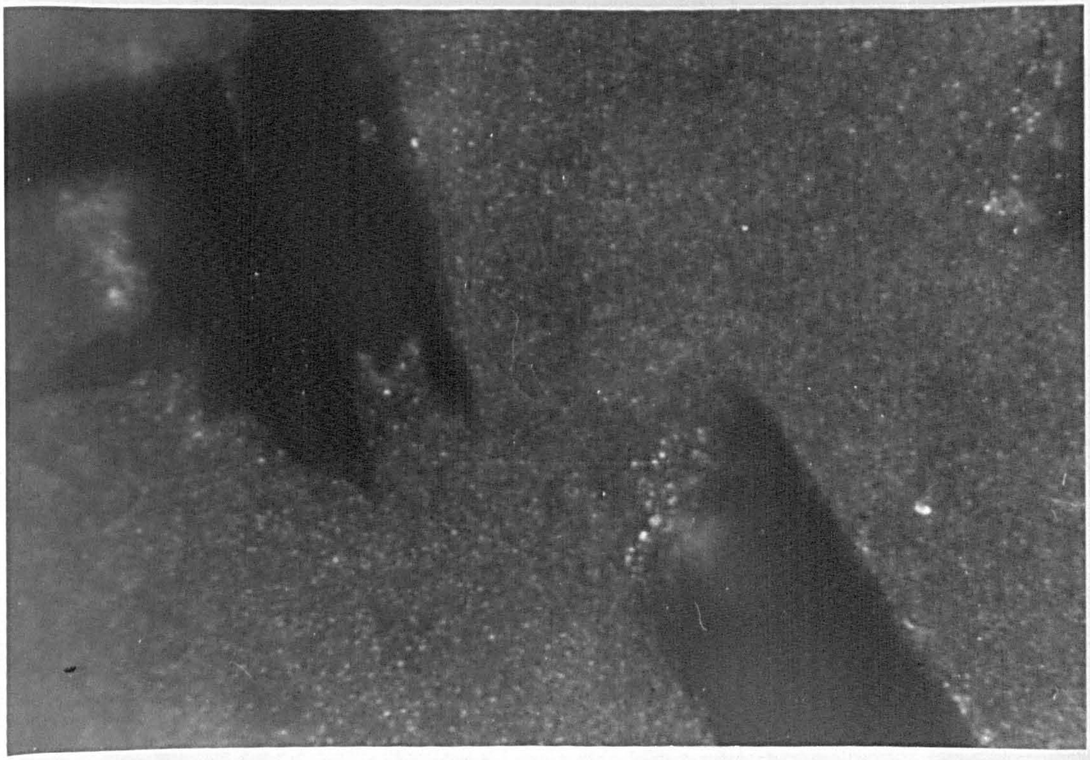
P. 4.7 Alteration in olivine after 1 day at 1000°C in air. The horizontal linear alteration is reddened. The vertical linear alteration is green.

P. 4.8 Linear green alteration elsewhere in same olivine as P. 4.7

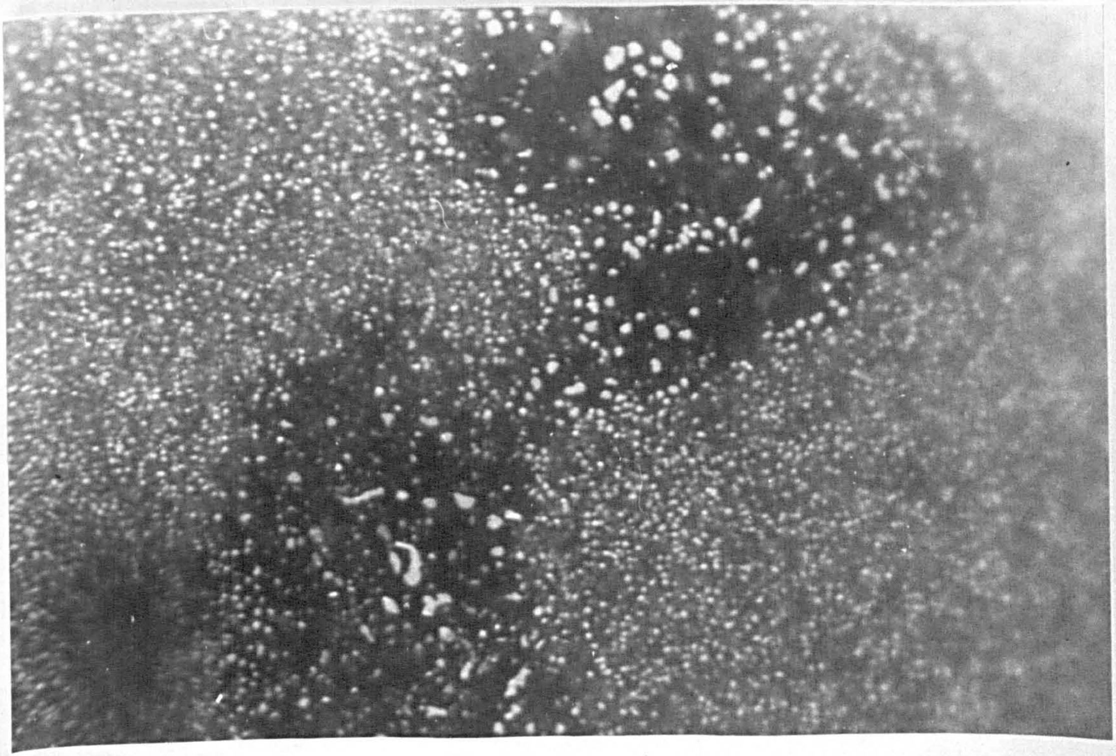
P. 4.9 The alteration in glass after 24 hrs at 1000°C in air, showing variation in alteration size and unaltered feldspars



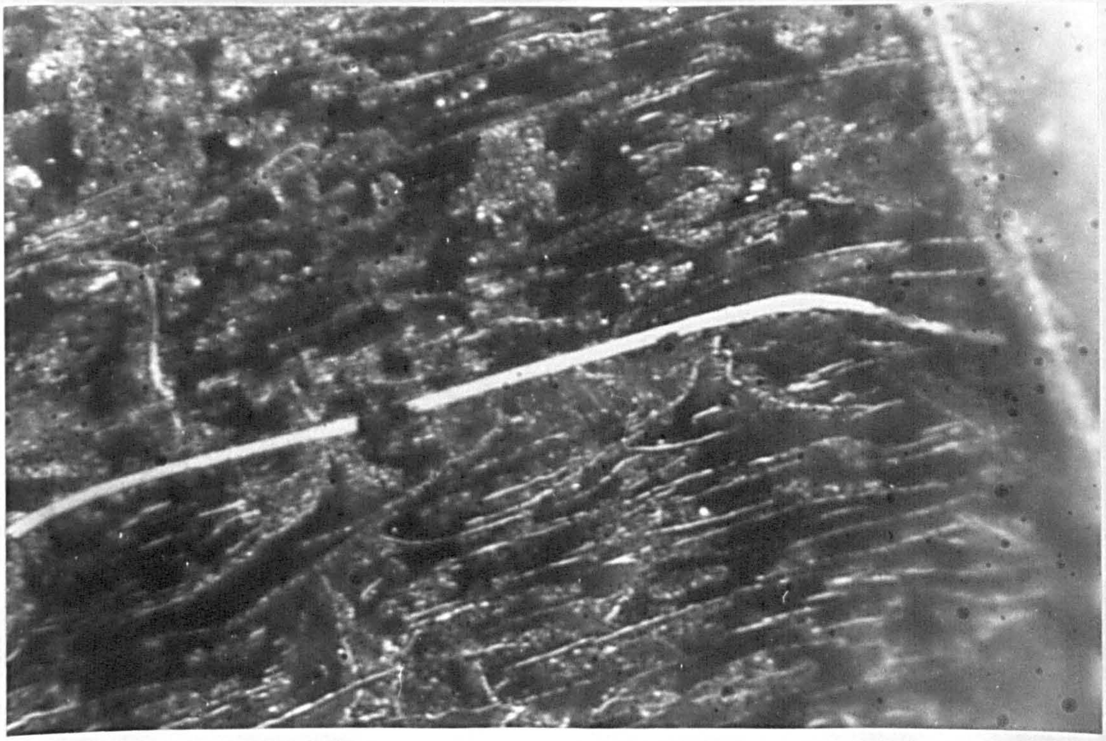
P. 4.10 The alteration in an included olivine crystal in glass of P. 4.9



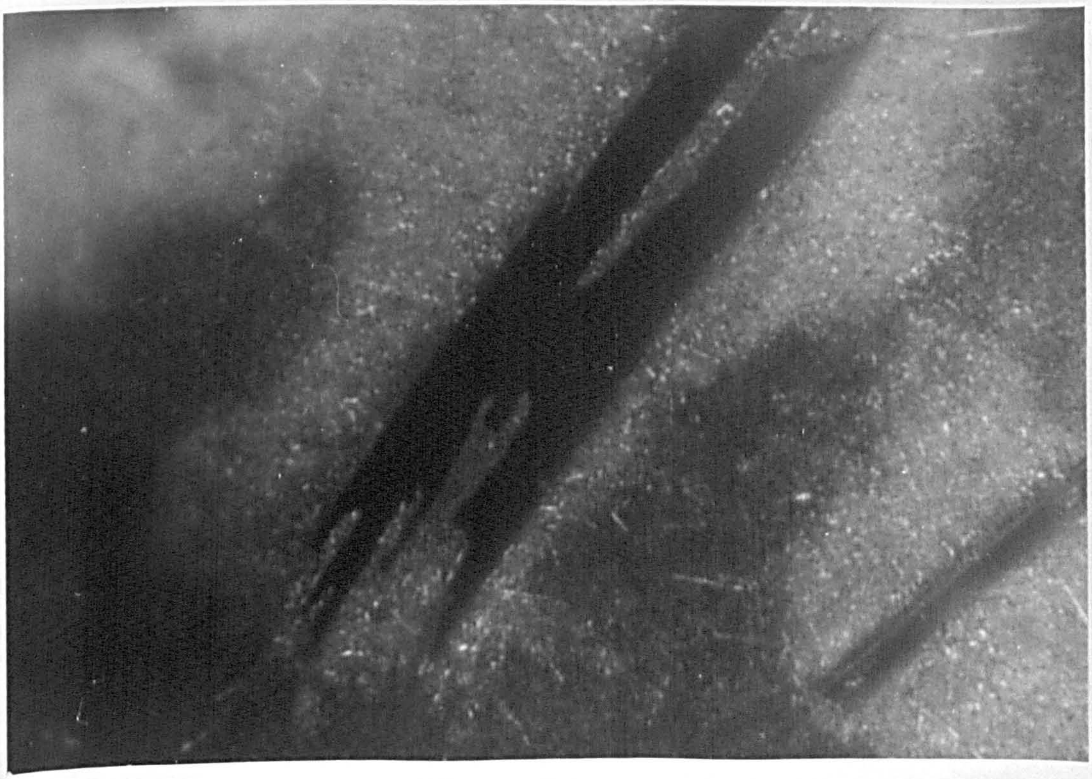
P. 4.11 The alteration in glass after 7 days at 1000°C in vacuum, showing unaltered included feldspar crystals



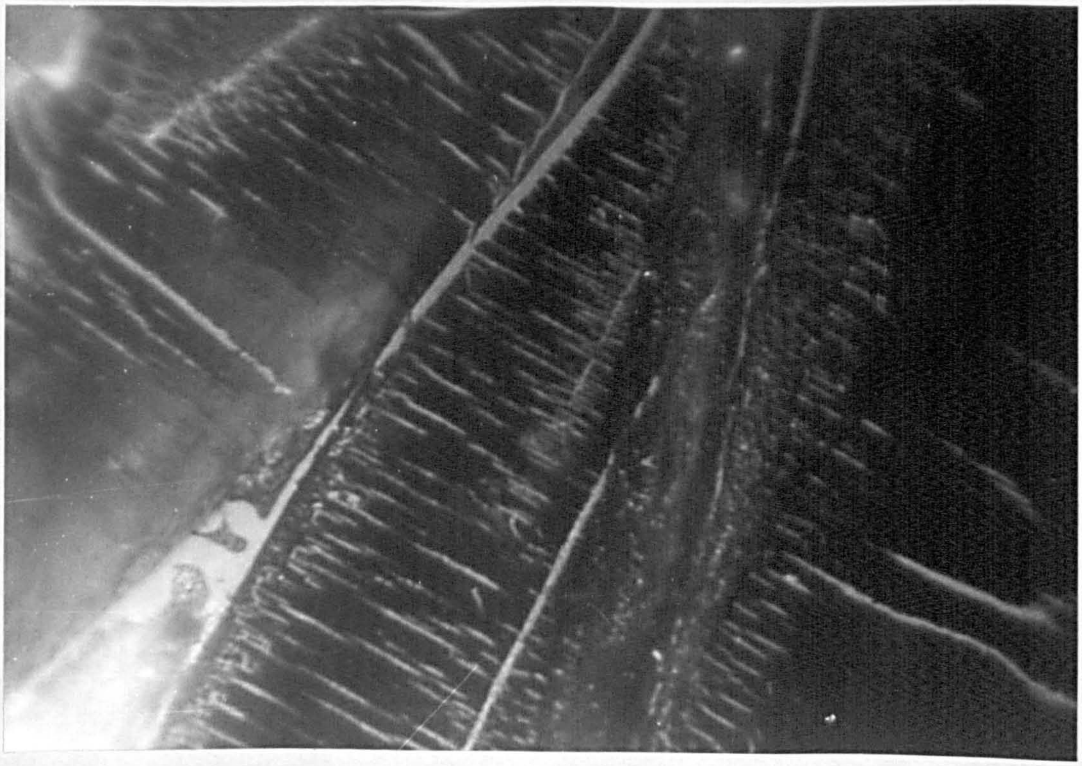
P. 4.12 The alteration in glass after 7 days at 1000°C in air showing the variations in alteration



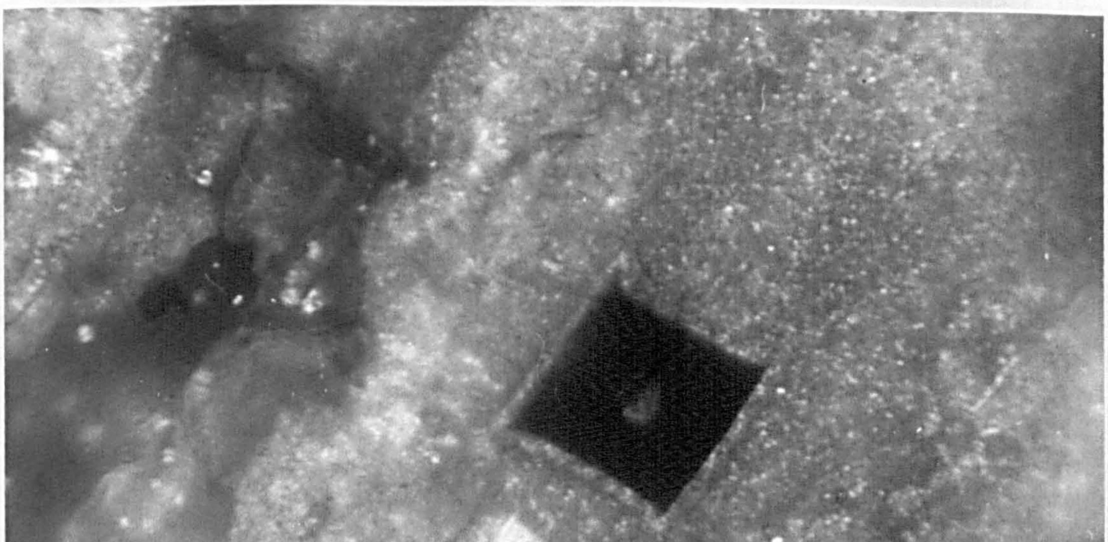
P. 4.13 Included olivine in glass heated 7 days at 1000°C in air



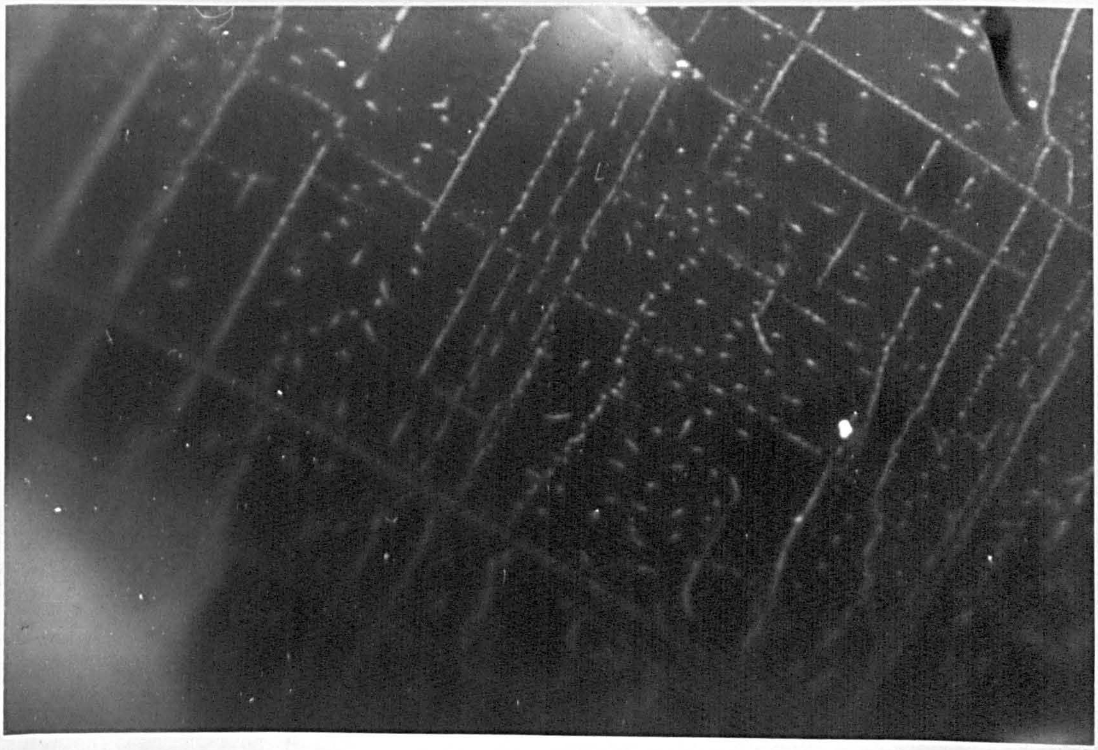
P. 4.14 Glass heated for 24 hrs at 850°C in air showing unaltered feldspars



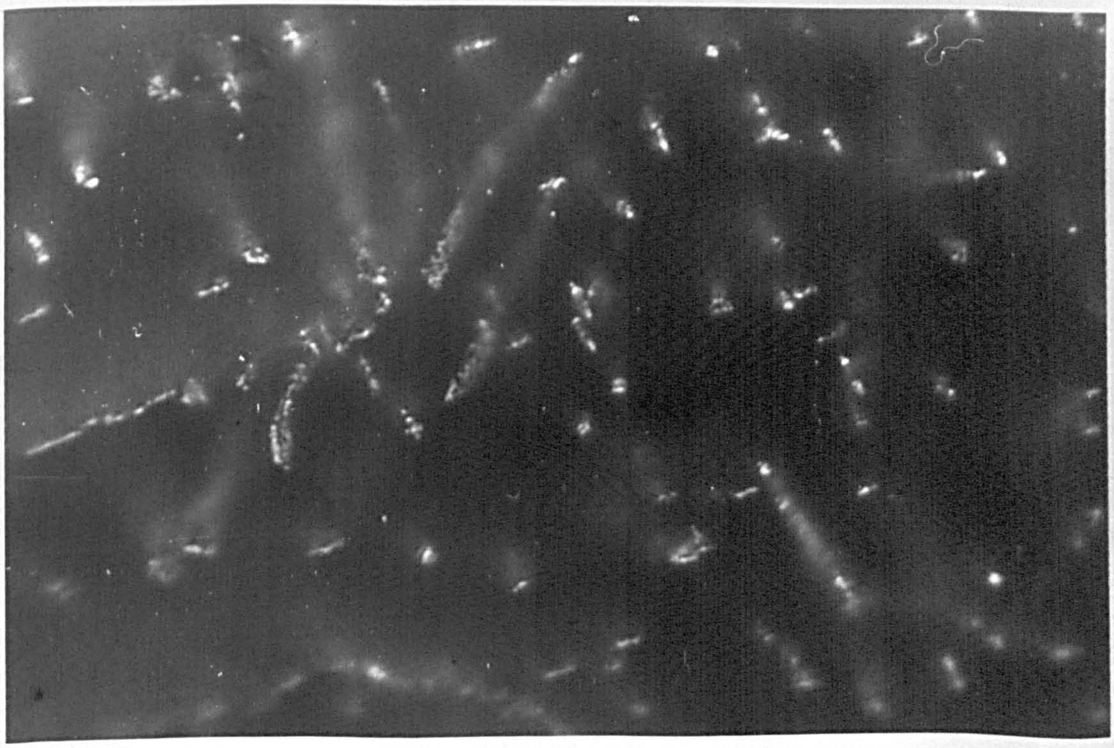
P. 4.15 Olivine included in glass heated at 850°C in air for 24 hrs



P. 4.16 Glass heated at 850°C in air for 7 days showing reddened altered edge with included crystal



P. 4.17 Olivine heated for 5 minutes at 1000°C in air

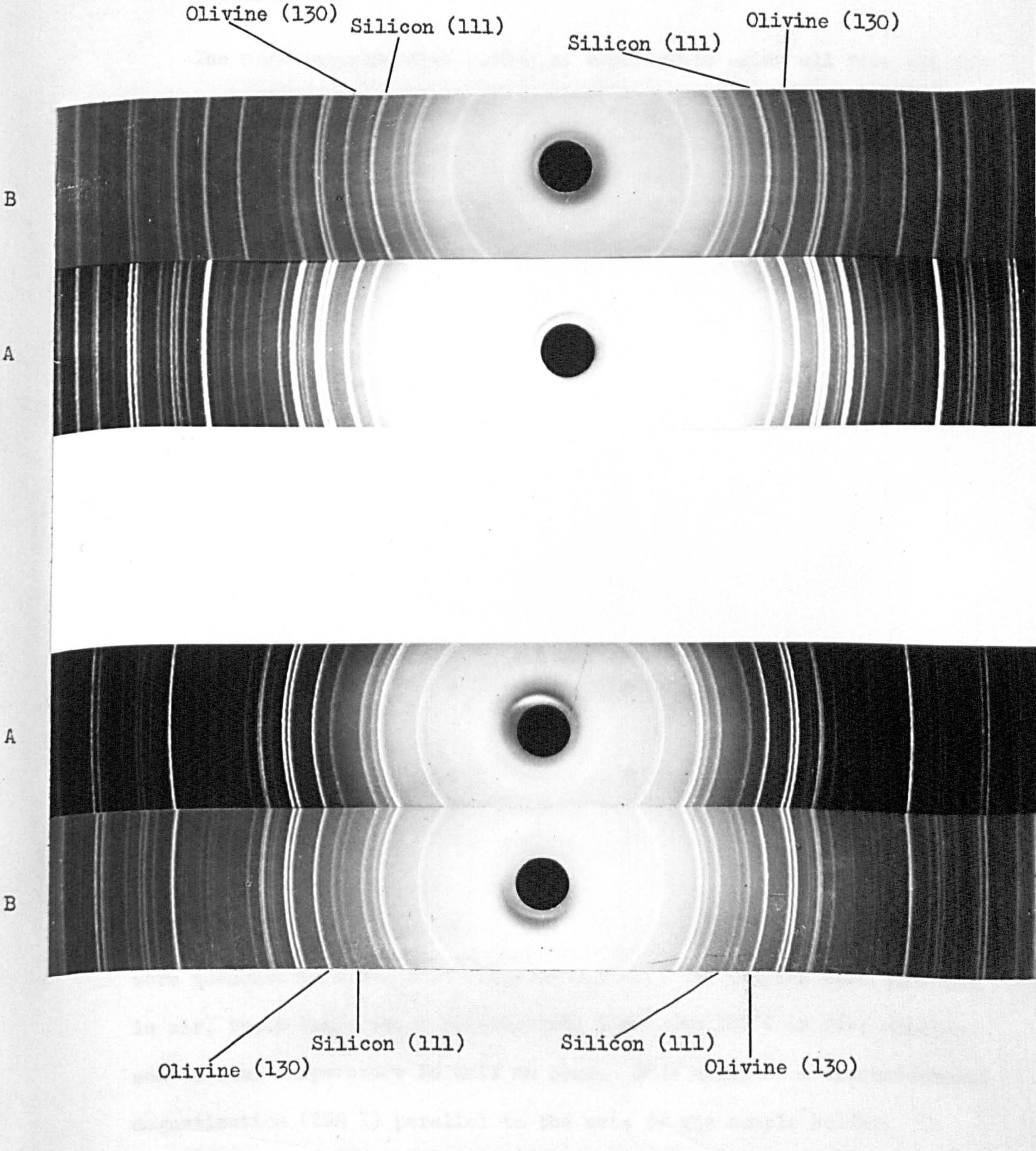


P. 4.18 Olivine heated for 20 minutes at 1000°C in air

X-RAY POWDER PHOTOGRAPHS OF SAMPLES 1 AND 2

(A) Natural Samples

(B) Samples containing Silicon



CHAPTER 5

THE RESULTS OF HEATING THE OLIVINE SAMPLES TO 1000°C

5.1 Introduction

The most comprehensive series of experiments using all five olivine samples, was the heatings to 1000°C in vacuum, 10^{-3} torr, and with samples open to the air. This choice of temperature proved most advantageous, as it gave a progression of alteration products in all of the samples, within a reasonable time scale. All five samples were heated under vacuum for one day and then in air for progressively longer periods from five minutes to nine days. The low iron content olivines, samples 1 and 2, as after having been heated for nine days they were not fully altered, were heated for longer periods, up to forty days. The samples 1 and 2 were also reheated, after having been heated for nine days in air, for periods up to six hours in a vacuum. During this reheating the oxidation effects in the samples showed remarkable reversibility. The results of all the samples may be conveniently divided into three sections, magnetic, optical and X-ray powder photograph results. However, each of these divisions show similar features during the development of the alteration.

5.2 The Magnetic Results

The samples, having been heated for the required period of time, were quenched in a magnetic field of 0.5 oe. The samples were quenched in air, their temperature falling from 1000°C to 100°C in five minutes and to room temperature in half an hour. They acquired a thermoremanent magnetization (TRM 1) parallel to the axis of the sample holder. In no experiment did a sample acquire a remanence in any direction, other than that of the applied magnetic field.

After the initial one day heating in vacuum the sample acquired a very low TRM 1. After the initial heating in air, five minutes, the magnitude of the TRM 1 had increased by factors up to 400. On further heating the samples showed similar variations in TRM 1. With all samples a peak value was obtained, after which time there was a steady decrease (Fig. 5.1). Samples 1 and 2 required twenty days of heating to reach a maximum TRM 1 (Table 5.1). From these results, it may be concluded that the magnitude of the TRM 1 depends on two factors, firstly the iron content of the olivine and secondly the state of alteration, that is the time for which the sample has been heated.

As previously described, the samples were given a second thermoremanent magnetization (TRM 2) by slowly cooling the samples in a 0.62 oe magnetic field, after they had been thermally demagnetized to temperatures above 700°C. The development of the TRM 2 with the heating of the samples was very similar to the development of the TRM 1 but there was an increase in magnitude (Fig. 5.2, Table 5.1). The ratio of the applied field during slowly cooling the sample and that applied during the quenching was 1.2 : 1. The ratio of TRM 2 to TRM 1 was never less than 1.2 : 1 and was usually close to 2 : 1.

During the experiments involving the longer period heatings of the samples 1 and 2, these two thermoremanent magnetizations were investigated more systematically. It was thought that after having been heated in air for ten days, a further heating for half an hour would not increase the alteration. As can be seen from the results (Table 5.1), TRM 2 can be closely repeated during the series of magnetic measurements. The TRM 1 was repeated by heating the samples for half an hour at 1000°C and then requenching them. This requenching gave a result close to that originally obtained for TRM 1. Whilst there was variation in the value of TRM 1 and TRM 2, the ratio of TRM 2 : TRM 1 was consistently in the region of 2 : 1 and never less than 1.7 : 1. This difference may be explained by the difference in cooling rate of the samples. On quenching magnetic equilibrium is not attained during the cooling of the sample.

All the samples showed a maximum value of TRM 2 of approximately 7.5×10^{-2} emu/gm, which would be equivalent to 6.25×10^{-2} emu/gm in a magnetic field comparable with that of the earth in high temperate latitudes. In a rock containing 5% of altered olivine, this result would imply a natural remanent magnetization (NRM) due to cooling in the earths magnetic field of 3.1×10^{-3} emu/gm for a rock sample, due solely to the magnetization of the altered olivine. A NRM of this magnitude would be considered average for a basaltic sample as used in rock magnetism.

The Curie points of the magnetic materials in the samples were measured by one or more of three methods. Firstly, the samples were heated in a saturating magnetic field (5000 oe) and the saturation magnetization measured as a function of temperature. Secondly, the samples were heated in zero magnetic field and the saturation remanence measured during thermal demagnetization. Thirdly, the samples were heated in zero magnetic field and a thermoremanence measured during thermal demagnetization. A maximum difference of 10°C was found between the Curie points obtained by these three methods for the same sample (Table 5.1). The measured Curie points indicated that all samples began after five minutes at 1000°C with a Curie point in the region of 520 - 550°C and this value decreased as the samples were further heated (Fig. 5.3). The Curie point was 480°C or less after long periods of heating. The appearance of a second Curie point at 690 - 700°C increased the rate of decrease of the first Curie point. The high Curie point was difficult to detect and measure, when the magnetization, which gave this Curie point, constituted less than 5% of the initial magnetization.

The saturation magnetization and saturation remanent magnetization followed very similar development. All samples developed maxima in both these magnetization (Figs. 5.4, 5.5). The size of the maxima and the length of time, the sample had to be heated to obtain the maxima depended on the iron content of the sample. The samples 1 and 2 required much longer heating and had smaller maxima than samples 4 and 5. The magnitude of the saturation magnetization for sample 5 had a maximum of one third that of pure magnetite, whilst the alteration product, that is the magnetic material, is optically only about half the material of the sample.

The magnetic hardness of the altered samples was looked at by AC demagnetizing both the TRM 2 and the saturation remanence. Samples 1 and 2 became progressively softer to AC demagnetization after a slight initial rise (Figs. 5.6, 5.7). Sample 3 became softer until it had been heated for nine days when it became harder (Fig. 5.8). Samples 4 and 5 showed the initial softening of the magnetization but after nine days of heating 30% of the magnetization remained after AC demagnetization in magnetic fields of 500 oe. In all samples the thermoremanence and the saturation remanence demagnetization curves were of very similar shape.

From these magnetic results three main conclusions can be drawn. The alteration of the olivine develops in two distinct stages. The initial alteration of the olivine is to a highly magnetic material. The secondary alteration is of this material to a far less magnetic material. The secondary material, from the development of the high Curie point would appear to be hematite. Secondly, the initial alteration is so highly magnetic, that it could be responsible for all the natural remanence of some rocks. Thirdly, the magnitude of the magnetization of the initial alteration is systematically dependent on the duration of its heating, and the composition of the original olivine.

5.3 Optical Results

All samples were examined with a Reichert Zeto-pan Pol microscope using an oil immersion objective at x 1200 magnification. The photomicrographs were taken with the same objective lens but at x 800 magnification. These magnifications gave a field of vision of diameter 120 μ and material described as submicroscopic would be less than 1 μ across. The photomicrographs were approximately 80 μ x 60 μ.

Several comments are applicable to all the olivine samples with regard to their optical alteration. The alteration began at the edges and along cracks in the interior of the crystal. After heating in a vacuum, opaque material was not formed, but often the crystal had an overall lighter colouration. The development of the alteration in air began with the appearance of a green material with a sponge-like texture. This green alteration resembled submicroscopic opaque grains in a semi-transparent material. The initial alteration, after further heating of the sample, became red. The opaque material in the alteration grew in size. All five samples followed this general sequence with minor variations.

Samples 1 and 2 followed similar patterns of alteration and can be described together. There was very little alteration until they had been heated for more than one day in air. Before then there were two types of alteration found in small areas about the edges. There were some fine strings of the green sponge-like alteration. These strings would all form in the same orientation. There were fine lines of opaque grains, 1 μ diameter, which again tended to have one direction throughout an area of alteration (P. 5.1, 5.3). The sponge-like alteration would grow on further heating. After nine days of heating the edges of the crystal would be reddened. The green sponge-like alteration would fill the crystal in two forms, either blotches of irregular shape about 10 - 20 μ in size or parallel bands of alteration. These two forms would be in separate areas (P. 5.2, 5.4).

Sample 3 showed the complete development of the alteration. After five minutes heating in air, a dark green sponge-like alteration had spread from the edge of the crystal. This alteration was of broad bands linked by fine threads of the same alteration (P. 5.5). After twenty minutes heating, the green alteration had spread throughout the crystal. The gaps in the green alteration were filled with bright red alteration of a similar sponge-like appearance (P. 5.6). After further heating the initial green material became bright red with high reflectivity because of submicroscopic opaque material (P. 5.7, 5.8). The alteration, through the crystal, was not uniform. Some areas were full of the bright red alteration. In other areas, the alteration was bright red but the structure of the initial green alteration could be seen (P. 5.9). In a few areas the green alteration could still be seen after heating for three days. After nine days heating, all the sample was red. Opaque material had grown in the alteration and was clearly visible (P. 5.10). About the edge of crystal and along some cracks opaque material 5 μ across, had grown. About this opaque material there was a deficiency of alteration, perhaps due to leaching of the surrounding material for the growth of the opaque material.

Sample 4 followed a similar development, except that after 120 minutes heating, it was similar to sample 3 after nine days heating (P. 5.11). From then, the opaque material grew in size. After nine days heating the sample was full of small, 5 μ and under, irregularly shaped opaque material (P. 5.12). Some of the material was elongated and the elongations tended to align in one direction.

Sample 5 followed a similar pattern but was even quicker. After just five minutes heating it was as progressed as sample 4 after 35 minutes heating (P. 5.13). After nine days the sample was similarly full of opaque material of irregular shapes. The size and density of the material varied through the crystal. The smaller sized opaque material was more prevalent than the larger material (P. 5.14).

From these optical results, two main conclusions can be drawn. The initial alteration of the olivine in air is to a green material, which is apparently a submicroscopic opaque material in a semi-transparent material. The further heating of the sample produces the reddening of this initial alteration product and the growth in the size of the opaque material in the alteration product.

5.4 Results from the X-ray Powder Photographs

X-ray powder photographs of each of the samples were taken after they had been heated for nine days in air. The samples were crushed to a fine powder and mixed with a small amount of gum and mounted on a quartz fibre. The samples were mounted in a powder camera and the photographs taken using Cobalt Kα radiation. Due to the small nature of the sample, exposures of eight to ten hours were required for clear photographs. The powder photographs of the natural olivine samples before heating, showed standard olivine patterns. These photographs provided standard patterns for comparison with those patterns obtained after the samples had been heated.

Samples 1 and 2 showed similar line patterns. The original olivine line structure was clearly present but displaced to suggest a more magnesium rich olivine. New lines were present on the photograph and fitted the pattern due to hypersthene (Mg,Fe) SiO_3, a pyroxene, an orthorhombic chain silicate. It was not possible to determine the position of the hypersthene in the series $MgSiO_3$ to $FeSiO_3$.

Sample 3 showed a more complicated pattern. The pattern of the original olivine was not present but the pattern of hypersthene was clear. A line pattern similar to that of hematite was on the photograph and the remaining lines fitted the pattern of magnesioferrite. No reliable data is available for the location of the composition of the ferrite in the series Fe_3O_4 to $MgFe_2O_4$.

The photographs from samples 4 and 5 showed the patterns of both hypersthene and hematite but no lines of either the original olivine or a magnesioferrite were visible.

These X-ray powder photographs indicated the alteration of olivine to hypersthene and hematite. Magnesioferrite may be present, possibly as an intermediate stage of the alteration.

5.5 Further Heating in Vacuum

Samples 1 and 2 were both heated in vacuum, after the series of experiments had ended when the samples had been heated for nine days in air. They were sealed in a vacuum of 10^{-3} torr and heated at 1000°C for up to six hours. The results were unexpected.

Magnetically the samples became nonmagnetic within the limits of the magnetometers. So both the TRM 1 and saturation remanence must have fallen by factors > 200. Optically the change was quite strange. All alteration of the usual form had disappeared. The sample was a very bright orange-yellow colour and semi-transparent with bright internal reflections. In the sample were black opaque grains, 5 μ across. These grains were scattered throughout the sample. The X-ray powder photograph showed a pattern similar to the original olivine. When compared to the photograph of the sample after nine days heating in air, the original olivine pattern was stronger and the hypersthene lines were much weaker.

The alteration is partially reversible although the original olivine cannot optically be reformed after this short heating in vacuum.

5.6 Discussion of the Results

The conclusions drawn after each of the sections of results can be combined into a two stage alteration process. The olivine is initially oxidized to hypersthene and a magnesium ferrite. The second stage involves the oxidation of the ferrite into hematite and a more magnesium rich ferrite.

Olivine + Oxygen -> Hypersthene + Magnesioferrite
Magnesioferrite + Oxygen -> Magnesioferrite + Hematite
(Magnesium rich)

The initial rise in the magnetization of the altered olivine samples is due to the formation of the highly magnetic magnesioferrite. The low Curie point also indicates the presence of magnesium in the ferrite. Unfortunately the change in thermoremanence, because of the different cooling rates, seems due to the lack of magnetic equilibrium during the quenching since it can be easily reversed. This change masks any alteration which should occur due to ionic reordering in the spinel structure. However, examination of the results of the saturation magnetization does indicate the presence of the reordering (Table 5.1). The saturation magnetization which is measured immediately after quenching the sample is consistently higher than the saturation magnetization measured after the samples had been slowly cooled. In the results (Table 5.1) the saturation magnetization measured after TRM 1 are higher by on average 20% than those measured after TRM 2. The quickly quenched samples having a higher equilibrium temperature have a more disordered structure, which implies a higher saturation magnetization. The slowly cooled samples having a much lower equilibrium temperature, have a more ordered structure, which gives a lower saturation magnetization. The green alteration product is the hypersthene - ferrite mixture.

During the heating of the samples the visible opaque material grows in size. This growth corresponds to the initial weakening of the material to A.C. demagnetization due to the growth in the domain size. The hardening of the material to demagnetization after prolonged heating is due to the formation of hematite. The hematite is formed by the oxidation of the magnesium ferrite. The change is first seen as the reddening of the polished sample. The Curie point of the sample decreases due to the oxidation forming a magnesium richer ferrite. The Curie point of hematite does not appear immediately, because, as has been shown, hematite can exist in the ferrite structure without its Curie point appearing (Fig. 2.5, Forestier 1928).

The ease of the reversal of the alteration when heated in vacuum, can be explained in terms of the crystallography of the alteration. During the alteration of olivine to hypersthene the oxygen close packed arrangement of ions is undisturbed. The alteration is purely a cation migration. With this relatively undisturbed ion formation the reversal of the alteration is apparently very easy. The black opaque grains may be hematite which has been formed and locally broken the crystal structure.

TABLE 5.1

THE MAGNETIC MEASUREMENTS FOR SAMPLES 1 AND 2 AFTER HEATING IN AIR AT 1000°C FOR PERIODS UP TO 40 DAYS

SAMPLE 1

Time the sample had been heated in air	TRM 1 $\times 10^{-4}$ emu/gm	TRM 2 $\times 10^{-4}$ emu/gm	J_{SAT} emu/gm	J_{REM} $\times 10^{-2}$ emu/gm	Curie Point °C 1	Curie Point °C 2	Curie Point °C 3
2 Days	248		3.75	127			500
10 Days	306_1		4.54_2	131_3	485_4		
		746_5	3.75_6	121_7	485_8		
		794_9				485_{10}	
		701_{11}					
	357_{12}		4.58_{13}	120_{14}			485_{15}
20 Days	323_1		3.94_2	97.8_3	470_4		
		685_5	3.49_6	106_7	470_8		
		690_9				480_{10}	
		688_{11}	3.53_{12}	94_{13}			480_{14}
	322_{15}		3.61_{16}	99_{17}			
40 Days	331_1		2.64_2	66.3_3	460_4		
		574_5					450_6

TABLE 5.1 (Continued)

SAMPLE 2

Time the sample had been heated in air	TRM 1 $\times 10^{-4}$ emu/gm	TRM 2 $\times 10^{-4}$ emu/gm	J_{SAT} emu/gm	J_{REM} $\times 10^{-2}$ emu/gm	Curie Point °C 1	Curie Point °C 2	Curie Point °C 3
2 Days			1.54	58.7			505
10 Days	362_1		5.65_2	136_3	450_4		
		868_5	4.66_6	126_7	455_8		
		930_9				460_{10}	
		880_{11}					
	445_{12}		5.58_{13}	127_{14}			455_{15}
20 Days	357_1		4.30_2	81.8_3	455_4		
		680_5	3.53_6	77.3_7	455_8		
		775_9				450_{10}	
		684_{11}	3.62_{12}	76.2_{13}			450_{14}
	402_{15}		4.42_{16}	72.7_{17}			
40 Days	229_1		1.62_2	45.1_3	450_3		
		374_5				440_6	

NOTES FOR TABLE 5.1

TRM 1 - thermoremanent magnetization acquired on quenching in a 0.5 oe magnetic field - 10^{-4} emu/gm

TRM 2 - thermoremanent magnetization acquired on slow cooling in a 0.62 oe magnetic field - 10^{-4} emu/gm

J_{SAT} - saturation magnetization in a 5000 oe magnetic field - emu/gm

J_{REM} - saturation remanence after being saturated in 5000 oe magnetic field - 10^{-2} emu/gm

Curie Point 1 - measured by measuring the saturation remanence during thermal demagnetization

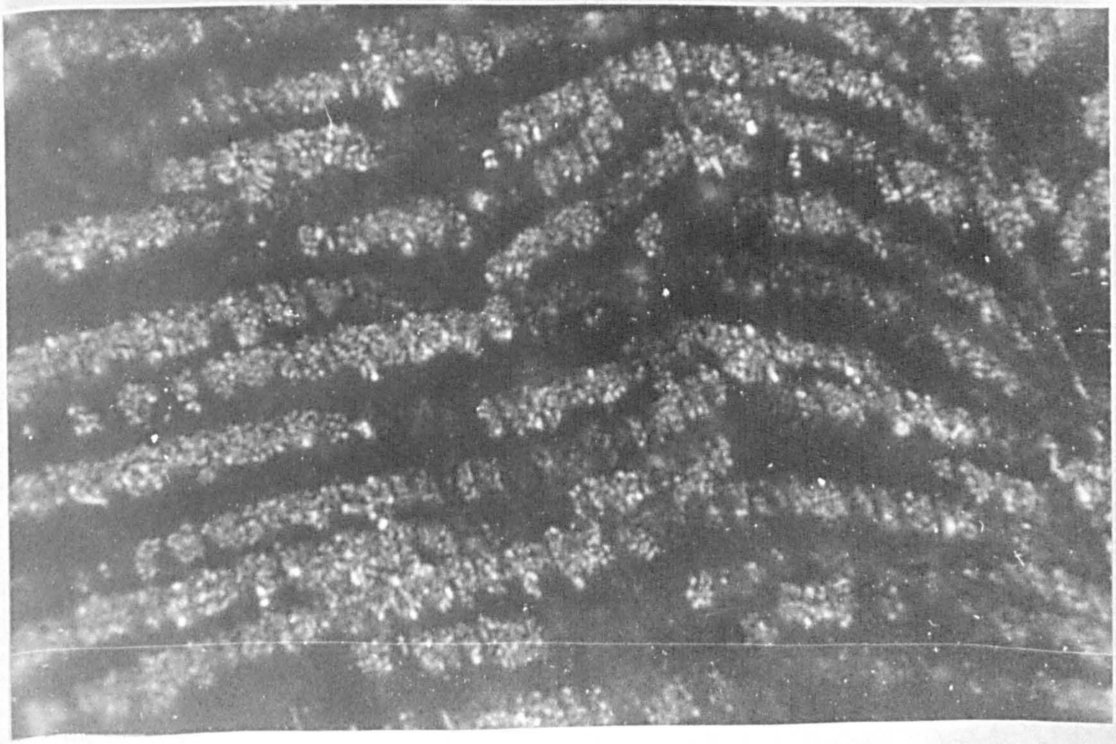
Curie Point 2 - measured by measuring the TRM 2 during thermal demagnetization

Curie Point 3 - measured by measuring the saturation magnetization during thermal demagnetization

The indices have been used to indicate the order in which the magnetic results were measured after each heating.

SAMPLE 1 HEATED AT 1000°C IN AIR

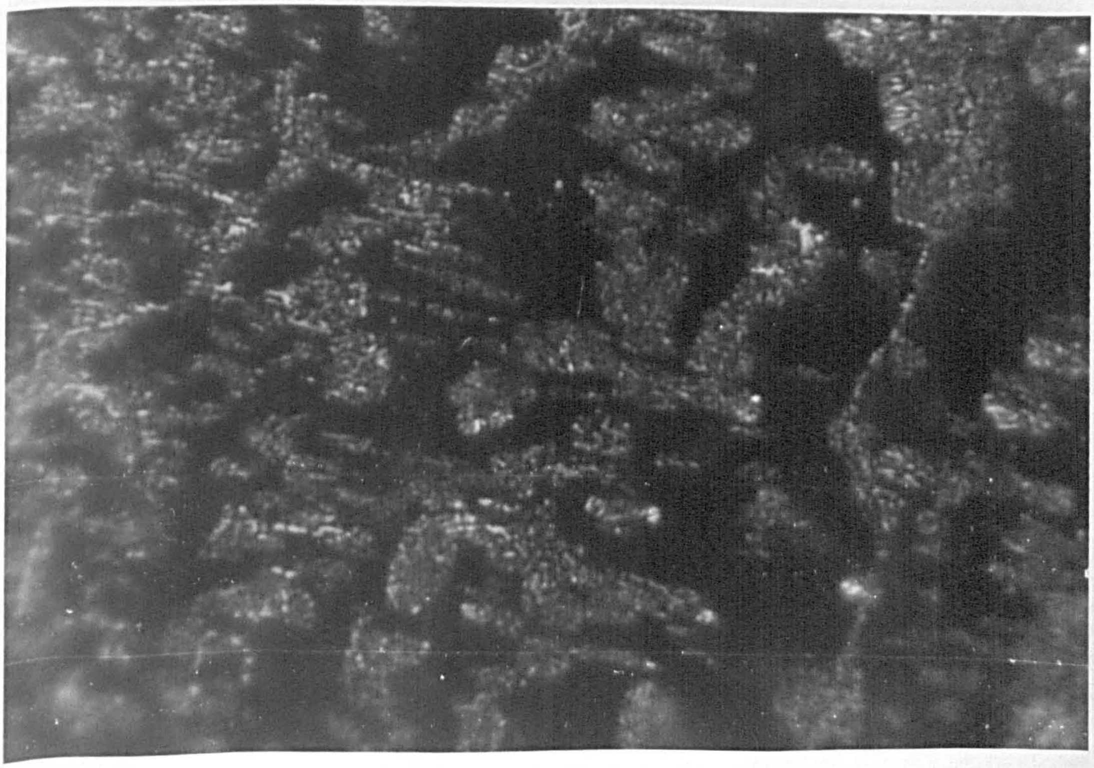
P. 5.1 after 35 minutes



P. 5.2 after 9 days

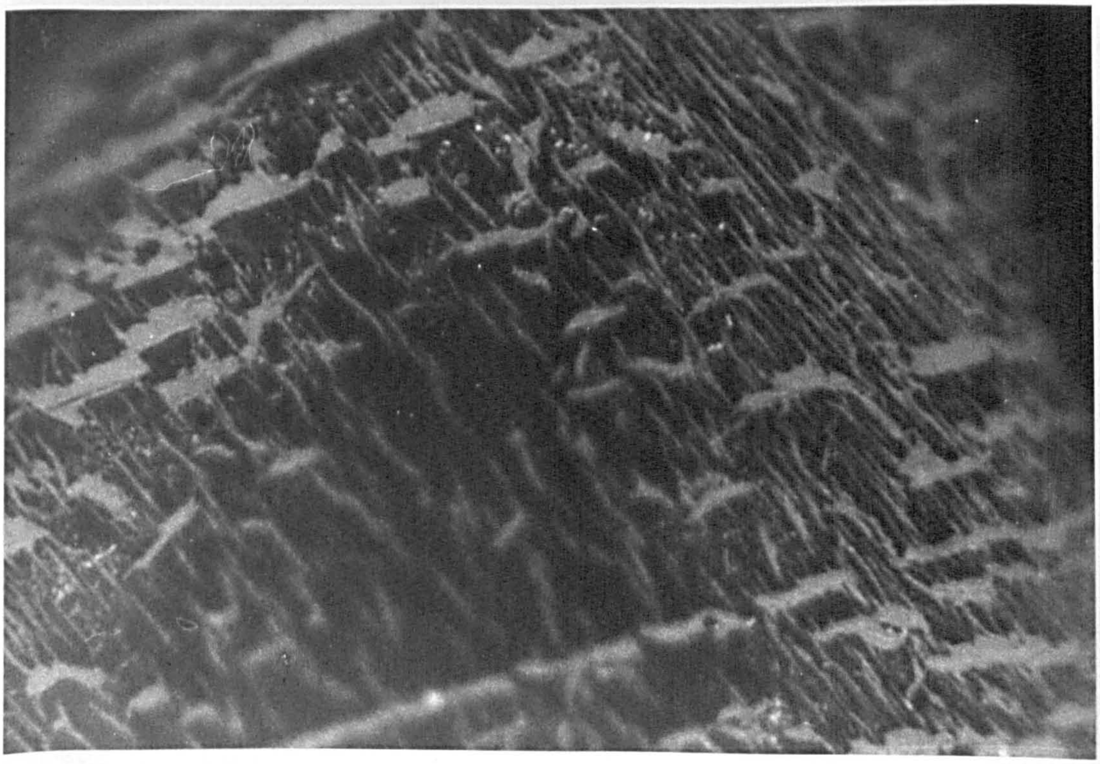
SAMPLE 2 HEATED AT 1000°C IN AIR

P. 5.3 after 35 minutes

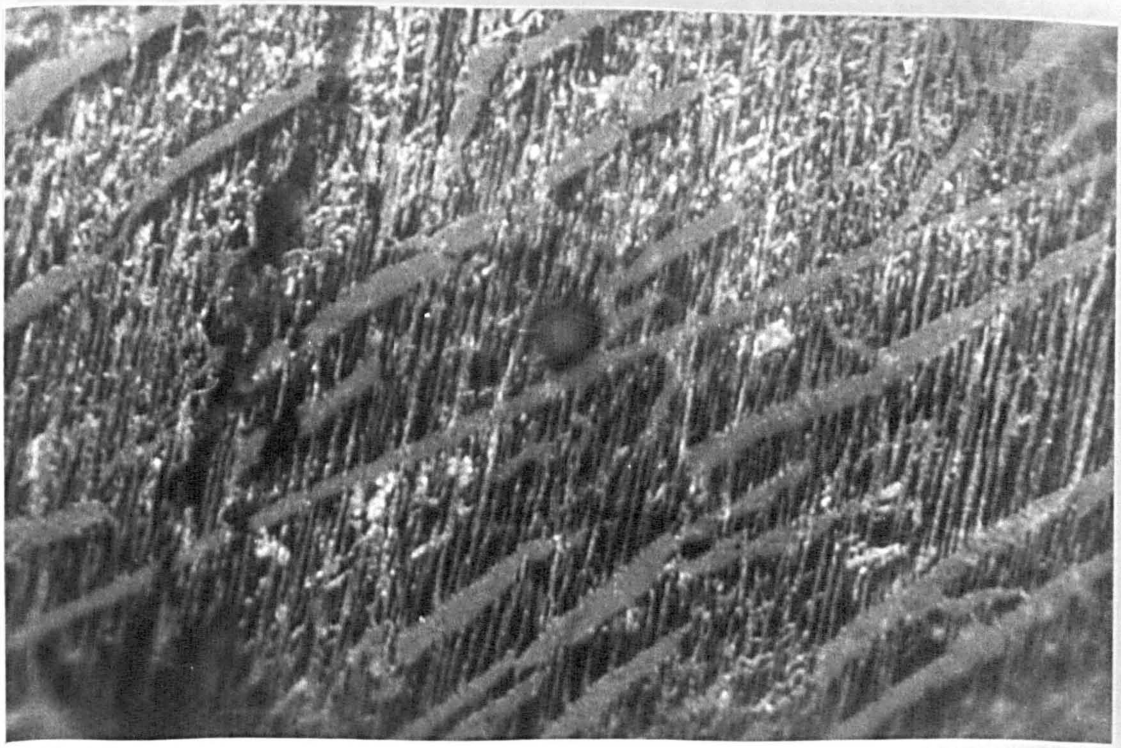


P. 5.4 after 9 days

SAMPLE 3 HEATED AT 1000°C IN AIR

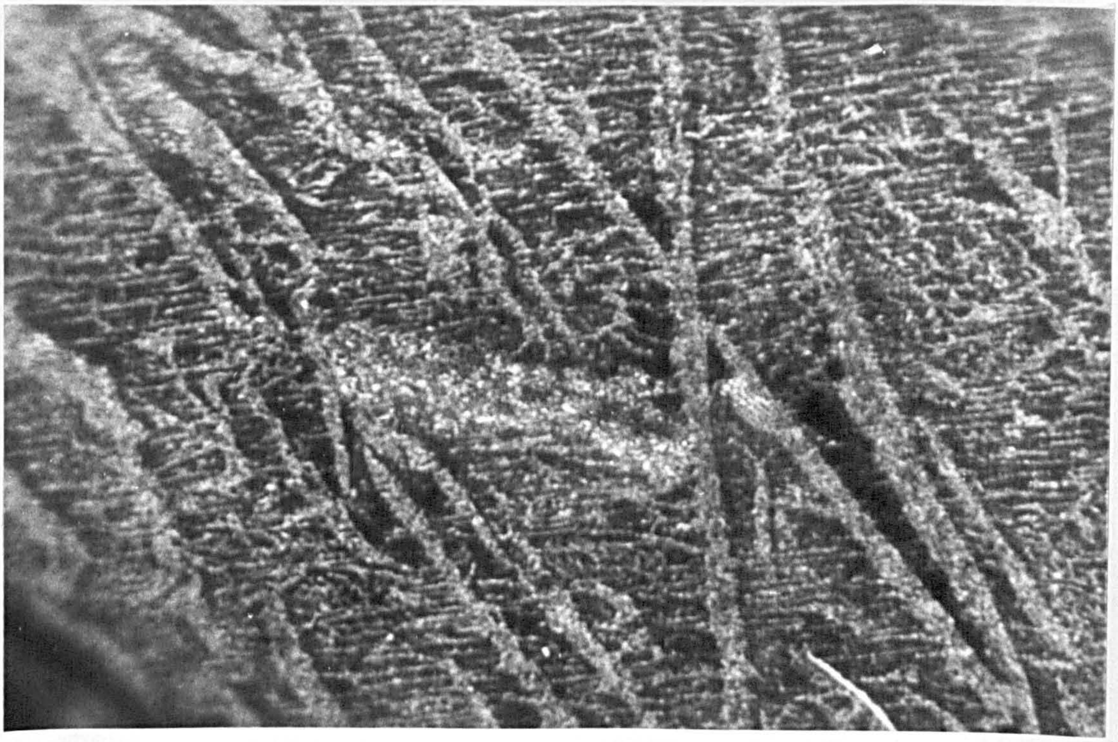


P. 5.5 after 5 minutes

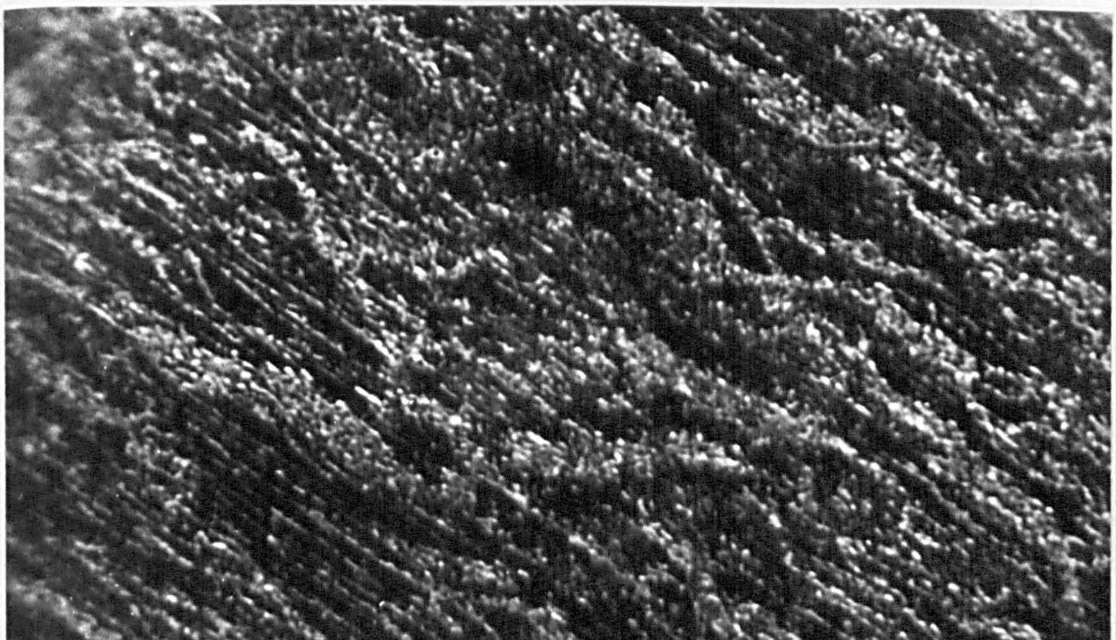


P. 5.6 after 20 minutes

SAMPLE 3 HEATED AT 1000°C IN AIR

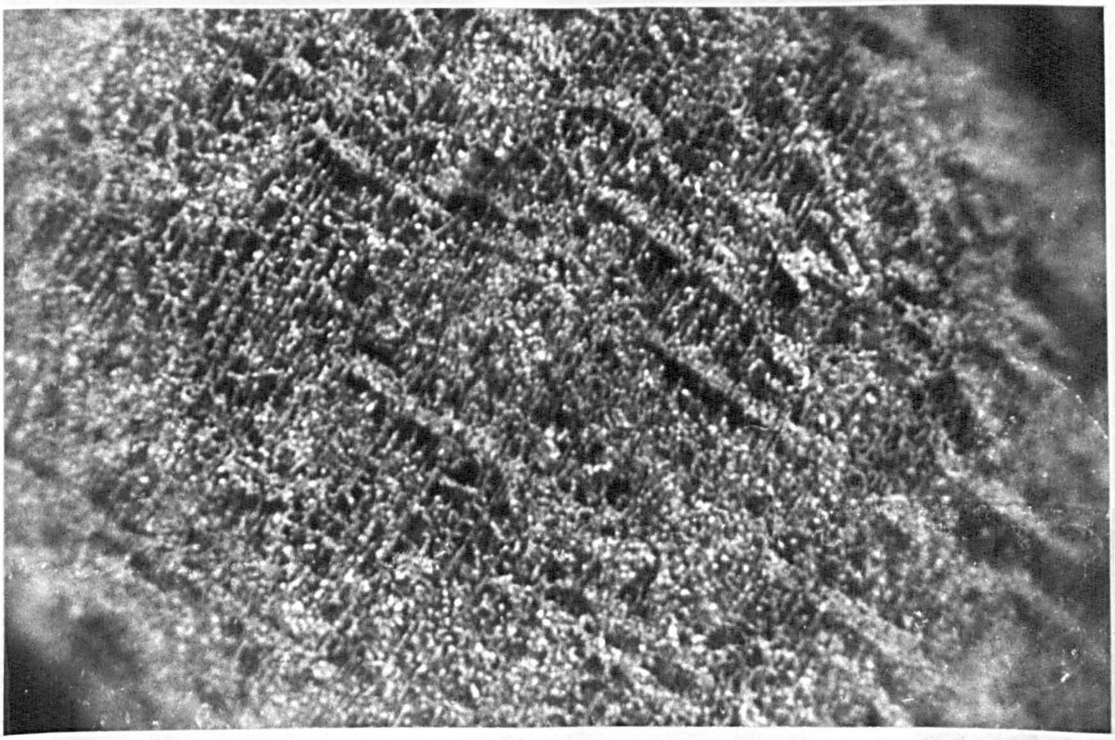


P. 5.7 after 3 hours

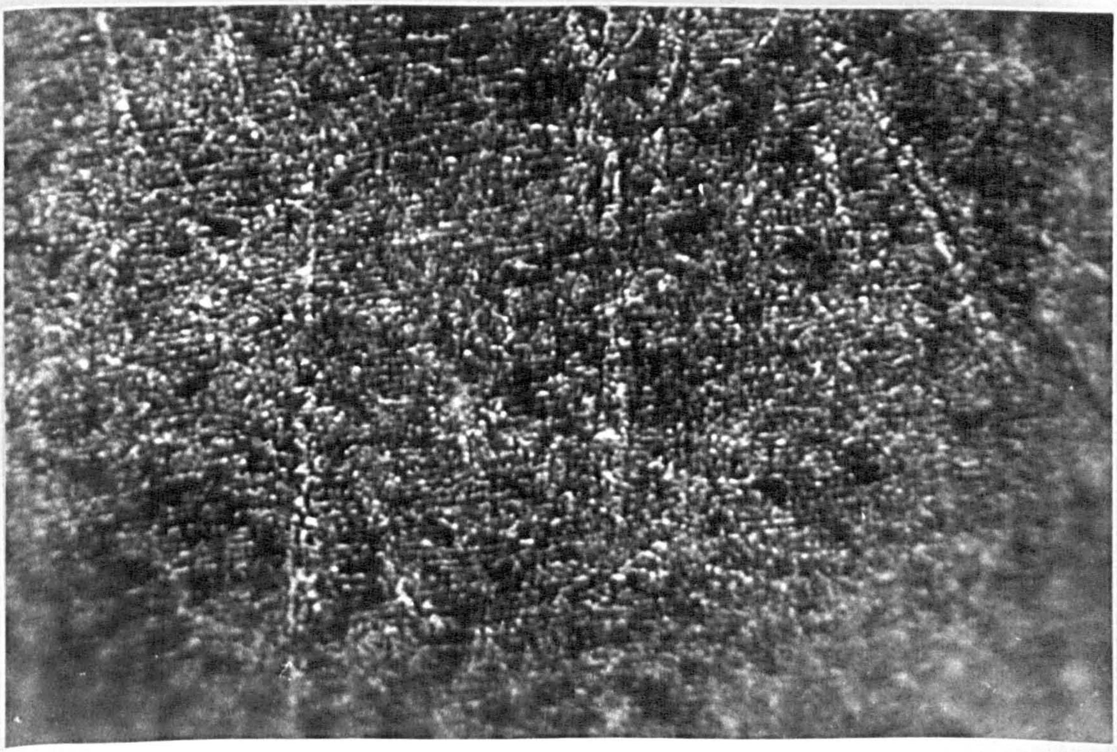


P. 5.8 after 12 hours

SAMPLE 3 HEATED AT 1000°C IN AIR

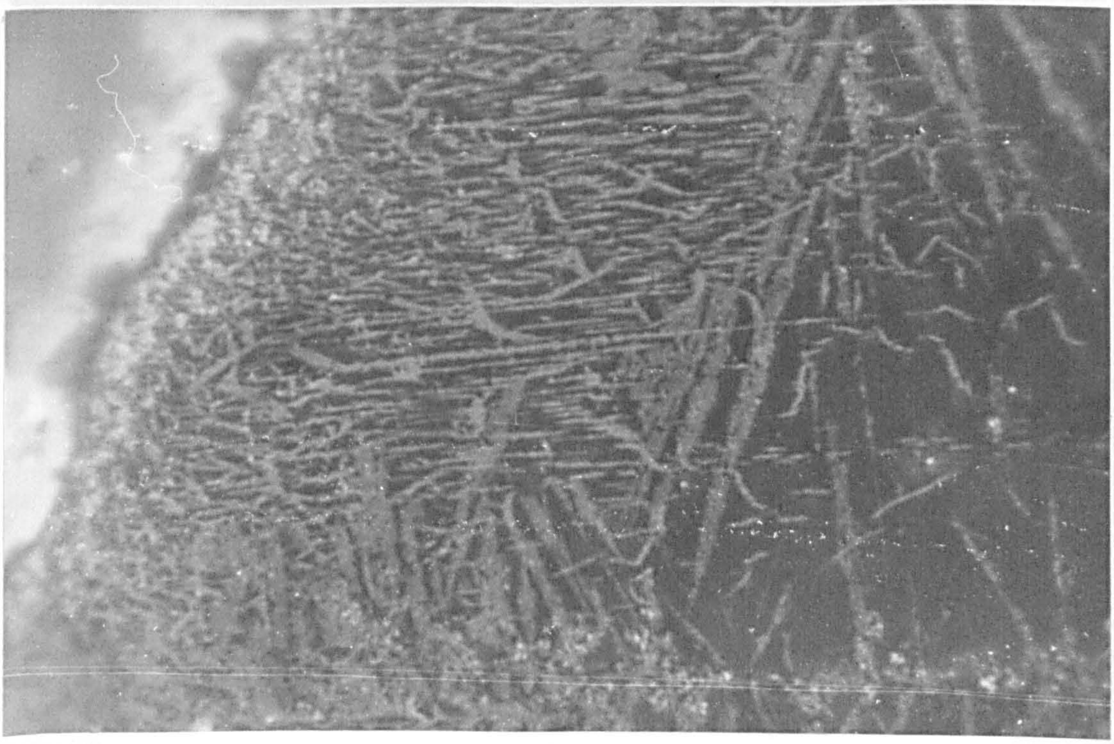


P. 5.9 after 3 days



P. 5.10 after 9 days

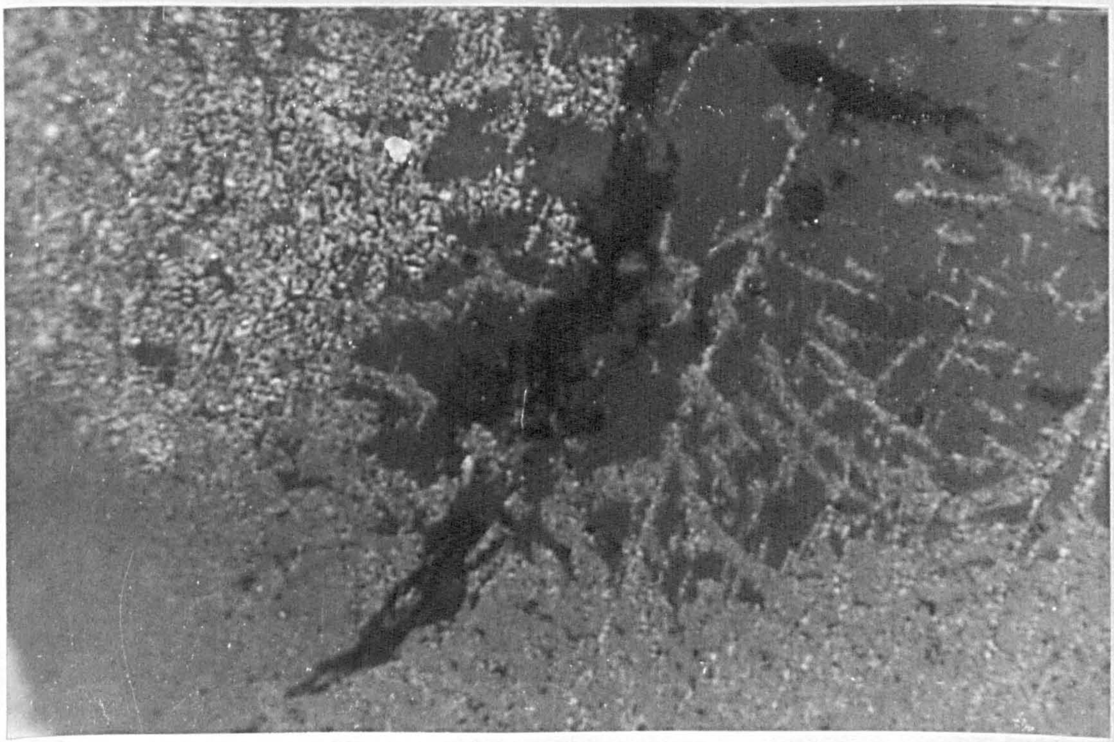
SAMPLE 4 HEATED AT 1000°C IN AIR



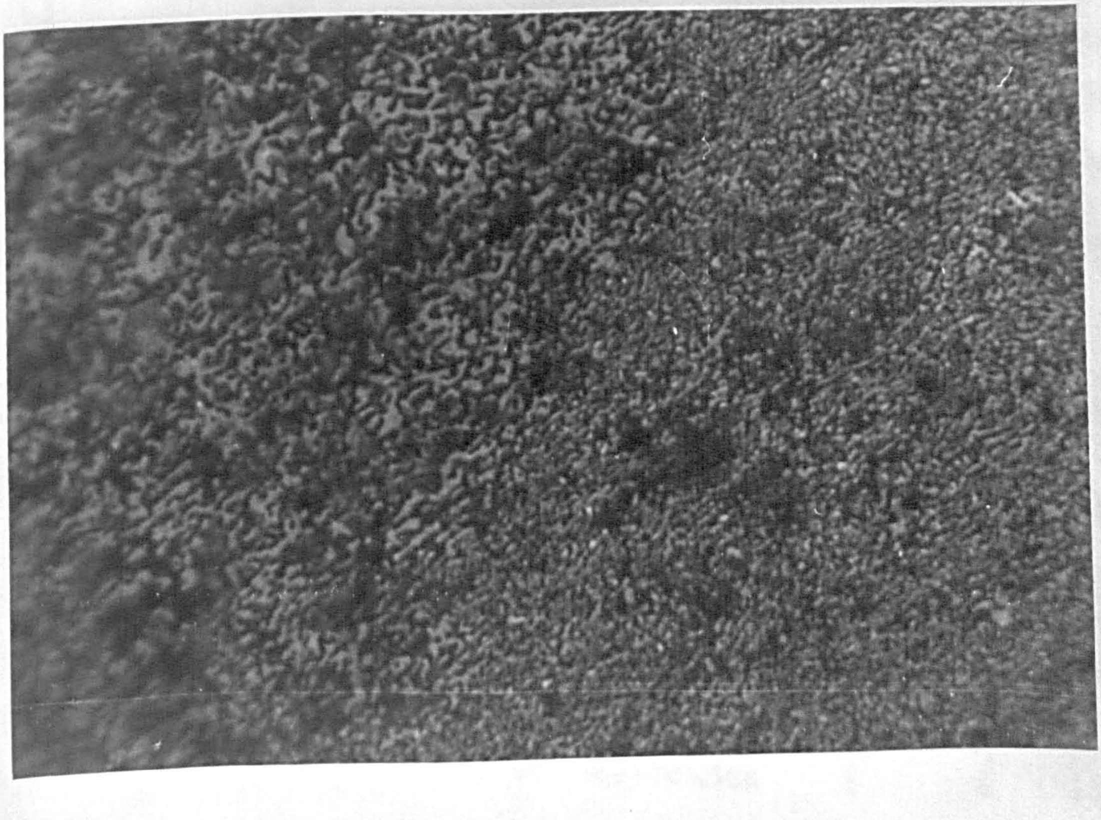
P. 5.11 after 5 minutes

P. 5.12 after 9 days

SAMPLE 5 HEATED AT 1000°C IN AIR



P. 5.13 after 5 minutes



P. 5.14 after 9 days

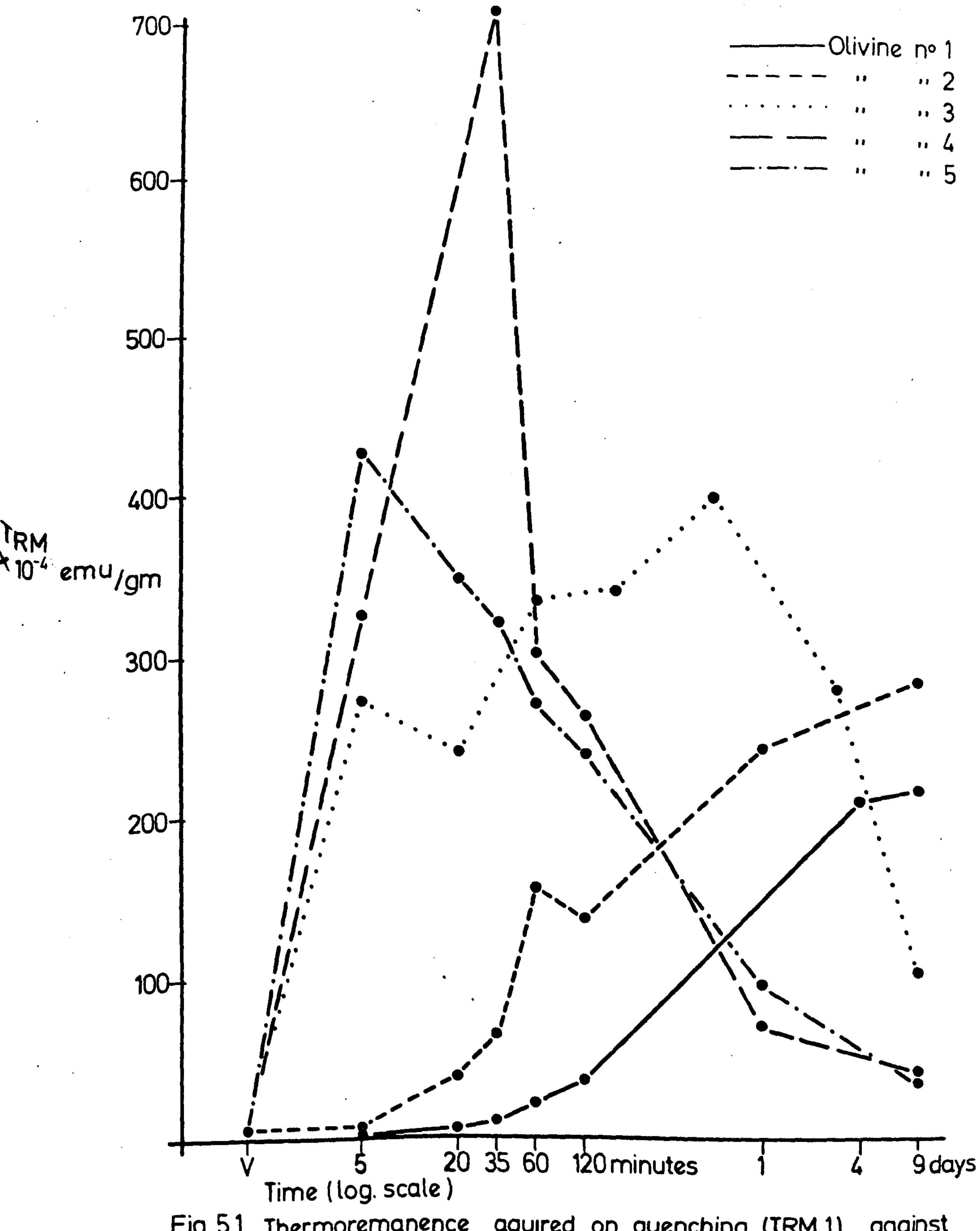


Fig 5.1 Thermoremanence aquired on quenching (TRM 1) against time heated at 1000°C in air

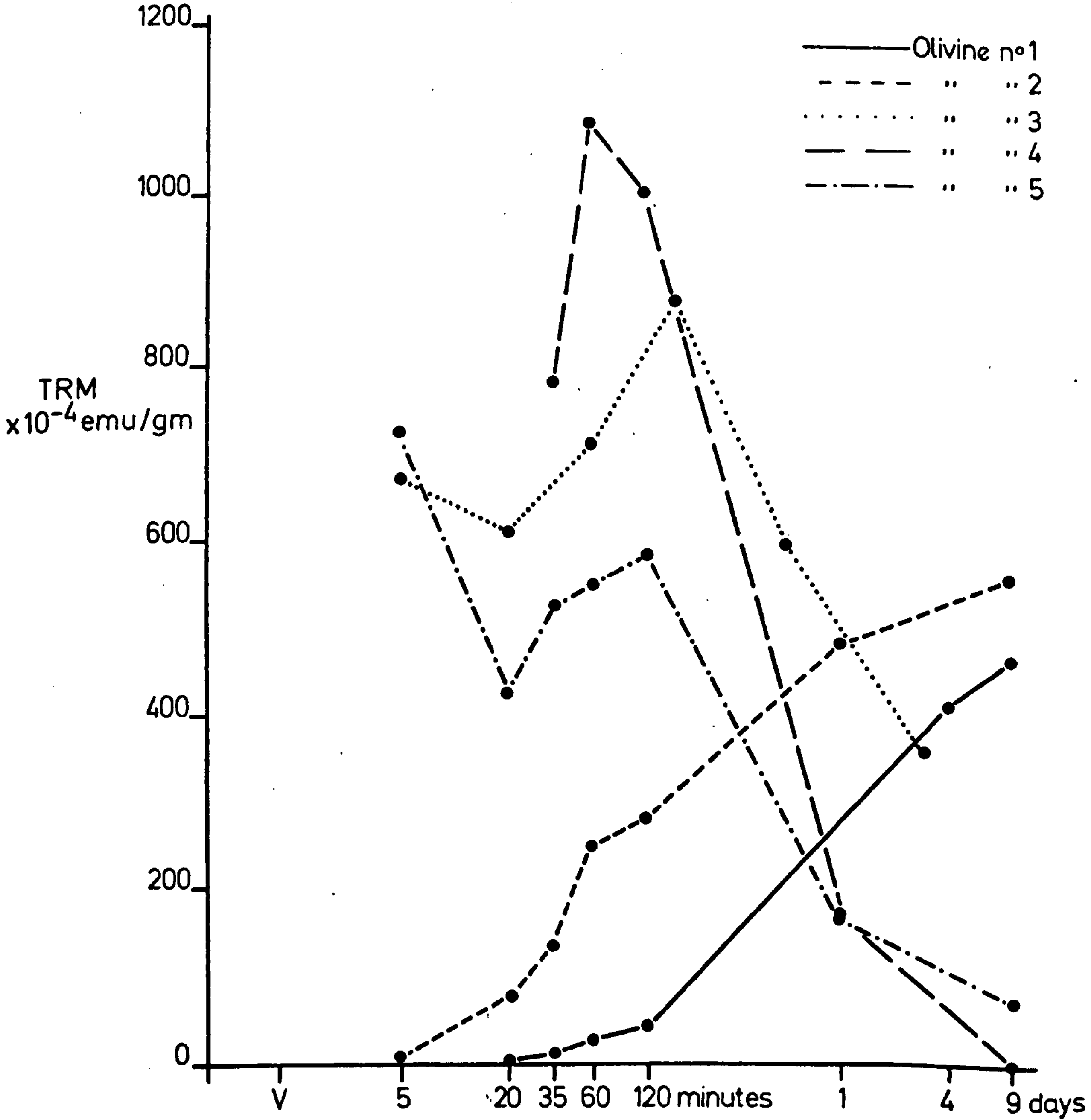


Fig. 5.2 Thermoremanence acquired on slow cooling (TRM 2) against time heated at 1,000 °C in air.

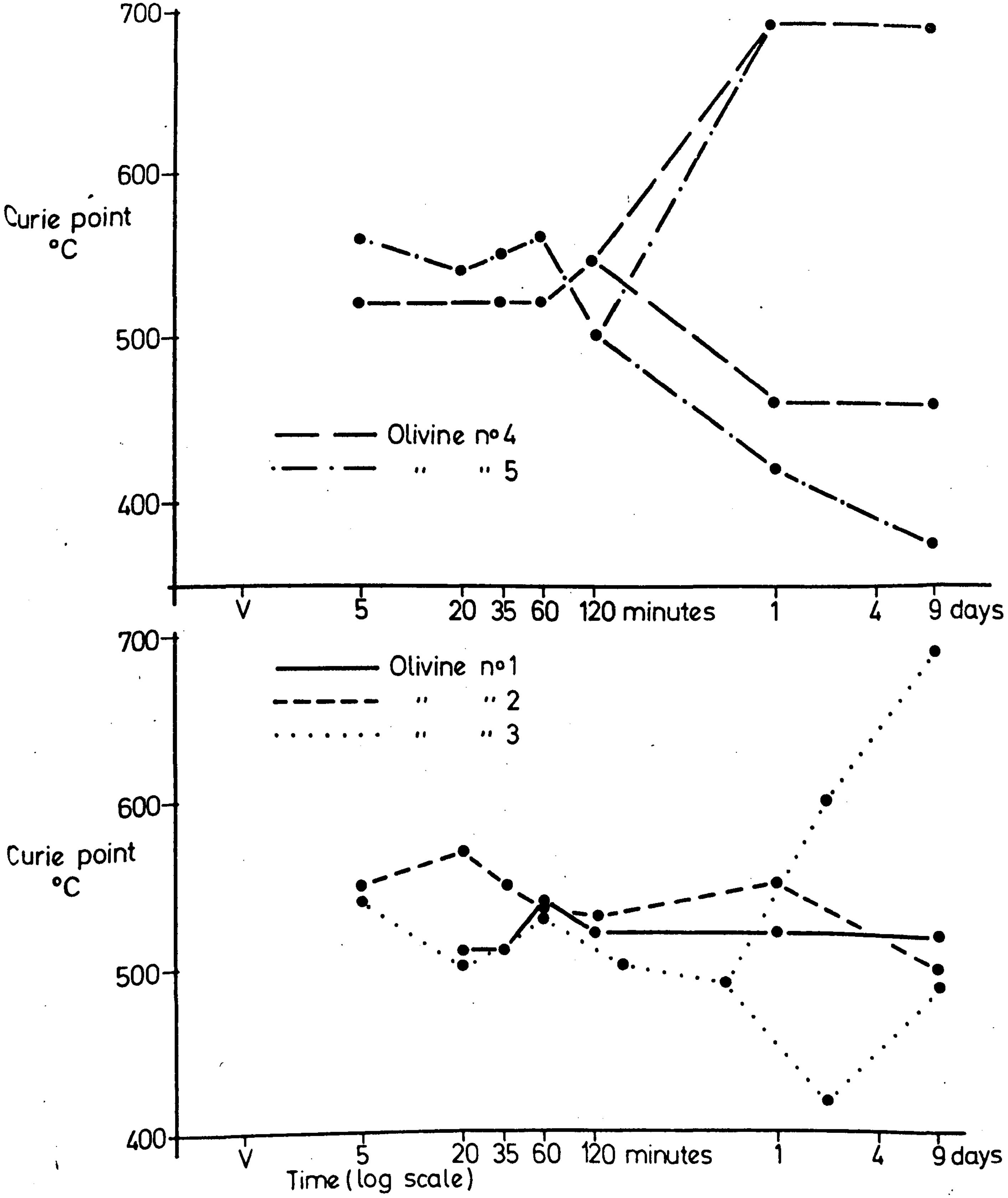


Fig. 5.3 Curie point against time heated at 1000°C in air

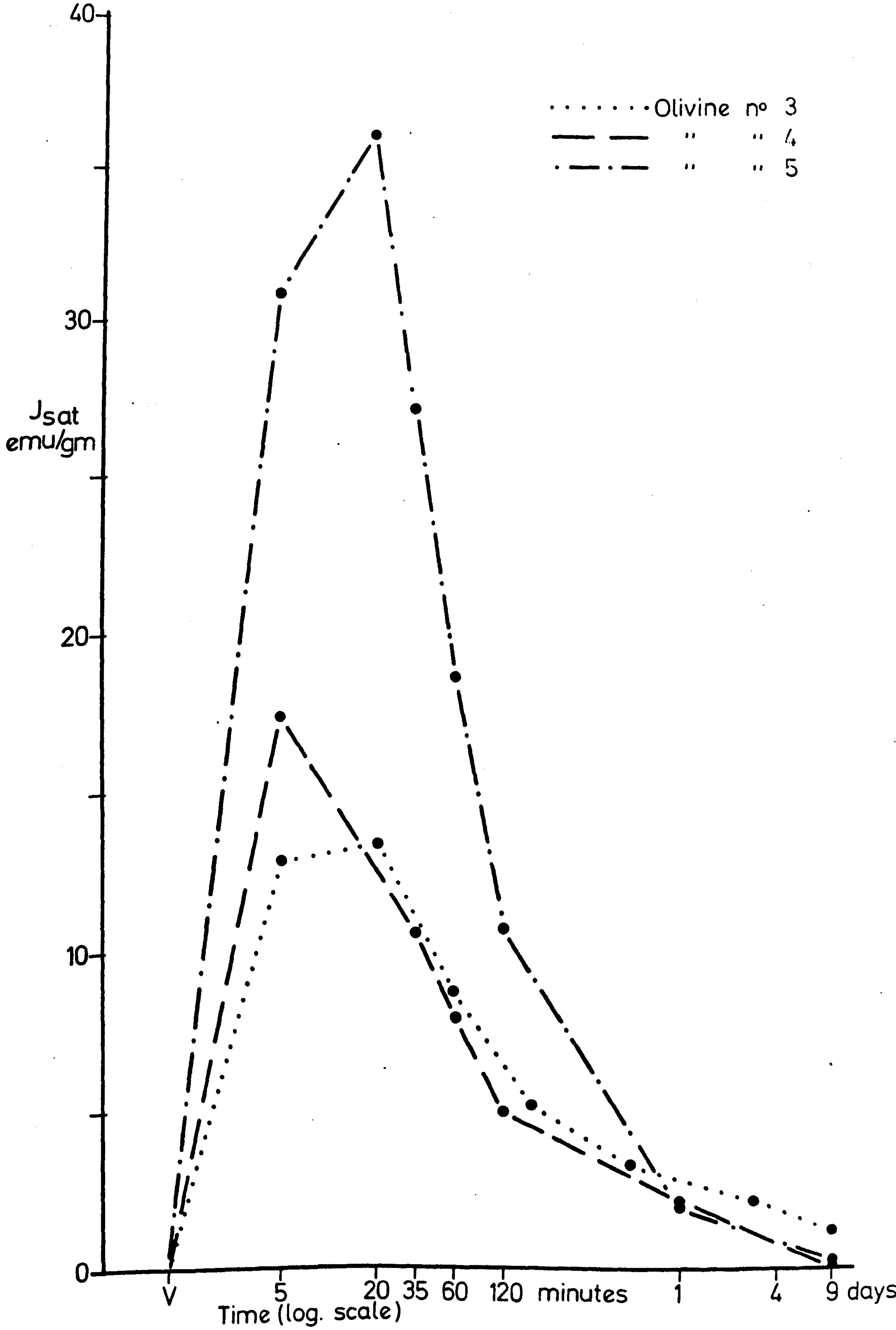


Fig. 5.4 Saturation magnetization against time heated at 1000°C in air

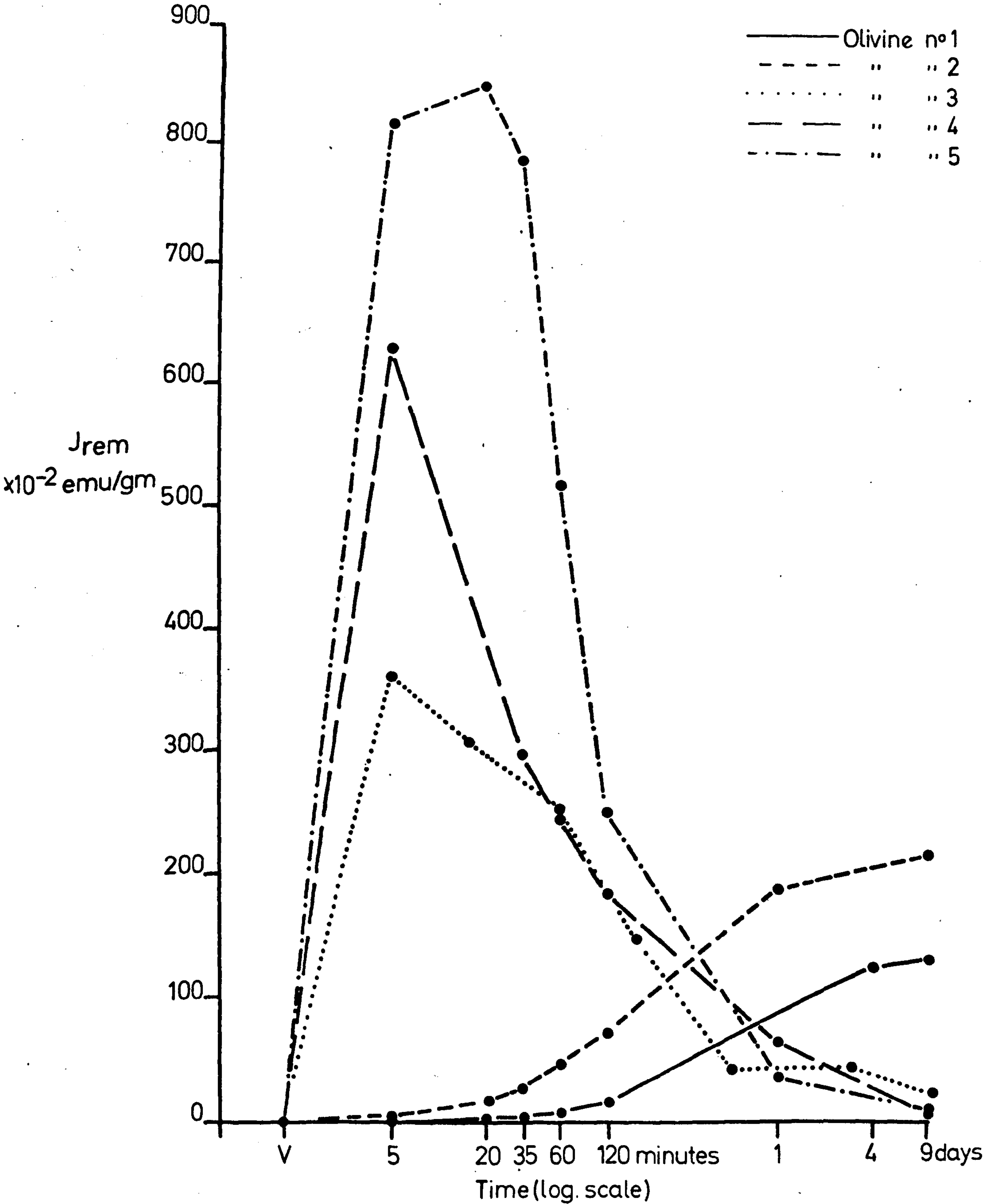


Fig. 5.5 Saturation Remanence against time heated at 1000 °C in air.

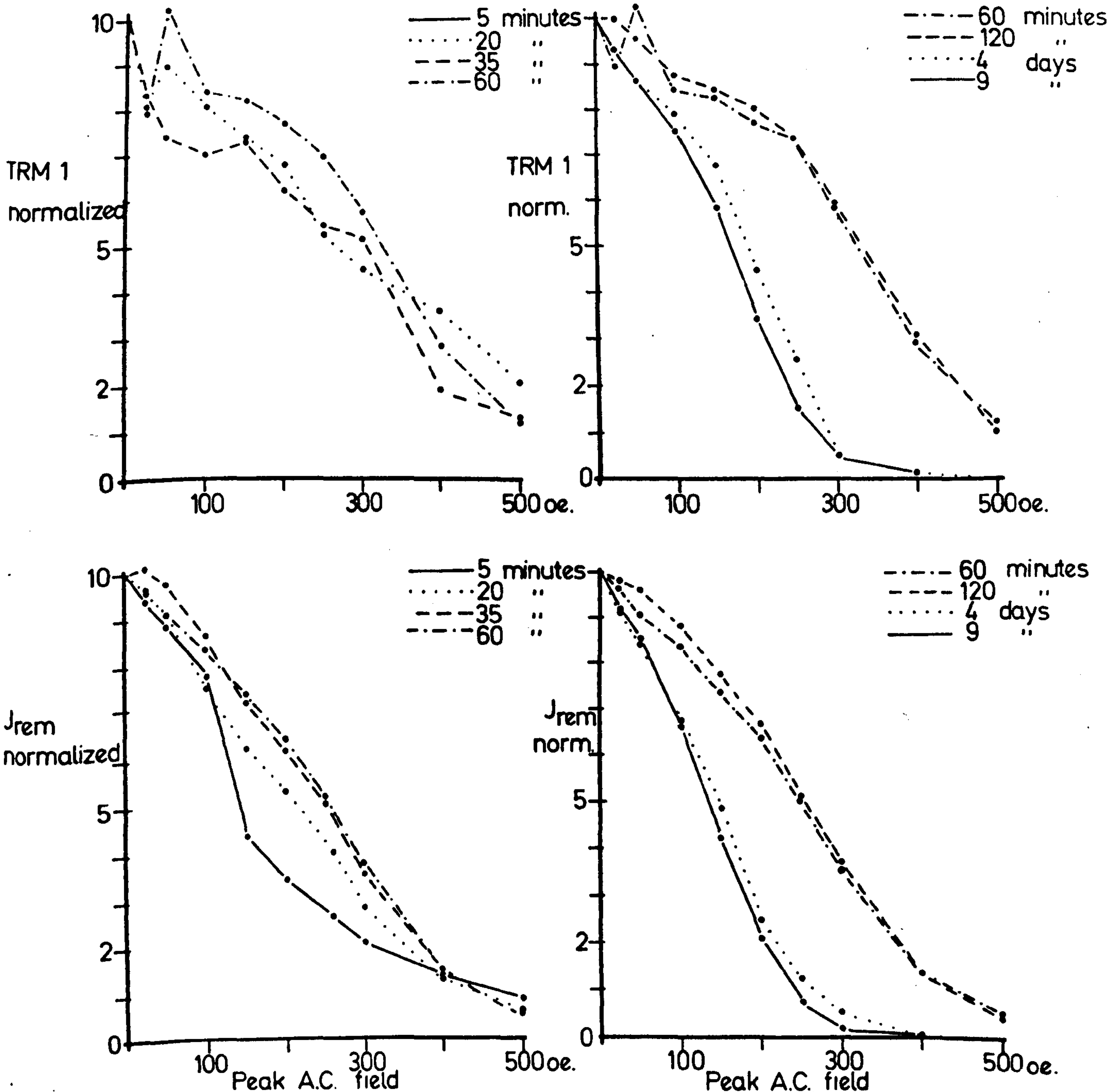


Fig. 5.6 A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 1 after heat treatments at 1000°C in air

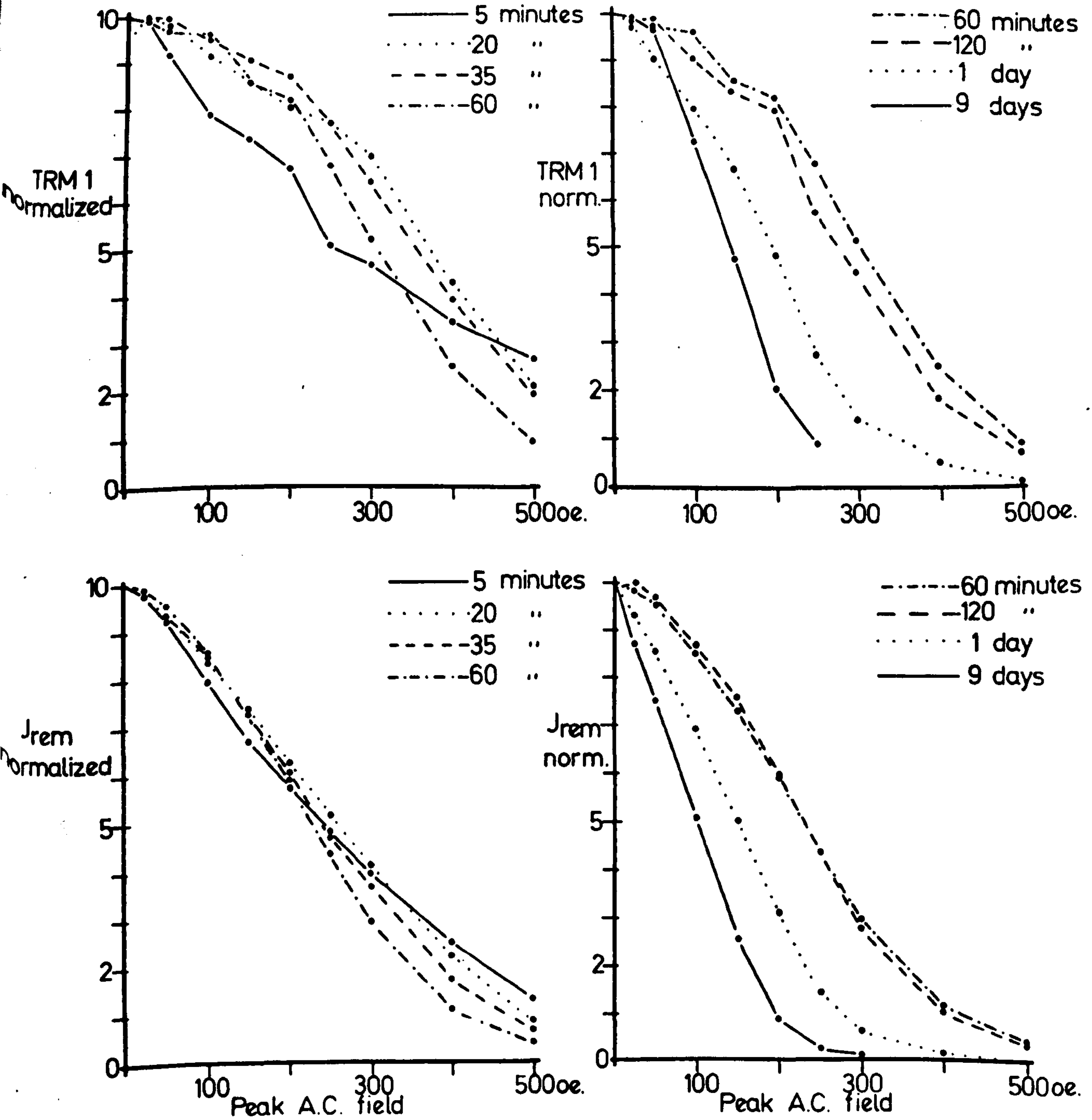


Fig. 5.7 A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 2 after heat treatments at 1000°C in air

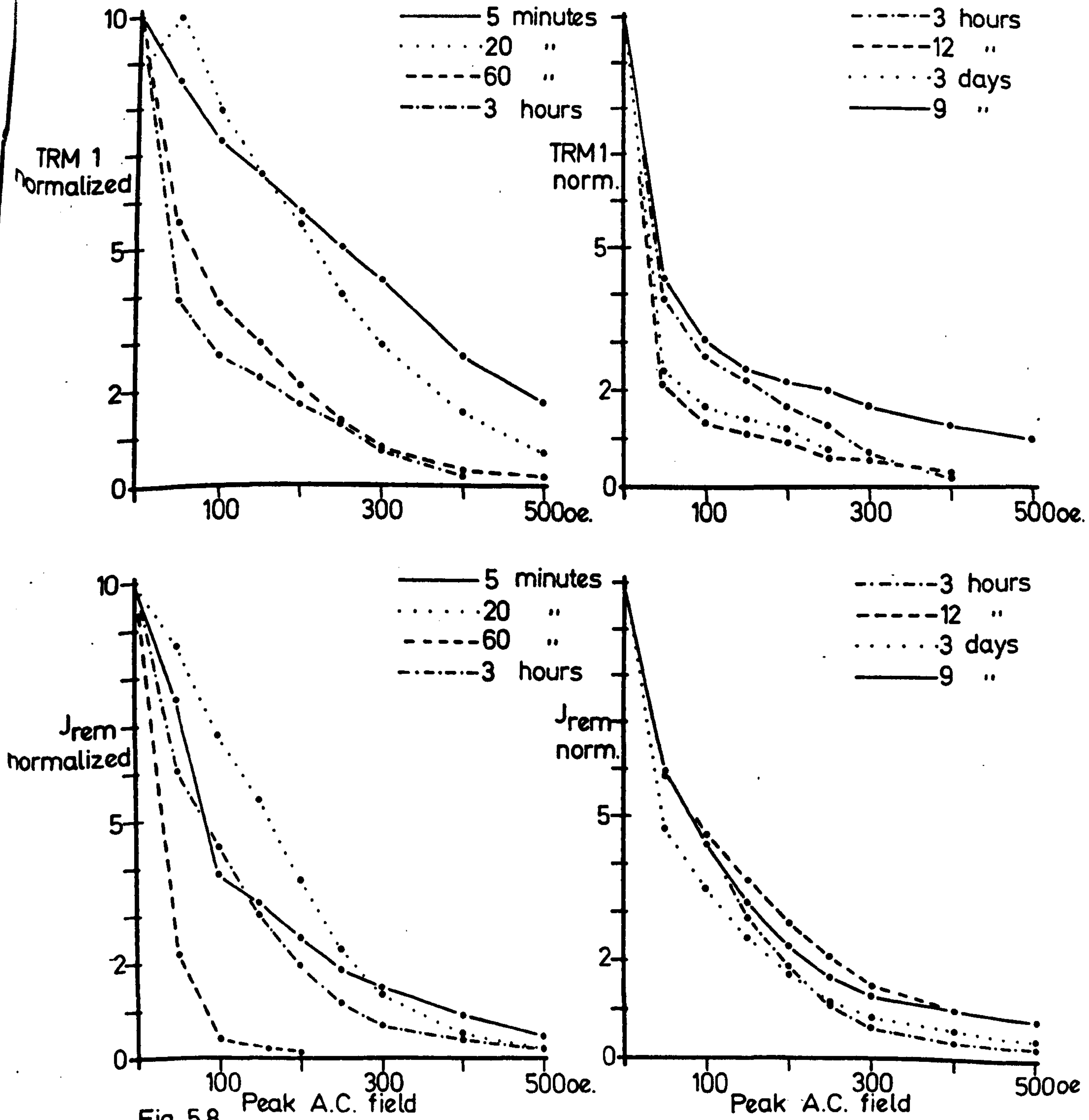


Fig. 5.8 A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 3 after heat treatment at 1000°C in ai

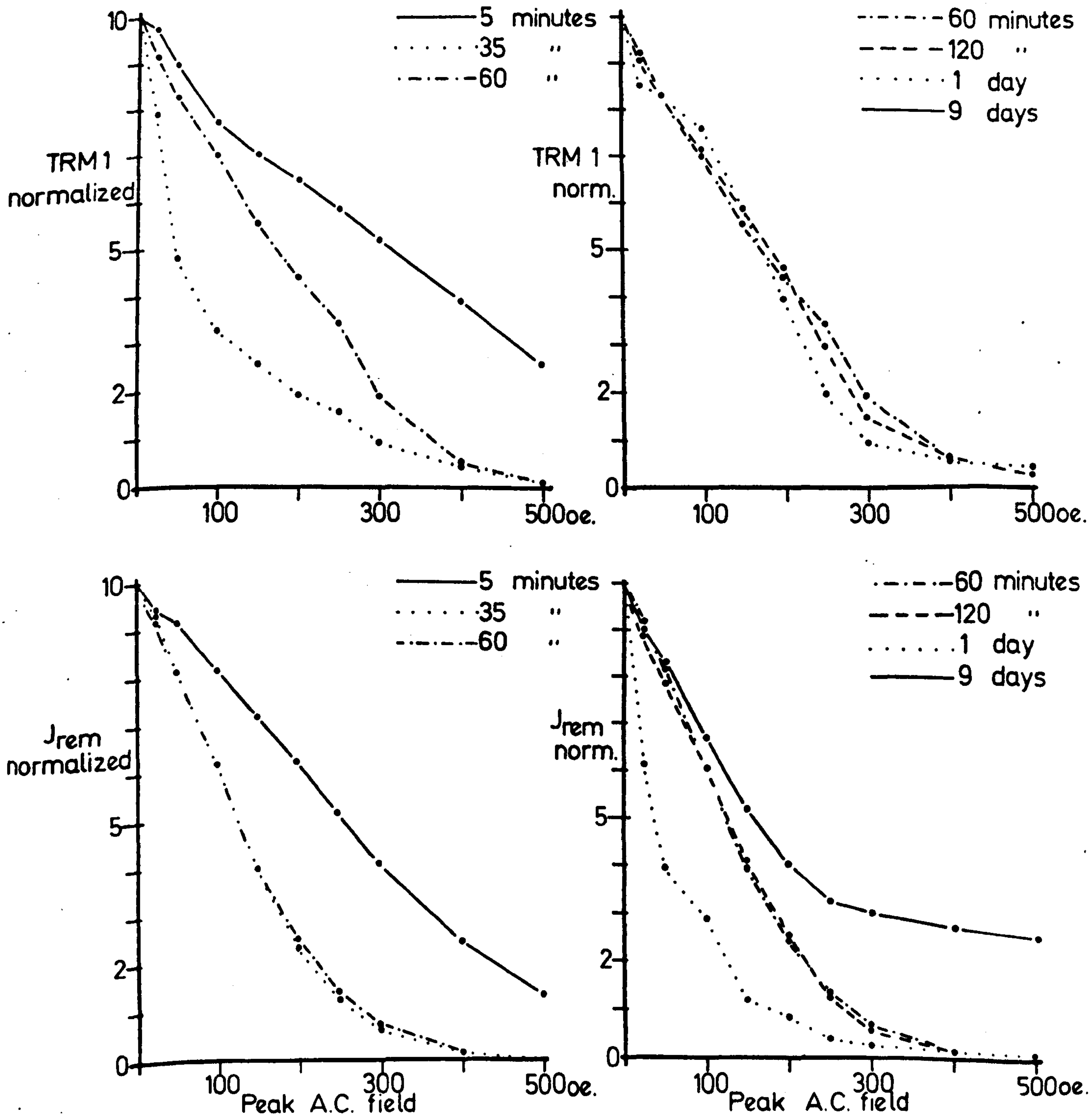


Fig. 5.9. A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 4 after heat treatment at 1000°C in air

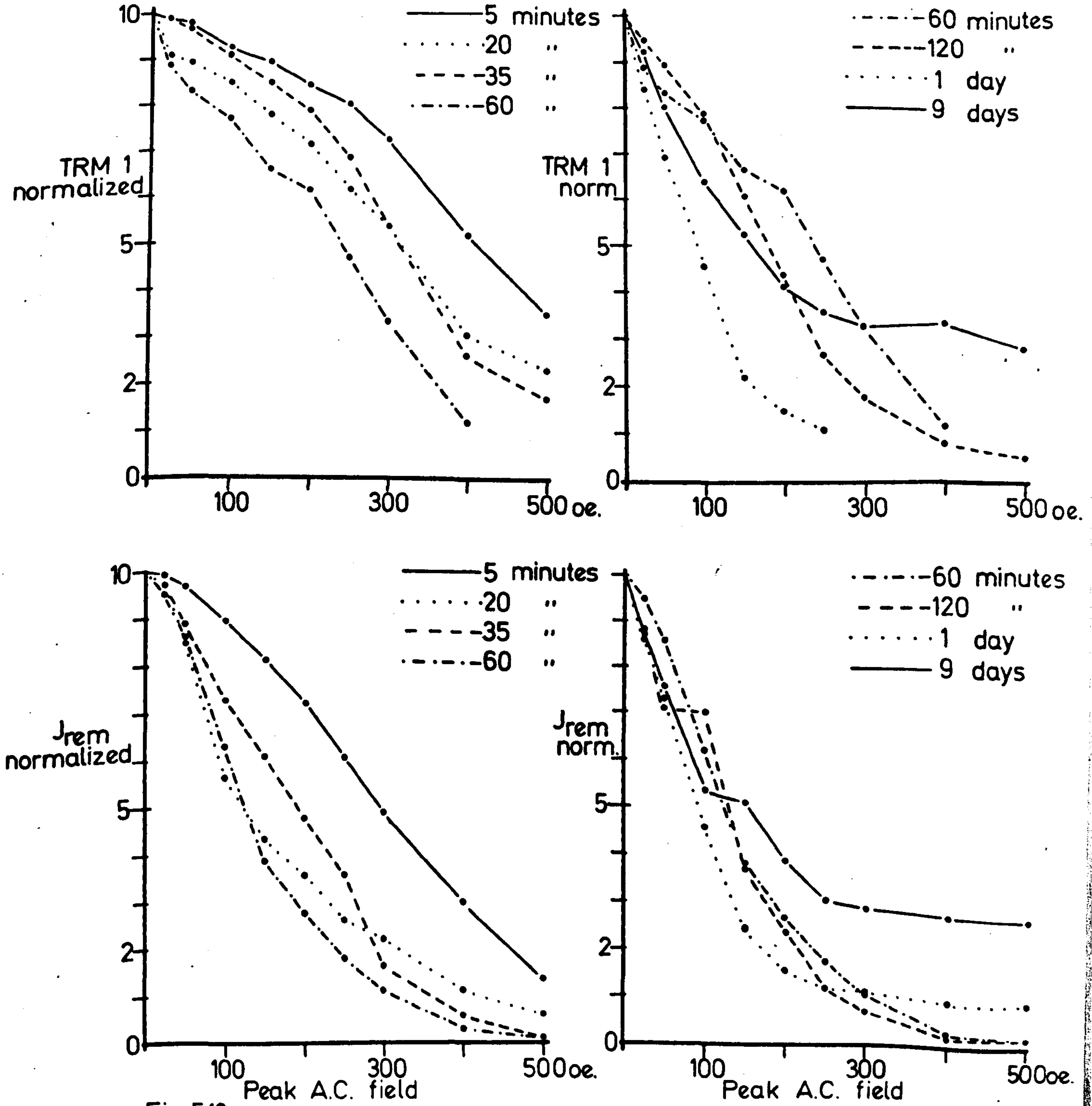


Fig. 5.10 A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 5 after heat treatment at 1000°C in air

CHAPTER 6

THE RESULTS OF HEATING EXPERIMENTS AT 650°C AND 850°C IN AIR

6.1 Introduction

Olivine samples of different compositions had been used to examine the variation of alteration formed, due to the composition of the original olivine. A second variable to be easily examined was the effect of the temperature to which the olivine was heated, on the alteration that was produced.

Samples 1 and 2, low iron content samples, were of most interest, as it is olivines of approximately these compositions which are found in rocks of common interest to paleomagnetism. These samples were heated for up to one day at both 850°C and 650°C to look for a possible lower limit to the formation of similar alteration. No alteration was found in either olivine sample when heated to 650°C for one day. Their magnetic properties were too weak to be measured on available instruments. No visible alteration could be seen with a microscope, at x 1200 magnification. For the samples heated to 850°C considerable rise in their magnetic properties was detected, together with visible alteration similar to that obtained previously.

These experiments showed that within convenient laboratory time scales, heating samples to 650°C would not produce similar alteration of olivine. So a second series of experiments with all five samples was started, to heat the samples to 850°C in air and vacuum. This temperature proved convenient as it slowed the alteration of samples 4 and 5, so the initial stages of their alteration could be examined more fully than during the heatings at 1000°C. The results again can be divided into magnetic, optical and X-ray results.

6.2 Magnetic Results

The magnetic results were not as extensive as the results for the previous series of experiments. The low iron content olivines were very slow in the development of their alteration and some of their magnetic properties were too small to be measured during the shorter duration heatings. In particular, the thermoremanence, acquired on slowing cooling the sample, was not measured as the thermal demagnetization which preceded it was not measurable. The results were generally similar, for all the samples, to those results obtained when heated to 1000°C, except that the alteration developed at a much slower rate.

The thermoremanence acquired on quenching in a 0.5 oe magnetic field showed a rise as before but only sample 5 showed a maximum of TRM 1. Samples 3 and 4 had values of TRM 1 at the end of nine days heating greater than any they acquired at 1000°C. Neither samples showed that the TRM 1 was approaching a maximum (Fig. 6.1).

The Curie points of the samples followed a development, similar to that of the previous series of heatings, except for sample 2 (Fig. 6.2). Sample 1 was magnetically too weak for its Curie point to be measured until it had been heated for one day. The behaviour of the Curie point of sample 2 could not be explained. The change of Curie point from 420°C to the more normal 560°C was unique, in all the experiments with this sample. The sample did not show any other deviations from the expected development in these experiments. The Curie points of samples 3, 4 and 5 were after five minutes heating between 520 and 550°C and on further heating decreased. Their Curie points after nine days heating were between 400°C and 420°C. A Curie point of this value would, according to Benard and Chaudron (1937) (Fig. 2.4), indicate a magnesium ion : ferrous ion ratio of about 9 : 1. The starting Curie points indicated an excess of ferrous ions over magnesium ions. The ratio of ions may be higher than indicated as the hematite formed may have increased the Curie point of the ferrite. Only sample 5 showed the high 690°C Curie point, indicating of hematite, in these 850°C experiments.

The variation of saturation magnetization and saturation remanence showed similar development (Fig. 6.3, 6.4). Samples 1 and 2 were magnetically very weak and showed only a slight rise of saturation remanence. Samples 3, 4 and 5 showed the forseeable large rise in magnitude, with a maximum and a decrease. The apparent anomaly of sample 5 may be due to an error in the result taken after 120 minutes heating as it is not reflected in the saturation remanence curve. The maximum value occurred after longer periods of heating than in the comparable curves at 1000°C and for samples 3 and 4 was smaller.

The slower development of the alteration showed clearly in the A.C. demagnetization curves (Figs. 6.5, 6.6, 6.7, 6.8). Samples 1 and 2 showed clearly a rise in the hardness of the saturation remanence, during the heating. This rise is due to the growth of smaller domains in the early slower development of the ferrite. For both samples there was a rise from 30% after five minutes heating to 70% after one day's heating of the saturation remanence remaining after A.C. demagnetization in peak magnetic fields up to 200 oe. Sample 3 showed this rise in hardness, followed by the rapid softening of the sample after three hours heating. Samples 4 and 5 showed no indication of the initial hardening but started with a hard magnetization. They both showed the rapid softening but only sample 5 showed the final hardening that was evident during the heating at 1000°C.

The magnetic results are very similar to those results after heating to 1000°C except that the alteration is much slower in development. The two distinct stages are not evident clearly except in sample 5. Samples 3 and 4 only show the rise and then fall in magnetization in the saturation magnetization and saturation remanence results. The main problem of these results is why does the thermoremanence of samples 3 and 4 rise throughout? This problem will be resolved later, in the discussion of the results.

6.3 Optical Results

The optical results may be briefly summarized as similar to the alteration after heating to 1000°C but slower to develop. There was also less reddening of the samples and the opaque material formed was much smaller in extent and size.

Sample 1 showed very little alteration until it had been heated for one day. The alteration began as fine green sponge-like alteration in lines about the edge of the sample. These lines often but not always had a common direction. They grew in size and in density with the further heating and developed into the interior of the sample. After nine days the alteration was seen throughout the sample, with varying density. In some areas the alteration had spread into broader lines. The edges of the sample were reddened in some places and some cracks were filled with opaque material (P. 6.1).

The alteration of sample 2 was very slow to develop. It began at the edges as small amounts of green sponge-like alteration in the form of shapeless blotches. After nine days heating the alteration had spread through the sample with the broadening of the alteration about the edges. There was no development of linear alteration with preferred directions. No opaque material of microscopic size developed (P. 6.2).

The alteration of sample 3 was much quicker. A green alteration was formed about the edges after five minutes heating. This alteration consisted of fine lines with a generally preferred direction. As the alteration developed the lines thickened and joined together (P. 6.3). After nine days heating a second stage of alteration had started. The green alteration was being replaced by a bright red sponge-like alteration with submicroscopic opaque material in this alteration. This alteration was mostly about the edges of the sample which were reddened (P. 6.4). There was no indication of the growth of the opaque material present.

Samples 4 and 5 were visually very similar during their alteration. After five minutes heating most of the crystal was filled with alteration. Clearly visible was the green sponge-like alteration in the form of bands of varying thickness but all of one direction. In some areas the gaps between the lines was filled with a brighter alteration which had a slight red colouration (P. 6.5). After twenty minutes the rim of the sample had turned red and less of the green band type alteration remained (P. 6.6). During the heating to two hours the green alteration was gradually altered to a bright red alteration, the structure of the original alteration could be seen in some areas of the red alteration (P. 6.7, 6.8, 6.9). After heating for one day all the sample was reddened and in some areas the opaque material had started to grow in size (P. 6.10). Finally, after nine days heating the sample was filled with the red alteration. The opaque material had started to grow and the grains were 1 - 2 μ across. Some cracks were filled with opaque material and in some places an opaque rim had formed around the crystal.

Within any sample the alteration may vary in condition within distinct areas. These areas may be due to differing composition within the olivine sample. The development of samples 3, 4 and 5 shows the two stage nature of the alteration. The red alteration forms on further heating pseudomorphs of the original green alteration. Visually there can be a continuation in structure of the alteration. The opaque material grew from this red alteration but did not become as extensive as after heatings to 1000°C.

6.4 X-ray Powder Photograph Results

As explained previously X-ray powder photographs of the samples after heating for nine days were taken and compared to photographs of the original olivine samples.

Samples 1 and 2 showed similar patterns to those obtained after heating to 1000°C. The pattern of the original olivine was very clear and a weaker pattern of hypersthene was present in both photographs. The pattern of the olivine did not give any indication of the alteration of the composition of the olivine.

Sample 3 gave the most complicated powder pattern of all the samples. The patterns of the original olivine and of hypersthene were clearly present in the photograph. On examination of the remaining lines, hematite was clearly present in the sample and lines indicating a ferrite structure remained.

Samples 4 and 5 gave similar powder photographs. Hematite was the main constituant of the pattern produced. In both samples the remaining lines indicated the presence of hypersthene and a ferrite.

These results show clearly that the alteration of olivine starts with the formation of hypersthene. The continuation of the alteration forms hematite and a ferrite in detectable quantities.

6.5 Discussion of Results

These results are both more complicated and simpler than the results of the heatings at 1000°C. The results are similar to those after the heatings at 1000°C, but are an indication of the slower development of the alteration. This slowing of the rate of growth has magnified some of the finer points of the alteration, which were masked by the speed of alteration at 1000°C.

The results can be explained by exactly the same alteration as was proposed for the heatings at 1000°C.

Olivine + Oxygen -> Hypersthene + Magnesium Ferrite

Magnesium Ferrite + Oxygen -> Magnesium Ferrite + Hematite
(Magnesium richer)

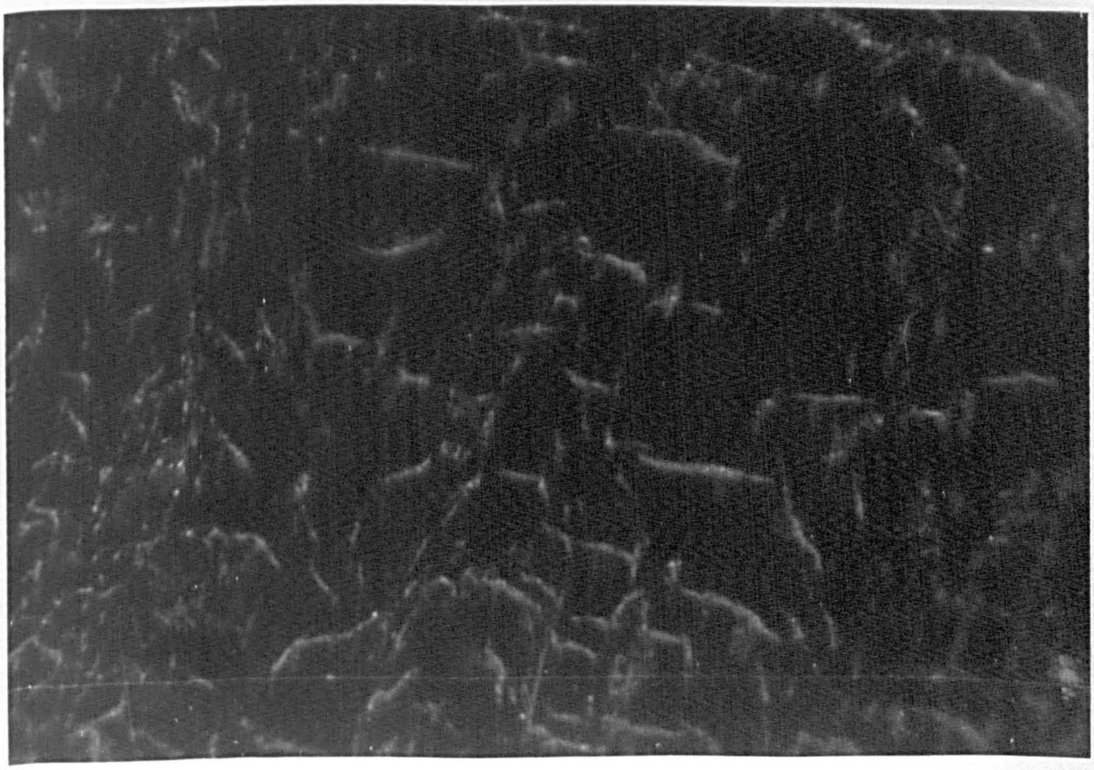
The first stage of the alteration accounts for the rise in magnetic properties because of the production of the ferrite. This alteration is optically the green sponge-like alteration. The second stage of the process gives the fall of saturation magnetization, the fall in the ferrite Curie point and the reddening in the optical specimens. The initial hardening of the samples to A.C. demagnetization is due to the slower development allowing the formation of the small domain opaque material. The softening of the magnetization is due to the growth on further heating of the grains and in this process the domain size. The X-rays results show that the alteration does not form two distinct stages. Both processes can occur at the same time within one sample.

The single problem to escape this simple explanation is the continued rise of the thermoremanence of some samples after the saturation remanence and saturation magnetization have decreased. It can be pointed out that the magnetic properties can be complicated as they are the result of the interplay of four factors. These factors are of varying importance throughout heatings. There is during the heating an increase in the amount of magnetic material present. This amount will at some time reach a maximum. Secondly, there is an increase in the size of the magnetical material. From the combination of optical and A.C. demagnetization results, there is a strong link between size of grains and magnetic domain size. Thirdly, the magnesium : ferrous ion ratio of the ferrite changes during the heating. During the second stage of the alteration process this ratio increases. Finally, the magnetic properties are altered by changes of ionic ordering within the spinel structure of the ferrite. The variation of importance of these four factors can lead to very complicated magnetic changes as the samples are heated.

If the results for this series of experiments of samples 3 and 4 are examined the consequences of these factors can be noticed. The initial rise of the saturation magnetization is due to the production of the highly magnetic magnesioferrite. The peak of the saturation magnetization is reached when the oxidation of the iron rich ferrite to hematite has a greater effect than the continued formation of iron rich ferrite. The fall in saturation magnetization is due to the oxidation of the ferrite to hematite and a magnesium richer, magnetically weaker, ferrite. This production of the magnesium rich ferrite is seen in the decrease of the Curie point of the sample. However, why does the thermoremanence continue to increase? The solution to the problem is indicated by the A.C. demagnetization curves. These curves show the progressive softening of the samples whilst the saturation magnetization falls and the thermoremanence rises. This softening of the magnetization implies the material is easier to magnetize. So while cooling in the magnetic field, the thermoremanence acquired will be greater.

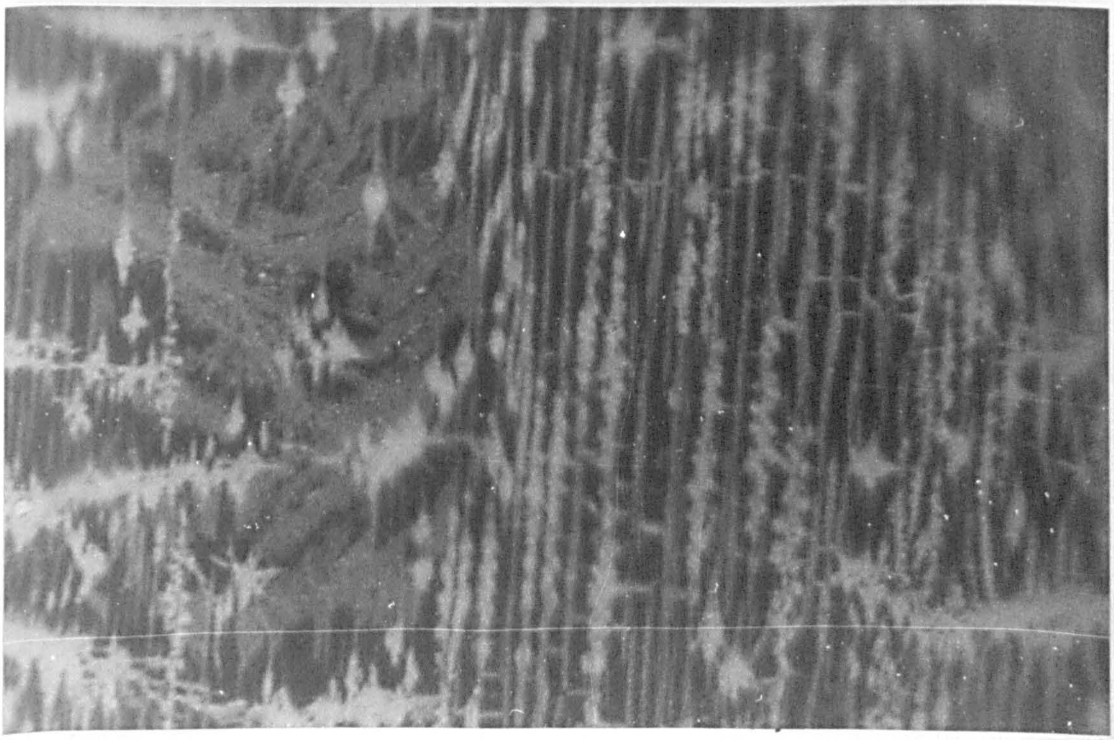
SAMPLES AT 850°C IN AIR

P. 6.1 Sample 1 after 9 days heating

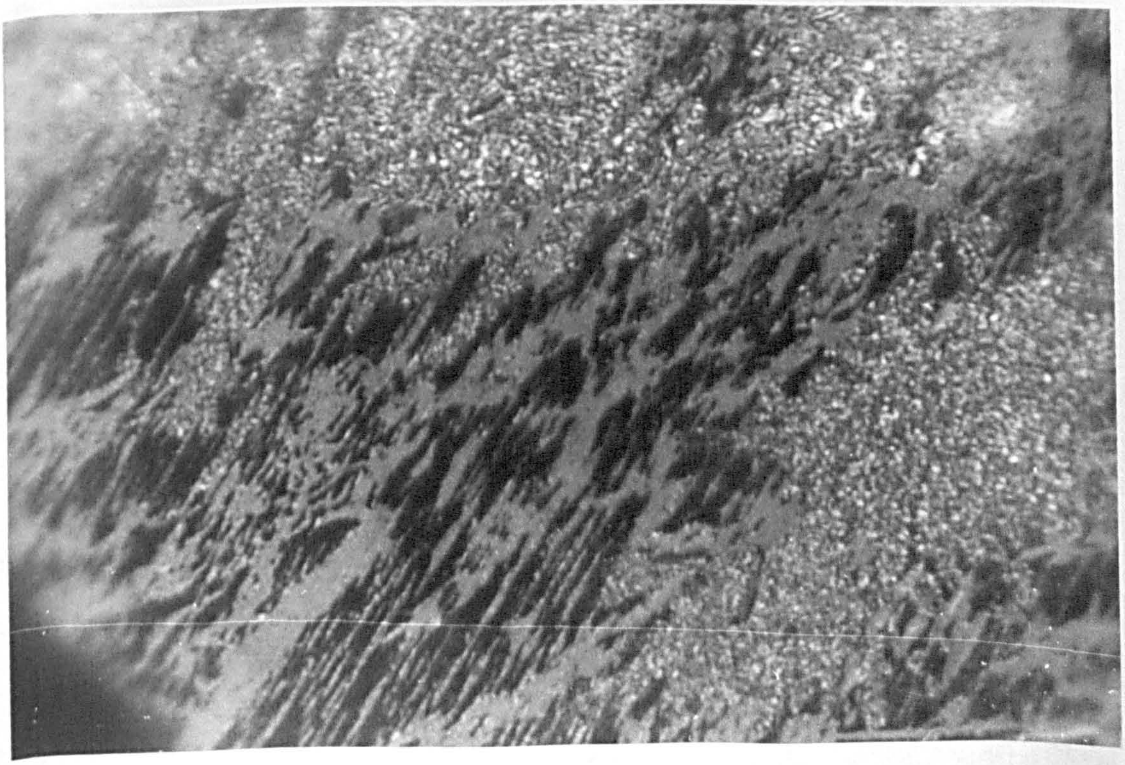


P. 6.2 Sample 2 after 9 days heating

SAMPLE 3 AFTER HEATING AT 850°C IN AIR

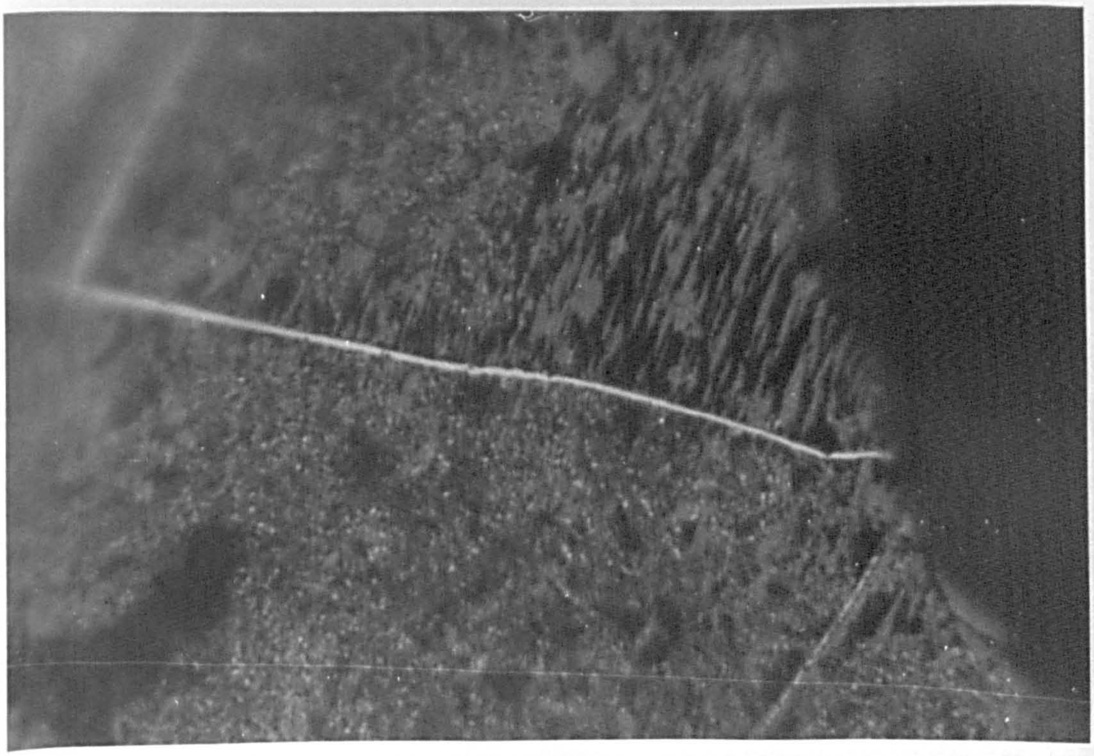


P. 6.3 after 3 hours heating



P. 6.4 after 9 days heating

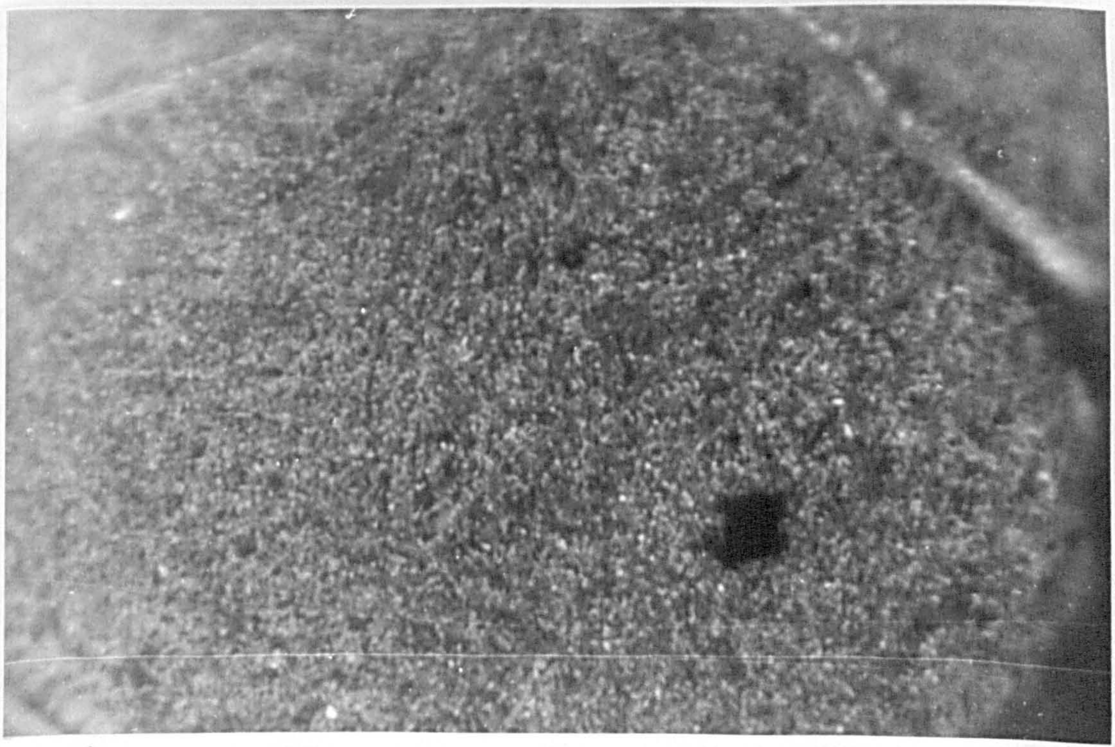
SAMPLE 4 AFTER HEATING AT 850°C IN AIR



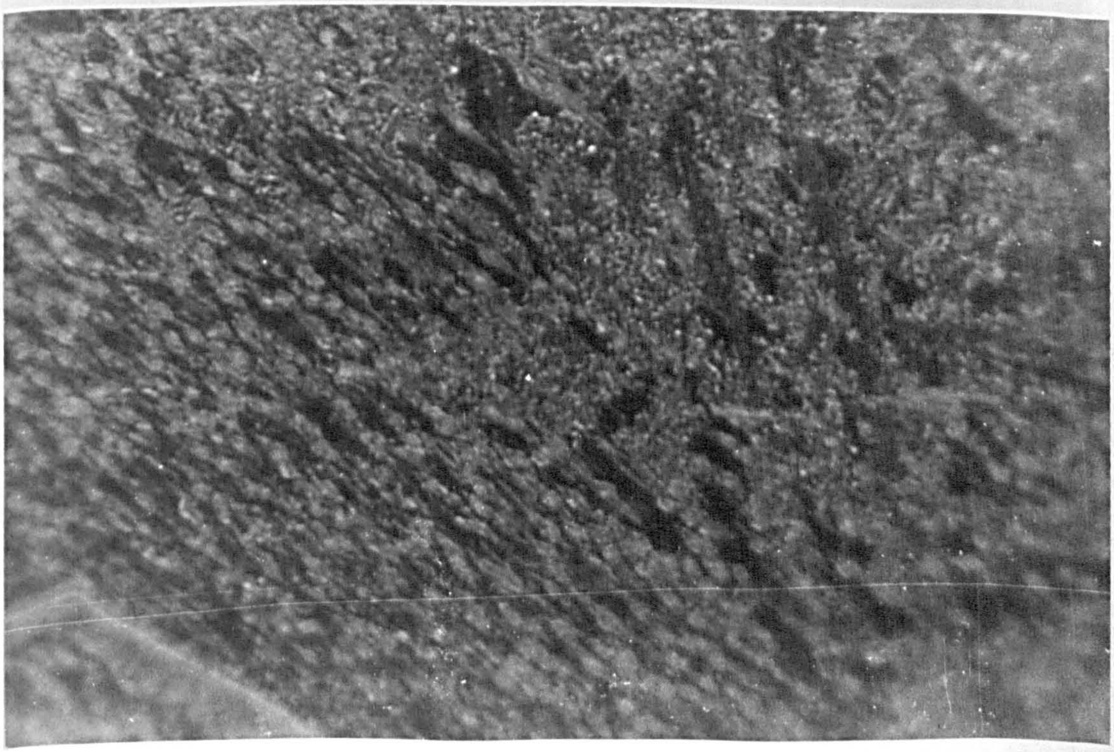
P. 6.5 after 5 minutes heating

P. 6.6 after 20 minutes heating

SAMPLE 4 AFTER HEATING AT 850°C IN AIR

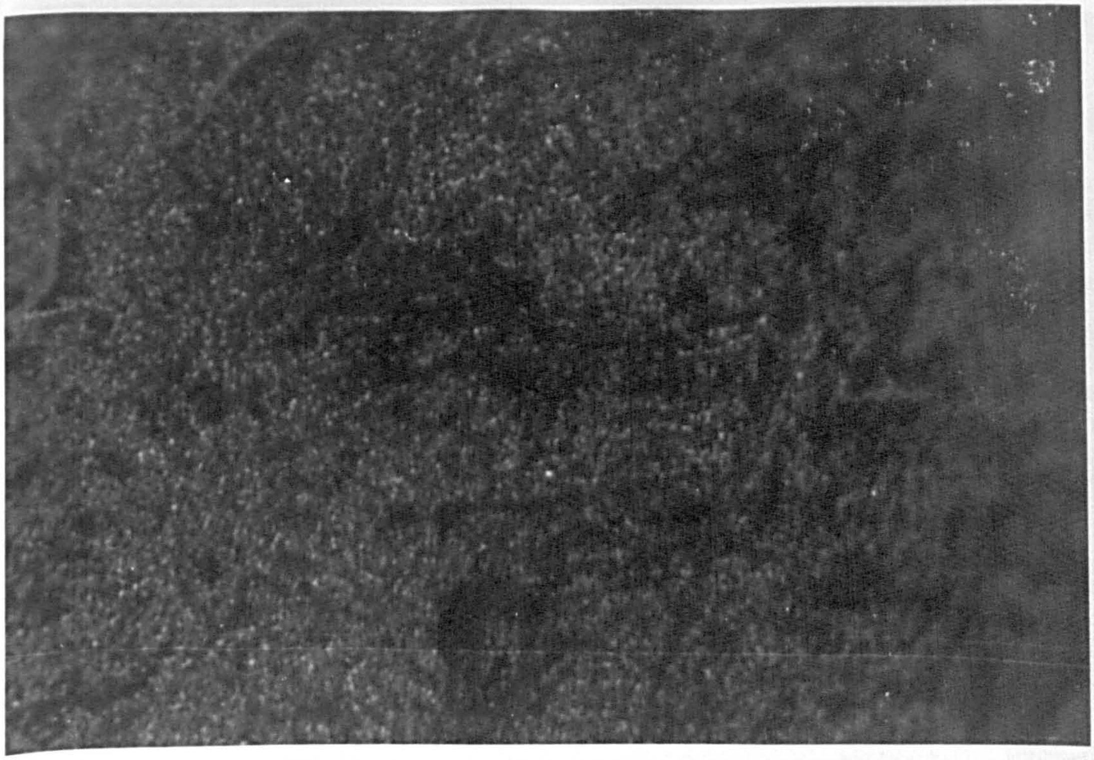


P. 6.7 after heating for 35 minutes

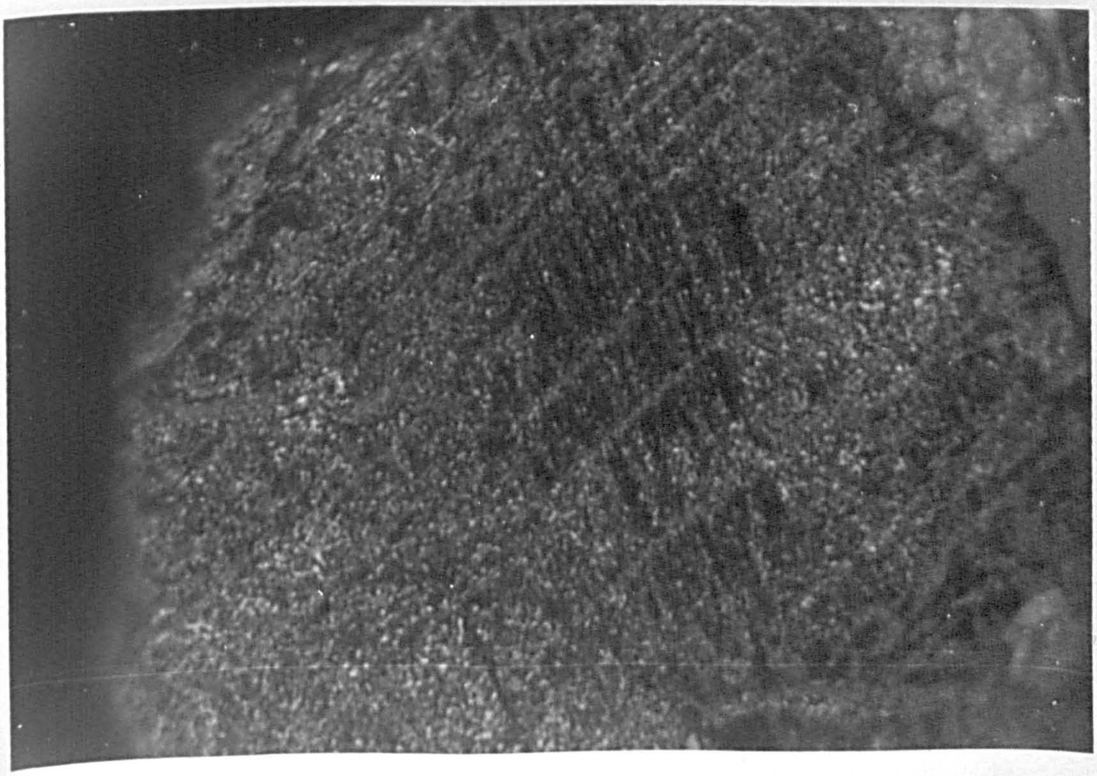


P. 6.8 after 1 hour heating

SAMPLE 4 AFTER HEATING AT 850°C IN AIR

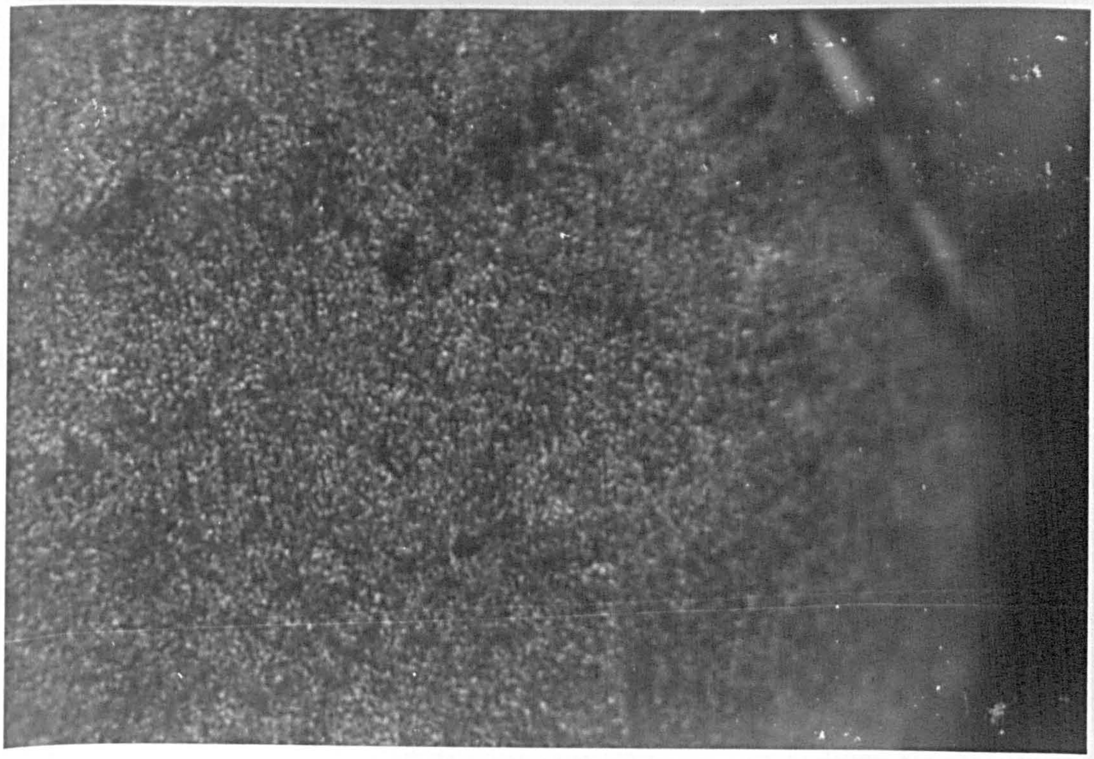


P. 6.9 after 2 hours heating



P. 6.10 after 1 day heating

SAMPLE 4 AFTER HEATING AT 850°C IN AIR



P. 6.11 after 9 days heating

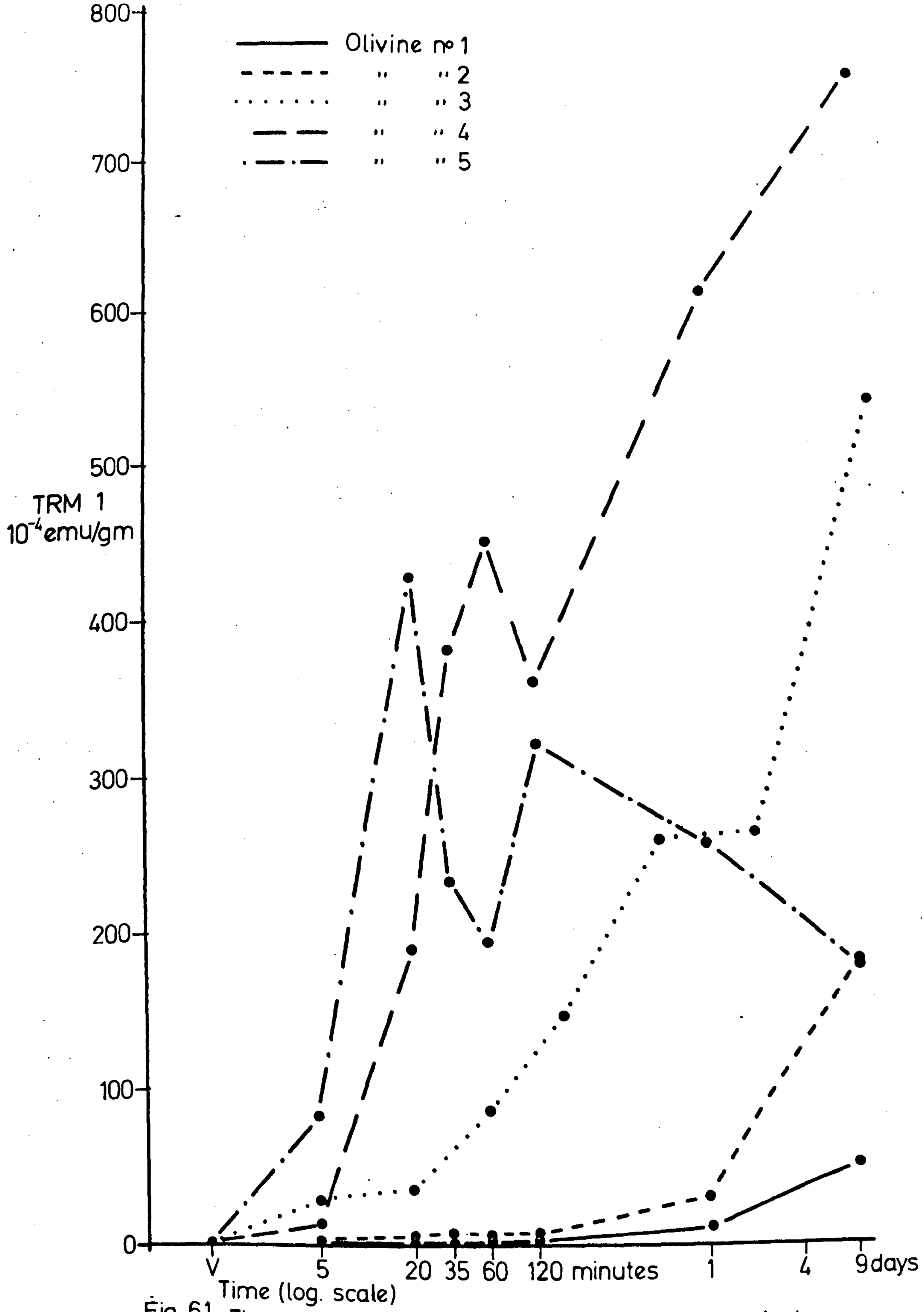


Fig. 6.1 Thermoremanence aquired on quenching against time heated at 850°C in air

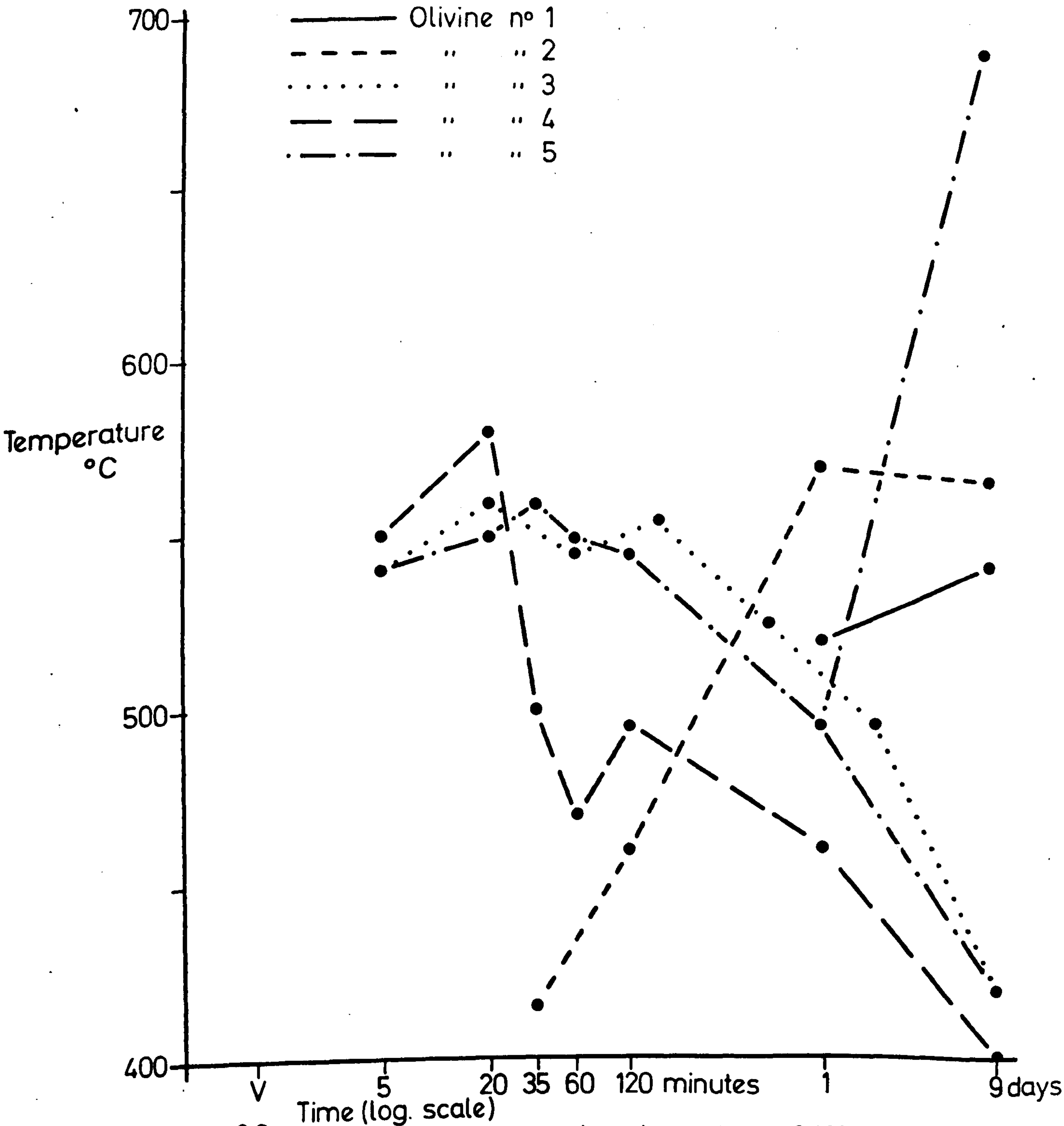


Fig. 6.2 Curie point against time heated at 850°C in air

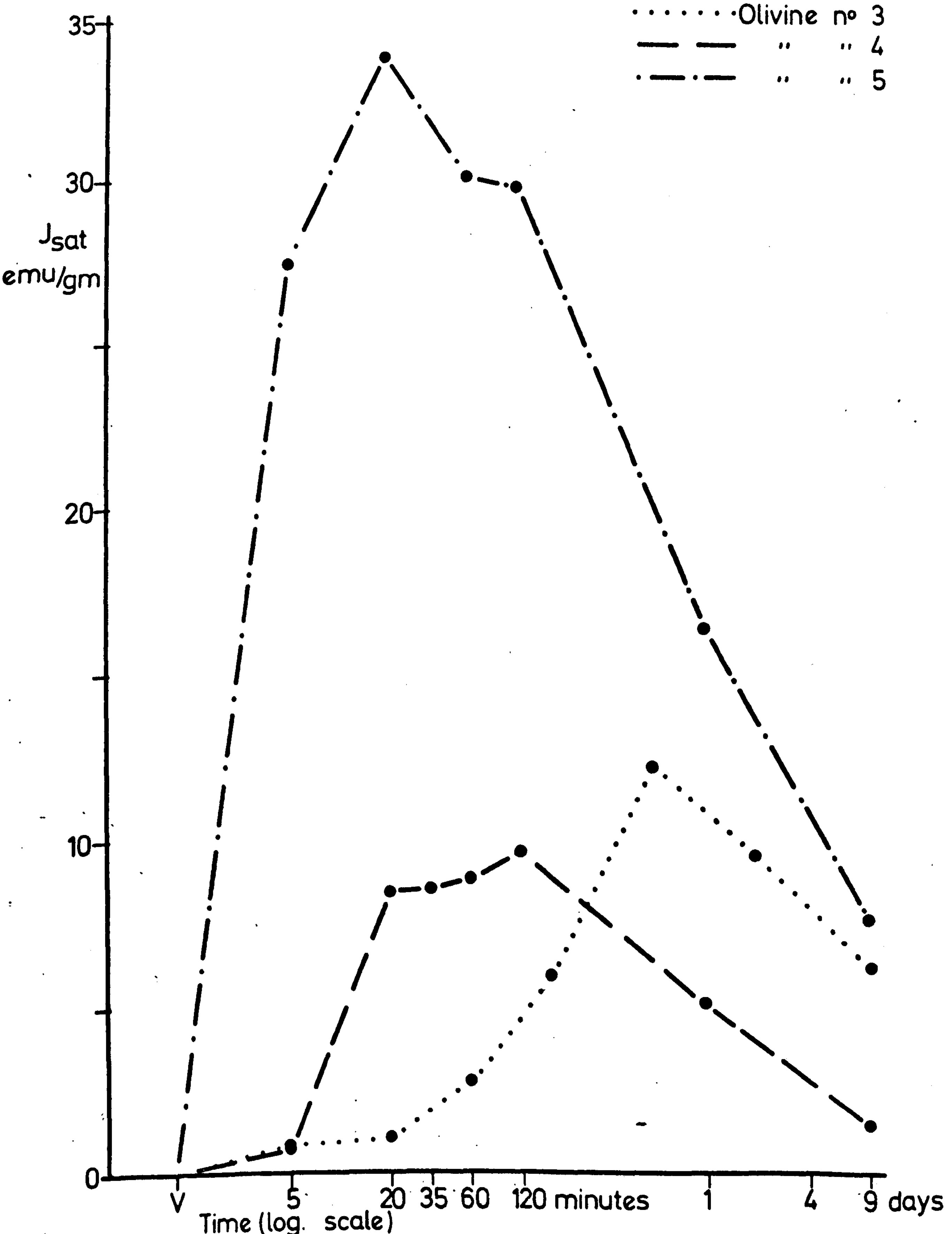


Fig. 6.3 Saturation magnetization against time heated at 850° C in air

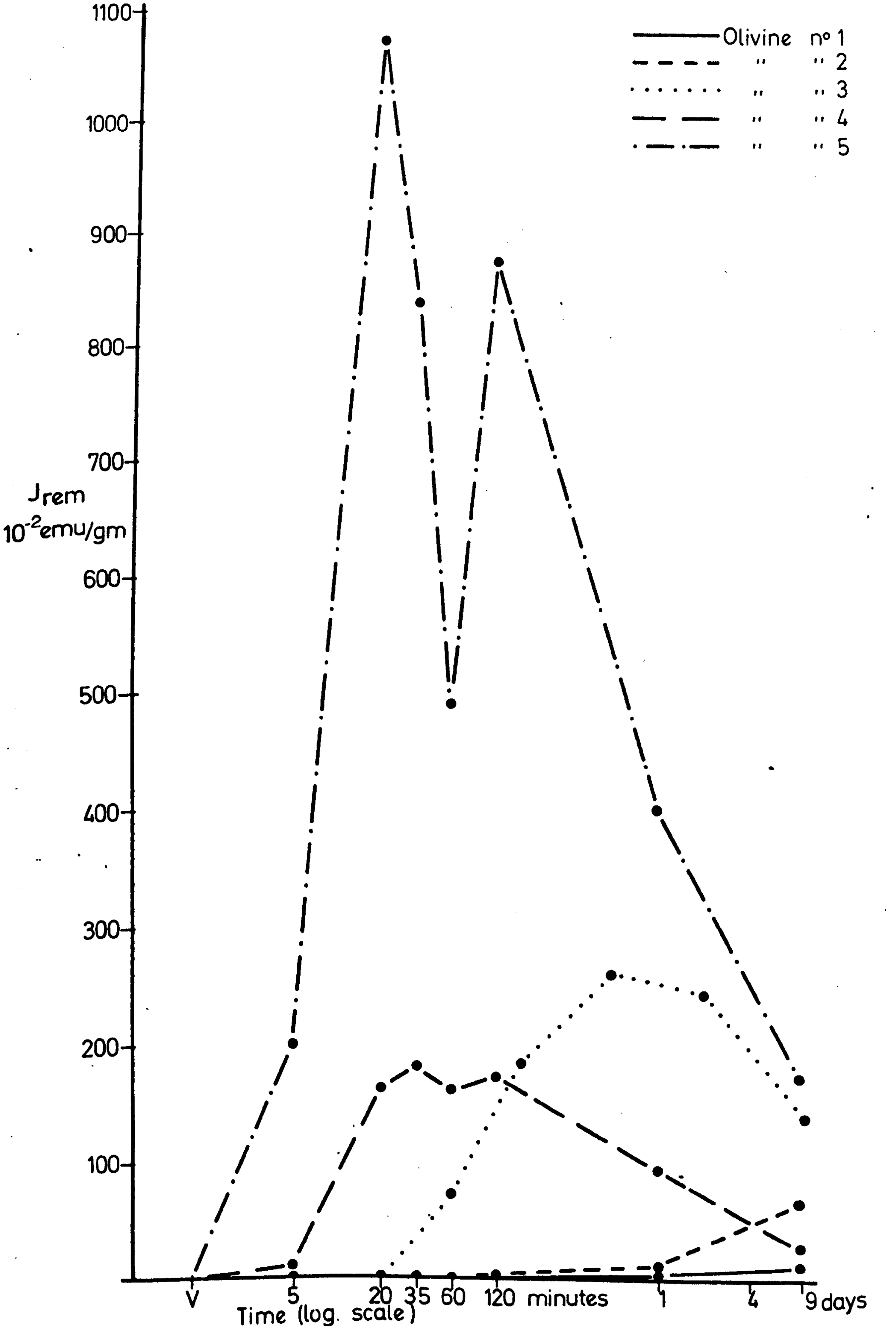


Fig. 6.4 Saturation remanence against time heated at 850°C in air

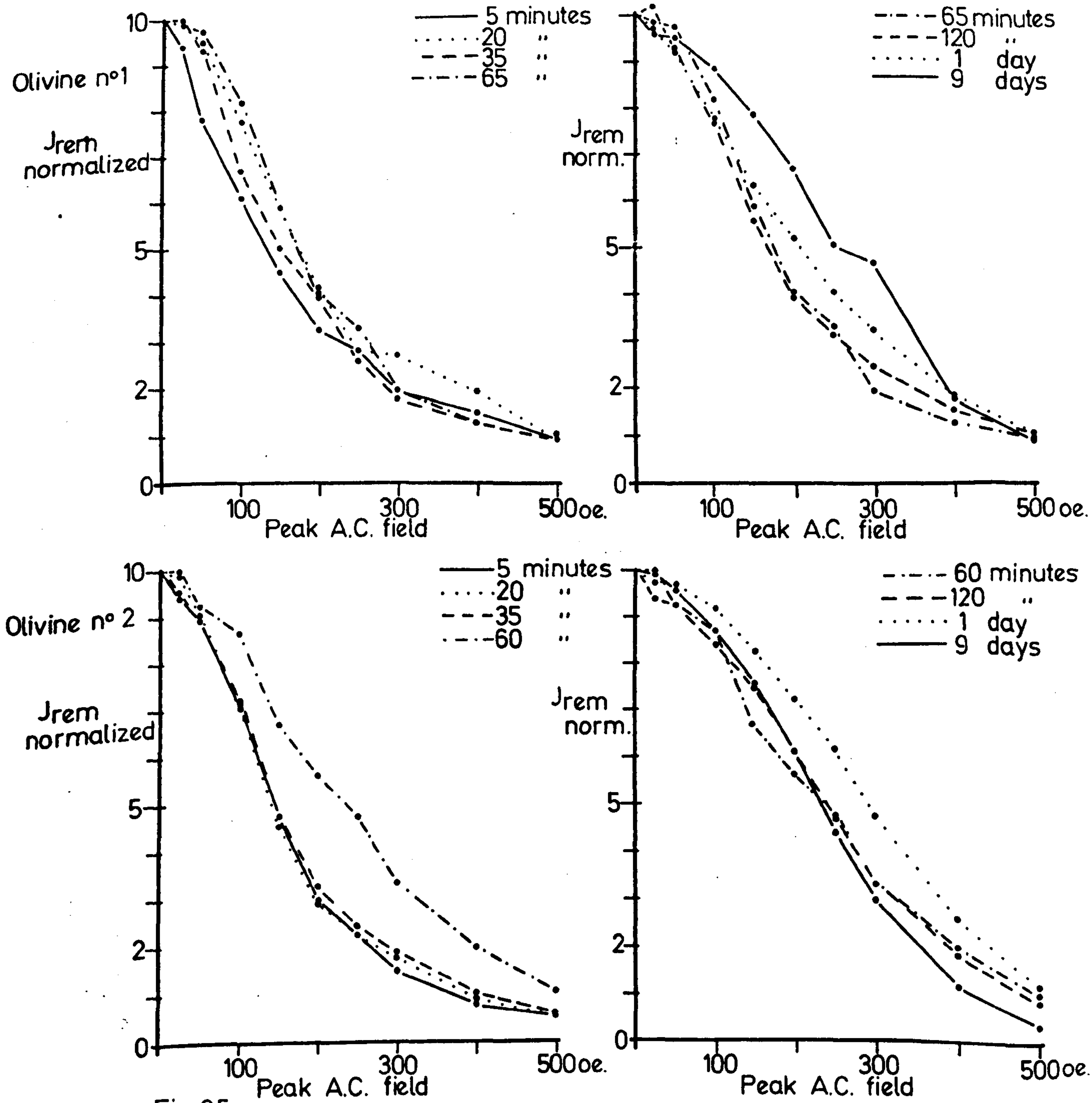


Fig. 6.5 A.C. demagnetization of saturation remanence for Olivine n° 1 and 2 after heat treatment at 850° C in air

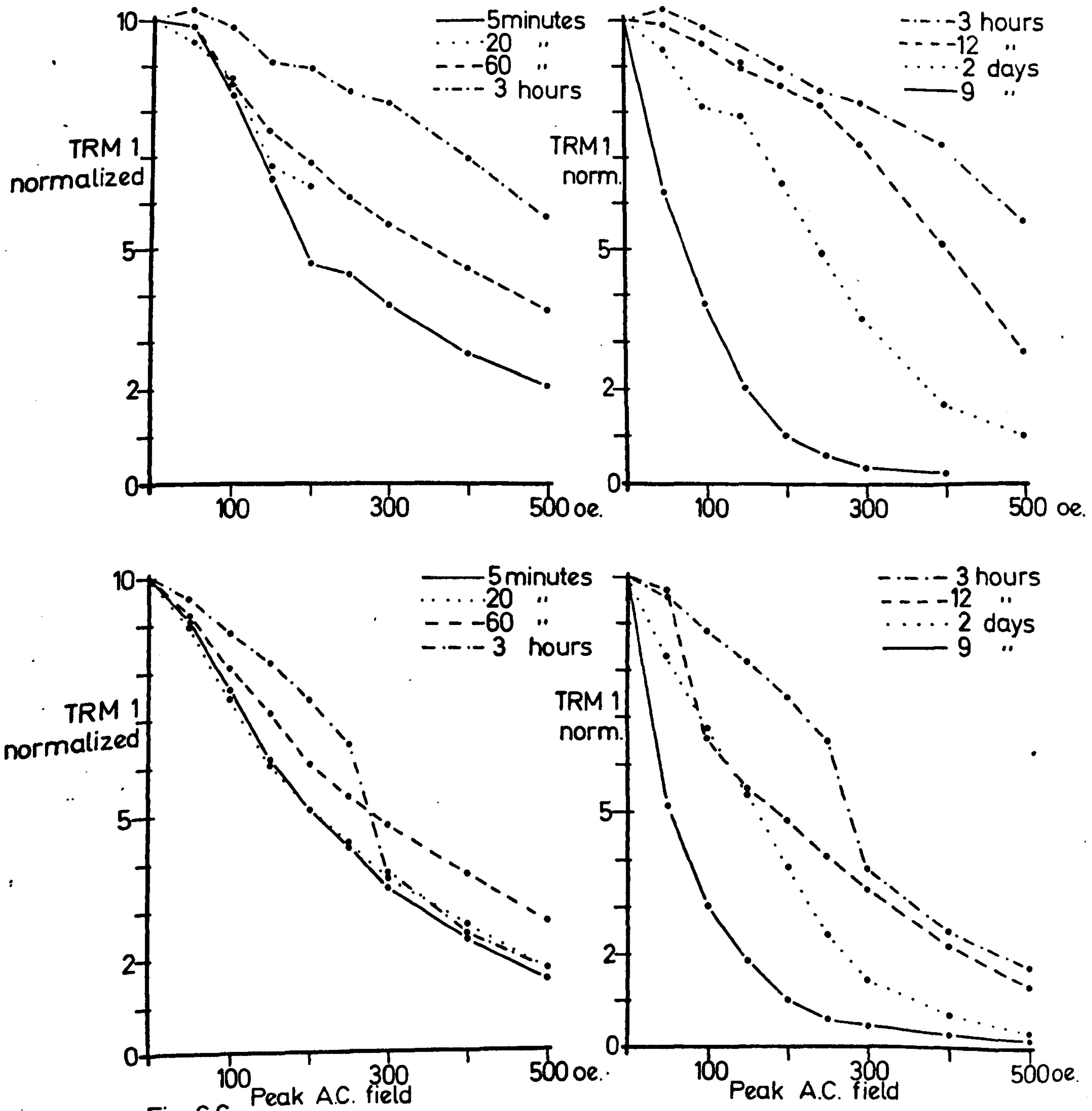


Fig. 6.6 A.C. demagnegzation curves of quenced thermoremanence and saturation remanence for sample 3 after heat treatments at 850°C in air

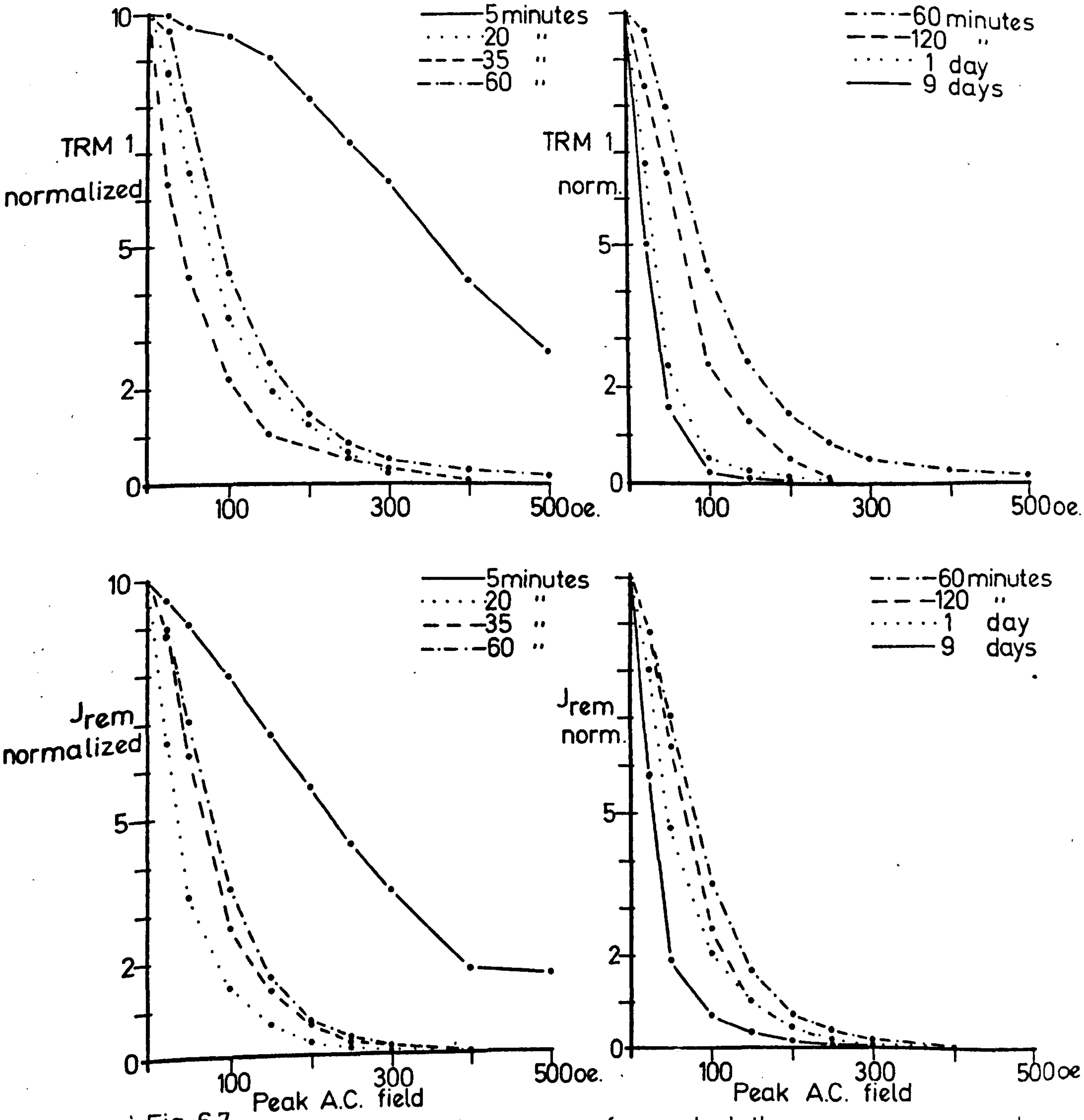


Fig. 6.7 A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 4 after heat treatment at 850°C in air

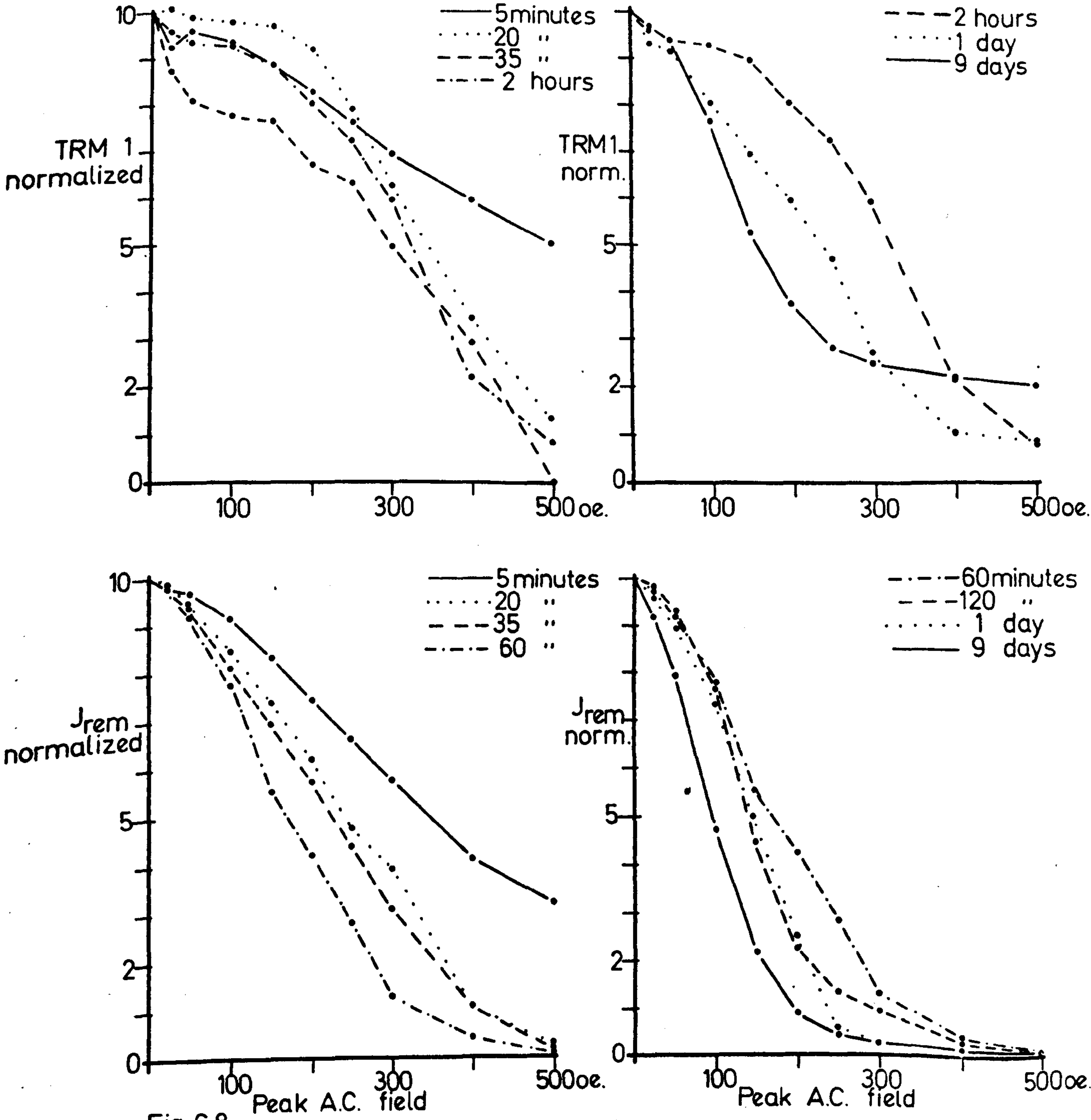


Fig. 6.8 A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 5 after heat treatment at 850°C in air

CHAPTER 7

FURTHER HEATING EXPERIMENTS ON LOW IRON CONTENT OLIVINES

7.1 Introduction

Two further series of experiments were carried out both using only samples 1 and 2. Samples 1 and 2 were the low iron content olivines. These olivine compositions, 5% and 14% Fa, are commonly found in the basaltic samples of use in paleomagnetism. As it was the consequences to paleomagnetism of the alteration of olivine which was being examined, it was decided to concentrate further work on these two samples.

The first series of heatings was at 1100°C in air. This temperature was the upper limit for this technique, for two reasons. The furnace, used in these experiments, burnt out in a very short period, if it was used above this temperature. At 1100°C, it had to be rebuilt after this series of experiments. Above this temperature, reaction with the quartz sample holder could be expected to occur. It was possible that certain reaction between the sample and holder occurred even at this temperature, 1100°C, but no visible evidence of this reaction was found.

The second series of experiments was at 1000°C but in an atmosphere saturated with water vapour. Water vapour is of importance as during the cooling of a rock, the water may be the primary or the only source of oxygen, for the alteration of olivine. As has been previously described, Chapter 4, the furnace was simply saturated with water vapour.

7.2 The Results of Heatings to 1100°C in Air

7.2.1 Magnetic Results

The thermoremanence acquired on quenching showed a steady rise in both samples throughout the heating (Fig. 7.1). If compared to the results acquired on heating at 1000°C in air, the final TRM 1 was approximately twice as great, when heated to 1100°C. The thermoremanence acquired on slowly cooling (TRM 2) of the samples followed a very similar pattern to TRM 1, again being approximately twice that acquired at 1000°C (Fig. 7.2). TRM 2 showed the increase in magnitude over TRM 1 due to the slower cooling. The ratio of TRM 2 : TRM 1 was between 1.6 and 2.1 for sample 2 and between 1.75 and 2.1 for sample 1.

The Curie points of the samples showed the expected fall. Sample 1 showed an initial fall to 490°C but then the Curie point remained fairly steady for the remainder of the heatings (Fig. 7.3). Sample 2 began at 560°C and decreased during the heating until after nine days heating had a Curie point of 460°C (Fig. 7.4).

As was found previously the saturation magnetization and saturation remanence have similar development (Figs. 7.5, 7.6). Sample 1 had a similar rise in both quantities. After nine days heating the magnitude of the saturation remanence was very close to that acquired when heated to 1000°C. Sample 2 showed a much more interesting development. After being heated for two days these quantities decreased.

Sample 1 showed an initial hardening to A.C. demagnetization (Fig. 7.7). But after twenty minutes heating the magnetizations began to soften. Sample 2 began after five minutes heating with hard magnetizations (Fig. 7.8). There was, on further heating, a rapid softening of magnetizations.

These results showed that after heating to 1100°C, the alteration of olivine produced magnetic effects similar to those results acquired after heating to 1000°C. The consequence of heating to a higher temperature was to increase the speed of the alteration. Just as when the samples 3 and 4 were heated to 850°C, differences between thermoremanence and saturation magnetization were apparent. For sample 2, the saturation magnetization decreased after two days heating but the thermoremanence rose throughout the heatings.

7.2.2 Optical Results

Both samples showed similar development when the alteration was viewed in polished section. Within a sample, there was often differences in the alteration. In a crystal, there were regions of different density and type of alteration. The average overall characteristics of the samples could be examined.

After twenty minutes heating sample 1 had thin blobs of green sponge-like alteration about the edges of the sample. Towards the centre of the sample, thin bands of the alteration could be seen (P. 7.1). After sixty minutes heating the alteration had grown in density and size. The bands of alteration were often aligned within one region of the sample (P. 7.2). On further heating the opaque material within the alteration grew in size and the bands of alteration became more disorganized (P. 7.3). After two days heating the edges of the sample were reddened. Within the sample there were two distinct areas and types of alteration. There were areas where the alteration had formed bands and other areas where the alteration was in irregular shaped blobs. There were definite boundaries between these areas (P. 7.4). After nine days heating both types of alteration were still visible but both had grown in size. The opaque material within the alteration was now clearly visible in the form of irregular shapes. When these shapes were elongated, there was a direction of alignment of the opaque grains (P. 7.5, 7.6). The reddening had spread into the crystal but all the sample was not reddening. In some places the edges of the sample had a rim of opaque material.

Sample 2 followed a very similar sequence of alteration. Again within a crystal, there was much variation in density and type of alteration. After nine days the sample was very similar to that for sample 1 but the opaque material was generally not as large within the alteration (P. 7.7).

The alteration was started with the formation of the green sponge-like material. The opaque material within this alteration grew throughout the heating and the alteration was gradually turned red from the edges inwards. This alteration did not divide very easily into the two distinct stages. The opaque material was much larger than before without the complete reddening of the sample.

7.2.3 X-ray Powder Photograph Results

As with previous heating X-ray powder photographs were taken of the samples after nine days heating and compared with photographs of the original olivine. Sample 1 showed the original olivine with additional lines. These lines fitted the hypersthene pattern. Sample 2 showed the original olivine but with many additional lines. These lines were fitted to three patterns, hematite, hypersthene and magnesioferrite. No more than precise identification of the minerals present could be obtained from these photographs.

7.2.4 Discussion of Results

These results follow the sequence of the series of heatings to 1000°C in air except that the higher temperature used has speeded the alteration. In sample 2, the alteration had progressed, after nine days, to the alteration of the magnesioferrite to hematite. The production of the hematite led to the decrease in saturation magnetization. The explanation of the continued rise of the thermoremanence is as before. The remaining ferrite of the original alteration is magnetically softer, from the A.C. demagnetization curves, and so acquires a relatively greater thermoremanence. Optically both samples appear highly altered after nine days. There is much opaque material present. However, the X-ray photographs show only olivine and hypersthene. The large amount of opaque material produced does not effect the lineation of the alteration, showing the continued effect of the original olivine crystal structure.

7.3 The Results of Heatings to 1000°C in Water Vapour

7.3.1 Magnetic Results

Both samples showed a steady rise in thermoremanence either acquired on quenching or by slowly cooling (Figs. 7.1, 7.2). After nine days heating there was an increase of 50 - 100% over the thermoremanence acquired on similar heating in air. The thermoremances for both samples were very close together throughout the entire period of heating, unlike the other heating experiments, when sample 2 had a greater thermoremanence after the same period of heating. In neither of the thermoremanences was there any indication of a maximum value being attained.

The Curie point of sample 1 was stable about 520°C after it had been heated for five minutes, until it had been heated for nine days when it fell to 480°C (Fig. 7.3). Sample 2 began with a higher Curie point, 560°C, but after heating for one hour showed a steady decrease to 490°C after nine days (Fig. 7.4).

The saturation magnetization development showed a steady rise (Fig. 7.5). The olivine samplos had similar magnetizations with sample 1 having a slightly greater magnitude for most of the heatings. The saturation remanence showed a similar progression of a steady rise but sample 1, the lower iron content olivine, was clearly more magnetic than sample 2 throughout (Fig. 7.6).

Sample 1 became magnetically harder to A.C. demagnetization until heated for one hour when on further heating it showed a rapid softening (Fig. 7.9). Sample 2 did not clearly show the initial hardening but after twenty-five minutes it slowly became softer (Fig. 7.10).

No indication of a two stage alteration process is evident in these results. The magnetizations become both magnetically stronger and softer with heating. The Curie points show a decrease but without a second Curie point appearing. The foremost difference with these results from other results of other heatings is the relative strength of sample 1 compared to sample 2. Throughout the heatings sample 1 is as strong as or even stronger than sample 2.

7.3.2 Optical Results

The alteration in sample 1 was the green sponge-like material in the form of fine lines around the edges of the sample. After further heating the lines of alteration broadened and spread into the sample. After one hour, the alteration had spread and in some areas it was in the form of elongated irregular shapes. The alteration formed with the longest dimensions having a preferred direction (P. 7.8). On further heating, the density and individual size of the alteration grew. The opaque material within the alteration became much denser (P. 7.9). The rim of the sample became reddened. The area of the alteration and the quantity of opaque material within the alteration grew with heating. The orientation of the opaque material and the general alteration was lost (P. 7.10, 7.11). After nine days, there was an opaque rim to the sample on some edges. Most of the sample was reddened. The opaque material had become as large, within the area of alteration, as seen in any other alteration. Some of the opaque grains were 5 μ across (P.7.12).

The alteration of sample 2 followed the same general trend. The opaque material within the alteration was not as well developed. More of the sample was reddened.

With this series of heatings the opaque material was as large as was formed in the high iron content samples heated at 1000°C in air. There is one important difference. With the other samples, the opaque material grew to comparable size after the samples were completely reddened. Also the opaque material and the red sponge-like alteration, which preceded it, filled the entire sample. With this series of heatings, the opaque material has only grown with the limits of the green alteration.

7.3.3 X-ray Powder Photograph Results

X-ray powder photographs of the samples after nine days heating were compared with photographs of the original olivine. Sample 1 showed the original olivine pattern with hypersthene and hematite like patterns. The hematite line was very faint. Sample 2 had a much more complicated pattern but again predominating was the original olivine line structure. The remaining lines indicated hypersthene, hematite and a ferrite were present, in the heated sample. A small amount of sample 2 was crushed and some material magnetically extracted, as previously described. The extracted material was used as a X-ray sample. The pattern of the extracted material was disappointingly similar to the pattern of the sample heated for nine days. However, closer examination showed that the lines of the pattern of the "nine day" photograph which were less intense in the extracted sample were the hematite lines and hematite would not have been extracted by the method used.

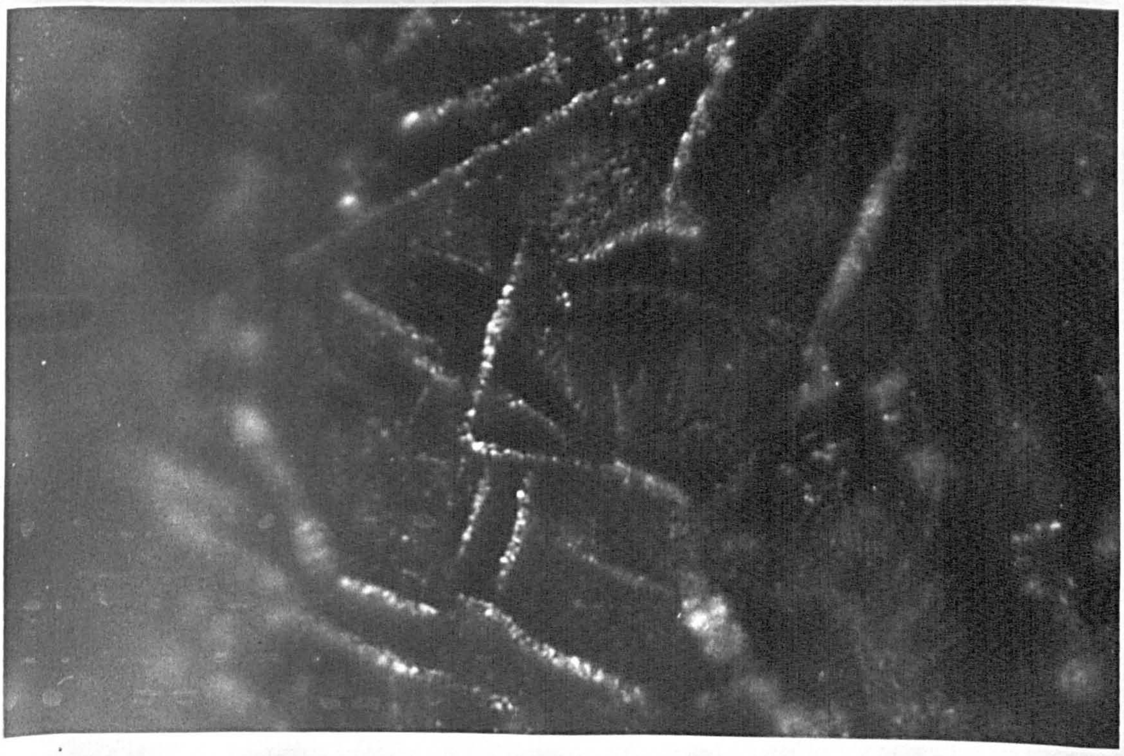
7.3.4 Discussion of the Results

These results do not show a distinct two-stage alteration process. The magnetic results show a continual alteration, producing increased magnetization. Optically, the green alteration is firstly formed but the reddening spreads evenly from the edges and the opaque material grows gradually from the alteration throughout the heating. The X-ray results show a conglomeration of the products proposed in other chapters as alteration products. It is possible that the water vapour allows both the stages to occur together much more readily than if the samples are heated in air. More probably the second stage of the alteration had started during the heating but the point for the completion of the initial alteration of the olivine had not been reached.

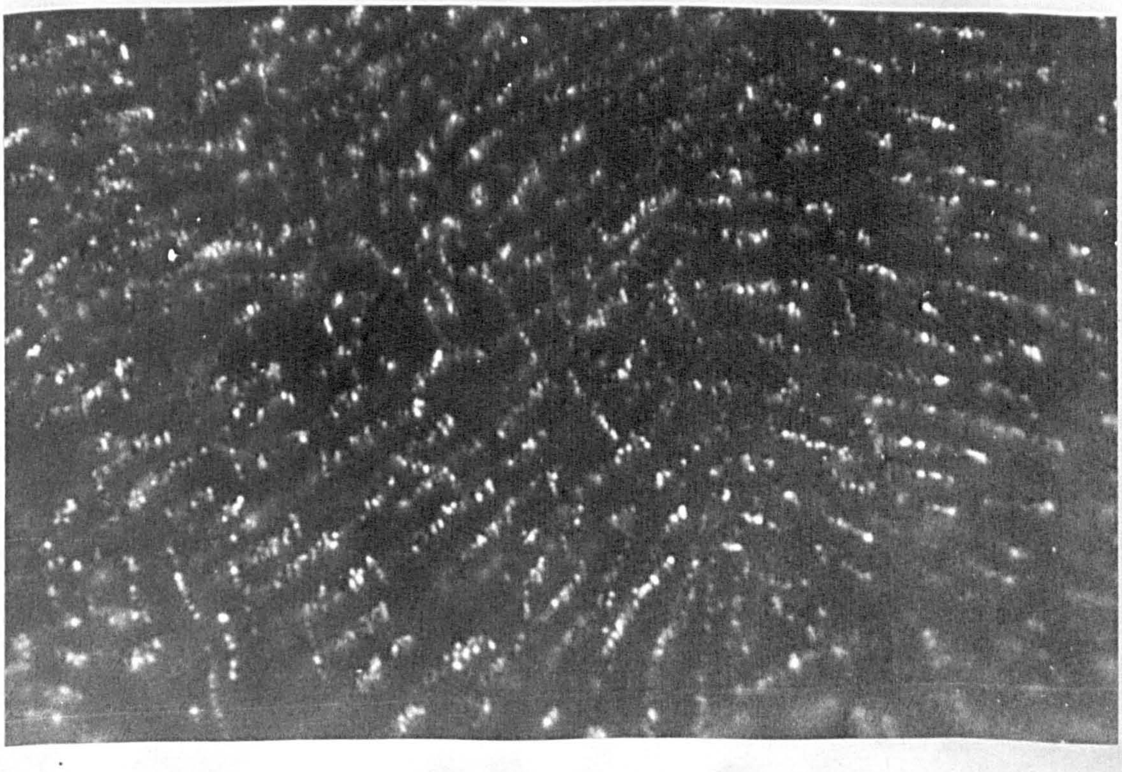
The presence of the water vapour has helped the formation of the opaque material without the reddened of the sample due to the formation of the hematite.

The X-ray results of the magnetic extraction of material from sample 2 would show one point clearly. The hematite when formed exists outside the original lattice. It is likely that the simple magnetic extraction did not separate the ferrite from the olivine and hypersthene because of crystallographic linkage of the three materials. This linkage is evident in the oriented growth of the alteration within the original olivine. This orientation is not only seen with the green sub-microscopic opaque alteration, but is evident in the reddened material and the microscopic opaque material.

SAMPLE 1 HEATED TO 1100°C IN AIR

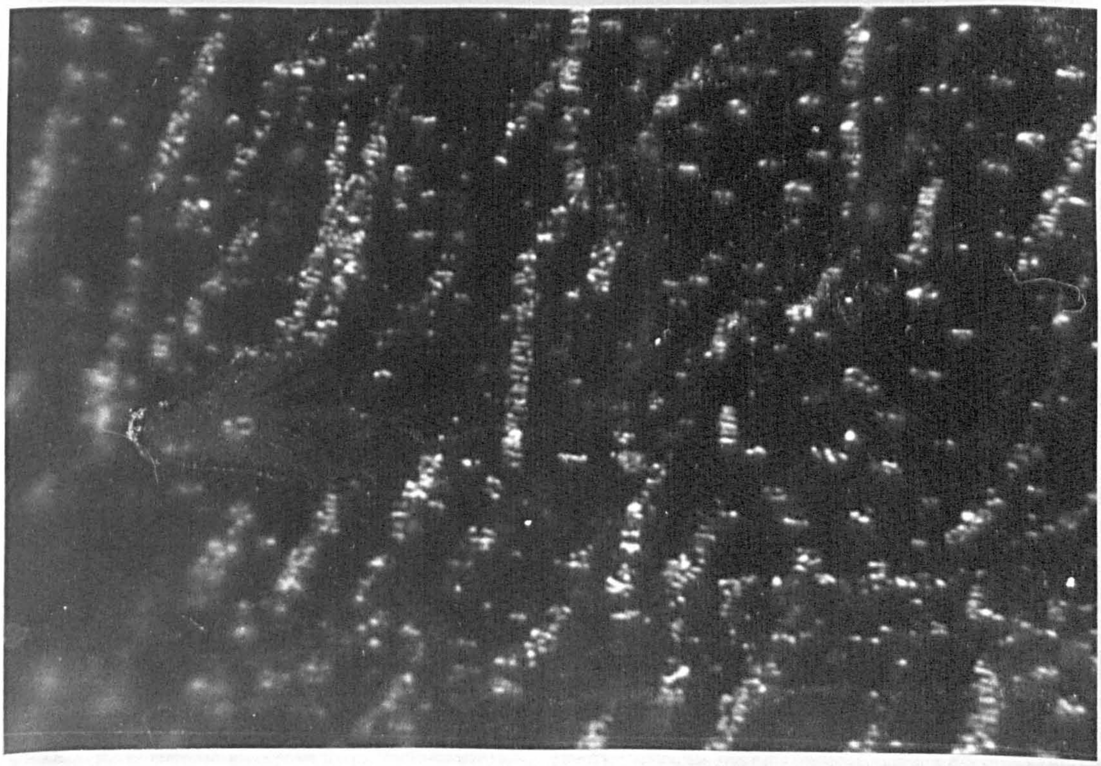


P. 7.1 after 20 minutes heating

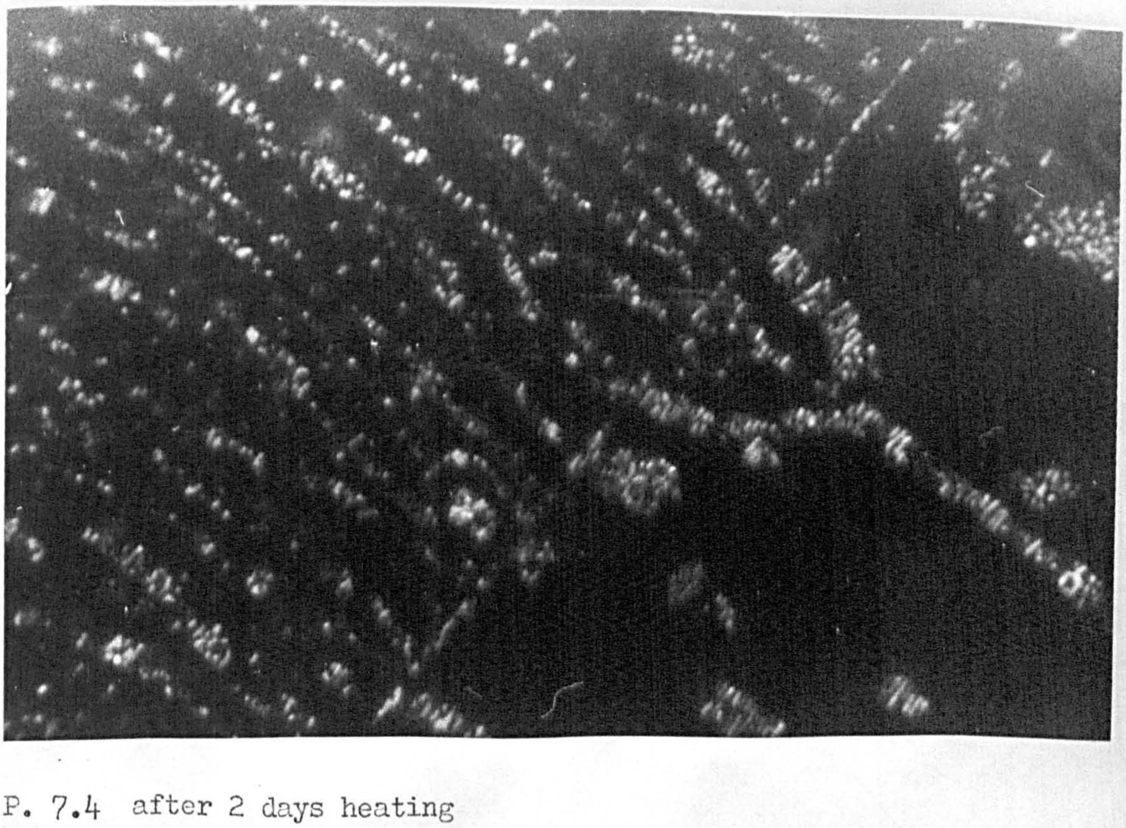


P. 7.2 after 60 minutes heating

SAMPLE 1 HEATED TO 1100°C IN AIR



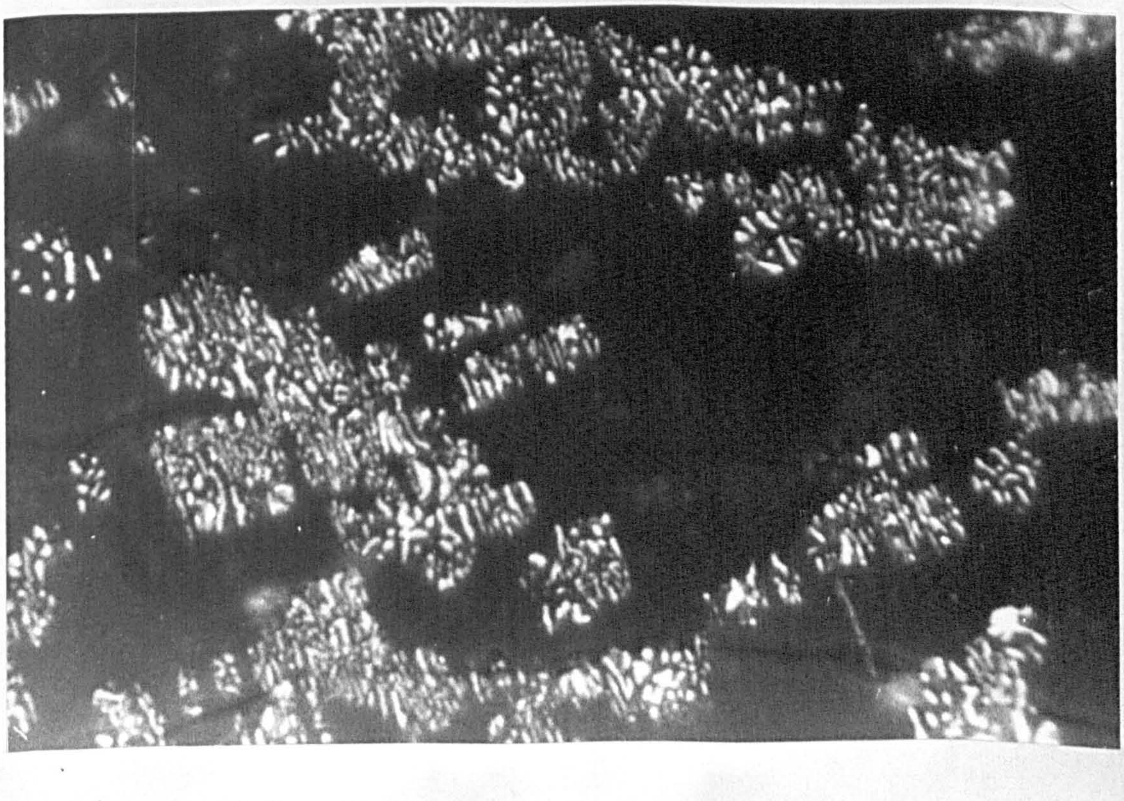
P. 7.3 after 3 hours heating



P. 7.4 after 2 days heating

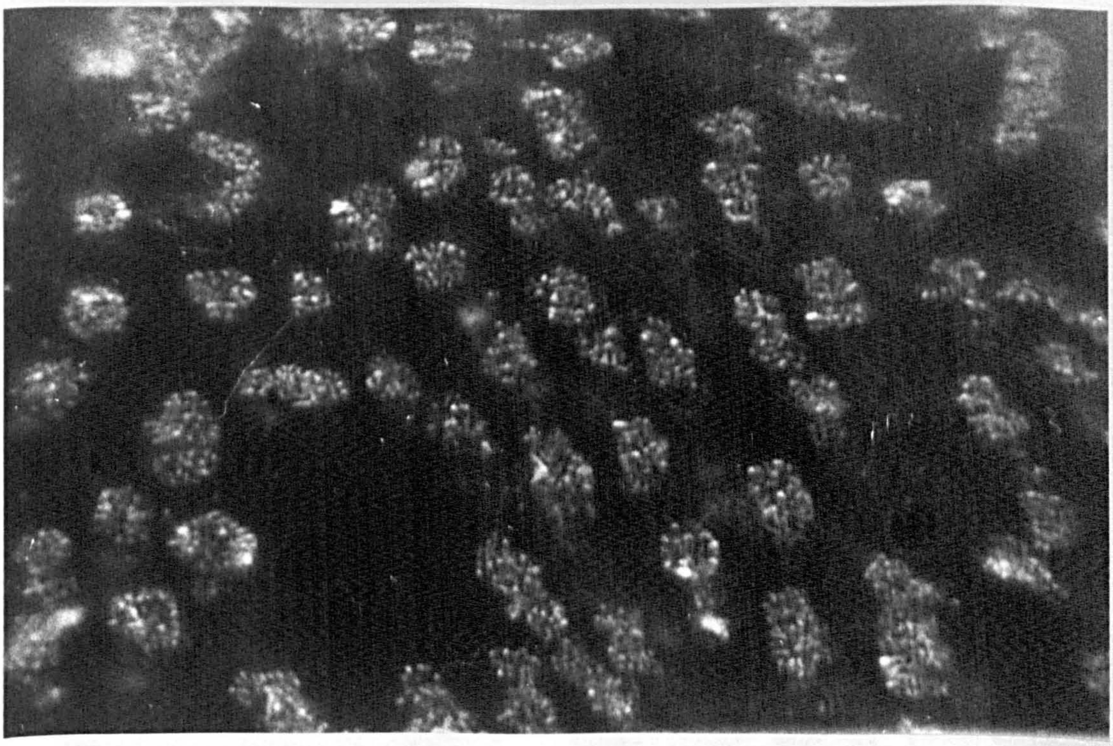
SAMPLE 1 HEATED TO 1100°C IN AIR

P. 7.5 after 9 days heating



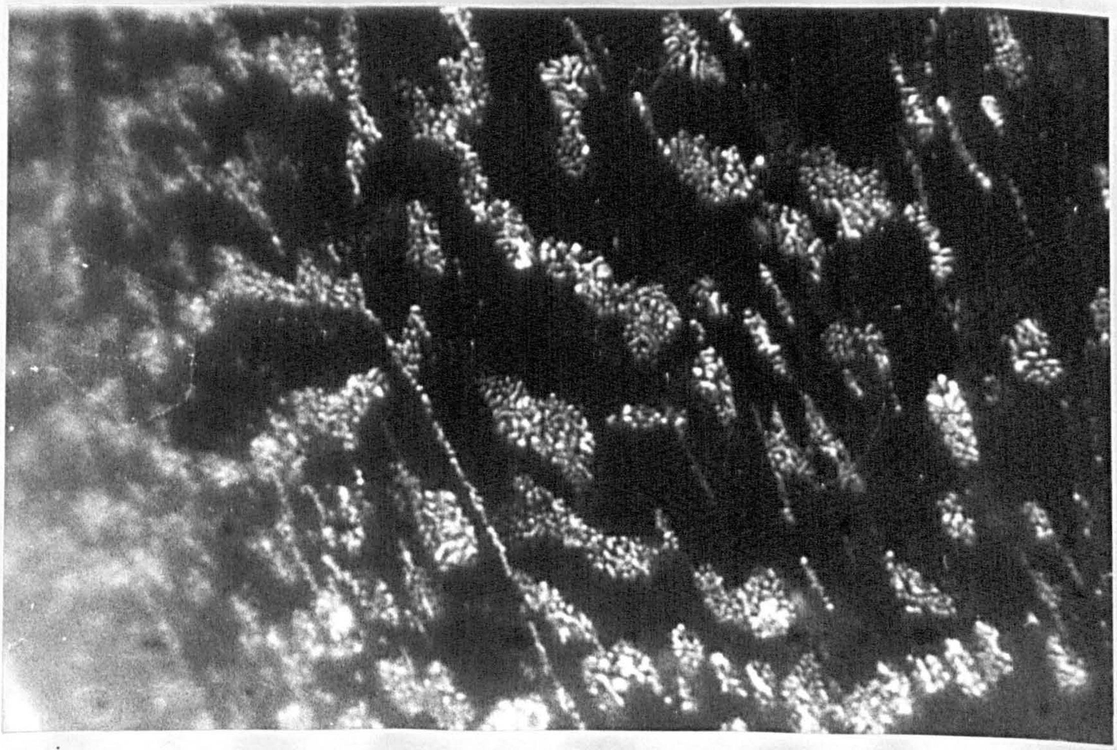
P. 7.6 after 9 days heating

SAMPLE 2 HEATED TO 1100°C IN AIR

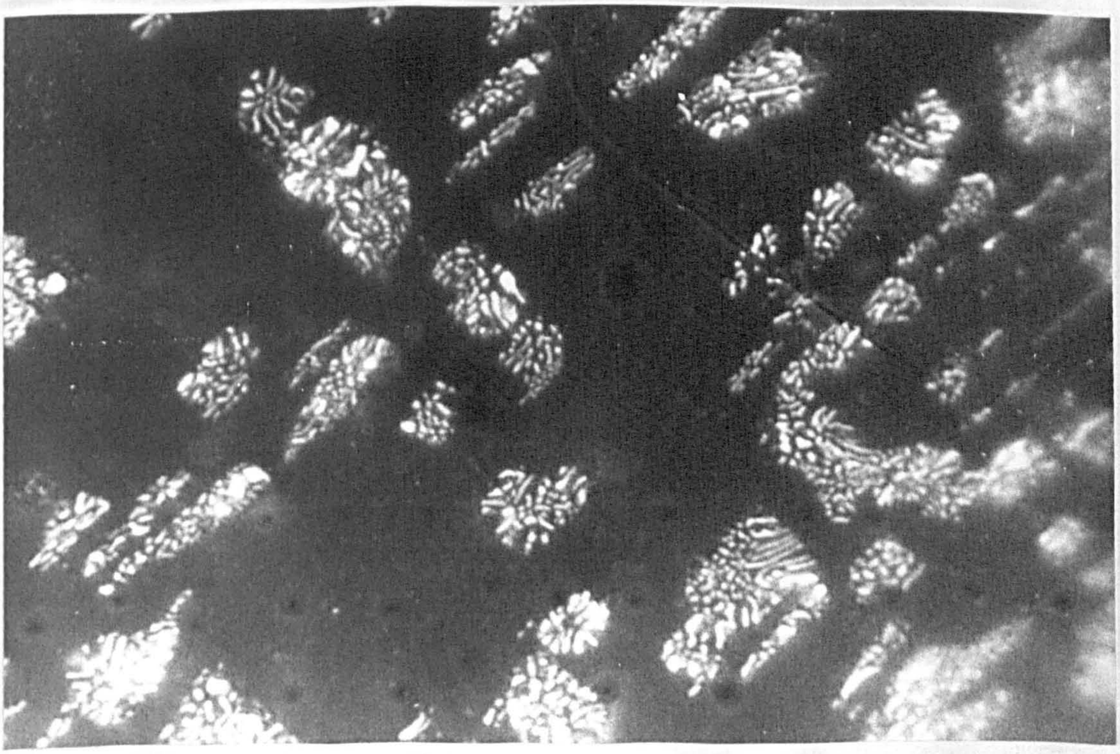


P. 7.7 after 9 days heating

SAMPLE 1 HEATED AT 1000°C IN WATER VAPOUR

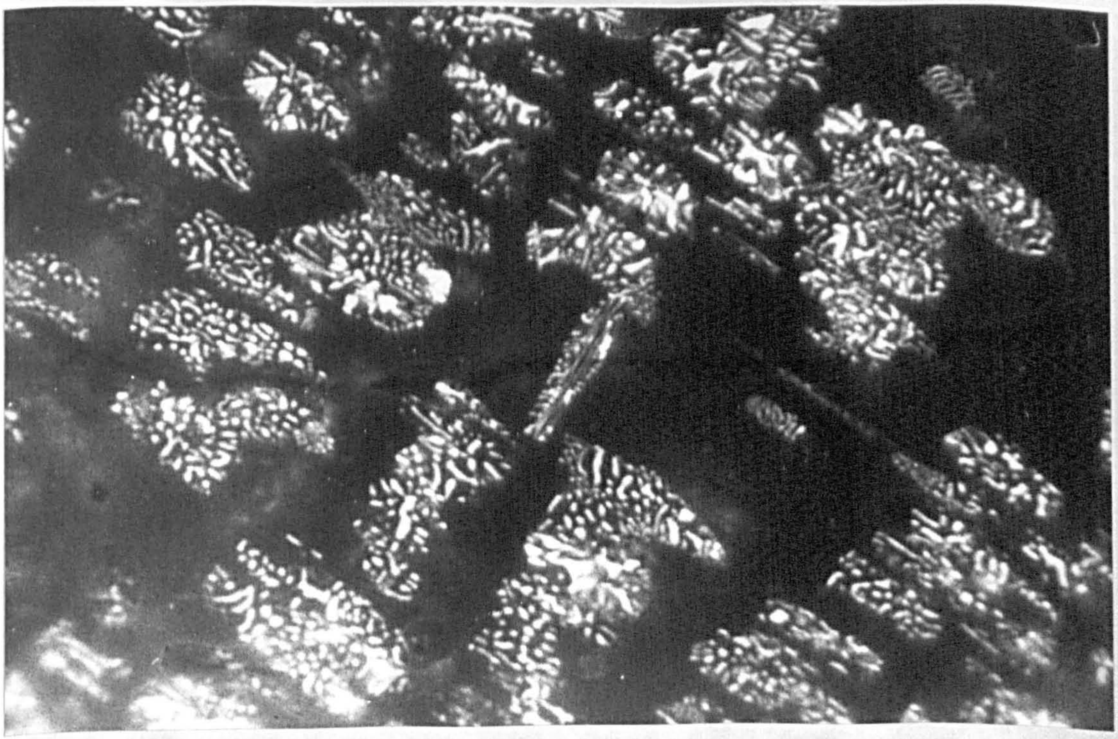


P. 7.8 after 60 minutes

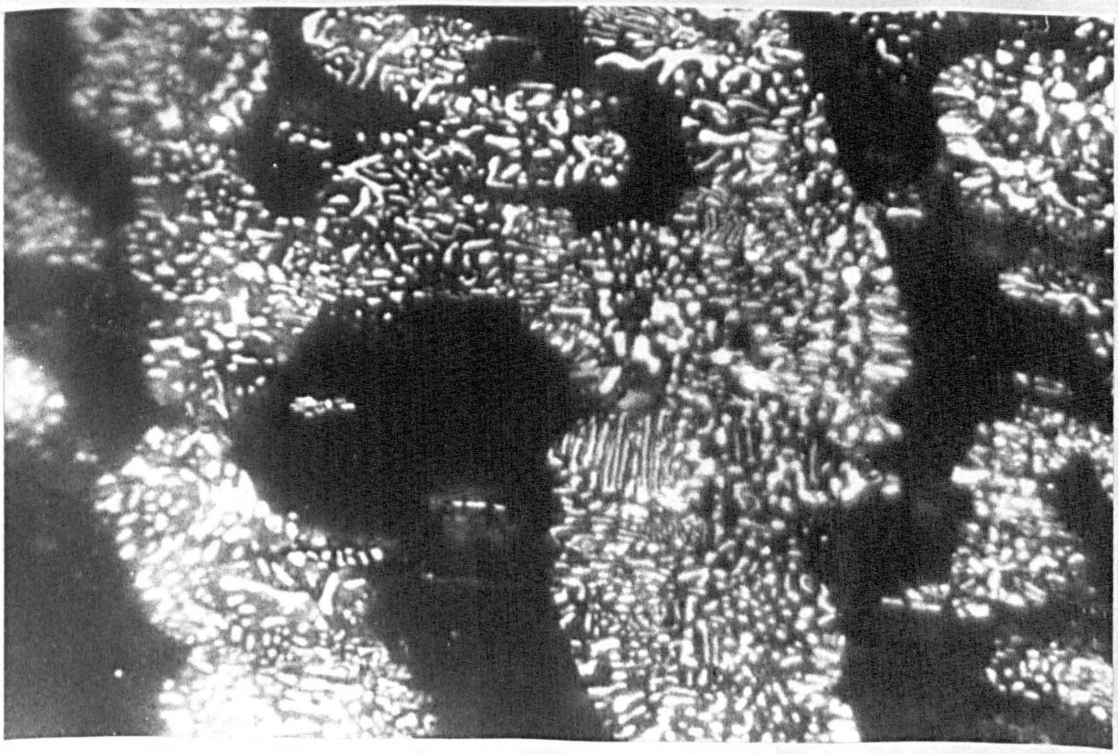


P. 7.9 after 3 hours

SAMPLE 1 HEATED TO 1000°C IN WATER VAPOUR

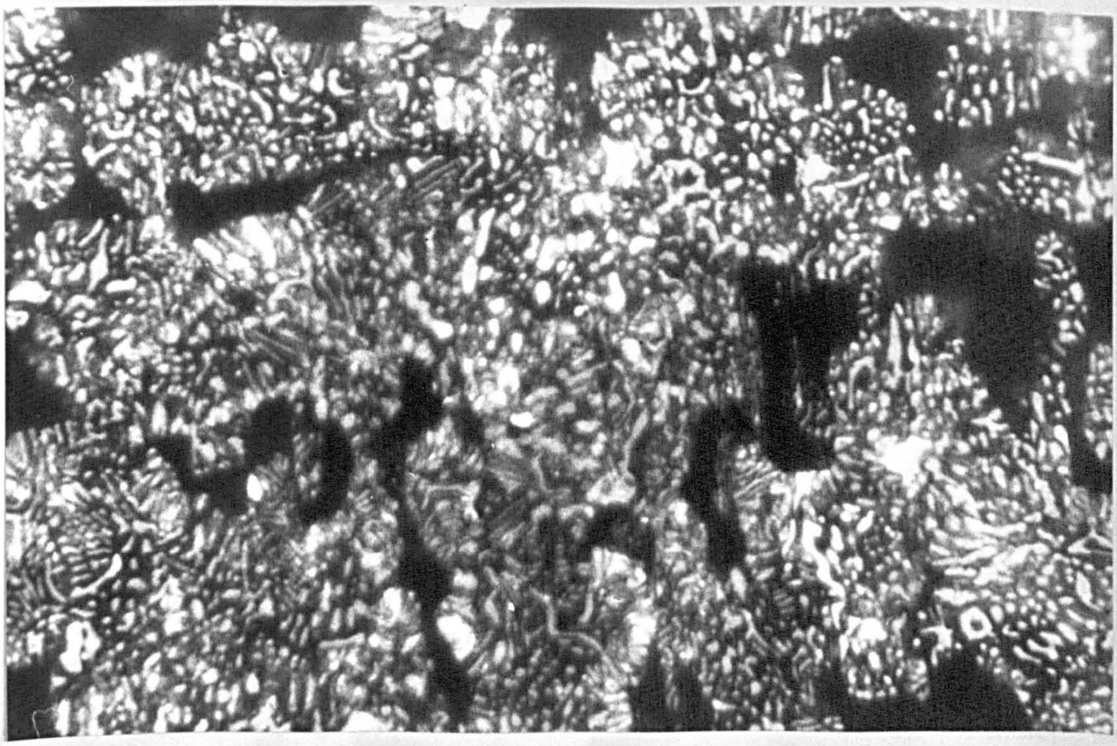


P. 7.10 after 12 hours heating



P. 7.11 after 2 days heating

SAMPLE 1 AFTER HEATING AT 1000°C IN WATER VAPOUR



P. 7.12 after heating for 9 days

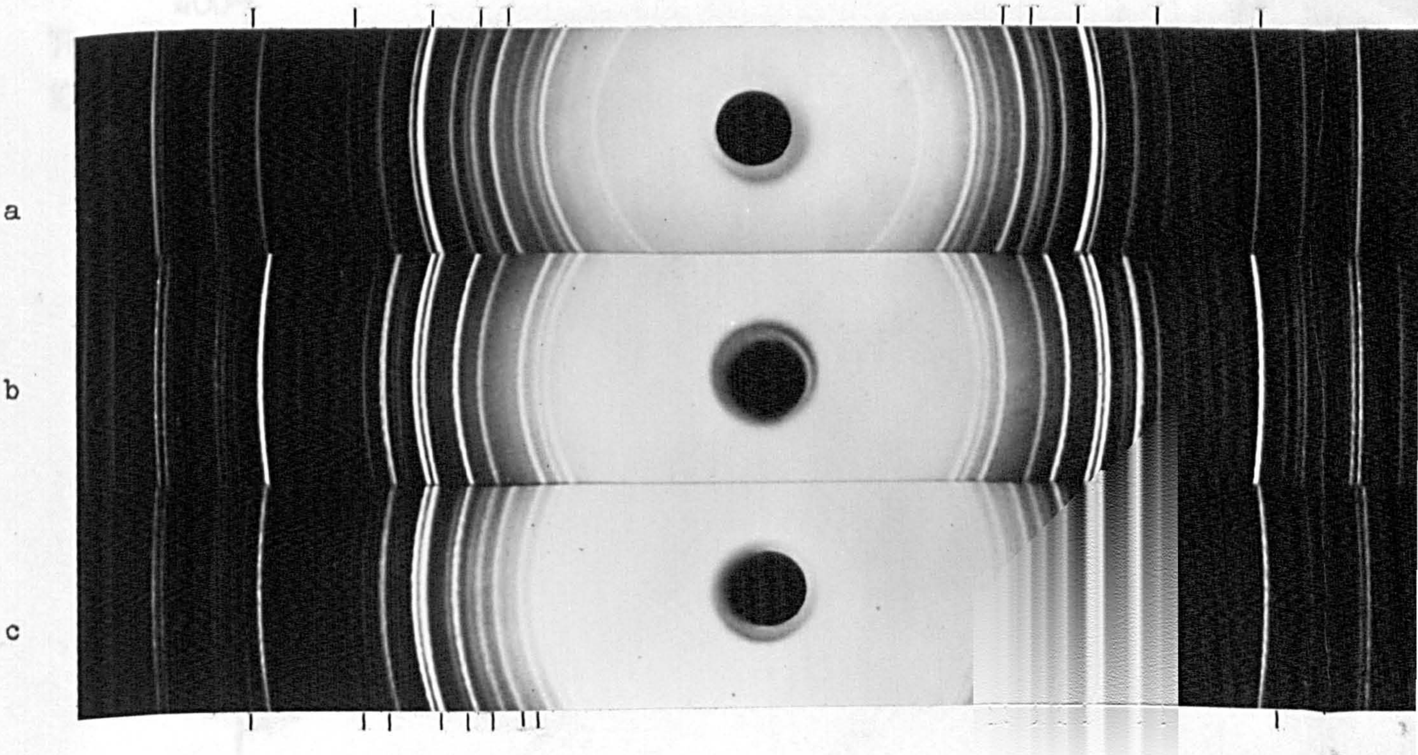
X-RAY POWDER PHOTOGRAPHS OF SAMPLE 2

(a) after 9 days heating at 1100°C in air

(b) natural sample

(c) after 9 days heating at 1000°C in water vapour

indicating lines due to alteration products



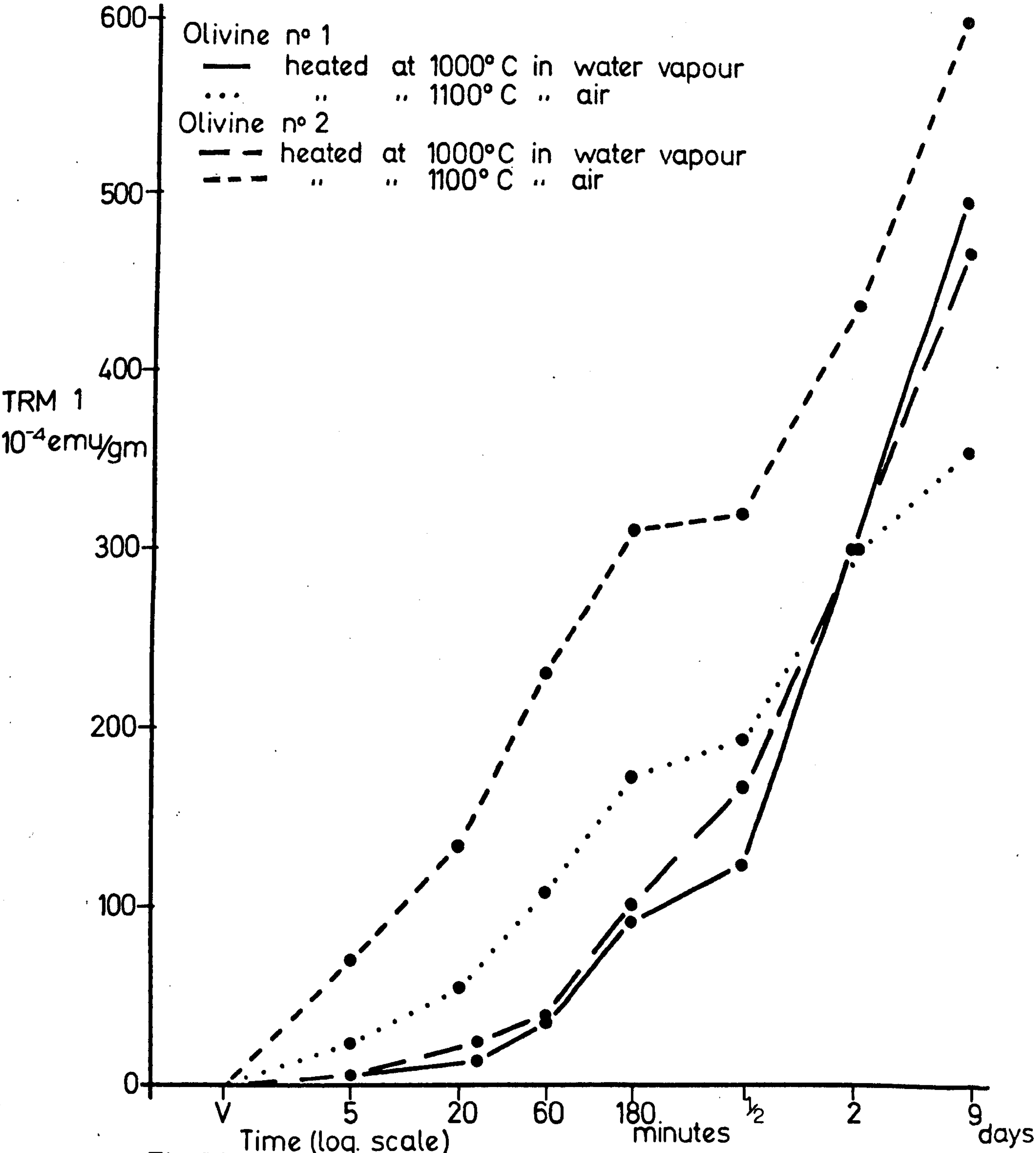


Fig. 7.1 Thermoremanence aquired on quenching against time heated

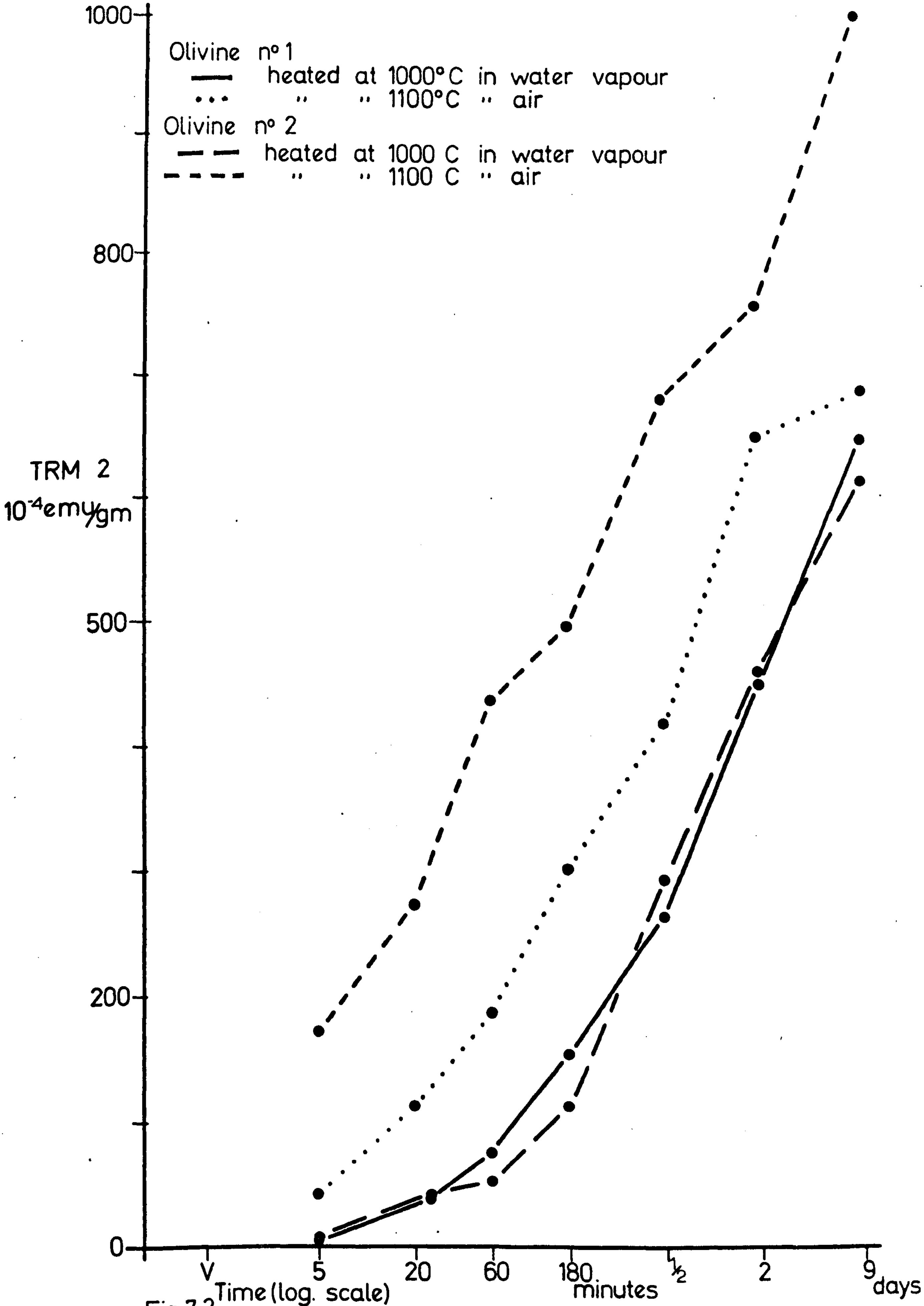
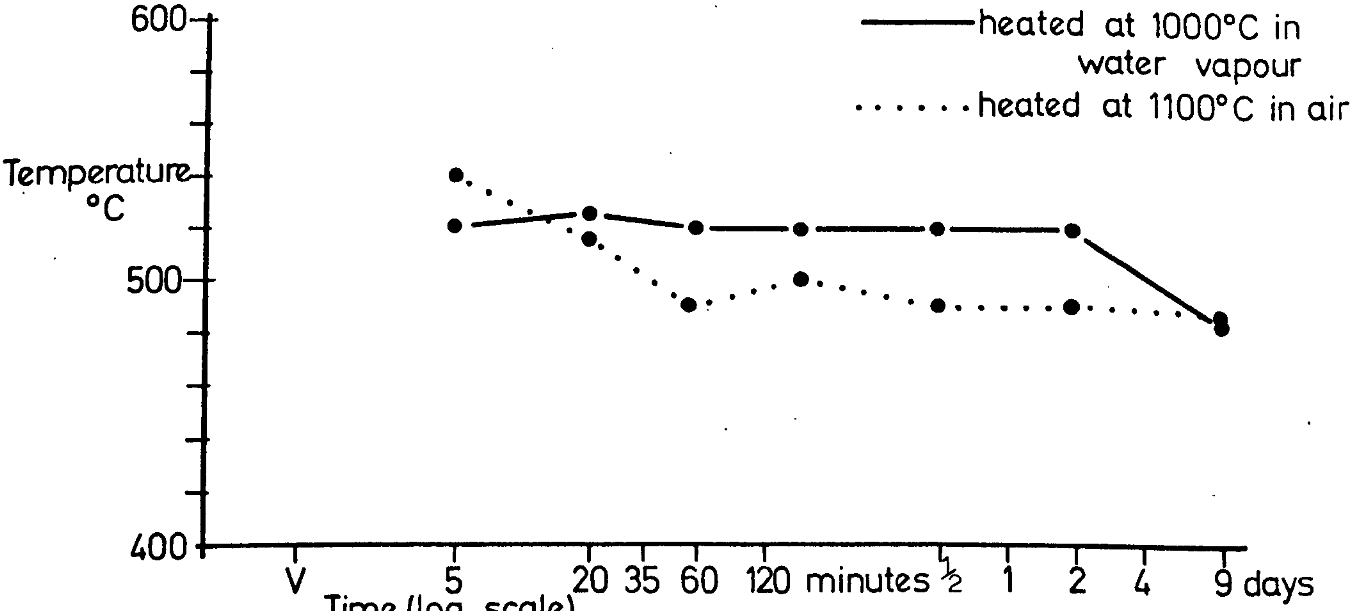
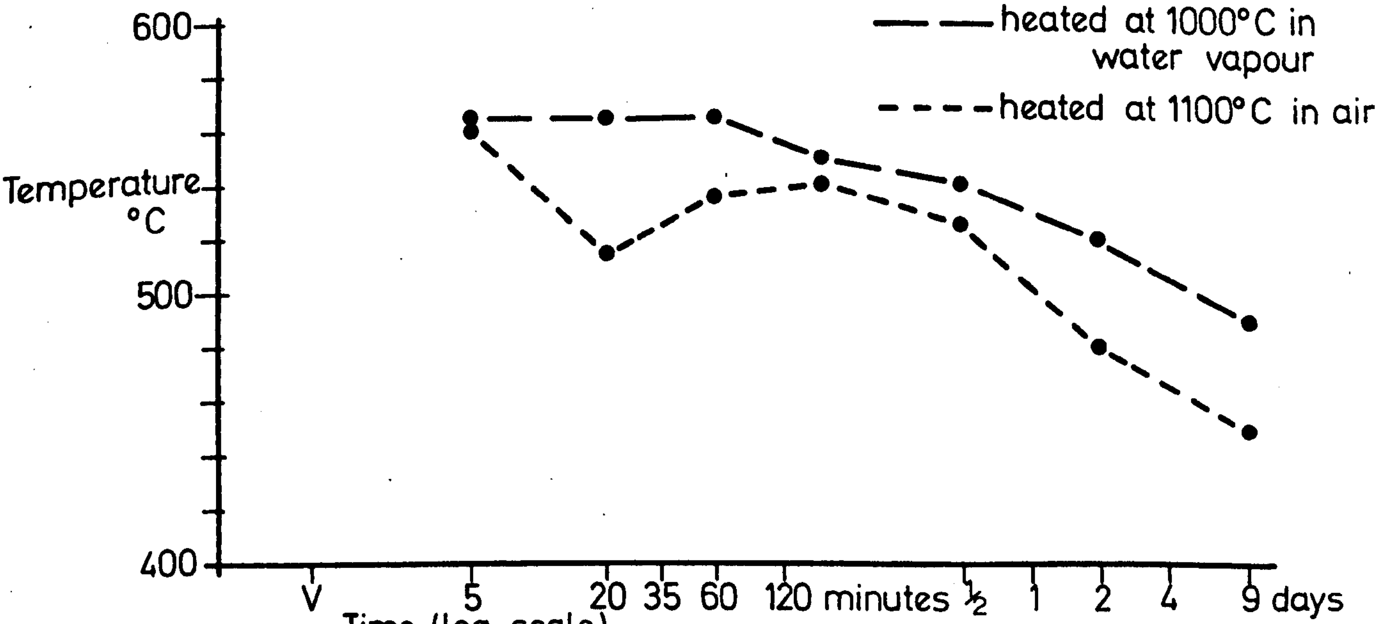


Fig. 7.2 Thermoremanence aquired on slow cooling against time heated



Time (log. scale)

Fig. 7.3 Curie point of Olivine nº 1 against time heated



Time (log. scale)

Fig. 7.4 Curie point of Olivine nº 2 against time heated

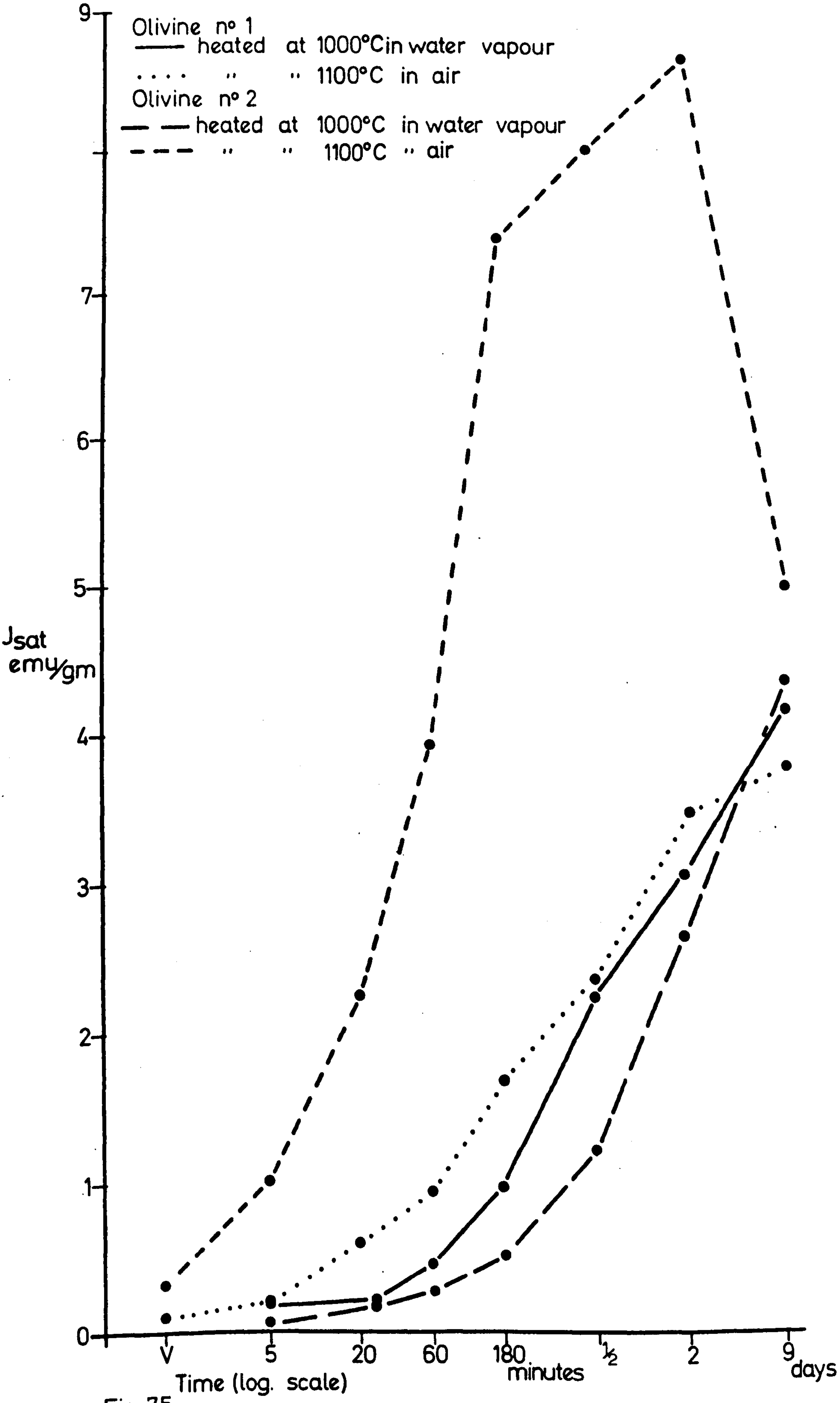


Fig. 7.5 Saturation magnetization against time heated

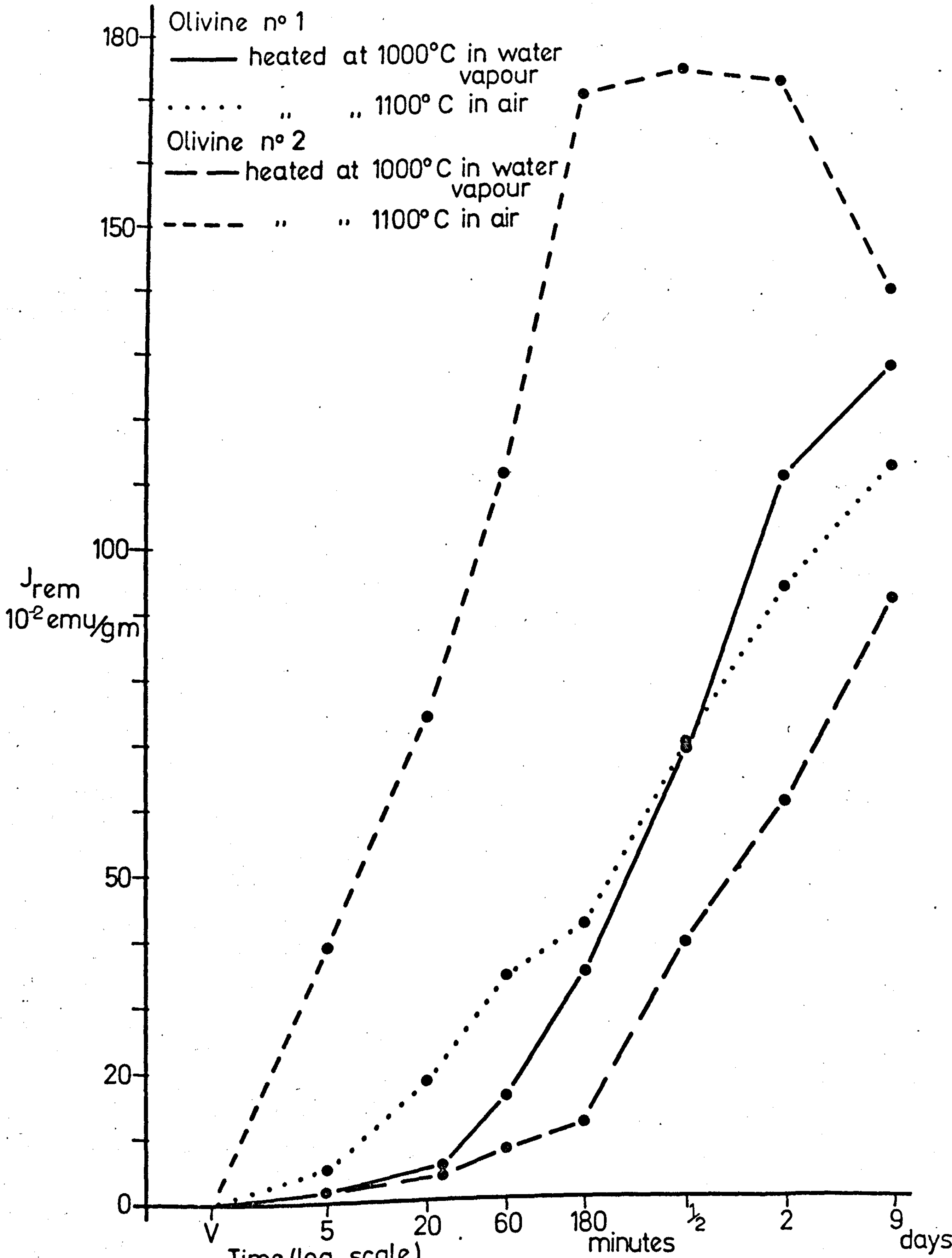


Fig. 7.6 Saturation remanence against time heated

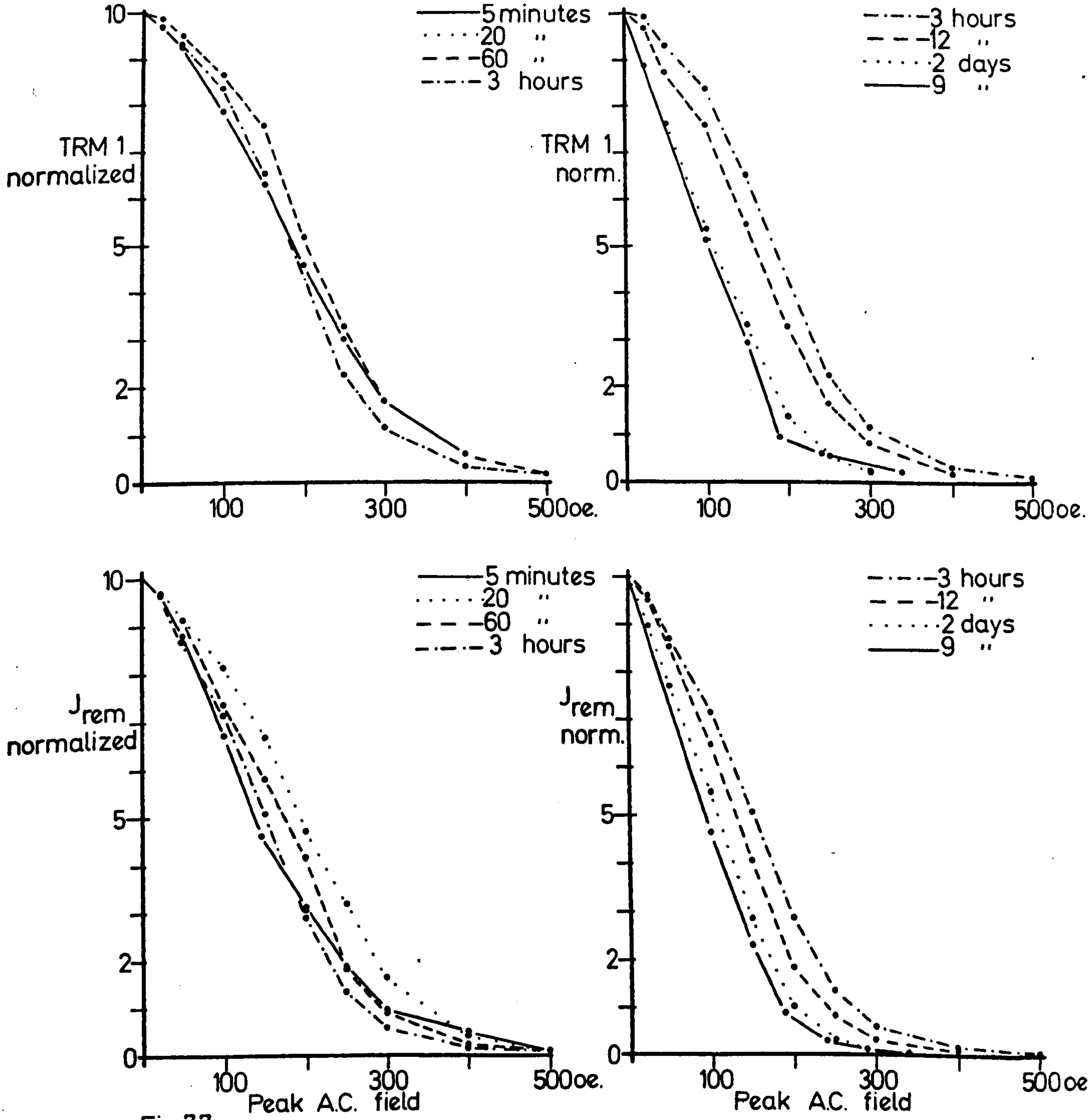


Fig. 7.7 A.C. demagnetion curves of quenched thermoremanence and saturation remanence for sample 1 after heat treatment at 1100°C in air

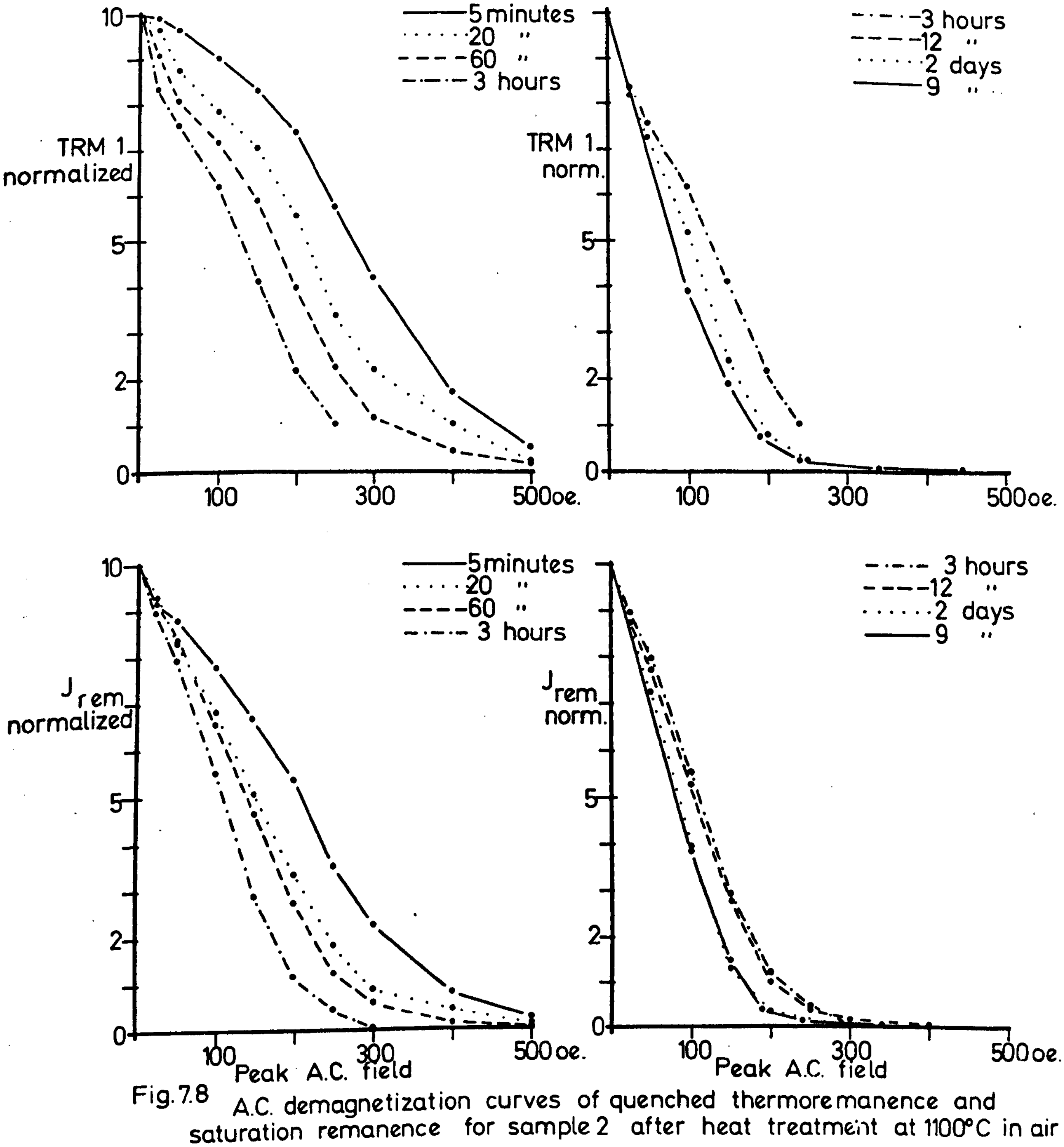


Fig. 7.8 A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 2 after heat treatment at 1100°C in air

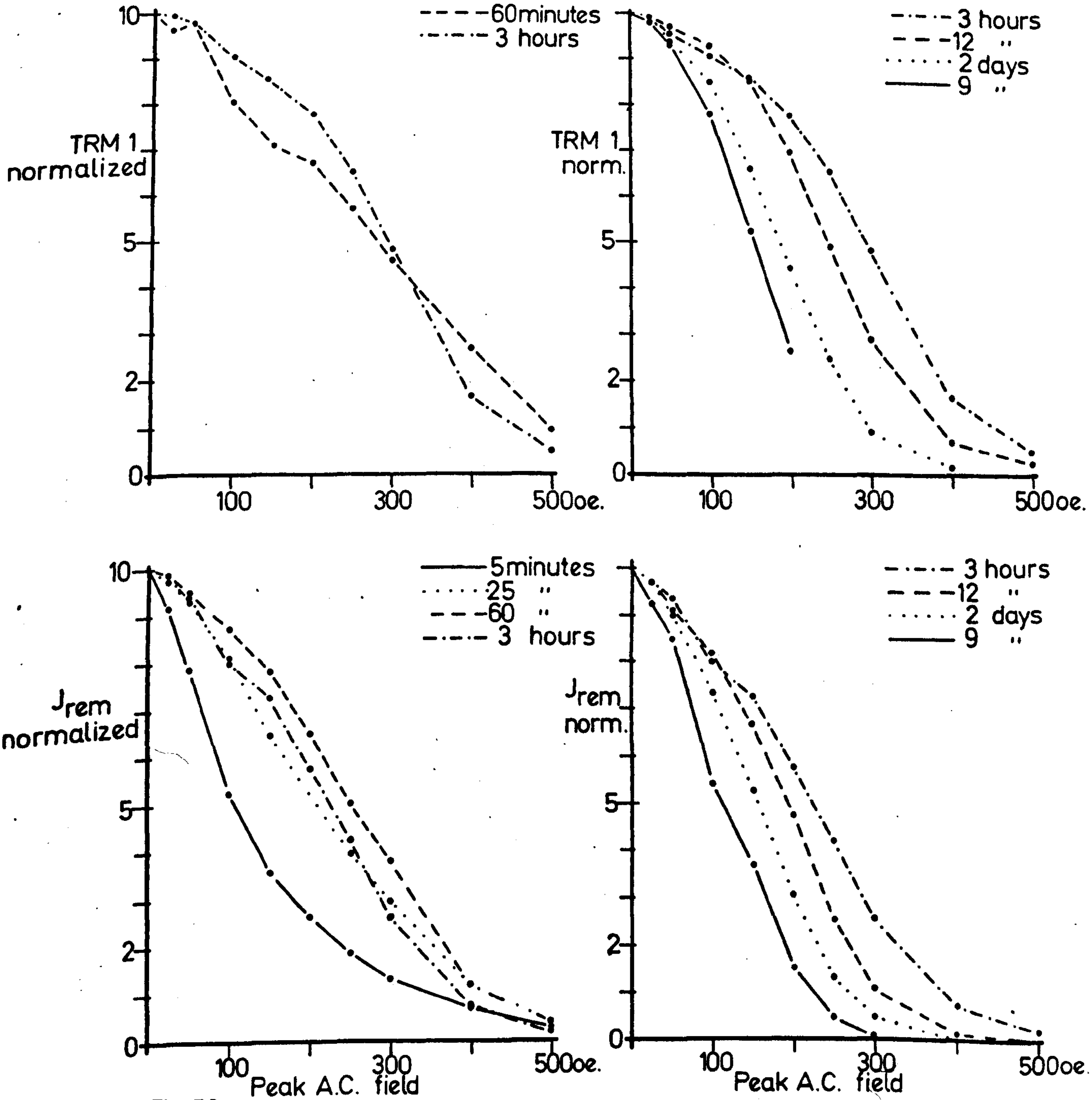


Fig. 7.9 A.C. demagnetion curves of quenched thermoremanence and saturation remanence for sample 1 after heat treatment at 1000°C in water vapour

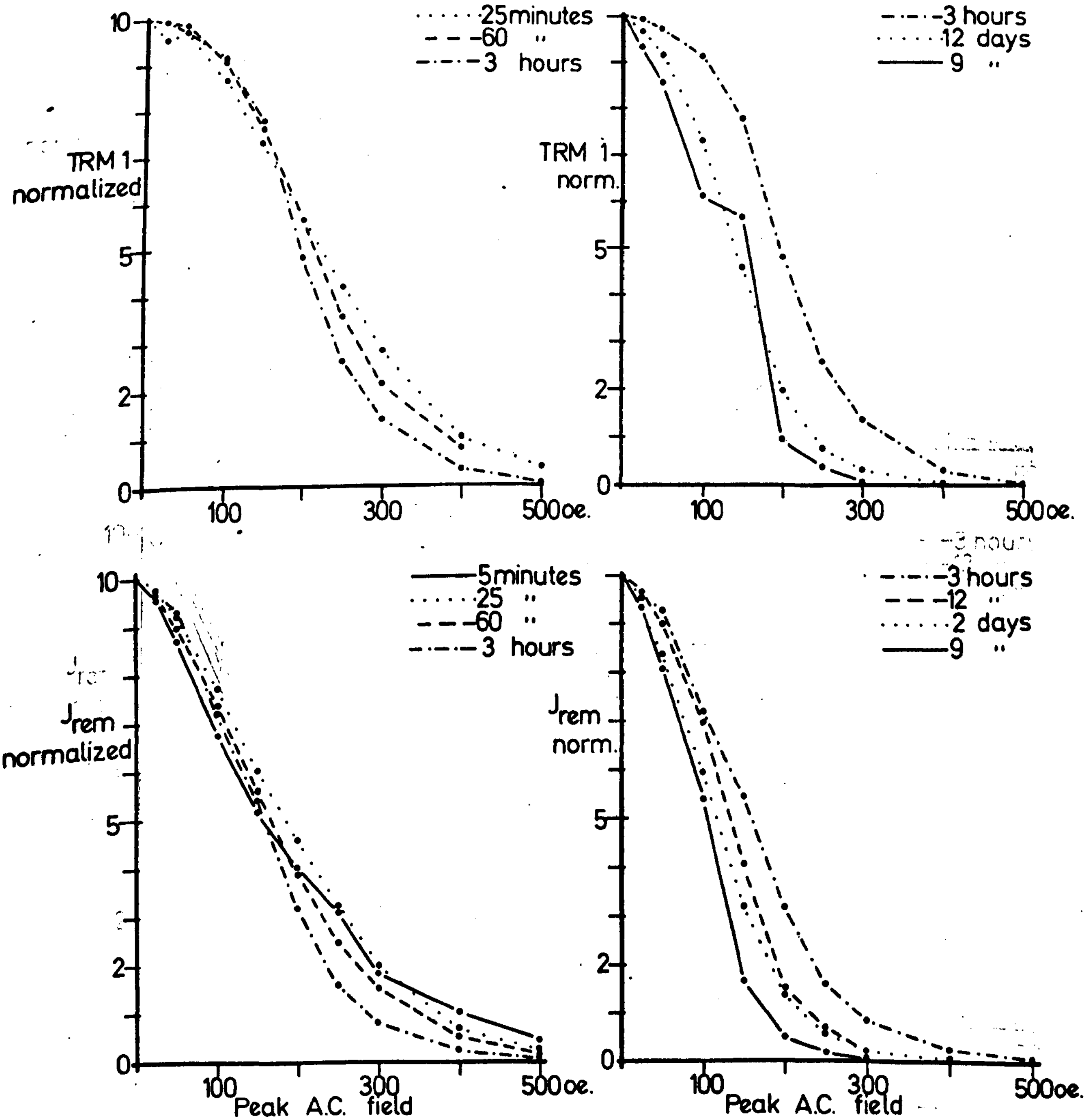


Fig. 7.10 A.C. demagnetization curves of quenched thermoremanence and saturation remanence for sample 2 after heat treatment at 1000°C in water vapour

CHAPTER 8

SUMMARY OF CONCLUSIONS

8.1 Introduction

The conclusions of this work are based on the series of results from simple heating experiments. Five samples of olivine were used in these experiments, with a spread of composition from 5% to 82% fayalite. The samples were variously heated for periods between 5 minutes and 40 days, at temperatures between 650°C and 1100°C in air, and at 1000°C in water vapour. The results were obtained from three methods of observation, magnetic, microscopic and X-ray powder photographic.

The results are similar for all the various heatings of all the samples, within two generalizations. At the lower temperatures, a longer period of heating was required to obtain the same alteration condition of the olivine sample, as was more quickly obtained at higher temperatures. The higher iron content samples required less heating, that is either a shorter period or a lower temperature, to produce a certain degree of alteration, than the magnesium rich samples.

8.2 A Short Summary of the Results

The samples were readily altered in the experiments within two limitations. No alteration was produced if the samples were heated in a vacuum, even with the high iron content, 82% fayalite, samples heated at 1100°C for 24 hours. Negligible alteration was produced under any conditions, if the samples were heated only to 650°C, for periods up to 24 hours. This result may indicate a lower limit to the temperature at which this alteration can be produced, at least within a laboratory time scale.

During all other heating experiments, alteration of the olivine samples was produced. The alterations were very similar, magnetically, optically and in X-ray powder photographs. The results may be reviewed generally as changes with increased time of heating the samples at the required alteration temperature.

The thermoremanent magnetization acquired by the samples on cooling in a known magnetic field showed an initial rise. On further heating, the TRM obtained a maximum value and then decreased. A typical peak value of sample 2, 14% Fa, was approximately 8×10^{-2} emu/gm. The TRM acquired on quenching a sample in a known magnetic field was consistently lower than the TRM acquired on slow cooling in a known magnetic field, when allowance was made for a slight difference in the two magnetic fields. The saturation magnetization, measured in a 5,000 oe magnetic field, and the saturation remanent magnetization were very similar in development. Both magnetizations showed an initial rise, a peak value then a decrease as the samples were heated further. Typically a peak value of saturation magnetization of sample 2 was 4.5 emu/gmbut for sample 5, 82% fayalite, it was 35 emu/gm. The peak values of saturation magnetization and the saturation remanence were acquired after the same duration of heating but did not necessarily coincide with the maxima of the TRM. The Curie points of the samples were, after five minutes heating, generally about 520 - 550°C but on further heating decreased to 450 - 400°C. A high Curie point of 690°C occurred after heating some samples for days at the experimental temperature.

Optically the samples showed a general trend of alteration during the heatings. After short periods of heating a green alteration was formed. This alteration appeared to be sub-microscopic opaque grains in a semi-transparent material, which gave it a sponge-like appearance.

This alteration began at the edges of the sample and spread inwards with further heating. Often this alteration was formed in long thin lenses of distinct orientation within the sample. Further heating of the samples caused the alteration to redden and fill the entire sample. This reddening precedes a growth in size of the opaque grains. In some samples the opaque material would coalesce to form large opaque grains, particularly in the high iron content samples.

The X-ray powder photographs were only taken of samples after they had been heated for long periods. This examination showed the presence of four minerals; olivine (remaining after low temperature experiments); hypersthene-like structure (present after experiments in the lower iron content samples); magnesioferrite-like structure (present after low temperature experiments with high iron content samples, and after high temperature heating experiments with low iron content samples); and hematite (present after most experiments).

8.3 Summary of Conclusions

The results showed a maximum value of thermoremanence of 8×10^{-2} emu/gm for sample 2, 14% fayalite. Sample 2 has an olivine composition similar to olivines found in basalts. In a basalt containing 5% of altered olivine, this TRM would indicate a natural remanence of a sample of this rock of about 4×10^{-3} emu/gm, which is average for basaltic samples used in paleomagnetism. This simple result implies that <u>all</u> the natural remanence of some highly oxidized rocks could be due to the magnetization of the altered olivine.

Alterations, visually identical when viewed in polished sections at 1200 x magnification, have been commonly seen in virgin paleomagnetic samples. The altered olivine is found in oxidized basalts, samples commonly used in paleo-intensity work. It is important to point out that the TRM obtained in these laboratory heating experiments may be identical with an original NRM mechanism of some rocks. These experiments do not just re-heat and re-cool existing minerals, but cool a newly formed mineral in a known magnetic field.

The conclusions of these experiments can be briefly summarized into two chemical processes.

Olivine + Oxygen -> Hypersthene + Magnesioferrite

e.g. $2Fe_2SiO_4 + 4Mg_2SiO_4 + O_2 \rightarrow 6MgSiO_3 + 2Fe_2MgO_4$

Ferrite + Oxygen -> Magnesium rich ferrite + Hematite

e.g. $6Fe_2(Mg_{\frac{1}{3}}Fe_{\frac{2}{3}})O_4 + O_2 \rightarrow 2Fe_2MgO_4 + 6Fe_2O_3$

An infinity of chemical equations can illustrate these processes, but an examination of the first chemical equation shows that for a ferrite to be formed in the initial process a ratio of 1 : 2 of fayalite : forsterite or a higher percentage of fayalite is required. This conclusion would imply a leaching of iron, during the formation of the ferrite, in samples of less than one-third fayalite content. The exact compositions of the hypersthene and ferrite depend on the initial Mg : Fe ratio of the original olivine.

These conclusions are drawn from the evidence of the heating experiments. The magnetic results of the experiments are complicated by four factors during the alteration. Firstly, the growth of the grain size of the magnetic material affects the coercivity of the sample. The Fe : Mg ratio of the magnesioferrite affects the magnetization of the sample. This ratio changes during the second stages of the alteration. The ionic ordering of the Fe^{2+} : Mg^{2+} ions within the ferrite structure affects most of the magnetic properties. The ordering is dependent upon the thermal history of the sample. Finally, the progression of the two stages of the alteration, at the same time, can produce complicated variation in the magnetic properties of the sample.

The two stage nature of the alteration is immediately obvious from the experimental results. The magnetizations show the initial rise then the decrease in magnitude on further heating. The Curie point of the material remains relatively constant, then falls and a second higher Curie point can appear. The samples become magnetically softer, then on further heating gradually harden. Optically the two stages are even more distinct. There is the initial green opaque alteration, followed by the reddening of the sample.

The necessity of oxygen is shown, as the alteration does not occur if the samples are heated in vacuum. However, the experiments indicated that water vapour could be the source of oxygen for this process of alteration.

The primary evidence for hypersthene as an alteration product comes from the X-ray powder photographs. It is clearly present in all photographs unless the entire photograph is masked by very strong hematite lines. The ease with which the alteration can be reversed on heating the altered samples in vacuum implies the alteration products must accept much of the original crystal structure of the olivine. This ordered nature of the alteration is evident in the initial optical results, where the opaque material forms linear patterns. Hypersthene is known to accept the oxygen close packed structure of olivine.

The magnesioferrite is indicated by the X-ray powder patterns, which show a magnetite-like spinel pattern. The magnesium ion replacement of the ferrous ion in the magnetite structure is clearly seen in the magnetic results. The high magnetization, coupled with a characteristic Curie point indicate a magnesioferrite. Conclusive evidence is seen in the variation of saturation magnetization with thermal history of the sample, showing the effects of ionic ordering within the spinel structure. The magnesioferrite is identified with the green sponge-like alteration product.

Evidence for the initial process is found in the leaching of the iron from the low iron content olivine samples. Optically the alteration is seen to progress with the growth of size of material by the loss of the surrounding alteration. The X-ray powder photographs of these samples indicated a magnesium richer olivine structure after heating. This leaching of iron is as was predicted in the formation of the ferrite.

The evidence for the second stage of the process is not as conclusive. The magnesium rich ferrite is not detected by X-ray photographs but the magnetic results show the decrease in Curie point as the incrase of the $Mg^{2+} : Fe^{2+}$ ratio would predict.

The final product of the alteration, hematite can be found in all of the results. The X-ray photographs show very clearly the hematite structure. Optically the red colouration of the sample is the first evidence of the production of hematite. The hardening of the magnetization of the sample to A.C. demagnetization, the appearance of a Curie point of 690°C show the presence of hematite.

8.4 The Importance of these Conclusions to Rock Magnetism

The prime importance of these conclusions lies in the recognition of a new common magnetic mineral, in rock magnetism. The high values of the magnetic parameters of magnesioferrites mean that the rock samples containing visually altered olivines should be critically examined. It is easily possible that the magnesioferrite material could be the cause of the entire natural remanence of this rock. The magnetic properties will depend on the thermal history of the sample, due to ionic re-ordering, and would render it unreliable for ancient field intensity measurements. It would be of prime importance to determine when the alteration occurred. If the alteration took place after the rock had been formed, the magnetic properties would represent the period of the alteration, not the period of the formation of the rock. Even a rock which now shows the fullest development of hematite in the altered olivine, at some intermediate stage would have contained the more magnetically significant magnesioferrite.

Despite the occurrence of the two distinct magnetic phases within the alteration no self-reversal was detected in these experiments. No tendency to self-reversal was ever observed with these samples. It is, however, possible that within a rock sample, this alteration could effect other magnetic minerals.

These conclusions are of interest in laboratory heating work. Any samples containing olivine, heated to 850°C and above, will contain altered olivine due to this heating. As these experiments indicate a lower limit to alteration of 650°C, this conclusion is of marginal significance in normal Curie point determinations. Of more importance is the effect of this heating on altered olivine already present. The presence of small amounts of magnesioferrite may not be visually detectable, but because of its strong magnetization, which depends on its ionic ordering it could have profound magnetic consequences. Hence, a laboratory heating experiment may not produce the alteration of the olivine but may affect the magnetic properties of the sample due to ionic re-ordering within any magnesioferrite, present in the sample.

CHAPTER 9

A PALEOMAGNETIC FIELD DIRECTION DETERMINED FROM A TRIASSIC SANDSTONE

9.1 Introduction

The aim of this work was to use the available techniques to obtain a Triassic paleomagnetic field direction for Britain. Due to the low intensity of the natural remanent magnetization (NRM) of sandstone samples and the scatter of NRM directions of samples from one site, as found by other workers, a large number of samples from one site was required for an accurate result. The local availability of New Red Sandstone made the requirements easier. Computer techniques were used to analyse the data collected more completely than in previous work. Throughout this work, a sample will mean a single rock core separately collected and oriented at the site. A specimen will refer to the one inch cylindrical piece cut from a sample. Several specimens may be cut from the same sample.

9.2 A Brief Review of Previous Work

There is a paucity of paleomagnetic work on rocks of Triassic age for Britain. Clegg et al (1954) collected 43 rock samples from nine sites throughout England. These samples were Keuper or Upper Triassic sandstones. Creer (1957, 1959) collected 35 samples from one site in Devonshire, of Keuper Marl. There are nine ancient field directions of Triassic age for N.W. Europe, reported by other workers (Irving 1964, McElhinny 1968 a,b). The mean of these results, calculated by Dr. P. Dagley (to be published), is listed in Table 1, together with individual results of particular interest.

The process of magnetization of red sandstones is still in some doubt. The iron content of sandstones is of two forms. Black specular hematite, which has been reported as containing magnetite (Creer 1962), is present as detrital grains. A red material, acting as a cement, forms a thin covering of the silicate grains. This material is either hematite or an iron oxyhydroxide. The exact composition of these materials varies in different sandstones, as does the relative abundance of these two materials (Collinson 1965 a). The hematite is probably formed by the oxidation of magnetite. This oxidation may occur before or after the formation of the sandstone.

The NRM of sedimentary rocks is due to either depositional remanent magnetization (DRM) or chemical remanent magnetization (CRM). The DRM can be acquired by two processes. Magnetic particles align themselves with the ambient magnetic field as they are deposited from water. This alignment produces a remanent magnetization. Magnetic particles can rotate within a wet sediment during the drying to align with the ambient magnetic field. Again this rotation will cause a remanent magnetization. CRM is acquired if a magnetic mineral is formed below its Curie point in a magnetic field. The magnetization of the new mineral is aligned with the magnetic field, producing a remanent magnetization.

DRM has been suggested as the cause of the large scatter of the direction of NRM of sediments. However, both theoretical and practical work have shown that turbulence during deposition will not give poor alignment with the magnetic field (Collinson 1965 b). Any scattering due to turbulence may be overcome by the post-depositional alignment of magnetic grains (Irving and Major 1963). It would appear that the NRM of sandstones may be due to either DRM or CRM, and possibly a combination of both magnetization (Picard 1964). Collinson (1965 a) found that the NRM of the Chugwater U.S.A. sandstones originated in the black hematite grains but could not differentiate between DRM or

CRM for these rocks. Later Collinson (1966) investigating the Taignati Bolivia sandstones, found the NRM to originate from the red pigment and to be of a chemical magnetization form.

9.3 The Geology of the Site

The collection was made from Woolton Quarry Liverpool 53.5N, 3W, which is at present worked for stone for Liverpool Cathedral. The quarry provided a sandstone face of which approximately 25 metres were sampled at 25 cm intervals. The face showed flat banding. The bands were of fine grained white sandstone, varying in thickness between 1-2 cm and 50 cm. Twelve bands passed through the sampled section at irregular intervals. The bands showed no signs of current bedding or internal deformation.

The section varied in composition from coarse grained, > 1 mm grains, to fine grained, < 0.1 mm grains. This variation appeared irregular. The sandstone contained pebbles from 1-5 cm in diameter. The colour of the sandstone was constant except for the white bands.

The New Red Sandstones were formed during the Triassic period (230 - 180 My). This quarry is of the Bunter Sandstone or Lower Triassic period (230 - 210 My). This period is subdivided into the Upper Mottled Sandstones, the Pebble Beds and the Lower Mottled Sandstones. The quarry is of the Pebble Bed period (Webb et al 1923, Edwards and Trotter 1954).

The tilt of the sandstones was clear from the bands in two orthogonal quarry faces. The tilt was $8\frac{1}{2}^{\circ}$ in a direction of 65° E. of N.

9.4 The Collection and Measurement of the Sandstone Specimens

The samples were collected with a portable drill. Cores, of one inch diametre were drilled with a water cooled diamond drill. These cores were 2 - 5 inches long and were oriented whilst still attached to the sandstone face (Methods in Paleomagnetism, Collecting). This method enabled 105 samples to be collected at intervals of approximately 25 cm down the rock face.

The samples were cut, firstly to remove the weathered end, then into one inch long cylindrical specimens. The NRM's of the specimens were measured using a sensitive astatic magnetometer. The specimen was mounted in a holder beneath the magnetometer and continuously rotated about an axis of the specimen. The component of the NRM along this axis of the specimen was measured. The cube was removed and replaced, rotated by 180°, perpendicularly to the axis of rotation and the same component of NRM again measured. The average of these two results would eliminate any induced magnetization or any magnetization of the cube holder and rotation equipment. This average was obtained for each of the three components of the NRM.

The sensitivity of the astatic magnetometer was adjusted by having an adjustable field gradient about the astatic pair. The field gradient was produced by attaching a magnet to the side of the magnetometer casing. By lowering the magnet the sensitivity of the magnetometer increased, as the effect of the field gradient opposed the restoring torque of the suspension. The sensitivity was limited by external magnetic disturbances and by the period of the magnetometer. A maximum working sensitivity of 10^{-5} emu/cm deflection could be used at magnetically quiet times.

The specimens were demagnetized in a tumbling A.C. demagnetizing apparatus. After each demagnetization the NRM was measured as previously explained. The specimen was then re-demagnetized at the same peak A.C. field and the NRM remeasured. The final mean paleomagnetic direction obtained after demagnetization to a given peak A.C. field, was the result of each component of NRM being measured four times. This repetition was thought necessary because of the small deflection obtained with the astatic magnetometer at this high sensitivity.

9.5 The Paleomagnetic Results

A group of 11 specimens from different samples was chosen for preliminary work. The samples were spread throughout the section, including one white sandstone. This latter specimen was found to be non-magnetic, within the limits of the magnetometer, as were all the other specimens of the white sandstone. Each of the remaining specimens were progressively demagnetized in peak A.C. fields of up to 400 oe in 50 oe steps, and then 100 oe steps to 800 oe. The direction of the NRM of each sample was calculated and the mean of the ten samples found at each demagnetization field. The precision parameter k and the semi-cone angle of 95% confidence, α_{95}, were calculated by Fisher statistics (1953) (Table 9.2). The results showed the samples were marginally better grouped after demagnetization to 25 and 100 oe. At higher demagnetization fields the scatter increased because the sample became magnetically weak and consequently difficult to measure accurately.

It was decided to proceed by demagnetizing one specimen from each sample at 100 oe peak A.C. field. On eliminating the white sandstone specimens, 84 specimens remained. The directions of their NRMs after demagnetization were taken in groups of seven and the mean direction of each group calculated (Fig. 9.1, Table 9.3). The mean direction of all the specimens was calculated together with k and α_{95}. The NRM directions of the individual specimens were sorted to determine if the scatter of the directions could be decreased.

The NRM directions of each specimen after the first and second demagnetization at 100 eo were compared. Specimens with high precision parameters k for these two directions were picked out, firstly $k > 1000$ and secondly $k > 500$. The mean of these two sets of specimens is shown in Table 9.4. The precision parameter k is the same for these sets as for the total collection, α_{95} was greater as fewer specimens were involved.

The magnitude of the NRM of each specimen was sorted. Two groups of specimens were selected, specimens with magnetization $> 10^{-6}$ emu/gm and those with magnetization $> 7 \times 10^{-7}$ emu/gm. The mean directions of these two groups are in Table 9.4. The precision parameter is largest for samples of high magnetization but α_{95} is still large as few specimens are included.

These results suggest that the scatter is inherent in the magnetization, rather than experimental. The slight increase in precision for the magnetically stronger specimens would imply slight experimental error in measuring the weaker specimens. However, with so small an improvement in scatter, the scatter would appear due primarily to other causes, either due to the magnetization process or secular variation of the magnetic field. The mean directions of the specimens with high precision parameters and the mean direction of the group with magnetization $> 10^{-6}$ emu/gm lie one degree outside the 95% circle of confidence about the mean direction of all the specimens. The mean direction of samples with magnetization $> 7 \times 10^{-7}$ emu/gm is within the circle of confidence.

Creer (1959) used A.C. demagnetization fields up to 800 oesteds to destroy secondary components of magnetization. No evidence for the existence of secondary magnetization was found with these sandstones. Streaking of the NRM towards the present magnetic field is a well known instability in sandstone. The effect is to spread the NRM directions measured along a great circle between their ancient field direction and the direction of the present magnetic field. No such spreading of results was found with this sandstone.

9.6 General Conclusions

The paleomagnetic field direction obtained from this Bunter Pebble Bed sandstone was declination 4.9° E. of N., inclination 34° downwards with α_{95} of 6.5°. When compared with other Triassic results from Britain, this result has a small declination and a slightly greater inclination. Due to the large number of specimens used the α_{95} is half other quoted results. The ancient pole position, latitude 55°N longitude 170°E, compares favourably with that obtained by Nairn (1960) from Bunter sandstones in Germany (Table 9.1).

The use of a large number of samples was able to give a better circle of confidence about the mean result. The sorting of these samples with the variation of certain magnetic parameters, showed that primarily the scatter is due to a scatter of the magnetization, not experimental imperfections. Only with large numbers of samples can accurate results be obtained from these red sandstones.

No samples were found in this collection which had a NRM in the opposite direction to the present earths magnetic field. In all the other results quoted, both normal and reversed magnetizations were found. This result suggests either that there was a long period of normal magnetization during the Bunter period or that this particular sandstone had a fast rate of deposition.

TABLE 9.1

TRIASSIC PALEOMAGNETIC DIRECTION FOR N.W. EUROPE

AFTER IRVING AND McELHINNEY

D	I	α_{95}	λ'	ϕ'	Reference Number
22	+28	13.1	-	-	1
17	+29	13	55	159	2
33	+26	12	43	131	3
30	+23		44	134	4
214	-48	21	54	118	5
5	+34	6.5	55	170	6

Ancient Field Direction

D : declination : °E of N

I : inclination : + downwards - upwards

α_{95} : semi-cone angle of 95% probability : Fisher Statistics

λ' : lattitude of paleomagnetic pole - °N

ϕ' : longitude - °E

Reference Number

1 - average of nine quote results for N.W. Europe (Dagley)

2 - Nairn 1960, Germany Bunter Sandstone 230-210 My

3 - Clegg et al 1954 British Keuper Sandstone 200-180

4 - Creer 1959 British Keuper Marl 200-180

5 - Irving 1959 Scottish Triassic Sandstone 230-180 My

6 - Riding 1969 British Bunter Sandstone 230-210 My

TABLE 9.2

RESULTS OF DEMAGNETIZING 10 SPECIMENS

A.C. Demagnetization field, oe	Declination °E of N	Inclination ° downwards	k	α_{95} degrees
0	10.8	31.8	6.0	21.5
25	6.8	33.3	11.0	15.2
50	11.8	38.9	5.2	23.3
100	12.3	21.4	7.9	18.3
150	9.9	35.7	6.8	20.0
200	12.1	15.0	6.5	20.5
250	17.6	16.9	6.7	23.1
300	15.4	23.8	5.0	25.8
350	18.3	24.5	7.0	27.4
400	11.6	22.6	3.5	34.8
500	23.3	41.1	6.5	23.5
600	4.8	25.8	2.2	49.8
700	10.4	24.8	3.1	38.0
800	14.85	38.3	2.2	68.9

TABLE 9.3

RESULTS OF NRM DIRECTIONS OF 84 SPECIMENS IN GROUPS OF 7 AFTER A.C. DEMAGNETIZATION TO 100 OE AND THE MEAN DIRECTION OF 84 SPECIMENS

Declination °E of N	Inclination ° downwards	k	α_{95}
353.2	32.4	9.8	20.3
352.5	31.7	6.4	26.0
357.79	17.4	5.6	27.9
341.67	39.93	7.7	23.1
24.37	31.72	9.0	21.29
6.33	34.84	15.9	15.6
5.91	35.42	11.3	18.8
6.88	45.46	11.8	18.3
30.8	37.7	4.1	34.2
356.1	50.9	5.0	30.14
11.02	25.7	5.2	29.4
11.42	17.2	7.7	23.2
4.87	34.05	6.7	6.5 Mean Direction

TABLE 9.4

MEAN DIRECTION FOR SELECTED GROUPS OF SPECIMENS

Group	
Specimens with k > 1000	A
Specimens with k > 500	B
Specimens with magnetization > 10^{-6} emu/gm	C
Specimens with magnetization > 7×10^{-7} emu/gm	D
All specimens	E

Group	No. in group	Declination °E of N	Inclination ° downwards	k	α_{95}
A	21	359.2	28.3	6.9	13.1
B	33	3.31	27.6	6.7	10.4
C	15	358.2	29.7	11.4	11.8
D	44	3.0	33.1	7.7	8.3
E	84	4.87	34.05	6.7	6.5

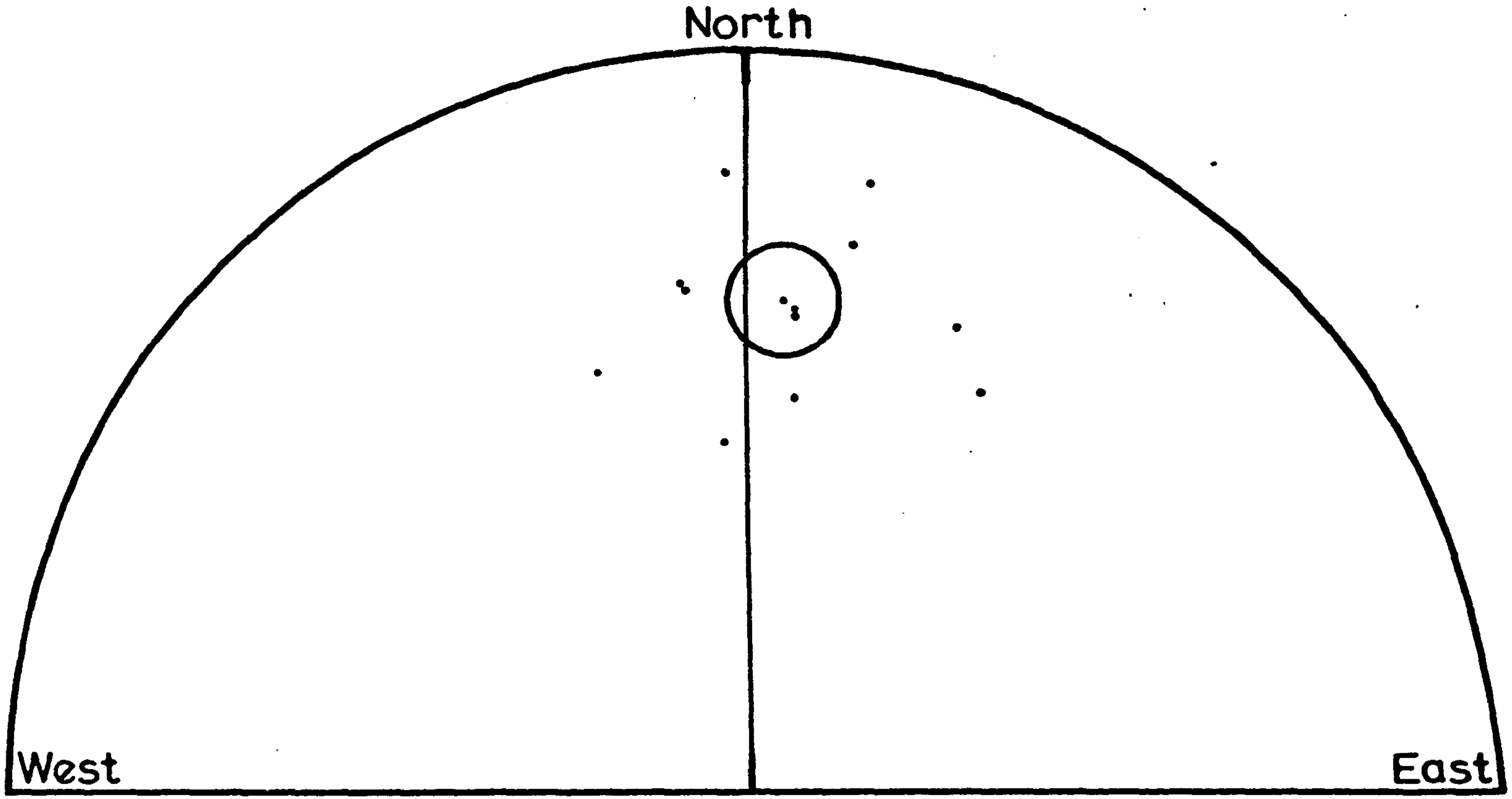


Fig 9.1 Directions of magnetization of all specimens, meaned in groups of 7, and the mean direction of all specimens

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