

# The Alteration of Olivine in Basaltic and Associated Lavas

## Part I: High Temperature Alteration

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*Abstract.* A study of the alteration products of olivines in lavas from a number of volcanic regions indicates the temperature and oxidation conditions under which deuteric alteration has taken place. High temperature oxidation of basaltic olivine results in either exsolution of hematite associated with a more forsteritic olivine, or formation of a symplectic intergrowth of magnetite and orthopyroxene. Continued oxidation of the metastable assemblage magnetite + orthopyroxene produces hematite + forsterite. Identical textures and mineralogical assemblages have been produced in a number of heating experiments, and compare closely with natural examples, and with reheated olivines from gabbroic and ultra-basic xenoliths. The advanced oxidation state of coexisting Fe-Ti oxides associated with highly altered olivines confirms the suggestion that processes of oxidation are the prime causes of high temperature deuteric alteration.

### Introduction

The aim of this study is an attempt to establish criteria for the recognition of processes resulting in the alteration of olivines in lava flows, and particular attention has been directed to the effect of oxidation at high temperatures.

Over 500 thin sections and nearly 2000 polished sections of basaltic and associated lavas were studied. Principally the rocks examined were from eastern Iceland and St. Helena, but collections from Fuertaventura, Teneriffe, Morocco and the British Isles were also studied. Olivine-bearing xenoliths from Lanzarote, the Auvergne and Faial (Azores) were also examined.

Most of the X-ray data were obtained from diffractometer traces but X-ray powder photographs were also used.

Heating experiments were carried out at atmospheric pressure on separate olivine concentrates of known composition, the alteration products being studied by the above techniques.

Unlike most mineralogical and petrological studies of basic igneous rocks, the emphasis in this study has been placed on the reflection microscopy examination of the opaque oxide phases. The reasons for this are threefold: first, magnetite and hematite feature prominently in the high temperature alteration of basaltic olivine; secondly, the intense development of these Fe-oxide phases produces nothing more than an unidentifiable "spongy opaque" in thin section; thirdly, the discrete Fe-Ti oxides although occurring in small proportions, are nevertheless sensitive and useful indicators of oxidizing conditions.

The term deuteric is used throughout in the sense of SEDERHOLM (1929), who defines deuteric alterations as "those that have taken place in direct continuation of the consolidation of the magma of the rock itself".



interesting comparison between metamorphic and oxidation symplectites has been revealed in an examination of a number of polished and thin sections from the Hamar meta-gabbro, Somalia. The opaque oxide phase in these symplectites is either magnetite or spinel plus enstatite, indicating that simple oxidation without metamorphic reaction has at times been operative.

With reference to the  $\text{MgO—FeO—Fe}_2\text{O}_3$  system, MUAN and OSBORN (1956) have discussed the effect of the partial pressure of oxygen on paths of primary equilibrium crystallization. MUAN (1958) has broadly defined paths of equilibrium crystallization in a closed system as “a continuous description of the changes in phase assemblage taking place as the temperature is lowered from liquidus temperature, and equilibrium maintained among the phases”.

It is well known that a continuous compositional change may take place in a solid solution series as a result of magmatic equilibration. The oxidation reactions referred to in this study, however, are considered to be effected during the late stages of crystallization and as such are dominantly gas-solid, rather than liquid-solid reactions. The latter reaction results in a fayalitic enriched component, whereas an oxidizing gas-solid reaction induces a separation of the olivine into two component phases (forsterite plus hematite).

On the basis of MUAN and OSBORN'S work, if one considers a continuous increase in  $P_{\text{O}_2}$  taking place with increasing crystallization, an increase in the  $\text{MgO}:(\text{MgO} + \text{FeO})$  and  $\text{Fe}_2\text{O}_3:\text{FeO}$  ratios is to be expected. MUELLER (1961) points out that both these ratios may reflect  $P_{\text{O}_2}$  conditions during late stages of consolidation, irrespective of previous  $P_{\text{O}_2}$  conditions, but adds that the  $\text{Fe}_2\text{O}_3:\text{FeO}$  ratio is the better of the two indicators.

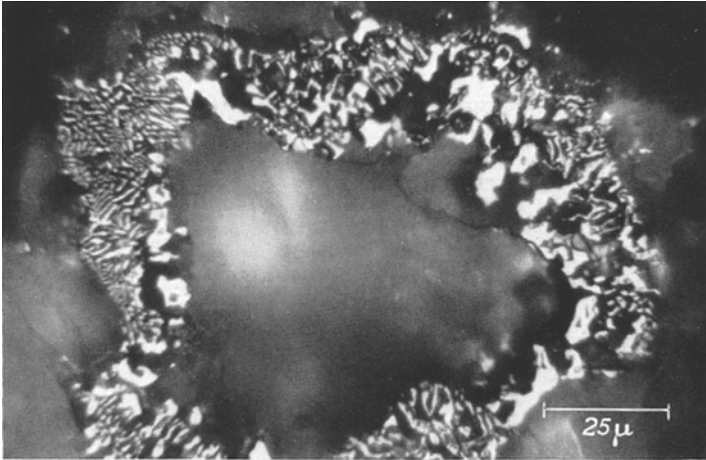
An increase in the  $\text{MgO}:(\text{MgO} + \text{FeO})$  and  $\text{Fe}_2\text{O}_3:\text{FeO}$  ratios is evident in the progressive high temperature oxidation breakdown of olivine. The former ratio is reflected in the development of the silicate phases (enstatite or forsterite) and the latter ratio is expressed in the opaque oxides (magnetite or hematite).

## Reflection Microscopy

### *a) Secondary Iron Oxides in Altered Olivine*

A wide variety of textural forms exists in the secondary opaque oxides associated with the oxidation breakdown of olivine at high temperatures. The progressive oxidation of each type may occasionally be followed within a single polished section, where oxidizing conditions have varied over small distances. Gross variations have been traced in vertical traverses across single lavas in which high temperature oxidation zones have been found to occur (WATKINS and HAGGERTY, 1965). These zones commonly occur towards the centre of a lava, and several factors suggest that the oxidation process is of a primary deuteric nature.

The coarser magnetite symplectites (Figs. 1 and 2) that have been observed in polished sections of basic lavas, may vary from true vermicules (single or multiple worm-like forms of the opaque phase) to rods, lamellae and irregular plates. Generally, individual vermicules are extremely fine, and at magnifications of  $\times 2000$  are only just within the resolving power of a good reflecting microscope. These magnetite vermicules constitute the microsymblectites (Figs. 5 and 6).



Figs. 1 and 2. Magnetite symplectites.

Fig. 1. Vermicular rods and irregular plates of magnetite forming an annulus to an altered olivine grain.

Photomicrographs: Oil immersion objectives have been used for all photomicrographs taken in reflected light. Figure 11 is an incident light photomicrograph and was taken using a conventional air objective

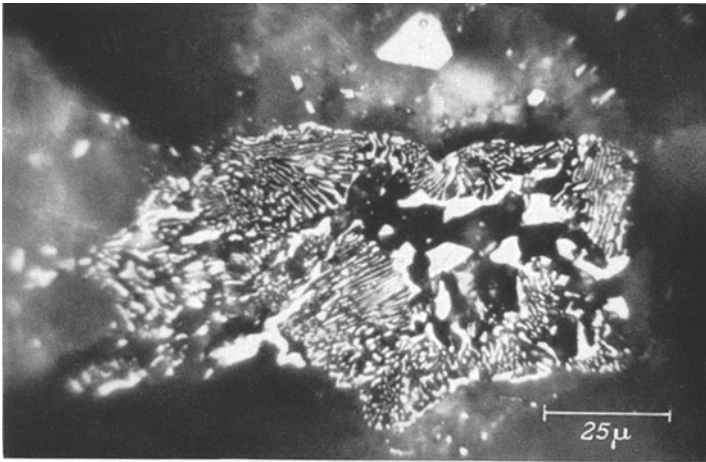
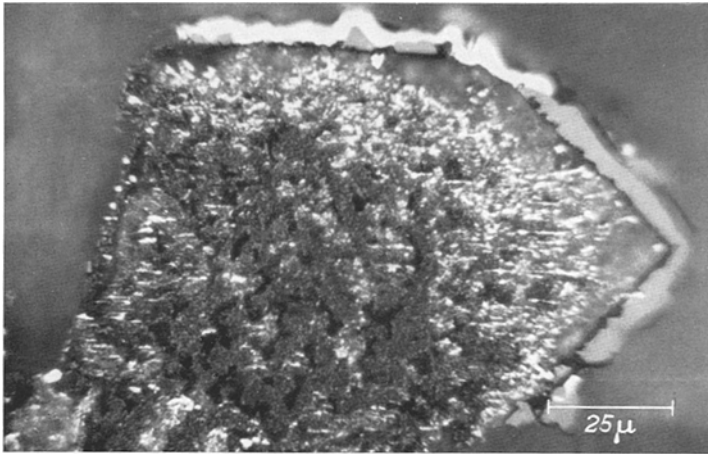


Fig. 2. An altered olivine grain containing radial ribs, subparallel rods and irregular plates of magnetite. Note the manner in which vermicular fingers of magnetite sometimes become attached to, or radiate from, the plates

In the coarser symplectites, massed vermicules of magnetite occur in jagged symplectic units which may be spheroidal, semi-spheroidal, lensoid or lamellar in form. Examples of these units are illustrated in Figs. 16—19. These units frequently show a perfect gradation of one form to another, in the order listed, as they develop from the centre towards the edge of a crystal. Symplectic units are generally oriented within the oxidized olivines, but local crystallographic control of individual vermicules does not seem apparent. Particle coarsening and



Figs. 3 and 4. The oxidation of magnetite symplectites

Fig. 3. The oxidation of vermicular magnetite to lamellar hematite taking place towards the edge of a densely packed symplectite intergrowth. The crystal is bounded by a hematite (white)-hercynite (grey) diffusion rim. Note the well defined oxide-deficient zone adjacent to the diffusion rim

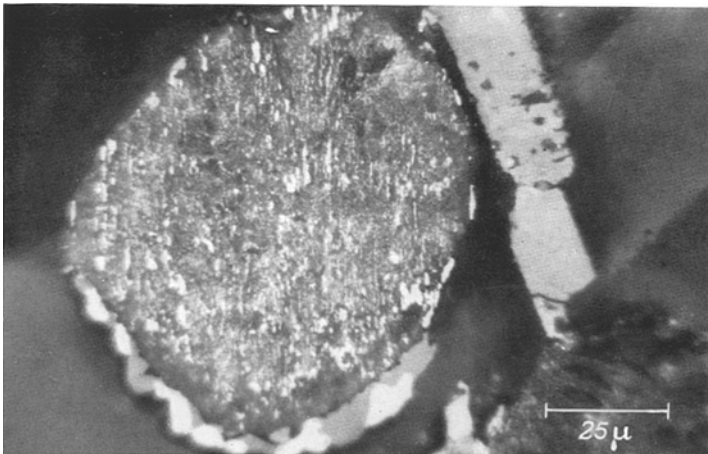
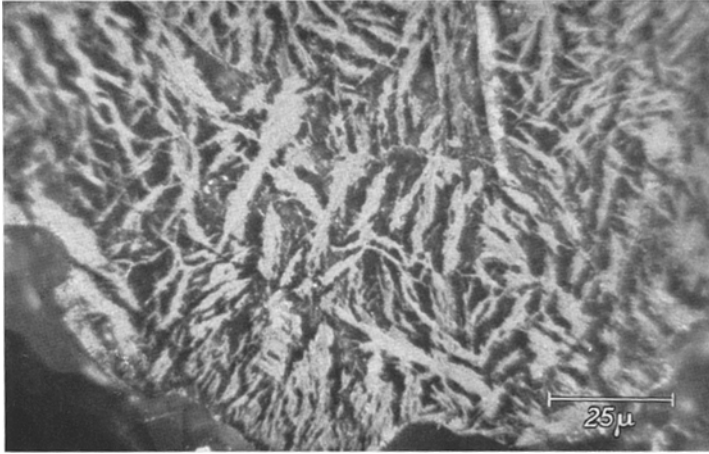


Fig. 4. Well oriented lamellae, irregular plates and finely dispersed hematite in a highly oxidized olivine. Small areas of relic symplectic magnetite still persist but in general the original texture has been completely transformed. The crescent-shaped diffusion rim consists of hematite (white) and hercynite (grey). The lath-shaped grain in the groundmass contains pseudobrookite, with small amounts of titanohematite and rutile, pseudomorphous after original ilmenite

gradual growth of the symplectites to solid lamellae and irregular plates takes place by a process of diffusion and agglomeration, and in this respect a very close analogy may be drawn between this process and the textural transformations which have been observed to take place in annealing experiments of eutectic binary alloys (GRAHAM and KRAFT, 1966; HUNT, 1966). Although the maximum oxidation reached in a grain is towards the edge of the grain, nucleation and



Figs. 5—8. Progressive oxidation of the microsymplectites

Fig. 5. Feathery microsymplectite intergrowths of magnetite in an altered olivine

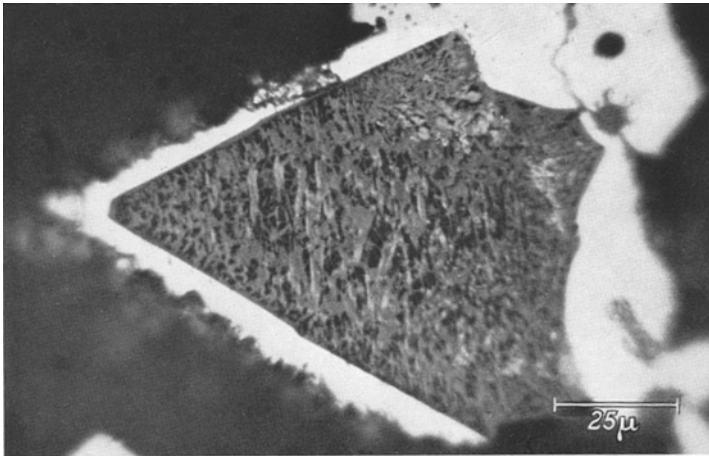


Fig. 6. A well developed hematite diffusion rim showing sharp straight edges towards crudely oriented microsymplectite lenses, and a cusped form towards the groundmass silicates. The discrete opaques at the jagged end of the olivine crystal are finely developed intergrowths of pseudobrookite, rutile and titanohematite after an original titanomagnetite-ilmenite intergrowth

particle coarsening of the magnetite is not restricted to any particular area or zone within the crystal.

The microsymplectites occur more commonly than their coarser counterparts. They characteristically occur in lens shaped bodies and yet may show some degree of orientation in one or more crystallographic directions (Fig. 5). Fine filamental symplectite stringers occur between the larger bodies and in irregular cracks, which give the grain an intricate net-like appearance (Fig. 12). These bodies tend to coalesce and become densely packed at the grain boundaries, where no apparent

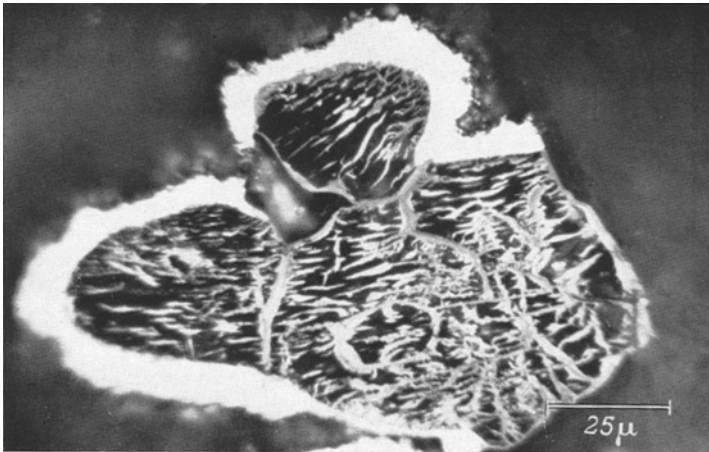


Fig. 7. Microcrystalline, flame-like bodies of hematite which have developed from the microsymplectite intergrowths shown in Fig. 6. Microsymplectitic magnetite is still evident in the irregular cracks which occur throughout the olivine

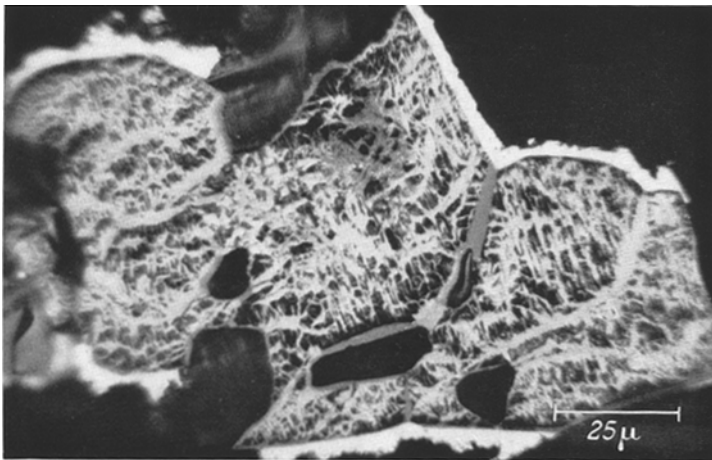


Fig. 8. Densely packed lenses and fine feathery stringers of hematite containing a small percentage of microsymplectitic magnetite, with an ill-defined and discontinuous diffusion rim of hematite along the grain boundary

orientation occurs. A perfect transition of this deterioration in orientation is evident in crystals which show a steep oxidation gradient from the crystal boundary to the centre of the crystal.

The micrographic nature of the microsymplectites is not evident in the photomicrographs. This feature is best observed under the microscope by racking the stage into and out of focus. Optically the opaque phase in the microsymplectites is isotropic, somewhat darker in colour, and has a lower reflectivity than the magnetite in the coarser symplectites. Microsampling and X-ray powder photography of a number of altered olivines of this type have confirmed that the

opaque phase is magnetite. The optically anomalous nature of the magnetite is considered to be partly due to its extremely fine grain size and to the fact that the Fe-oxide to Mg-silicate ratio is far less than in the coarser symplectites.

It follows that subsequent or continued oxidation of the magnetite phase produces hematite. Hematite may also be produced directly from the olivine without passing through this intermediate magnetite-enstatite assemblage.

Olivine grains which are highly oxidized are characterized by thick diffusion rims of  $\text{Fe}_2\text{O}_3$  along the grain boundaries (Figs. 6—8). These hematitic rims develop within the olivine, and do not mantle the olivine in the sense of an overgrowth. The outer margin of the rim tends to be irregular, whereas the inner contact frequently shows sharp, straight edges (Fig. 6). A concentric opaque-oxide deficient zone generally forms adjacent to this rim (Fig. 12); the Mg-enriched silicate phase assumes a spongy appearance and becomes intensely reddened when viewed under oil immersion. The rate and direction of solid diffusion of the iron seems to be variable, and as a result, perfectly continuous oxidation hematite rims are rarely seen. While in a majority of cases the diffusion rim is hematite, a small number of samples also showed associated hercynite (Figs. 3 and 4). The identification of this phase has been confirmed by electron probe microanalysis. The Al, as pointed out by KUSHIRO and YODER (1966), is probably derived from reaction with adjacent plagioclase.

Two distinct textures are produced in the oxidation of magnetite to hematite. The micrographic form of the magnetite phase may give rise to fine orientated laths of hematite (Figs. 3 and 4), or to solid microcrystalline areas of hematite (Figs. 7 and 8). The former texture is the result of a direct transformation and recrystallization of vermicular magnetite to lamellar hematite, whereas the latter texture appears to be the result of an internal migration and nucleation of  $\text{Fe}^{+2}$  ions into well-defined lens-shaped bodies. These bodies gradually invert to hematite as diffusion and oxidation proceed (Figs. 5—8). Fig. 3 illustrates the structural transformation that takes place towards the grain boundaries in the oxidation of magnetite to hematite. It is important to note that pseudomorphic hematite after magnetite only occurs when the magnetite is in a lamellar or plate form; vermicular hematite is only rarely seen. The vermicular to lamellar transformation is typical of the coarser symplectites (Figs. 3—4), whereas a gradual concentration with accompanying oxidation of the ferrous iron into flame-like bodies is typical of the microsymplectites.

Olivines from samples which show positive reheating effects, as in thin pahoehoe flow units, olivine nodules and scoriaceous crusts at the tops of lava flows, tend to contain hematite rather than magnetite in their secondary assemblage. This applies equally to samples immediately adjacent to the high oxidation zones within single lavas. The hematite characteristically segregates into irregular cracks throughout the olivine (Fig. 10), and also diffuses towards the grain boundaries, as in the symplectites. Flame-like segregations of  $\text{Fe}_2\text{O}_3$  are typical of thin pahoehoe flow units. These may be crudely orientated, and are indistinguishable from the massive microcrystalline  $\text{Fe}_2\text{O}_3$  lenses referred to above. There is no evidence from the large number of samples examined, in spite of the fact that variable oxidation conditions may exist within one grain (Fig. 13) or within



one sample, to suggest that these lenses are the oxidized equivalents of magnetite microsymplectites. They appear to be derived directly as hematite.

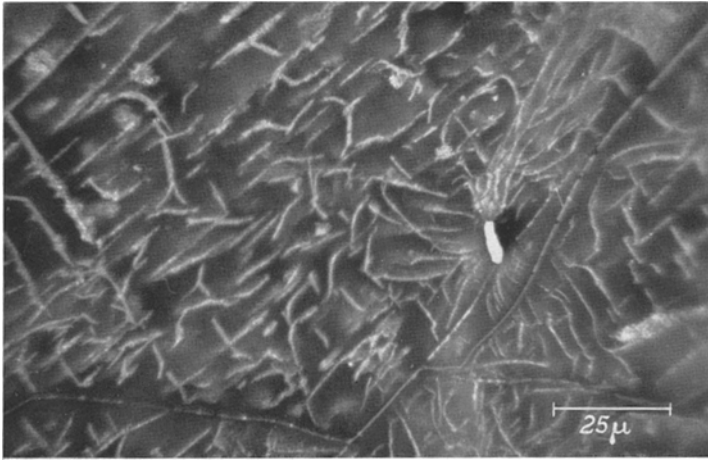
**Stability of Symplectic Magnetite.** In spite of the high oxidation states shown by the discrete Fe-Ti oxides, symplectic magnetite may be well preserved and unaffected in many highly oxidized olivines. There are two possibilities which may account for this fact. Firstly, the formation of the  $\text{Fe}_2\text{O}_3$  diffusion rim, which appears to form early on in the oxidation process, may protect the magnetite-pyroxene assemblage from being extensively oxidized. It may act almost as a semi-permeable membrane, allowing oxidation to continue, but only to a very limited extent. The alternative is that small amounts of MgO which may be present in the magnetite will have a stabilizing effect on it (TSVETKOV *et al.*, 1966).

There is some evidence to suggest that a well established diffusion rim of hematite may act as a preventative barrier against further oxidation. Olivine grains in the state of oxidation shown in Fig. 14 illustrate the preservation of a well-defined symplectite zone between the hematite diffusion rim and the rest of the grain. Mass diffusion of iron has taken place only in part of the grain, towards what appears to be a natural crystal termination. It would appear that oxidation may have terminated, or was prevented from continuing, once the symplectite and diffusion rim had been produced. The initiation of fresh oxidizing conditions, or sustained oxidation at low temperatures (since the rate of diffusion has been rather sluggish) has effectively attacked the olivine away from the diffusion rim. In these areas, limited segregation of the iron has taken place within the olivine, into thin stringers and irregular lenses, and has not migrated in the normal sense towards the grain boundaries. The oxidation front now moves towards the hematite rim from within the crystal, gradually disrupting not only the magnetite vermicules, but also the well-defined symplectite lenses. The arrow in Fig. 14 illustrates a perfectly gradational transformation in the oxidation of magnetite to hematite.

The effect of thermal-oxidation gradients across single crystals of olivine will be dealt with more fully in a discussion of the heating experiments. The oxidation asymmetry of the type shown in Fig. 14 is extremely common, and one which probably reflects, in addition, the effectiveness of grain boundary seal to oxidation processes at different temperatures.

#### *b) Iron-Titanium Oxides*

LINDSLEY'S work (1962, 1963) in the system  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$  permits determination of the temperature and oxygen fugacity of formation of coexisting pairs of titanomagnetite and ilmenite. VINCENT and PHILLIPS (1954) concluded from their detailed work on the Fe-Ti oxides in the Skaergaard intrusion that the  $\text{Fe}^{+2}$  iron "locked up" in the silicates is less susceptible to oxidation than the iron in the discrete opaque oxides. These oxides are extremely sensitive indicators of oxidation and reduction conditions, and as such may record not only the primary, but also the magmatic-deuteric and post-crystallization history of the rock. The degree of oxidation of basic lavas, as determined chemically, has been qualitatively assessed from a study of the state of oxidation of the Fe-Ti oxides, in traverses across several single lavas from Iceland (WATKINS and HAGGERTY,



Figs. 9—11. The oxidation and reheating effects on an olivine-bearing xenolith

Fig. 9. This grain is located immediately adjacent to the basaltic host rock. Oriented lenses of microsymplectic magnetite and derived hematite occur along perpendicular planes. The structurally controlled pattern is complicated by the formation of irregular sigmoidal lenses which occur at an angle to the oriented lenses. The bright inclusion is hematite derived probably from an original included grain of magnetite

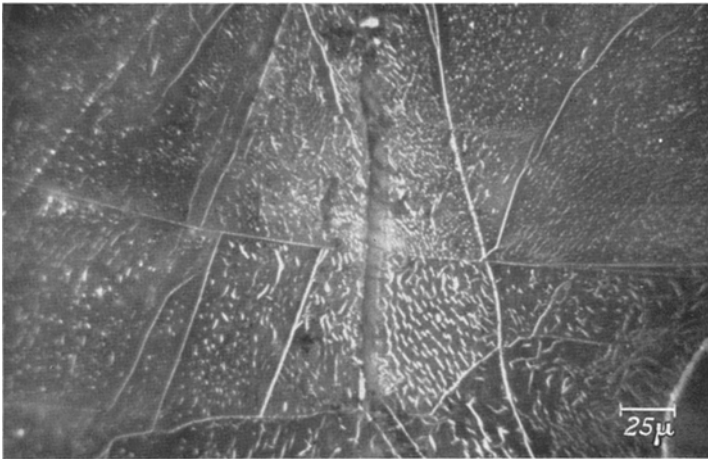


Fig. 10. A single crystal of olivine, located in the centre of the xenolith, which has been segmented by diffusion veinlets of hematite along original cracks within the grain. The amount of hematite, and the degree of orientation of the "exsolved" phase, varies greatly from one segment to the next. The hematite is derived directly from the olivine and because of the thermal gradient across the xenolith has formed at a lower temperature than that of Fig. 9

1965 and 1967), and in a large suite of alkaline lavas from the island of Tenerife (HAGGERTY *et al.*, 1966). The progressive oxidation of titanomagnetite and ilmenite, within densely sampled traverses across single lavas, has resulted in a well defined high temperature oxidation classification, in which homogeneous



Fig. 11. A thin section of an olivine grain in the xenolith showing a complex development of the opaque phase (black) into separate units, and along diffusion cracks. The vertical sub-parallel bars in the photomicrograph are semi-opaque, intensely red and strongly pleochroic

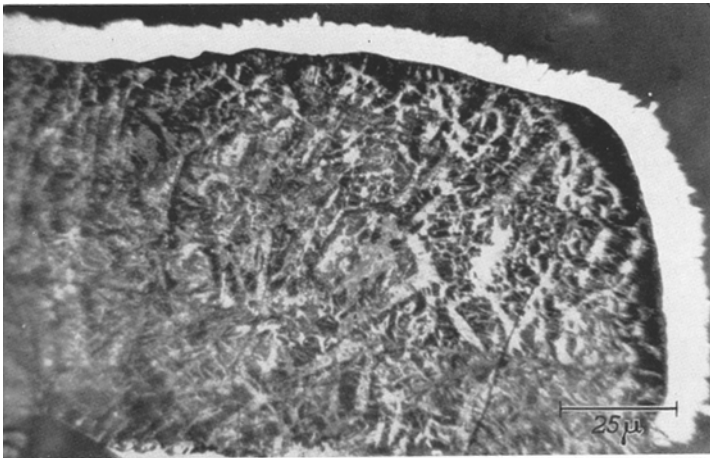


Fig. 12. Densely packed microsymplectic magnetite showing incipient oxidation to hematite. The most significant feature in this photomicrograph is the excellent development of the black, oxide-deficient zone between the hematite diffusion rim and the microsymplectite

titanomagnetite represents the primary state of oxidation, and the index mineral pseudobrookite ( $\text{Fe}_2\text{TiO}_5$ ) the highest state of oxidation.

The initial subsolidus oxidation of titanomagnetite produces "oxidation-exsolution" lamellae of ilmenite along (111) parting planes. In volcanic rocks this oxidation probably takes place above  $600^\circ\text{C}$  but may continue to lower temperatures (BUDDINGTON and LINDSLEY, 1964). Subsequent oxidation of the titanomagnetite-ilmenite intergrowth produces rutile and titanohematite. This latter assemblage finally breaks down to a pseudomorphic intergrowth of pseudobrookite and titanohematite, with minor rutile. A more detailed sequence following the same trend has been traced in discrete grains of ilmenite. The high

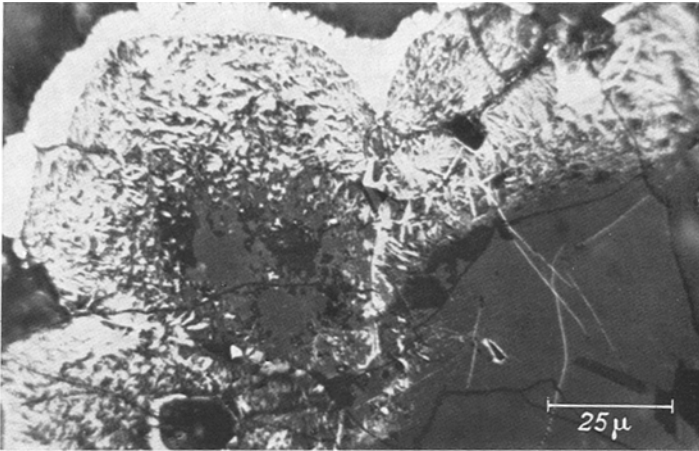


Fig. 13. A partly altered olivine grain, from a thin pahoehoe flow unit, showing a well formed diffusion rim and flame-like inclusions of hematite. It is considered that the hematite has formed directly from the olivine and has not passed through microsymplectic magnetite as an intermediate stage

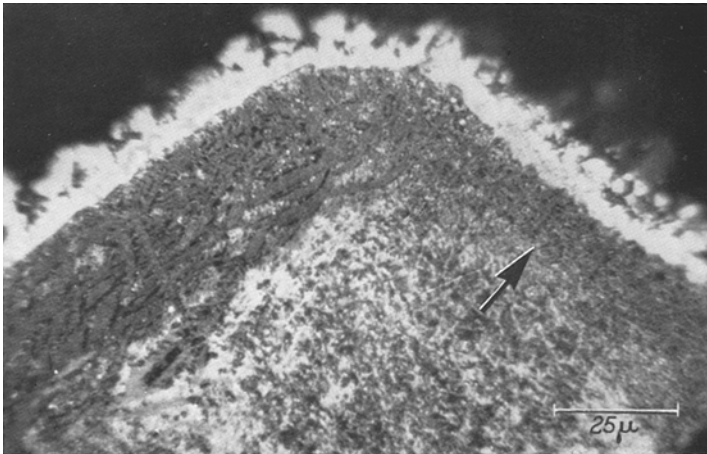


Fig. 14. A highly altered olivine grain in which a zone of microsymplectic magnetite has been preserved between the diffusion rim and an area of hematite after magnetite. For a detailed description of this photomicrograph see text, under, stability of symplectite magnetite

temperature oxidation nature and the progressive sequence of these products has been confirmed in a series of heating experiments on basaltic ilmenite, in which pseudobrookite, rutile and titanohematite have been produced at temperatures above  $650^{\circ}\text{C}$  in an oxidizing atmosphere. Samples from unoxidized parts of a lava have also been heated, and the reproduced phases are identical in textural form and composition to those of the high temperature (pseudobrookite) zones. LINDSLEY (1965) in addition has shown that pseudobrookite cannot form below  $580 \pm 15^{\circ}\text{C}$ . Below this temperature pseudobrookite breaks down to rutile plus a member of the rhombohedral, hematite-ilmenite solid solution series.

Pseudobrookite has been used as an indicator of high temperature oxidizing conditions, and was found to be present in all lavas with highly oxidized olivines containing symplectic magnetite intergrowths or hematite after magnetite. In lavas containing predominantly titanohematite and rutile, or for example, in zones of oxidation immediately adjacent to pseudobrookite zones, hematite rather than symplectic magnetite is produced directly from the olivine. The heating experiments on olivine have demonstrated that this primary formation of  $\text{Fe}_2\text{O}_3$  is temperature controlled, but within a lava volatile activity and/or rate of cooling may also influence the conditions of formation.

Maghemite is regarded as being extremely unstable as it readily inverts to hematite. In spite of this it has been found to be a very common oxidation product of titanomagnetite in the Icelandic and St. Helena lavas.

In reflected light titanomaghemite may be white or pale blue in colour, it is isotropic and has a lower reflectivity than titanohematite, but is brighter than the titanomagnetite which it replaces. Hematite, as is well known, may replace magnetite directly and is frequently controlled by (111) parting planes. Titanomaghemite however, characteristically occurs along curved conchoidal cracks and is not crystallographically controlled. In the single lavas containing high oxidation zones, titanomaghemite has been found to occur in zones of minimum oxidation, generally replacing homogeneous titanomagnetite or titanomagnetite with a small number of ilmenite lamellae. Titanomaghemite occurs most commonly however, in lavas showing distinct weathering features, particularly at the tops of lava flows, and in weathering rinds. The inversion of titanomaghemite to titanohematite has not been observed, and neither has titanomaghemite been found to occur in close association with pseudobrookite. While it is difficult to discount the possibility that maghemite may be of deuteric origin, it is certain that in a large number of cases its formation is due to post-crystallization processes.

Heating experiments by LEPP (1957) have shown that the oxidation of magnetite to maghemite starts at  $200^\circ\text{C}$  and culminates at  $375\text{--}400^\circ\text{C}$ ; the inversion of maghemite to hematite starts at  $375^\circ\text{C}$  and is complete at temperatures between  $525\text{--}550^\circ\text{C}$ . In contrast, BERNAL *et al.* (1957) have shown that maghemite, formed by the dehydration of lepidocrocite, inverts completely to hematite at temperatures below  $250^\circ\text{C}$ . No data exist on the effect of titanium on either the temperature of formation or the temperature of inversion of maghemite.

The importance of maghemite in this study has been to show that it is a common low temperature oxidation product, but more important than this is the fact that it has been found in each and every lava containing "iddingsite" as an alteration product after olivine.

Although the thermal stability of titanomaghemite as opposed to pure maghemite, is not known accurately, the close association of this phase with "iddingsite", which contains goethite, having an upper stability limit of  $140^\circ\text{C}$  (TUNELL and POSNJAK, 1931), lends support to the evidence that this assemblage owes its origin to a low temperature formation. This assemblage contrasts strongly with the oxidation group of minerals formed at temperatures in excess of  $600^\circ\text{C}$ , in which the Fe-Ti oxides are replaced by pseudobrookite, rutile and titanohematite, and the olivine by either symplectic magnetite plus enstatite or hematite plus forsterite.

*c) Spinels*

Primary spinels occur in very small quantities in normal olivine basalts. They tend to crystallize at an early stage, and hence are frequently included within grains of olivine. They are less susceptible to oxidation than the Fe-Ti oxides, but nevertheless may give some indication, internal to the olivine, of the temperature at which oxidation takes place. When these spinels occur as discrete grains within a basaltic groundmass they are usually zoned by rims of primary titanomagnetite, whereas when they occur in olivine or pyroxene they are usually

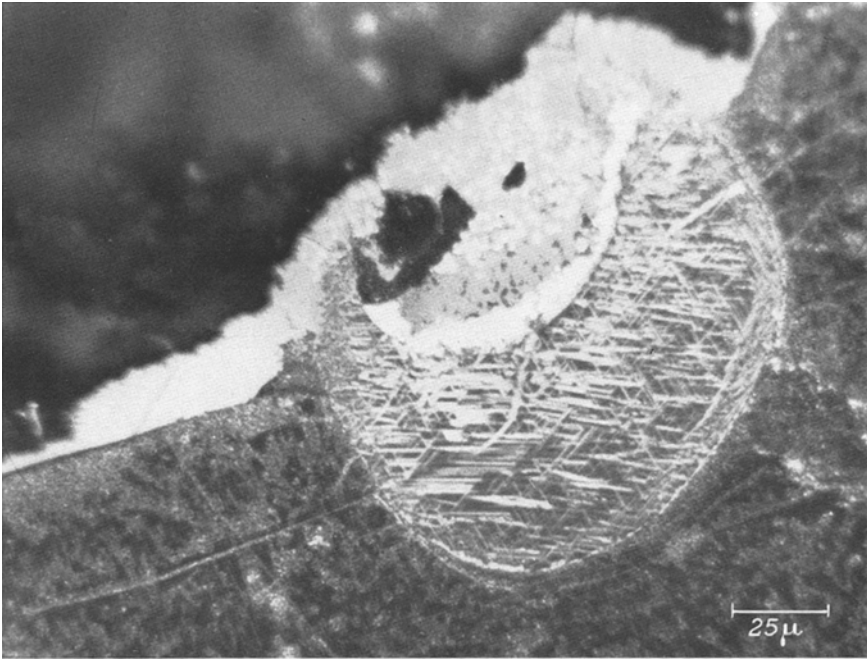


Fig. 15. An irregularly shaped spinel partly included in a highly altered olivine grain. The olivine contains abundant microsymplectic magnetite units. The spinel is densely packed with hematite lamellae along (111) parting planes. An overgrowth of pseudobrookite (grey) plus titanohematite (white), pseudomorphous after original titanomagnetite, occurs in the groundmass along the free spinel edge

homogeneous. Fig. 15 shows an oxidized spinel partly included in a high temperature oxidized olivine crystal, mantled in the groundmass by a pseudomorphic assemblage of rutile, titanohematite and pseudobrookite, after what was an original titanomagnetite overgrowth. Fine oxidation lamellae of hematite are evident in the spinel along octahedral parting planes. A thin diffusion rim of hematite, from the olivine, has developed adjacent to the spinel. Note that the density of hematite lamellae within the spinel increases towards the spinel grain boundary. Oxidation of these spinels (which are of the Cr, Al, Fe type) has the effect of darkening the spinel; this is probably caused by diffusion of the iron into (111) parting planes. Spinels, whether partially or totally included within highly oxidized olivines, provided they are closely associated with magnetite

symplectites or derived hematite, are themselves highly oxidized. It seems a relevant point to emphasize that primary titanomagnetite and ilmenite, associated with spinels in this high oxidation state are replaced by the high temperature ( $> 600^{\circ}\text{C}$ ) assemblage pseudobrookite, titanohematite and rutile.

By contrast, spinels have also been found in highly "iddingsitized" olivines, but they in no way show any sign or form of alteration. This applies equally to those spinels occurring in cores of "iddingsite" mantled by fresh olivine, or in rims of "iddingsite" around olivine. As far as the Fe-Ti oxides are concerned, titanomagnetite always shows signs of maghematization, whereas ilmenite remains completely unaffected.

The importance of pseudobrookite and maghemite as temperature indicators has already been stressed. The spinels therefore provide additional proof that the characteristic associations produced simultaneously in olivine and the Fe-Ti oxides under highly oxidizing, high temperature, conditions are quite different from those associations formed under conditions of lower temperature oxidation.

### Heating Experiments

The purpose of the heating experiments has been to determine the thermal stability of basaltic olivine under oxidizing conditions in the temperature range  $600\text{--}1000^{\circ}\text{C}$  at atmospheric pressure. An attempt has been made through these experiments to throw some light on the obvious mineralogical and textural changes that are effected within olivines of highly oxidized basaltic lavas.

Starting material for the oxidation experiments consisted of hand picked, unzoned basaltic olivine grains of composition  $\text{Fa}_{20}$ . The grain size of the starting material was of the order of 0.5 mm but additional runs were also made on material which was crushed to pass a  $-120$  mesh screen ( $< 0.01$  mm). Debye-Scherrer X-ray powder photographs were made from the material of each run using conventional glass fibre mounts. Diffractometer traces were made of several of the alteration products when sufficient material was available. Polished sections, for obvious reasons, were made only of the coarser grained material.

The experiments were carried out in air in a muffle furnace, with a temperature control unit accurate to  $\pm 10^{\circ}\text{C}$ . Runs were made in open high temperature ceramic boats; silver capsules and silica glass tubes were used in a series of further experiments. Samples from all runs were quenched in air.

Details of the duration, temperatures and results of the oxidation experiments carried out on these basaltic olivines at atmospheric pressure are summarized in Table 1.

The results of these experiments indicate that on oxidation in air at temperatures above  $600^{\circ}\text{C}$ , olivine "exsolves" its iron to form hematite, leaving behind a forsteritic enriched matrix. At  $820 \pm 10^{\circ}\text{C}$  a metastable and intermediate magnetite-pyroxene assemblage makes its first appearance. This metastable assemblage was detected in all the non-equilibrium runs up to  $1000^{\circ}\text{C}$ . It is evident from microscopic examination that the assemblage forms a symplectitic intergrowth. The symplectite inverts, with continued oxidation at constant temperature, to the stable forsterite-hematite assemblage.

Table 1. *Temperature, duration of experiment and phases present in equilibrium (< 0.01 mm) and non-equilibrium (approx. 0.5 mm) runs. Note that enstatite + magnetite make their first appearance at 820° C and also that equilibrium is reached in the 950° C experiment after 100 hours. The phases in parentheses indicate trace amounts. En = enstatite; Fo = forsterite*

Temp. °C	Duration of run in hours	Phases present	
		Grain size of starting material	
		< 0.01 mm	approx. 0.5 mm
600	100	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub>
750	100	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub>
800	100	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub>
810	100	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub>
820	24	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub>
	100	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub> (En + Fe <sub>3</sub> O <sub>4</sub> )
830	24	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub>
	100	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub> (En + Fe <sub>3</sub> O <sub>4</sub> )
850	48	Fo + Fe <sub>2</sub> O <sub>3</sub>	En + Fe <sub>3</sub> O <sub>4</sub> + Fo + Fe <sub>2</sub> O <sub>3</sub>
	100	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub>
950	24	Fo + Fe <sub>2</sub> O <sub>3</sub>	En + Fe <sub>3</sub> O <sub>4</sub> + Fo + Fe <sub>2</sub> O <sub>3</sub>
	48		En + Fe <sub>3</sub> O <sub>4</sub> + Fo + Fe <sub>2</sub> O <sub>3</sub>
	72		En + Fe <sub>3</sub> O <sub>4</sub> + Fo + Fe <sub>2</sub> O <sub>3</sub>
	100	Fo + Fe <sub>2</sub> O <sub>3</sub>	Fo + Fe <sub>2</sub> O <sub>3</sub>
	120		Fo + Fe <sub>2</sub> O <sub>3</sub>
	360		Fo + Fe <sub>2</sub> O <sub>3</sub>
1000	24	Fo + Fe <sub>2</sub> O <sub>3</sub>	(En + Fe <sub>3</sub> O <sub>4</sub> ) + Fo + Fe <sub>2</sub> O <sub>3</sub>

### X-Ray Data on Runs from Heating Experiments

X-ray powder photographs were taken of samples from each run using an 11 cm Phillips powder camera. Diffractometer traces were also made using Ni filtered Cu radiation. Small amounts of additional material were extracted from polished sections using the microsampling techniques described by HIEMSTRA (1956) and KINGSTON (1966).

The interpretation of X-ray powder photographs or diffractometer traces of multi-component assemblages may be extremely difficult. A large majority of the runs, however, contain simply hematite and forsteritic olivine of varying composition. It was only in the coarse grained material heated above 820° C, where equilibrium had not been reached, that four components were detected. These phases were identified as magnetite, hematite, enstatite and forsteritic olivine. Some difficulty naturally arises where a single reflection may be attributed to more than one phase.

The composition of the olivine formed during each of the runs has been calculated according to the method of JAMBOUR and SMITH (1964). The forsterite content of the olivine is determined by substituting the  $d(\text{Å})$  value of the (174) back reflection line in the equation:

$$(\text{mole } \%) \text{Fo} = 4151.46 - 3976.45 d_{174}$$



Table 2. *Temperature, duration of experiment, the  $d_{174}$  value from X-ray powder photographs, and the mole % forsterite as determined on coarse grained olivine (approx. 0.5 mm)*

	Temp. °C	Duration of run in hours	Olivine composition	
			$d_{174}$ (Å)	Mole % Fo
Starting material			1.0238	80.4 ± 0.6
	600	100	1.0238	80.4 ± 0.6
	750	100	1.0230	83.5 ± 0.6
	800	100	1.0228	84.3 ± 0.7
	810	100	1.0228	84.3 ± 0.7
	820	100	1.0206	93.1 ± 0.8
	830	100	1.0205	93.5 ± 0.8
	850	48	1.0202	94.7 ± 0.8
	950	24	1.0200	95.5 ± 0.8
		48	1.0192	98.7 ± 0.9
		72	1.0192	98.7 ± 0.9
		100	1.0189	99.9 ± 0.9
		360	1.0190	99.5 ± 0.9
	1000	24	1.0197	96.7 ± 0.9

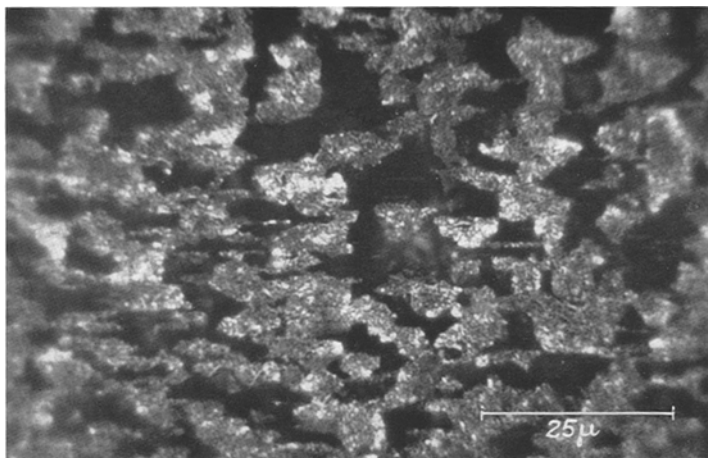
The error at 100 mole % Fo is  $\pm 0.87\%$  and at 80 mole % Fo is  $\pm 0.57\%$ . The  $d_{174}$  values and the forsteritic compositions of the olivines formed between 600 and 1000° C are listed in Table 2.

Samples from all runs above 820° C were found to be highly magnetic. It is known that continued replacement of Fe<sup>+2</sup> by Mg may take place in magnetite to form magnesioferrite, MgFe<sub>2</sub>O<sub>4</sub> (DEER, HOWIE and ZUSSMANN, 1962). The possible presence of magnesioferrite rather than magnetite has been considered in the high temperature oxidation of olivine, but has as yet not been detected. While only small differences exist in the unit cell dimensions (Fe<sub>3</sub>O<sub>4</sub>,  $a = 8.391$ ; MgFe<sub>2</sub>O<sub>4</sub>,  $a = 8.383$ ) the intensity of the (111) reflection at 8.84 Å is quite distinct (BERRY and THOMPSON, 1962). The X-ray data are supported by the mineralogical evidence in polished sections, suggesting that the opaque symplectic phase is magnetite and not magnesioferrite. The reflectivity of the (Mg, Fe, Al, Cr) spinel group is lower and the colour darker than that of magnetite. Small amounts of MgO may nevertheless be present in the magnetite. The fineness of the magnetite symplectite, and the fact that it is closely associated with enstatite, has precluded the positive confirmation or absence of Mg even by electron probe microanalysis.

Microsampling traverses across four olivine grains, selected from polished sections of non-equilibrium runs, has confirmed that towards the edge of an olivine grain forsterite is associated with hematite, and that towards the centre, the symplectite consists of enstatite and magnetite.

### Reflection Microscopy

By using relatively coarse grained material, the oxidation and temperature gradients that are set up within single grains have permitted a detailed study to be made optically of the progressive textural and oxidation changes that occur from the edges, where equilibrium is reached, to the centre, where in the experiments of shorter duration the olivine is completely unaltered.



Figs. 16—25. Illustrate the results of heating experiments on olivine under oxidizing conditions

Fig. 16. Sub-spherical magnetite symplectic units near the centre of an olivine grain. Finer oriented lens-shaped units also occur (950° C/48 hrs.)

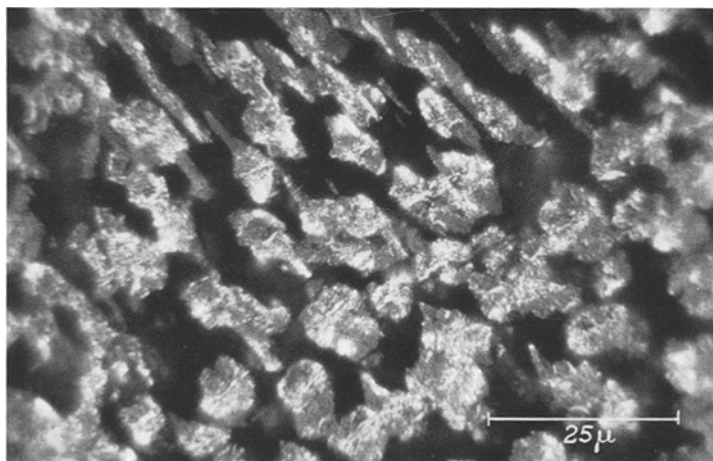


Fig. 17. The sub-spherical units gradually develop into lens-shaped forms, and in doing so a crystallographic lineation of the symplectic units becomes apparent (950° C/72 hrs.)

Samples heated above 820° C all showed hematite diffusion rims and the magnetite-pyroxene symplectite. The degree of development and complexity of these intergrowths, and the thickness of the rims varied with the duration of the experiment. A common feature in all of these experiments is the initial development of small spherical to sub-spherical symplectic nuclei. As these nuclei grow and become more numerous they tend to become lens shaped. Individual units may show a remarkable degree of orientation (Fig. 17). The gradual coalescing of these lens shaped units produces the symplectic pinch and swell structures illustrated in Fig. 18. Symplectites also develop from narrow cracks and flaws in

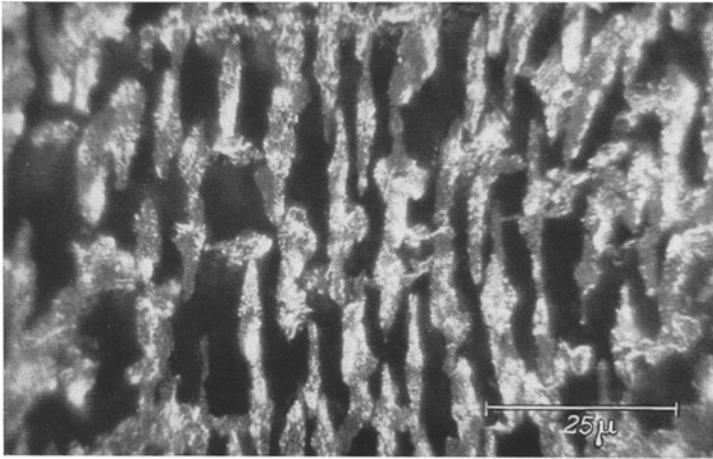


Fig. 18. Well oriented magnetite symplectic units in a groundmass of unaltered olivine. Although the units are well defined, and are structurally controlled, the symplectic intergrowths within the units are quite haphazard (950° C/72 hrs.)

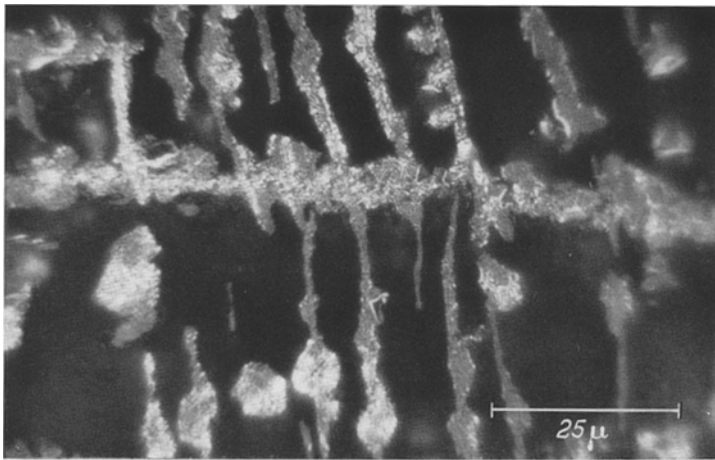
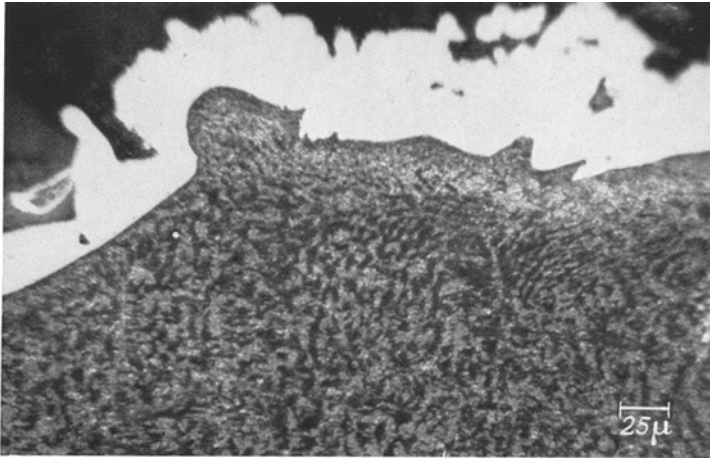


Fig. 19. A herringbone texture of symplectic magnetite which has developed along flaws within the olivine (950° C/48 hrs.)

the olivine. Branches, sub-branches and budding of the symplectite may take place, which then results in a herring-bone structure of the type shown in Fig. 19. Towards the grain boundaries and concentric to it, lenses, pinch and swell symplectites and fine inter-unit symplectic lamellae all merge into a densely packed halo adjacent to the hematite zone. These grains, in common with the naturally occurring olivines, show the vermicular to lath transformation that occurs during the oxidation of symplectic magnetite to hematite (Figs. 21 and 22). It is within this outer zone that equilibrium conditions are reached, and it is here that forsterite is the chief magnesium silicate.

Hematite diffusion rims are extremely well developed in the higher temperature runs. These rims are generally continuous but tend to be irregular (Fig. 20) and



Figs. 20—22. This series illustrates the magnetite symplectite to lamellar hematite transformation which takes place on oxidation

Fig. 20. A large fragment of olivine containing massed symplectitic units of magnetite and an irregular bulbous diffusion rim of hematite (950° C/24 hrs.)

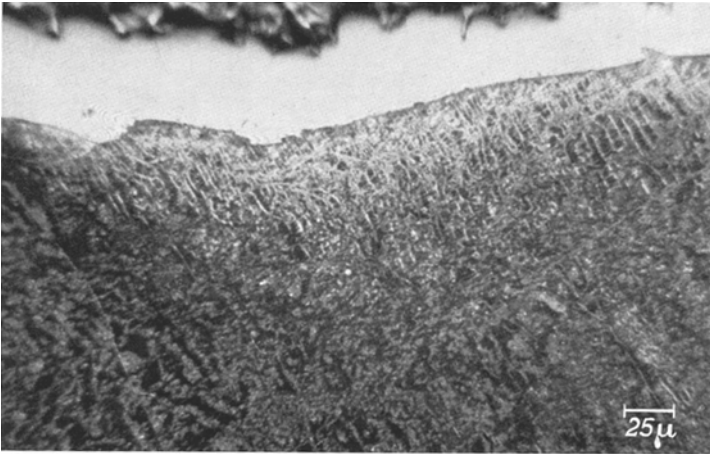


Fig. 21. A more advanced stage of oxidation in which the magnetite symplectite to lamellar hematite transformation begins to appear towards the edge of the grain, adjacent to the diffusion rim (950° C/48 hrs.)

are often of a rather bulbous nature. This feature is undoubtedly related to the fact that the grain boundaries in the heating experiments are unrestricted and not confined as in a crystalline basaltic host. Jagged saw tooth growths of diffused hematite frequently develop within the olivine along fine hair-line cracks.

Although hematite diffusion rims around olivine were found to be extremely common in the highly oxidized lava samples examined, it was nevertheless considered that these rims may owe their origin, in part, to primary marginal fayalitic zoning. The textural evidence however, supports the idea that diffusion

and migration does take place, not only within the crystal, but also towards the crystal boundaries. Great care was taken in the initial choice of the starting material to ensure that the olivines were free of magnetite, and Cr-spinel inclusions, and were unzoned. The textural interpretation that  $\text{Fe}_2\text{O}_3$  concentrations at the crystal boundaries are the result of an oxidation-diffusion process at high temperatures is supported by the heating experiments. The starting material for the heating experiments was fragmented. It is unlikely therefore, that continuous oxidation diffusion rims of hematite are in any way related to iron-rich zones

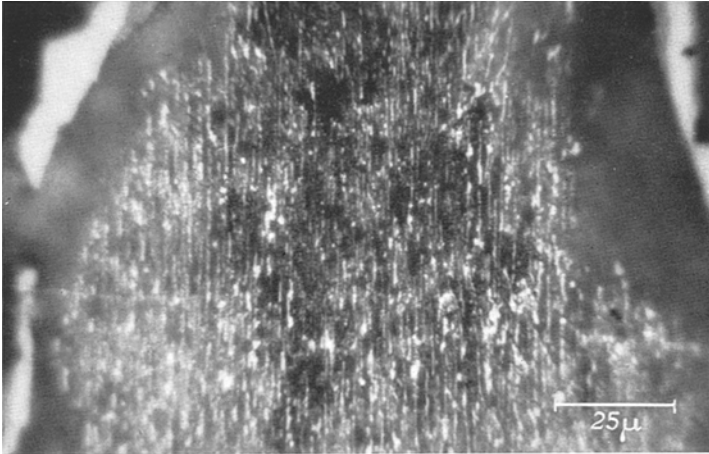
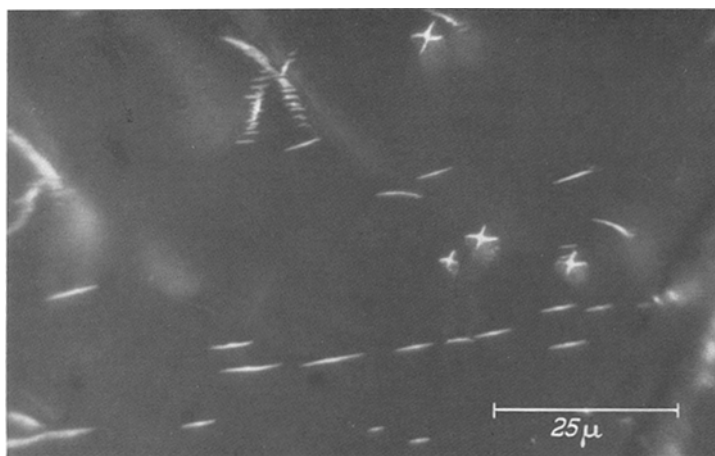


Fig. 22. The final stage in which all the magnetite has inverted to hematite. A prominent iron oxide-deficient zone occurs adjacent to the narrow irregular diffusion rim (950° C/100 hrs.)

within the olivines, and although fayalitic zoning will undoubtedly effect a concentration of iron towards the margins, processes of diffusion play the major role.

The  $\text{Fe}_2\text{O}_3:\text{Fe}_3\text{O}_4$  ratio increases rapidly with longer periods of heating. No magnetite was detected in the coarse grained material at 950° C for example after 100 hours. The final product in polished section contains thin oriented laths of hematite in an intensely reddened forsteritic matrix and is zoned by the characteristic  $\text{Fe}_2\text{O}_3$  diffusion rim. The textural form of this assemblage is identical to the natural sample and is illustrated in Fig. 22.

Samples heated below 820° C all showed the direct segregation of hematite from within the olivine. Hematite rims were found to be common but generally less well developed than in the higher temperature runs. In the 600° C run, after 100 hours, the olivine became intensely reddened and only small amounts of hematite were detected at the grain boundaries. The rather unusual textural forms of the opaque phase in the 600—810° C experiments are illustrated in Figs. 23 and 24. Unlike the spherical nuclei of the symplectites, the onset of alteration is marked by the development of minute star shaped bodies and en echelon lenses of hematite. These gradually develop with intriguing structural complexity towards the crystal boundaries. It is evident from the photomicrographs that these bodies are crystallographically controlled. The phases and textural form of the alteration



Figs. 23—25. Olivine grains heated at 800° C for 100 hours

Fig. 23. Bright star-shaped forms and narrow lenses of hematite occurring towards the centre of an oxidized olivine grain. The halo effect, around the stars, is caused by internal reflections of the lamellae at depth

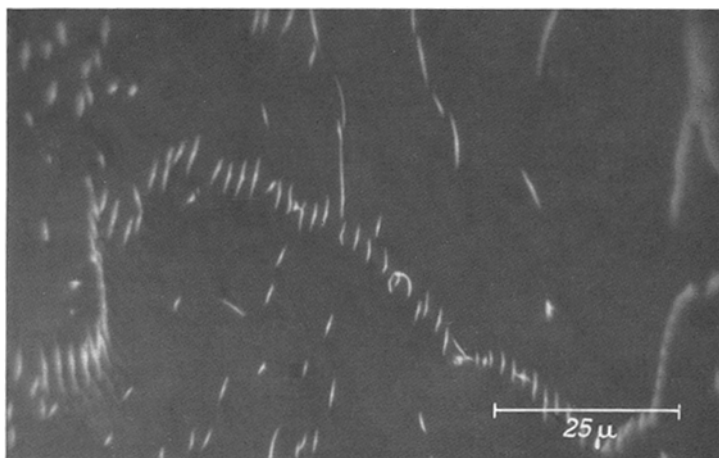


Fig. 24. A sinuous train of hematite lenses showing some degree of orientation, parallel to the long axis of the lens

products in these runs compare favourably with naturally reheated olivines in pahoehoe flow units and in olivine-bearing xenoliths.

The X-ray data indicate that with continued exsolution of the iron the olivine becomes more forsteritic in composition.

An important point to note with reference to the high temperature alteration of olivine, is that only oxygen needs to be added to effect the mineralogical changes that are observed in nature. No further introduction or removal of material is necessary. This contrasts greatly with the low temperature alteration of olivine which is discussed in Part II of this paper.

The production of fine magnetite intergrowths in highly oxidized olivines should be of extreme importance to research workers engaged in studies of the petrology of rock magnetism. WATKINS and HAGGERTY (1965) have shown, for example, that the intensity and stability of magnetization increases with increasing oxidation. The increase in intensity of magnetization is undoubtedly due to the production of symplectic magnetite, whereas the stability may owe its origin to its extremely fine grain-size (LARSON *et al.*, 1966). The highly oxidized parts of a lava are characterized by the weakly magnetic assemblage pseudobrookite,

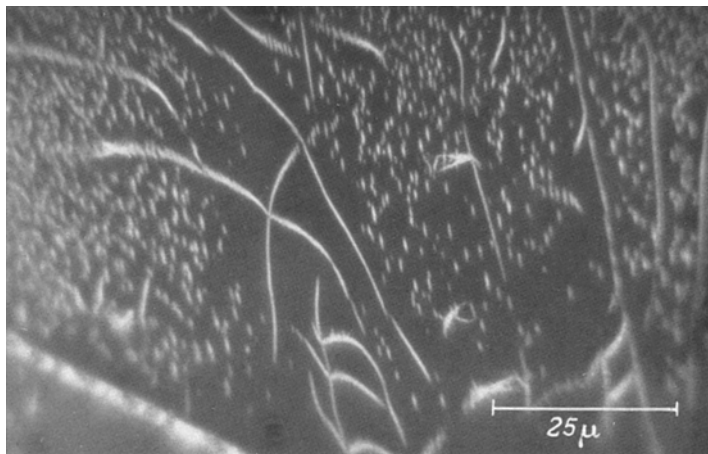


Fig. 25. Short parallel lenses, composite stringers and complex en echelon star-shaped bodies of hematite, in an area towards the edge of an altered olivine grain

titanohematite and rutile. In addition, the distinction between high and low temperature, deuteric and post crystallization alteration features and the production of non-titaniferous magnetite, are all important considerations to be taken into account in mineralogical studies of magnetic self-reversal processes.

### Conclusions

1. The high temperature oxidation of olivine may produce either magnetite plus enstatite, or hematite plus forsterite.
2. Heating experiments on basaltic olivine ( $\text{Fa}_{20}$ ) at atmospheric pressure in the temperature range 600—1000° C have shown that forsterite plus hematite is the stable assemblage.
3. Magnetite plus enstatite is an intermediate and metastable assemblage. Its first appearance has been noted at 820° C, and it continues to appear up to 1000° C. With sustained oxidation, magnetite plus enstatite inverts to forsterite plus hematite. This latter assemblage also develops between 600 and 820° C.
4. The discrete Fe-Ti oxides, which accompany the development of magnetite + enstatite or derived forsterite + hematite assemblages in altered olivine, are typically pseudobrookite, rutile and titanohematite, which have formed by oxidation after original titanomagnetite and ilmenite. The presence of pseudobrookite in particular, having a lower thermal stability limit of  $580 \pm 15^\circ \text{C}$ ,

supports the high temperature origin of iron oxide intergrowths in altered olivines.

5. Texturally the opaque phases of oxidized olivines are characterized in polished section, by the following features:

- i. Vermicular magnetite forms symplectic and microsymplectic intergrowths.
- ii. A progressive transformation of vermicular magnetite to lamellar hematite takes place with progressive oxidation.
- iii. Hematite derived directly from olivine is lensoid or flame-like in form.
- iv. Hematite or hematite-spinel rims develop towards the edge, but within, the crystal boundaries of highly oxidized olivines.

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