

# A Detailed Opaque Petrological and Magnetic Investigation of a Single Tertiary Lava Flow from Skye, Scotland—I

## Iron-Titanium Oxide Petrology

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### *Summary*

The iron–titanium oxides of 45 samples from a single tertiary lava flow from Skye, Scotland, have been subjected to detailed examination and quantitative measurement.

A basically simple assemblage of titanomagnetite (93–100 per cent) and discrete ilmenite (0–7 per cent) has, in most samples experienced one or both of two types of alteration, titanomagnetite high-temperature oxidation and ‘titanomagnetite granulation’, which we define in this paper.

Titanomagnetite high-temperature oxidation, describing the process of ilmenite exsolution and further oxidation, varies rapidly but largely systematically within the flow. Parallel alteration of discrete ilmenite and olivine also occurs.

Titanomagnetite granulation, describing the alteration of titanomagnetite to impure rutile granules, only affects samples with limited development of high-temperature oxidation and varies throughout the lava in a rather unsystematic fashion. While high-temperature oxidation is almost certainly wholly of deuteric origin titanomagnetite granulation is shown usually to require burial to greater than 900 m for its formation, and thus may not take place until several million years after the extrusion of a lava flow. The mechanisms by which these two types of alteration take place, and their implications for palaeomagnetic interpretation, are discussed.

### 1. Introduction

The purpose of the series of three papers is to describe the results of a wide range of magnetic and opaque petrological measurements carried out on 45 cores from a single basaltic lava flow. We were encouraged to carry out this study by the interesting discovery of considerable variation of properties within a single Icelandic lava flow by Watkins & Haggerty (1965). In attempting to understand the complex relationships between magnetic properties and opaque mineralogy we have accumulated data that is best described in separate papers (Parts I and II). Part III deals with attempts to obtain a value for the intensity of the ambient magnetic field ( $F_{ANC}$ ) at the time of cooling of the lava using different techniques and groups of samples of different titanomagnetite oxidation states. In this paper we first describe different

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types of titanomagnetite alteration, their quantitative measurement, and related effects on the silicate minerals. We continue by describing the spatial distribution and inter-relationships of alterations and conclude by a discussion of the origin of the alterations.

## 2. The lava flow

The lava was sampled in detail by one of us (M.A.K.) during a systematic survey of the palaeomagnetism of the tertiary (probably Palaeogene) Skye plateau basalt lavas (Khan 1960). This particular olivine basalt flow is number eleven of the Storr succession (Khan 1960, Fig. 1; Anderson *et al.* 1966, p. 83) and is located at 6° 10·0' W and 57° 30·5' N at an elevation of 600 m. Two vertical sections, separated horizontally by approximately 16 m, were sampled with an average interval of about 15 cm, using a coring drill clamped to the rock face by expansion bolts (Brown & Khan 1960). At one position the section sampled was about 6 m in vertical extent (Section 1) and at the other about 4 m (Section 2). Three-quarter inch length and diameter cylindrical samples taken from about half the drill hole locations have been used in this detailed study.

Olivine is generally abundant and tends to occur in clusters where it is associated with spinel and poikilitic rounded titanomagnetite (elsewhere titanomagnetite is typically anhedral to ophitic in form, e.g. Plate 1). The zeolite chabazite occurs within the flow (Anderson *et al.* 1966).

## 3. Iron-titanium oxide petrology

A simple iron-titanium oxide mineral facies characterizes unaltered samples. The dominant mineral is titanomagnetite, accounting for between 93 and 100 per cent by area of the total opaque mineral content. Discrete ilmenite is the remaining iron-titanium oxide mineral. With the exception of occasional rounded poikilitic grains associated with olivine clusters, the titanomagnetite occurs as anhedral to ophitic grains. Ilmenite usually occurs as elongate or needle-like grains.

Few samples contain titanomagnetite grains in an unaltered state. In most cases one or both of two types of titanomagnetite alteration occur and since these types of alteration are found to largely control the variation of magnetic properties, considerable effort was given to identification of phases and quantitative measurement.

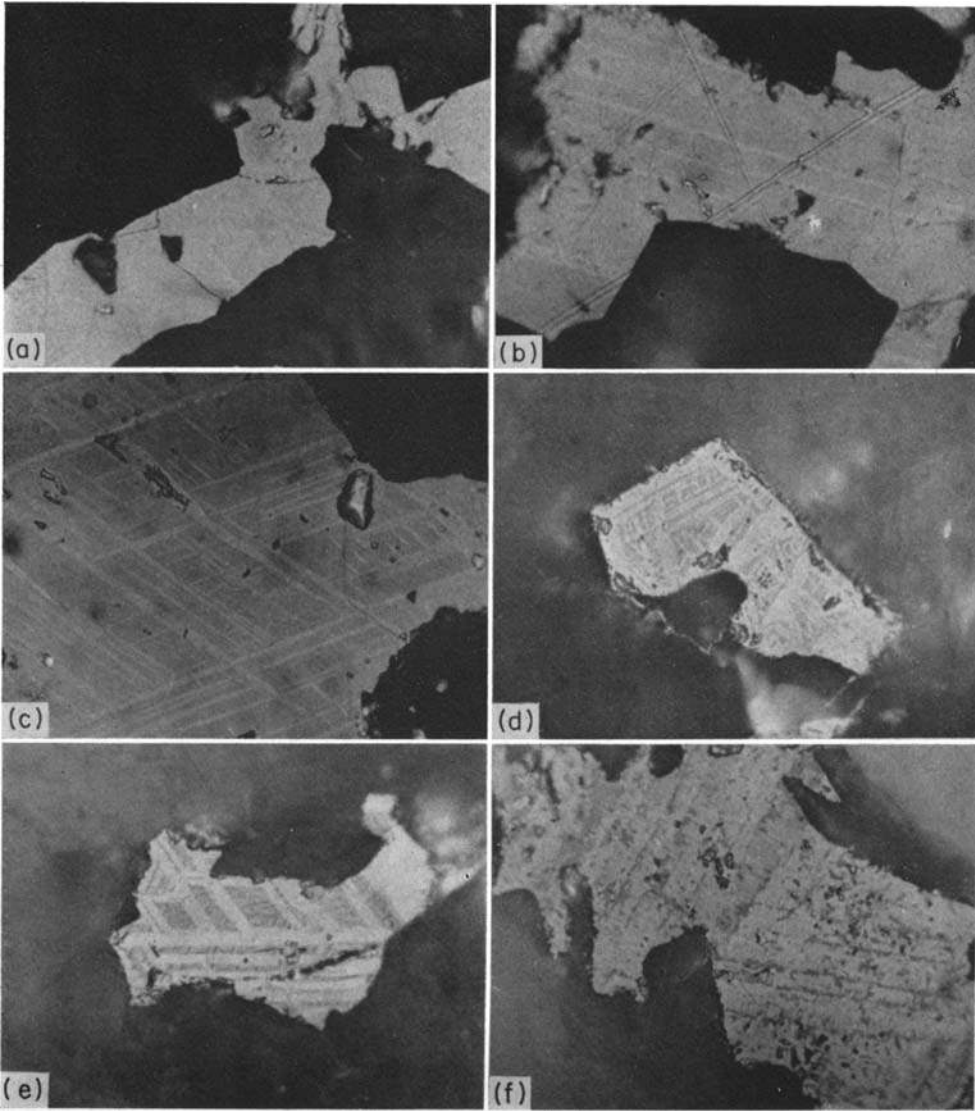
These two alteration processes are designated titanomagnetite high-temperature oxidation and titanomagnetite granulation and are described in detail below.

### 3.1 Titanomagnetite high-temperature oxidation (Plate 1)

This type of alteration consists of the rather well-known process of sub-solidus oxidation followed by aggregation into an octahedrally directed exsolution-like texture of ilmenite in titanomagnetite, together with further stages of oxidation to a final form consisting of an aggregate of rutile (at least largely  $\text{TiO}_2$ ), pseudobrookite (at least largely  $\text{Fe}_2\text{TiO}_2$ ) and titan-hematite. Laboratory studies on the rate of reactions involved in the process and the stability field of pseudobrookite (Lindsley 1965 and personal communication) suggest that the process can only take place at temperatures in excess of approximately 600 °C. Since such temperatures are usually only experienced by a lava during initial cooling, the time at which high-temperature oxidation takes place is limited to this period, that is, it is a deuteric process.

During recent years considerable interest has been shown in the relationship of magnetic properties to titanomagnetite high-temperature oxidation state (Ade-Hall & Wilson 1964; Ade-Hall, Wilson & Smith 1965; Watkins & Haggerty 1965; Larson & Strangway 1966; Wilson & Watkins 1967, etc.) and various schemes of

Plate 1



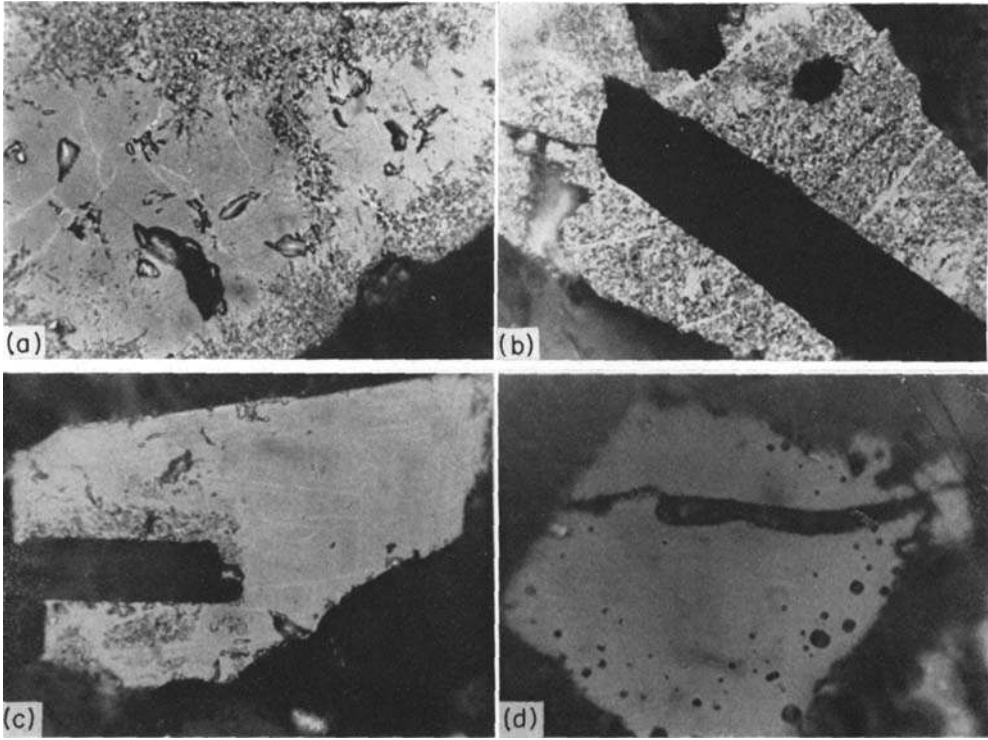
100  $\mu$

( $\times 750$ )

- (a) Class 1 titanomagnetite.
- (b) Class 2 titanomagnetite.  
White—exsolved ilmenite; light grey—titanomagnetite.
- (c) Class 3 titanomagnetite.  
Light grey—exsolved ilmenite; darker grey—titanomagnetite.
- (d) Class 4 titanomagnetite.  
White—hematite and other products of the decomposition of ilmenite lamellae; light grey—magnetite.
- (e) Class 5 titanomagnetite.  
White—titanomagnetite; light grey—cubic phase; black—spinel rods.
- (f) Class 6.  
White—titanomagnetite; light grey—rutile; dark grey—pseudobrookite.

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## Plate 2



100  $\mu$

( $\times 750$ )

- (a) Granulation developed peripherally and internally so as to subdivide the grain. Light grey—titanomagnetite.
- (b) Titanomagnetite almost completely covered by granules.
- (c) A titanomagnetite grain showing the effects both of high-temperature oxidation and granulation. White—exsolved ilmenite; light grey—titanomagnetite. The distribution of granulation is clearly controlled by the ilmenite lamellae.
- (d) Poikilitic magnetite (light grey) with a core of spinel (darker grey).

classification allowing quantitative measurement have evolved. In the most detailed of these schemes high-temperature oxidation has been divided into six progressive stages, each represented by a 'class'.

The oxidation classes used here only differ from those defined by Wilson & Watkins (1967) in that Class 5 has been subdivided, into a more strictly defined Class 5 and a new Class 6.

The definitions of these six classes are:

*Class 1.* (Plate 1(a)) Titanomagnetite with absolutely no ilmenite exsolution. Initially the titanomagnetite is light tan or brown (at  $\times 1200$  with oil immersion and no colour filters using a Reichert Zeto-pan Pol Microscope). It may, however, develop ill-defined whitening and also a feature which we proposed to call granulation. A description of granulation is given later. The titanomagnetite is neither pleochroic nor anisotropic.

*Class 2.* (Plate 1(b)) Titanomagnetite which may have any of the characteristics of Class 1, but in addition one or more ilmenite lamellae have been developed in *some parts* of the grain. The maximum degree of exsolution described by this class is where just less than 50 per cent of the grain area contains dense ilmenite exsolution. The ilmenite lamellae may be very fine, whitish but of low reflectivity, or pink. The ilmenite is pleochroic and anisotropic.

*Class 3.* (Plate 1(c)) As for Class 2 but *more* than 50 per cent of the grain area contains dense ilmenite exsolution.

*Class 4.* (Plate 1(d)) Titanomagnetite containing a high density of highly reflecting white pseudomorphs after ilmenite lamellae.

*Class 5.* (Plate 1(e)) The original ilmenite lamellae have now recognizably become replaced by fine aggregates of hematite, rutile and sometimes pseudo-brookite. These are all pleochroic and anisotropic to different degrees. The cubic phase is relatively dark brown, typically with short black exsolution rods, probably of a spinel different from magnetite. These spinel rods follow different crystallographic directions from the pseudomorphs after ilmenite lamellae.

*Class 6.* (Plate 1(f)) The grain now consists of an aggregate of hematite and pseudobrookite and sometimes rutile. The lamellae structure has either completely disappeared or remains as a crude relic structure. The hematite is white and highly reflecting, pseudobrookite dark grey, rutile medium grey.

This definition of Class 6 differs slightly from that used in Wilson, Haggerty & Watkins (1968), where the presence of pseudobrookite is the only criterion for inclusion in Class 6. That is, a grain containing both a cubic phase and pseudobrookite would be classified as Class 5 in this paper and Class 6 by Wilson, Haggerty & Watkins.

Many samples contained grains representing several different classes; titanomagnetite high-temperature oxidation in these samples typically varied considerably over very small distances, sometimes only a few tens of microns, and it was found by trial to be necessary to classify and measure the areas of each of 100 opaque grains, well spread over the polished specimen, to obtain a representative average for the titanomagnetite high-temperature oxidation state of a sample. The mean degree of titanomagnetite high-temperature oxidation was expressed by a *magnetite oxidation number*,  $M$ , defined as

$$M = \sum_{1=n}^6 (n \times \text{percentage of total magnetite area represented by Class } n)$$

giving a number between 1.00 and 6.00, the two limits of the titanomagnetite high-temperature oxidation scale as defined here. (The program for the computation of  $M$ , and other calculations utilizing the Chadwick Laboratory IBM 7040 computer, are the work of Dr P. Dagley.)

What are probably also high-temperature alteration effects were also recognizable in other minerals. Discrete ilmenite showed exsolution of ferri-rutile and other phases (Wilson & Haggerty 1966) in samples where titanomagnetite high-temperature oxidation was well developed. Quantitative measurement of ilmenite alteration resulted in the definition of an ilmenite oxidation number. Two ilmenite classes were established: Class 1 contains homogenous or patchily altered discrete ilmenite and Class 2 contains ilmenite with any degree or form of ferri-rutile exsolution. The ilmenite oxidation number is exactly analogous to the magnetite oxidation number and varies between 1.00 and 2.00.

The nature of the very slightly developed alteration products of olivine also correlates with the development of titanomagnetite high-temperature oxidation. In samples where oxidation is well developed olivine is characterized by reddening along and adjacent to cracks. In samples where oxidation is weakly developed or absent, olivine alteration is characteristically in the form of small greenish areas. Babkine (1965) describes the association of olivine 'iddingsitization' in a basaltic lava with maximum titanomagnetite oxidation, in that case to hematite.

### 3.2 Titanomagnetite granulation (Plate 2)

This is an apparently undescribed form of titanomagnetite alteration consisting of the development of irregular areas of fine granular texture. The individual granules are  $1\mu$  and smaller in size and have not been identified unambiguously using the microscope. Granulation may be developed peripherally (Plate 2(a)), along the margins of cracks (Plate 2(a)) or in irregular areas that are apparently unrelated to any features of the grain. Granulation and titanomagnetite high-temperature oxidation effects are generally inversely related in their development. That is, granulation occurs most frequently in Class 1 titanomagnetite grains (where it can cover a grain completely, Plate 2(b)), less frequently in Class 2 grains, very rarely in Class 3 grains and has never been found in titanomagnetite of Classes 4–6. Granulation has been noted in other Scottish tertiary basaltic rocks and in limited development in Eastern Icelandic basalts.

**3.2.1 Composition of granules.** As mentioned above, the small size of granules precludes certain microscopic identification. However, occasional red and blue-green internal reflections suggest a transparent phase.

Magnetic separation by crushing to 400 mesh and magnetic extraction has been carried out on three samples where granulation is well developed, and these extracts were examined using an 11.5-cm diameter Debye–Sherrer powder camera (16 h exposure, Co  $K\alpha$  radiation, Fe filter). In each case the presence of two phases was recognizable on the film. The majority of the lines were identified as originating from a spinel structure but three or four small angle lines originated from a separate structure. Table 1 lists these non-spinel lines.

**Table 1**

#### *Lattice parameters for non-spinel lines*

Sample	$d$ (Å) (in order of relative intensities)	Tetragonal cell parameters		
		$a$ (Å)	$c$ (Å)	$(c/a)$
1212	3.27, 1.756, 2.616, 2.294	4.70	3.14	0.66
1292	3.28, 1.753, 2.292	4.63	3.25	0.70
233a	3.26, 1.753, 2.608, 2.286	4.72	3.13	0.67
		mean $a$ : $4.68 \pm 0.04$ Å		
		mean $c$ : $3.17 \pm 0.05$ Å		
		mean $c/a$ : $0.68 \pm 0.02$		

Comparing with iron-titanium oxides\* in the ASTM index, card no. 4-0551 (synthetic rutile,  $\text{TiO}_2$ ) agrees most closely in relative intensity and magnitude with the lines for the unknown phase, with  $d$  lines 3.25 (100), 1.69 (50) and 2.49 (41) and cell parameters  $a = 4.59 \text{ \AA}$ ,  $c = 2.96 \text{ \AA}$  and  $(c/a) \approx 0.643$ . Since there is significant difference between the calculated cell parameters for the non-spinel phase and those for synthetic rutile it seems most probable that the non-spinel phase is an impure rutile.

**3.2.2 Genesis of granules.** In this section the more definite evidence for the conditions of formation of granules is described. In a later section (5.2) there is a more general discussion of the problems associated with the formation of granules and some of the implications of the occurrence of this type of titanomagnetite alteration.

Microscopic observation shows that the granules were formed *after* the exsolution of ilmenite had taken place. This can be seen from Plate 2(c) in which the pattern of ilmenite exsolution clearly controls the distribution of granules.

Evidence on the conditions and time of granule formation also arises from unpublished opaque petrological data on basaltic lavas from Eastern Iceland described by Dagley *et al.* (1967). Walker (1960) has been able to demonstrate the existence of a series of zones, based on zeolite assemblages, within the Eastern Iceland lava sequence. Field evidence suggests that these zeolite assemblage zones, which clearly transgress the lava stratigraphy, are related to the depth of burial below the original surface of the lava pile. The basaltic material described by Dagley *et al.* has been classified by Walker (personal communication) into five zeolite assemblage zones, and these were related to depth of burial beneath the original surface of the lava pile. Granulation occurs in 40 of the 207 Eastern Iceland samples examined. Of these 40 samples, 37 from two separate parts of the succession are restricted to the *two deepest* zeolite assemblage zones, zone D at 900–1200 m below the original lava surface (14 samples) and zone E at greater than 1200 m below this surface (23 samples). Fig. 1 illustrates this result in histogram form.

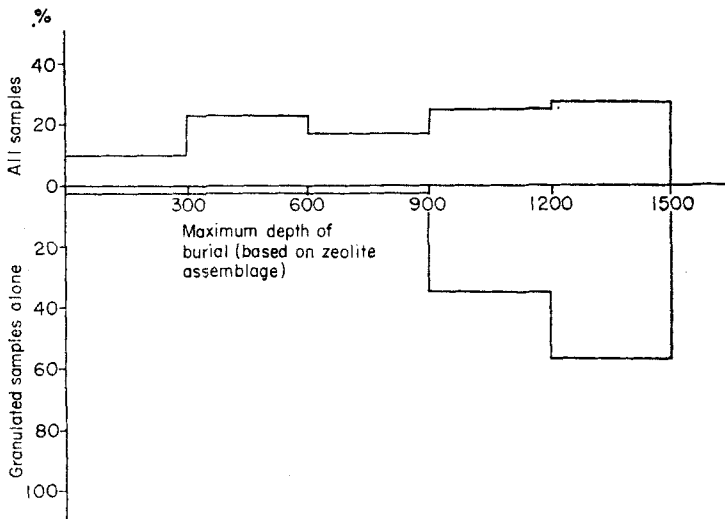


FIG. 1. Zeolite zone distribution of eastern Icelandic samples with granulated titanomagnetite.

\* The values of  $a$ ,  $c$  and  $c/a$  obtained from the X-ray powder diffraction films are actually closer to those reported for tin oxide,  $\text{SnO}_2$  ( $a$ : 4.74,  $c$ : 3.19,  $c/a$ : 0.67) which has a very similar structure to rutile. However, the order of the lines on the basis of relative intensity agrees with rutile and not with  $\text{SnO}_2$ .

This evidence from the Eastern Icelandic lavas suggests that titanomagnetite granulation usually does not take place until considerable burial has been achieved. Thus the alteration is most likely to take place at a very much later time, perhaps several million years later, than the formation of the flow.

3.2.3 *The magnetite granulation number.* Measurements of the development of granulation in a sample have been expressed as a magnetite granulation number,  $G$ . The basic measurement is of the area percentage of granulation for each grain, estimated to the nearest 10 per cent.  $G$  is calculated from the mean area percentage of granulation for a sample as:

$$G = \left( \frac{P}{20} \right) + 1$$

where  $P$  is the mean area percentage of granulation for 50 titanomagnetite grains per section. Expressed deliberately in this rather artificial way  $G$  varies between 1.00 (granulation absent) and 6.00 (every grain completely granulated) and thus has the same numerical range as the magnetite oxidation number,  $M$ .

### 3.3 *Poikilitic magnetite (Plate 2(d))*

Mention should be made of the fact that this type of magnetite responds to the causes of high-temperature oxidation and granulation in a different manner to the common ophitic magnetite. In samples where high-temperature oxidation is well developed in the ophitic titanomagnetite, the poikilitic magnetite rarely shows any indication of high-temperature oxidation. When there is any response to the conditions causing this type of oxidation, it is in the form of occasional thin white octahedrally directed exsolution lamellae. In this lava poikilitic magnetite *never* shows the development of granulation. The explanation for these different responses is unknown to us but would be consistent with the poikilitic magnetite being relatively titanium deficient compared with the ophitic magnetite.

## 4. Spatial variation and interrelationships between iron–titanium oxide parameters

Tables 2 and 3 list values of  $M$ ,  $I$  and  $G$  together with other parameters obtained during the same calculations. These are magnetic grain dimension (MGD), a mean linear dimension for the magnetite grains examined, ilmenite grain dimension (IGD), and magnetite percentage (MAGPERC) titanomagnetite as an areal percentage of the total titanomagnetite and discrete ilmenite. The magnetite and ilmenite grain dimension parameters are obtained from the average grain *areas* respectively not the average grain volumes as used by Wilson *et al.* (1968). Following Wilson *et al.* the grains chosen for measurement in a sample were restricted to those with volumes in excess of 3 per cent of the volume of the largest grain seen in a preliminary survey. Figs 2 and 3 show profiles of these parameters.

The systematic and parallel variation of  $M$  and  $I$  in each section is striking. It is also important that the form and magnitude of this parallel variation is quite different for the two sections although they are separated horizontally by only 16 m. It is worth noting that in contrast with this result, Watkins & Haggerty (1967) find only a small difference between adjacent oxidation profiles through an Icelandic basalt flow. Test correlation of  $M$  and  $I$  gives a certainty of a linear relationship of over 99 per cent with a value of  $r$  of +0.88 (Fig. 4). In Section 1 there is a zone of about 250 cm thickness with *high*  $M$  and  $I$  within the lower half of the flow and a similar zone of about 280 cm thickness of *low*  $M$  and  $I$  at the top of the flow. Three thin zones of rapid change in oxidation also occur; a low centred on 70 cm above the base, a high centred at 375 cm and another high at the very top of the section.



**Table 2**  
*Iron-titanium oxide parameters for Section 1*

Sample	Position (cm)	<i>M</i>	<i>G</i>	<i>I</i>	MGD ( $\mu$ )	IGD ( $\mu$ )	MAG PERC (%)
1001	30	2.59	1.00	1.20	30	15	97.5
1011	42	4.31	1.00	2.00	24	12	98.8
1012	42	4.43	1.00	1.66	30	13	98.4
1013	42	3.75	1.00	1.40	26	13	99.2
1021	56	4.45	1.00	2.00	30	12	99.2
1022	56	4.11	1.00	1.93	26	15	96.4
1032	70	1.00	1.23	abs.	31	—	100.0
1033	70	1.00	1.32	abs.	27	—	100.0
1041	84	2.00	2.67	1.00	50	12	99.7
1042	84	2.55	1.00	1.79	35	14	99.1
1051	99	3.52	1.00	1.34	36	12	97.0
1052	99	3.52	1.00	2.00	29	9	99.5
1093	152	3.27	1.00	2.00	34	25	95.7
1132	209	2.95	1.00	1.72	43	17	92.7
1141	222	3.84	1.00	1.93	43	18	97.7
1151	236	3.77	1.00	2.00	57	20	98.9
1163	251	3.14	1.01	1.91	47	23	95.5
1172	257	2.84	1.03	1.86	48	15	97.7
1181	284	2.53	1.07	1.80	58	15	99.2
1191	299	2.18	1.27	1.48	63	20	98.3
1201	314	1.34	2.43	1.20	65	16	98.5
1212	328	1.12	3.60	1.05	62	18	97.9
1213	328	1.00	3.87	1.00	60	6	99.9
1221	346	1.04	2.46	1.00	51	16	98.7
1231	360	1.07	3.40	1.04	61	14	98.8
1242	375	1.72	1.43	1.10	55	16	99.0
1252	383	1.05	2.41	1.14	42	14	94.4
1293	436	1.03	3.72	1.00	60	13	98.8
1331	485	1.00	2.95	1.00	44	8	98.8
1363	518	1.00	4.15	1.00	70	19	95.9
1401	566	1.00	3.33	abs.	39	—	100
1431	594	1.34	2.14	1.00	43	9	99.7
1444	607	3.27	1.29	abs.	48	—	100

**Table 3**  
*Iron-titanium oxide parameters for Section 2*

Sample	Position (cm)	<i>M</i>	<i>G</i>	<i>I</i>	MGD ( $\mu$ )	IGD ( $\mu$ )	MAG PERC (%)
2013	0	1.26	1.10	1.00	26	11	96.4
2062	66	1.08	5.00	1.00	30	10	98.0
2093	102	1.00	1.94	1.00	64	13	99.1
2123	140	1.00	1.10	1.00	49	12	99.0
2153	178	1.00	1.38	1.00	107	22	98.8
2183	214	1.00	1.46	1.00	77	16	98.7
2212	256	1.00	2.94	1.00	67	7	98.5
2243	294	1.02	1.88	1.00	60	11	98.7
2271	334	2.11	1.36	1.74	55	6	99.9
2312	366	1.00	1.00	1.00	125	12	99.4
2321	380	1.01	4.12	1.00	43	11	99.7
233a	390	1.00	3.02	1.00	32	9	99.9

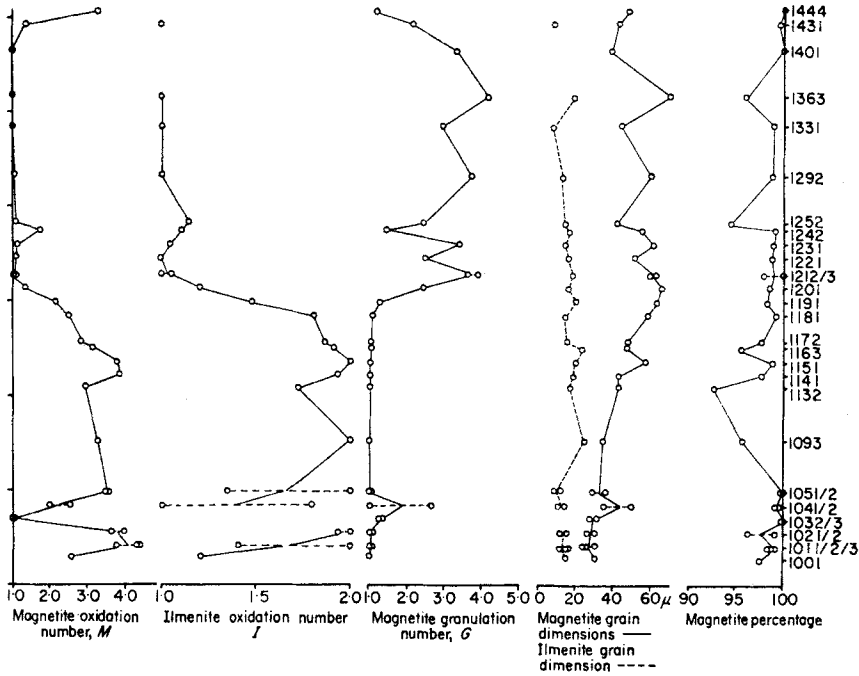


FIG. 2. Spatial variation of opaque petrological properties in Section 1.

In Section 2, apart from a weakly developed zone of oxidation at the base, only an isolated sample at 334 cm shows appreciable oxidation.

The largely mutually exclusive relationship between *G* and *M* (and *G* and *I*) is clearly seen in Figs 2 and 3 and is illustrated graphically in Fig. 5. Test correlation of *G* and *I* gives a *negative* linear relationship.

Magnetite grain dimension varies symmetrically about the central part of each section. This would be the expected relationship to the cooling surfaces and, in fact, has been described for Icelandic basaltic lava flows by Watkins & Haggerty (1965).

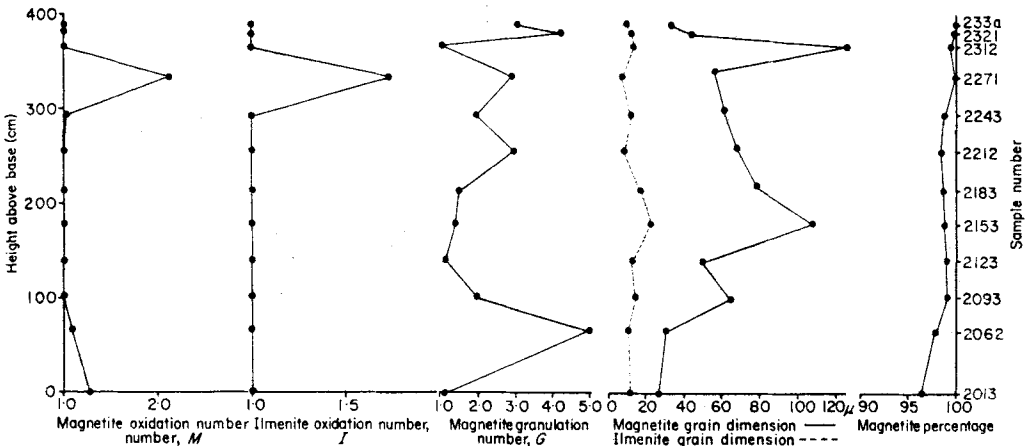


FIG. 3. Spatial variation of opaque petrological properties in Section 2.



### 5.1 Titanomagnetite high-temperature oxidation

Lindsley (1962) has produced ilmenite exsolution from titanomagnetites, in controlled experiments, which appears to be identical with the exsolution observed in natural titanomagnetites. In the laboratory temperatures of between 600 °C and 1000 °C and water vapour pressures between 670 and 2000 bars were used to produce exsolution. If the minimum temperature of 600 °C at which exsolution takes place in laboratory conditions is applicable under natural conditions, then exsolution in basaltic titanomagnetites must take place during initial cooling.

Analysis of volcanic gases (see Eaton & Murata (1960) for a summary of analyses and a list of references) indicates that steam is by far the most abundant constituent. So far as the availability of water vapour is concerned, Lindsley's mechanism would seem to be compatible with natural conditions.

Several other suggestions have been made regarding the process of high-temperature oxidation within a cooling body of lava. Watkins & Haggerty (1965) found a close similarity between the vertical variation in oxidation and calculated temperature profiles during cooling, and originally suggested that a relationship existed between the two parameters. However, such a relationship does not generally exist. In the lava described in this paper the *gross* variation in Section 1 (a broad high oxidation zone in the lower half of the section) might be matched with a temperature profile during cooling. But the generally low level of oxidation in Section 2 and the sharp irregularities of limited vertical extent in Section 1 are not compatible with any reasonable temperature profiles provided complicated flow patterns did not exist. Again Butler & Burbank (1929) find high-temperature oxidation in the Keweenawan lavas to increase typically towards the *top* of the flows. Wright & Sato (1966) describe a process of oxidation taking place in a Kilauea lava lake which is probably equivalent to high-temperature oxidation as described in this paper (personal communication). These authors suggest the oxidation may take place when part of the cooling lava behaves as a semi-permeable membrane, permeable to hydrogen but not to oxygen. Then, dissociated water vapour would lose its hydrogen so leaving the remaining oxygen free to react with the  $\text{Fe}^{2+}$  of titanomagnetite, ilmenite and olivine. Since such a membrane might be developed irregularly within a cooling body of lava, this mechanism inherently seems more likely to explain the observed spatial variation in oxidation than any *simple* relationship to temperature profile. However, the possibility that *irregular* temperature profiles occurred, resulting from complicated flow patterns beneath the chilled crust of the flow, must also be kept in mind.

The origin of the gases associated with cooling (and oxidizing) lavas is of considerable interest. While observers report great amounts of gases to be associated with volcanic activity it is possible that these derive from ground water which came into contact with the cooling lava and are thus not magmatic in origin. Butler & Burbank (1929) discuss at length the geological evidence for the origin of volcanic gases. They conclude, for the Keweenawan lavas, that the gases were magmatic in origin. The two most convincing points of their argument are the uniformity of the oxidation of the upper parts of flows over wide areas and the occurrence of oxidized zones *beneath* rafts of included non-oxidized lava within flows, which seems to exclude the atmosphere as a source of oxidizing agents. Evidence from another aspect might be expected to decide the origin of these gases. This is the study of the iron oxide petrology of basaltic dykes, which may, at least in some cases, have been lava feeders. From the work of Smith (1967), Haggerty & Watkins (1968) and unpublished work on the Mull, Scotland, dyke swarm, it seems that the titanomagnetite of basaltic dykes is on the average in a much lower state of high-temperature oxidation than titanomagnetite of basaltic lavas. Taken alone, this fact suggests that the oxidation in lavas is due at least in part to ground water contamination. However, the situation is complicated by the common presence of sulphides in dykes and their general absence

from lavas. Lindsley (personal communication) suggests that the presence of sulphides in dykes may indicate that, while potentially oxidizing gases could be present, conditions prevented the partial loss of volatiles necessary for the oxidation of precipitated minerals to take place. Thus the basaltic dyke iron titanium oxide petrology results do not settle the issue of the origin of the oxidizing gases.

The petrology of large basic intrusions also may have a bearing on the origin of volcanic gases. In many cases, e.g. the Bushveld and Skaergaard complexes, chemical analysis indicates the presence of  $H_2O^+$  (0.34 to 5.20 per cent by weight for the Bushveld complex (Hall 1932) and 0.20 to 1.13 per cent by weight for the Skaergaard complex (Wager & Deer 1939)). Since these masses may represent basaltic magma that failed to reach the surface, the presence of contained water suggests that at least some of the steam associated with erupting lavas is magmatic in origin.

In conclusion, it seems likely, although not definitely proven, that most of the gases associated with basaltic lavas are of magmatic origin, but that other conditions are not always appropriate for the gases to oxidize the iron titanium oxides.

## 5.2 Titanomagnetite granulation

As described in Section 3.2.2 there is good evidence that granules usually form within the titanomagnetite grains as a result of burial to a depth of at least 900 m. However, there is little evidence concerning the nature of the physical and chemical environment at this depth in a laval pile. Of the many aspects of granule formation three have been selected for discussion here:

- (i) the temperature at which granulation takes place;
- (ii) the time at which granulation takes place;
- (iii) the possibility of surplus iron being available after granule formation, and its disposal.

**5.2.1 The temperature at which granulation takes place.** Apart from its importance in defining the conditions for granulation, maximum temperature is also important from the palaeomagnetic aspect, as will be discussed in Part II. The influence of temperature can be approached from the evidence of geothermal gradients, from studies on the formation of rutile, and from the conditions required for zeolite formation. Geothermal gradients in active volcanic regions may be expected to be higher than the average of about  $3^\circ C/100$  m. Heat flow measurements in such areas (Lee *et al.* 1965) suggest that a value one order greater than the average value can be taken as the maximum gradient likely to occur. Thus, with a gradient of  $30^\circ C/100$  m a temperature of  $300^\circ C$  would occur at a depth of 1000 m. This is known to occur in Iceland now, for example (Askelsson *et al.* 1960). It follows that since granulation usually occurs in Icelandic lavas which have been deeper than 900 m, a temperature of  $300^\circ C$  may have been sufficient to cause granulation. Since this figure was obtained using a *maximum* gradient it is possible that granulation could occur at temperatures below  $300^\circ C$ .

While no laboratory studies appear to have been made on impure rutiles, the temperature range over which *pure* rutile is stable has been studied by Czanderma *et al.* (1958) and others. Czanderma finds rutile to be the stable form of  $TiO_2$  only above about  $600^\circ C$ . At lower temperatures the polymorph anatase ( $a : 3.78$ ,  $c : 9.51$ ,  $c/a : 2.52$ ) appears to be the stable form. However, petrological evidence suggests that rutile is probably stable relative to anatase and brookite well below  $600^\circ C$ . It is widely reported that iron and other rarer elements (Nb, Ta) can enter into solid solution in rutile but the effects of these substitutions on the transition to anatase appear to be unknown.

Rather close estimates are available for the temperature ranges in which zeolites are formed (Coombs *et al.* 1959). In a study that includes the results of both field and laboratory observations, Coombs and his co-authors find evidence for the formation of some of the zeolites which occur in this flow in the 200–300 °C interval (Coombs *et al.* 1959, pp. 77, 88, 89).

We may tentatively accept the combined evidence of the Icelandic observations, the estimated maximum thermal gradients and conditions for zeolite formation to define the conditions for magnetite granulation. Rejection of the applicability of the laboratory evidence for the stability field of rutile is based on the complete absence in our lava of mineralogical evidence of reheating to temperatures approaching 600 °C. It is possible that in the hydrothermal conditions of zeolite formation the temperature stability of rutile extends to considerably lower temperature than indicated by the laboratory experiments.

*5.2.2 The time at which granulation takes place.* The time necessary for the onset of granulation can be estimated from data on the Eastern Iceland lava pile. Here some 10 km of lavas were formed over a period of approximately 20 million years (Dagley *et al.* 1967). Thus for this lava pile an approximate interval of 2 my was required for sufficient cover (usually greater than 900 m) to be formed for granulation to take place.

The elapse of this considerable period, which is long enough for the Earth's magnetic field to reverse its polarity several times, before granulation takes place within the titanomagnetite, has serious implications for palaeomagnetism. These will be discussed in Part II.

*5.2.3 Surplus iron produced during granulation and its disposal.* Although the impurity content of the rutile granules is unknown it seems unlikely that they contain sufficient iron in solid solution to account for all the iron present in the original titanomagnetite. If this is the case it is necessary to explain how the surplus iron is disposed of. One possible explanation is that surplus iron is utilized in the formation of interstitial chlorite type minerals—the presence of which is a common feature of basalts in the deeper zeolite assemblage zones. A second possible explanation, that granule formation results in the remaining titanomagnetite being relatively titanium deficient, is not in accord with the magnetic evidence described in Part II. That is, there is no correlation between titanomagnetite granulation and the development of high-temperature (pure magnetite) Curie points.

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