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CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF MAGNETITE FROM THE EJECTED PLUTONIC BLOCKS OF THE SOUFRIÈRE VOLCANO, ST. VINCENT, WEST INDIES

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ABSTRACT

An homogeneous magnetite containing 6 percent Al_2O_3, 4 percent MgO and 7 percent TiO_2 by weight is present in the ejected plutonic blocks of the Soufrière, St. Vincent. The cell size of 8.372 ± 0.002 Å appears to be the smallest yet recorded for a magnetite which is not cation deficient. Reflectivity values are appreciably lower and microindentation hardness readings (VHN) appreciably higher than those for pure magnetite. Magnetic properties have also been determined, and it is concluded that it is not possible to satisfactorily deduce the composition oi a magnetite from measurements of cell size and Curie temperature.

INTRODUCTION

Polished sections of ejected plutonic blocks from the Soufrière volcano, St. Vincent showed an homogeneous magnetite to be the only opaque oxide mineral present, an unusual feature in basic and ultrabasic rocks. Furthermore, X-ray powder photographs indicated this magnetite to have a cell size appreciably less than that of pure magnetite and it was therefore decided that a fairly detailed study should be made of this mineral.

The St. Vincent ejected blocks consist of the mineral phases plagioclase (An_{96}-An_{89}, average An_{93}); olivine (Fo_{79}-Fo_{67}, most frequent interval Fo_{74-72}), salite containing 5–6 percent Al_2O_3, and hastingsitic amphibole together with the magnetite. The minerals occur in various proportions and textures.

Magnetite is present in the majority of the St. Vincent blocks but in some it is only a minor constituent. It is most abundant in the more melanocratic rocks and is closely associated with clinopyroxene and amphibole. The grain size varies from 0.1 to about 3 mm and the average size is about 1–2 mm for discrete grains.

This report on the composition and physical properties of the magnetite forms part of a detailed study of the mineralogy and petrology of the ejected plutonic blocks collected by the late Professor L. R. Wager from the Soufrière, St. Vincent. The blocks are regarded as igneous cumulates (Wager, 1962; Lewis, 1964, 1968). Aspects of the mineralogy of other mineral phases are considered separately (Lewis, 1967; Lewis

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1969). I have considered the paragenesis of the magnetite and other phases in a general paper (submitted for publication) on the plutonic blocks.

The terminology used here largely follows that of Buddington *et al.* (1963) and Buddington and Lindsley (1964). The term "iron oxide minerals" refers to the iron-bearing phases within the system Fe–Ti–O and with small amounts of other oxides in solid solution. 'Magnetite' is used in a somewhat broader sense than perhaps implied by Buddington and Lindsley (1964) and applies to all minerals within the magnetite series of Palache *et al.* (1944, p. 698).

CHEMISTRY

Complete chemical analyses of two magnetites from the St. Vincent blocks are given in Table 1. The numbers of cations have been calculated on the basis of 32 oxygens in the unit-cell. Analyses for FeO made on four further samples are also given in Table 1. Analytical methods used are summarized in the Appendix.

Great difficulty was experienced in obtaining a magnetite sample absolutely free from contamination by silicates although samples were ground (under acetone) to less than 250 mesh and repeatedly centrifuged in clerici solution. Sample T774I is estimated by grain counting to be 99.5 percent pure and sample T774Q to be 99.1 percent pure. The four samples on which Fe_2O_3 alone was determined are between 99.0 and 99.3 percent pure.

The St. Vincent magnetites belong to the magnetite series of Palache *et al.* (1944, p. 698). The analyses show the magnetites contain significant quantities of TiO_2, Al_2O_3 and MgO in solid solution. The total of 24 cations demonstrates that the magnetites are not cation deficient.

The small percentage of SiO_2 in the analyses is probably mainly impurity due to the minor amount of silicate present in the samples. It is unlikely that calcium occurs in the magnetite lattice (Wright and Lovering, 1965) and the small percentage of CaO is also possibly due to contamination by silicate, but there is also the very good possibility that some MgO was not completely separated from the CaO during the analysis, although a double precipitation was made, and it may be that some MgO has been recorded as CaO.

Cr_2O_3 is recorded as less than 0.05 percent. It was thought that Cr_2O_3 may have been suppressed by the presence of excess of other ions in the colorimetric method used for its determination (Sandel, 1959, p. 398), but spectrographic examination of the magnetite samples showed that this oxide is indeed present in trace quantities.

The FeO content of the other samples, not completely analyzed at this

TABLE 1. CHEMICAL ANALYSES AND PHYSICAL PROPERTIES OF MAGNETITES FROM THE EJECTED BLOCKS OF THE SOUFRIÈRE, ST. VINCENT

			Number of ions on the basis of 32 oxygens		
	1 T774I	2 T774Q		1 T774I	2 T774Q
FeO	32.33	32.23	Fe^{2+}	7.779	7.710
MgO	4.02	4.32	Mg	1.744	1.841
MnO	0.23	0.21	Mn	0.055	0.052
CaO	0.14	0.18	Ca	0.043	0.055
Fe_2O_3	50.04	50.02	Fe^{3+}	10.836	10.769
Al_2O_3	5.88	6.08	Al^{3+}	1.995	2.049
V_2O_3	0.16	0.14	V^{3+}	0.034	0.031
Cr_2O_3	(<0.05)	(<0.05)	Cr^{3+}	—	—
TiO_2	7.10	7.43	Ti^{4+}	1.537	1.597
SiO_2	0.05	0.08	Si	0.014	0.022
Total	99.95	100.71	Total	24.04	24.13

Analyses for FeO: T771 32.04; T896 32.54; T748A 32.63
Chemical analyses by J. F. Lewis

		T774I	T774Q
Unit cell		8.372±0.002 Å	8.370±0.002 Å
Specific gravity		4.91 ±0.02	4.87 ±0.02
Saturation magnetisation at 17°		55.7 e.m.u./g	43.9 e.m.u./g
Curie temperature		480°C	400°C
Reflectivity % white light		15.8	14.7
	589 nm	15.8	14.8
Microindentation Hardness (*VHN*)	(min.)	803	743
	(max.)	847	813
	(mean)	824±16	782±21

stage, is very similar to that of the complete analyses, suggesting the magnetites from the St. Vincent blocks are all of very similar composition. Measurements of the cell sizes support this.

UNIT-CELL DIMENSIONS

The cell size of the magnetites was measured from X-ray powder photographs taken with filtered Fe radiation ($K_\alpha = 1.9373$ Å) using a 114.59 mm camera. The film was mounted and measured according to the Straumanis method. The values from the analyzed samples determined from the 422, 533, 553 and 800 relections are given in Table 1.

The strong lines in the photographs were all sharp. There were no shadowy or doubled lines, as found in photographs of samples containing exsolved phases such as ulvöspinel.

The cell size of 8.372 for the analyzed and other magnetites from the St. Vincent blocks is considerably smaller than the value of 8.396 for pure magnetite (Basta, 1957). The St. Vincent magnetites are not cation deficient and contain considerable quantities of Ti, Al and Mg in solid solution. Of these elements, the substitution of Ti^{4+} (0.68 Å)[1] increases the cell size as shown in synthetic samples (Pouillard, 1950) and in natural magnetites (*e.g.* Basta, 1960). It is unlikely that Mg will have much effect on the cell size since the ionic radius (0.66 Å) is not far removed from Fe^{2+} (0.74 Å) for which it presumably substitutes. The cell size of the spinel $MgFe_2O_4$ is 8.38. Substitution of the small Al^{3+} (0.51 Å) for Fe^{3+} (0.64 Å), however, should cause a marked decrease in the cell dimensions, and the reduction in cell size with substitution of Al has been shown using synthetics by Pouillard (1950) and by Turnock and Eugster (1962) for the system $FeAl_2O_4$–Fe_3O_4. The cell size of hercynite ($FeAl_2O_4$) is 8.154 (Turnock and Eugster, 1962).

The analyzed St. Vincent magnetites contain 6 percent Al_2O_3. This more than compensates for the increase due to 7 percent TiO_2, and the reduction in cell dimensions may be attributed to this unusually large amount of Al_2O_3 in solid solution. This may be tested by assuming straight line relationships between the molecular concentrations of end members and their cell dimensions (Zen, 1956). The normative values have been calculated from the analyses of sample T774I following the scheme devised by Chevallier (*in* Vincent *et al.*, 1957) and are listed in Table 2. Neglecting calcium and vanadium the calculated unit-cell dimension for St. Vincent magnetite sample T774I is 8.380 in reasonable agreement with the observed value and considerably lower than the value for pure magnetite.

However, a further manner in which cell size of natural magnetite and titanomagnetite can be reduced is by partial oxidation to maghemite or titanomaghemite. Natural samples have been examined by Basta (1959) and Katsura and Kushiro (1961), and it has been shown that these cation deficient samples have a cell size considerably lower than that of pure magnetite.

The writer, however, has not found in the literature the chemical analysis of a homogeneous magnetite without cation deficiencies and a cell size as low as that of the St. Vincent magnetites. The analysis of magnetite from Magnet Cove, Arkansas, by M. G. Keyes, recorded by Newhouse and Glass (1936), shows 15 percent Al_2O_3 and the cell size

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[1] Ionic radii (six fold coordination) are taken from Ahrens (1952).

TABLE 2. POTENTIAL NORMATIVE COMPOSITION (MOLE %) OF MAGNETITE SAMPLE T774I

$FeO \cdot Fe_2O_3$	54.57
$MgO \cdot Fe_2O_3$	12.05
$MnO \cdot Fe_2O_3$	0.41
$CaO \cdot Fe_2O_3$	0.28
$FeO \cdot Al_2O_3$	10.07
$MgO \cdot Al_2O_3$	2.21
$MnO \cdot Al_2O_3$	0.06
$CaO \cdot Al_2O_3$	0.04
$FeO \cdot V_2O_3$	0.19
$MgO \cdot V_2O_3$	0.04
$2FeO \cdot TiO_2$	15.48
$2MgO \cdot TiO_2$	3.41
$2MnO \cdot TiO_2$	0.11
$2CaO \cdot TiO_2$	0.08
Excess FeO	0.79
Excess MgO	0.17
Total	99.96

for this specimen was given as 8.371. Basta (1957; 1959, p. 707) has since disputed this data and gives the analysis recorded in Table 3, anal. 4. The percentage of Al_2O_3 is 3.62 percent and the cell size, 8.396 given by Basta (1957), is identical with that of pure magnetite. The amount of Al_2O_3 is presumably just sufficient to compensate for the apparent increase resulting from the substitution of 7.18 percent TiO_2.

Basta (1959, p. 708; 1960, p. 1033) has listed a number of occurrences of magnetites with cell dimensions slightly less than that of pure magnetite (but not as low as those of the St. Vincent magnetites), and has tentatively proposed that these natural magnetite samples are partially oxidized to maghemite.

The data given here indicate that this is not necessarily the case, and that the small cell size may perhaps be due to Al in solid solution. It is clear that a complete chemical analysis is necessary, and attempts to correlate cell size with composition of magnetites simply on the basis of determinations of Fe_2O_3, FeO and TiO_2 on only partially purified samples (*e.g.*, Akimoto and Katsura, 1959) is unsatisfactory.

MAGNETIC PROPERTIES

The saturation magnetization and the Curie temperature of the analyzed specimens were kindly determined by Mr. W. O'Reilly at the Physics Department, University of Newcastle upon Tyne, England, through the courtesy of Dr. K. M. Creer of the same department.

TABLE 3. CHEMICAL ANALYSES OF SOME HIGHLY SUBSTITUTED NATURAL MAGNETITES FROM VARIOUS ENVIRONMENTS FOR COMPARISON

	1	2	3	4	5	6
FeO	38.2	36.21	26.69	21.83	33.30	33.79
MgO	3.7	3.25	5.15	7.18	5.54	1.49
MnO	tr.	0.74	n.d.	1.82	0.39	0.28
CaO	n.d.	1.56	0.10	0.94	0.74	0.20
Fe_2O_3	36.0	28.96	54.97	57.11	41.97	51.68
Al_2O_3	8.0	6.64	5.64	3.62	6.50	2.91
V_2O_3	n.d.	0.22	n.d.	0.10	tr.	0.58
Cr_2O_3	n.d.	0.01	n.d.	0.01	0.42	0.13
TiO_2	14.5	16.22	7.57	6.98	10.83	9.36
SiO_2	n.d.	4.38	0.14	0.38	0.64	0.05
Total	100.4	98.17	100.26	99.97	100.33	100.47

Key to magnetite analyses

1. Titanomagnetite, Ankaratra, Madagascar, average of three analyses (Chevallier, Bolfa and Matthieu, 1955).
2. Titanomagnetite from augitite, South of Ngong, Nairobi, Kenya (S595) (Basta, 1960). Analyst H. B. Milner.
3. Titanomagnetite (titaniferous magnesioferrite), Norway (Newhouse and Glass, 1936). Analyst Mary G. Keyes.
4. Titanomagnetite, Magnet Cove, Arkansas, U.S.A. (Basta, 1957). Analyst H. B. Milner.
5. Titanomagnetite from Beach Sand, Monti Rossi, Etna, Sicily (Starrabba, 1939). Analyst Stella Starrabba.
6. Titanomagnetite, anorthosite, Schmoo Lake, Quebec, Canada (Vincent *et al.*, 1957). Analysts E. A. Vincent and J. B. Wright.

Determinations of the Curie points were made with a photographically recording Chevallier balance. The thermomagnetic curve for sample T774I reproduced in Figure 1 shows a sharp decrease at a well-defined temperature indicating the magnetic, and therefore compositional. homogeneity of the sample. The curve for T774Q was similar.

The determinations of Curie temperature and saturation magnetization for the St. Vincent samples are given in Table 1. In comparison, the Curie temperature and saturation magnetization for pure magnetite (Fe_3O_4) are 580°C and 93 e.m.u./g respectively.

Most of the work to date on the magnetic properties of natural and synthetic magnetites has been connected with titaniferous magnetites containing low amounts of other impurities. It has been found that there is a gradual decrease in the Curie temperature and saturation magnetization with increase in TiO_2. The TiO_2 can be regarded as a diluent and the magnetic measurements can be expressed in terms of the Fe_3O_4 con-

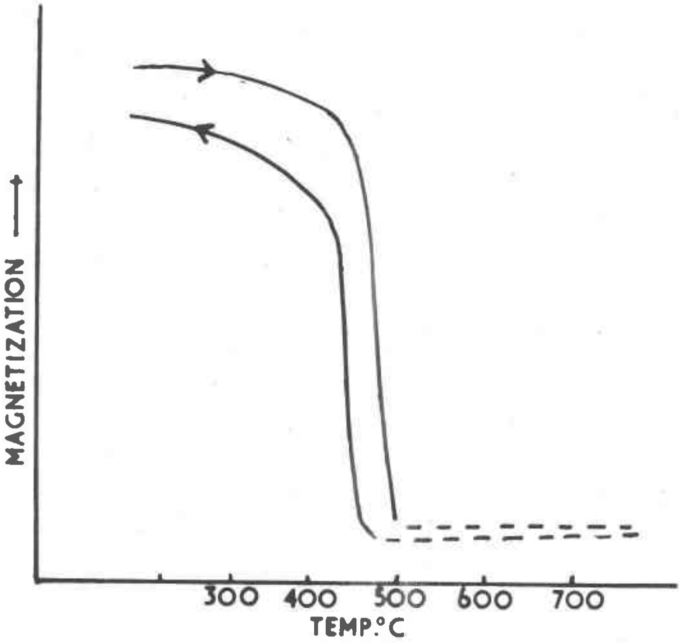

FIG. 1. Thermomagnetic curve for magnetite sample T774I.

tent of the magnetite (*e.g.* Chevallier *et al.*, 1955; Vincent *et al.*, 1957; Akimoto and Katsura, 1959).

Vincent *et al.* (1967) have constructed curves relating the weight percentage of Fe_3O_4 in homogeneous titanomagnetite with (a) Curie point and (b) saturation magnetization. The calculated total Fe_3O_4 in sample T774I is 72.53 percent by weight and a good correlation is found between the observed saturation magnetization measurements for sample T774I and that read from the graph of Vincent *et al.* (1957) but according to the graph the Curie temperature should read approximately 390°C. Sample T774Q has almost the same composition as T774I but the Curie temperature and saturation magnetization are lower. The absence of a good correlation between Curie temperature and Fe_3O_4 content might be related to the high Al_2O_3 contents of the St. Vincent samples.

Pouillard (1950) and Pickart and Turnock (1959) showed that the addition of Al_2O_3 to Fe_3O_4 does lower the Curie point, but the effect does not appear to be as great as found for the addition of TiO_2. According to Pouillard (1950) the addition of 10 mol. percent Al_2O_3 to Fe_3O_4 lowered the Curie point by only 40°C (*i.e.* from 575° to 535°).

The fact that the Curie temperature found on cooling the St. Vincent samples was significantly lower than that given on the initial heating may possibly be of some significance (Fig. 1). Verhoogen (1956) has noted that such a feature might be given by magnetites showing self-reversal of magnetization. The St. Vincent magnetites which have a high Al content and have been quenched from a high temperature may be slightly disordered. These features need further investigation.

DISCUSSION ON CORRELATION BETWEEN COMPOSITION, CURIE TEMPERATURE AND CELL SIZE

Carmichael and Nichols (1967) have estimated that the composition of the β phase in a basalt should contain at least 50–85 percent of the R_2TiO_4 component. Thus the measured Curie temperatures of the β phases should be below 200°C and basalts with Curie temperatures higher than 200°C must have been subsequently oxidized. Magnetite in the St. Vincent blocks is an example of a single homogeneous β phase which has crystallized in equilibrium with silicates from a basalt magma. The phases have been quenched and no unmixing or post-crystallization oxidation processes have occurred. The St. Vincent magnetites have only 19.1 percent normative ulvöspinel (R_2TiO_4) but 24.3 percent of normative $MgO \cdot Fe_2O_3$, $FeO \cdot Al_2O_3$ and $MgO \cdot Al_2O_3$ and have Curie temperatures in excess of 400°C. It is apparent that a sub-alkaline basalt magma can precipitate more than one variety of iron oxide depending on the conditions of crystallization. Even a single basalt lava may contain several varieties of iron oxide depending on the crystallization history of the basalt, particularly if the basalt inherits crystals separating at depth from an early fractionating state (Lewis, 1969). This statement has relevance to recent studies on the magnetic properties of iron oxides and paleomagnetic studies. Ade-Hall (1964), Ade-Hall *et al.* (1965) and Smith (1967) have found a wide discrepancy between measured and calculated Curie points on apparently homogeneous titano-magnetites. This has been attributed to oxidation of the magnetic iron oxides (see Akimoto and Katsura, 1957; Wright and Lovering, 1965). In determining their analyses these authors analyzed several individual grains in the rock but the magnetic measurements were made on a sample of whole rock. In a basalt that has undergone several stages of fractionation not only will the groundmass iron oxides differ in composition and magnetic properties from the phenocrysts but the phenocrysts themselves may also show a range in composition and magnetic properties (Nagata, 1961, p. 93; Carmichael and Nichols, 1967). Thus a good correlation between calculated Curie points based on the composition of a few individual phenocrysts and Curie points determined on a sample of the rock should not be expected.

It is apparent that the addition of small ions such as Al and Mg to magnetite, besides oxidation, will cause a reduction in cell size. However, Al and Mg decrease the Curie temperature whereas oxidation causes an increase in Curie temperature. Ti increases the cell size but lowers the Curie temperature. Thus, it may be impossible to deduce the composition of a magnetite from magnetic and X-ray parameters. In order to correlate magnetic measurements of rocks with mineralogy, complete analyses of all iron oxide phases present in the rock are required.

Reflectivity and Microindentation Hardness

Reflectivity and hardness measurements were kindly made by Dr. M. Gallagher of the Atomic Energy Division, Geological Survey of Great Britain, through Mr. S. H. U. Bowie of the same Division. Mr Bowie reported (pers. commun. 20th Feb., 1964) that the reflectivity was measured by selenium barrier-layer cell using a tungsten-filament lamp with colour temperature of 2850°K. The monochromatic value was obtained using a Schott continuous-band interference filter with a half-height band width of 25 nm hence this value is not dependent on colour temperature or cell characteristics as is the "white light" value. Hardness was measured with a G.K.N. indenter with 136° pyramid. Ten separate measurements were made on each of two grains in each polished section. No significant variation from grain to grain was found in the same specimen.

The measurements on the analyzed St. Vincent magnetites are given in Table 1 and are also compared below with those for pure magnetite (Bowie and Taylor, 1958). These results have been published in part by Gallagher (1965).

Specimen No.	*R*% of Magnetite 'White Light'	*R*% of Magnetite 589 nm	*VHN* of Magnetite mean
T774I (St. Vincent)	15.8	15.8	824±16
T774Q (St. Vincent)	14.7	14.8	782±21
Pure Magnetite (Fe_3O_4)	21.1	—	560

It is seen that the values recorded for the St. Vincent magnetites are decidedly different from those of pure magnetite. This is apparently the first time that such quantitative measurements have been recorded for a magnetite, although Jourasky (1936) noted that some highly substituted magnetites from Ankaratra, Madagascar, showed low reflectivity compared with that ordinarily given by magnetite.

The reflectivity of magnetite T774Q from St. Vincent is about 1 percent lower than that of T774I. The hardness is also somehwat lower in

T774Q. It is uncertain how much value can be attached to these differences since T774Q was not as well polished at T774I.

COMPARATIVE CHEMISTRY

The TiO_2 content of the St. Vincent magnetites is low compared with that of magnetites from basic igneous rocks assembled by Buddington *et al.* (1955) and by Buddington and Lindsley (1964). The TiO_2 values determined for the St. Vincent magnetites resemble more closely those reported for magnetites from acid-igneous rocks and some metamorphic rocks.

Although complete chemical analyses of magnetites containing more than 3 percent Al_2O_3 and 3 percent MgO are extremely rare, a number of recent studies by electron microprobe (*e.g.* Wright and Lovering, 1965; Carmichael, 1966) have shown that 3 percent each of MgO and Al_2O_3 is quite common in homogeneous magnetites from igneous rocks. Smith and Carmichael (1969) report up to 5.0 percent MgO and 3.9 percent Al_2O_3 in magnetites from trachybasalts from south-eastern California, and a compilation by Fleischer (1965) suggests that magnetites in alkaline igneous rock types generally show relatively high MgO, Al_2O_3 and MnO contents. Unfortunately, many of the magnetite analyses quoted in the literature are incomplete, reporting only Fe_2O_3, FeO and TiO_2. Clean separation of magnetite from silicates is often very difficult and a determination of MgO and Al_2O_3 on a sample containing appreciable silicate is generally of little value. In most cases, however, it is clear from the analysis that the magnetite does not contain significant amounts of spinel-type cations, but this is probably not always the case. It is unfortunate that Al_2O_3 and MgO have not been determined on at least some of the homogeneous magnetites from the Japanese volcanics which have been the subject of extensive investigation by Akimoto, Nagata and co-workers. It is to be noted that the sum $FeO+Fe_2O_3+TiO_2$ in the analyses quoted by Akimoto (1955) and Akimoto and Katsura (1959) in no case exceeds 95 percent by weight and in many cases is appreciably less than this. These incomplete analyses disallow a detailed comparison of their results.

Analyses Nos. 1–5, Table 3, are complete analyses of magnetites which contain significant quantities of Al_2O_3 and MgO and which resemble those from the St. Vincent blocks. Unfortunately only in a few instances are the parageneses of these magnetites known.

The material of volcanic origin from Ankaratra, Madagascar, (Table 3, anal. 1) is found in loose volcanic ejecta and river gravels. This magnetite is reported to be perfectly homogeneous and is a "véritable titanomagnétite" (Lacroix, 1922–23, I, p. 334).

The volcanic homogeneous titanomagnetite from an augitite, Nairobi, (Table 3, anal. 2) contains 6.64 percent Al_2O_3 but also contains appreciable SiO_2, hence the sample is presumably impure.

Newhouse and Glass (1936) do not give the exact locality and association of their material from Norway (Table 3, anal. 3), nor of the similar material from Siberia. The exact association of the magnetite specimen from Magnet Cove (Table 3, anal. 4) is also unknown to the writer.

Magnetite containing 6.57 percent Al_2O_3 has been described from Schelengen, Kaiserstuhl, Germany, by E. Hugel (1912) but the exact locality and association are not given. A further analysis of a magnetite containing 6.80 percent Al_2O_3, 2.59 percent MgO and 4.70 percent TiO_2, from limestone, Vogtsburg, Kaiserstuhl, is given in the same reference. The association here is with syenite intruded into limestone (Palache *et al.*, 1944).

Magnetite (magnesioferrite) containing 12.58 percent MgO has been reported from Vesuvius (Rammelsburg, 1875, p. 133). This material is intergrown with hematite and was formed through fumarolic activity.[1] The same paragenesis is likely for occurrences of similar material associated with hematite in porous lava from Stromboli and from Etna (Bergeat, 1899). The origin of the Beach Sand grains from Monti Rossi, Etna (Table 3, anal. 5) is not known to the writer.

In so far as the overall FeO, Fe_2O_3 and TiO_2 content is concerned, the St. Vincent magnetites resemble an analysis of a magnetite from an anorthosite, Schmoo Lake, Canada (Table 3, anal. 6). The Schmoo Lake material consists of an intergrowth of magnetite, ulvöspinel and ilmenite. Girault (1953) notes exsolved hercynite in some specimens from the same area.

It is clear from the above assessment that magnetite analyses showing significant quantities of Al_2O_3 and MgO are rare, and that some of those available are unsatisfactory. Whether this is merely a sampling problem or whether such magnetites are really rare in nature cannot be estimated until more complete analyses are available. Evidence that some magnetites from gabbroic and some volcanic rocks may have an appreciable Al_2O_3 content in solid solution on initial crystallization is found in the occurrence of hercynite exsolution intergrowths in magnetite (e.g. Ramdohr, 1960, p. 835).

SOLID SOLUTION IN MAGNETITE

Studies in the system Fe-Al-O by Richards and White (1954) and Atlas and Sumida (1956), in the system $MgO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$ by Muan and

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[1] Pure magnesioferrite can readily be made by passing HCl gas over powdered Fe_2O_3 and MgO at about 900°C and reactions of this nature no doubt account for the occurrence of magnesioferrite around volcanic fumaroles.

Osborn (1956), and in the system Fe-Ti-O (Taylor, 1964) show that extensive substitution of Al, Mg and Ti might be expected in magnetite separating at a high temperature from a polycomponent system such as a natural basalt magma.

The homogeneity and extensive solid solution within the St. Vincent magnetites has resulted from the fact that they have crystallized at, and have been quenched from, a comparatively high temperature. The St. Vincent magnetites, therefore, are comparable with the phases that have been prepared and quenched from a high temperature in the synthetic experiments, and in many cases to the homogeneous phenocrysts contained in lavas where these have not undergone subsolidus oxidation.

From their study of the system Fe_3O_4-$FeAl_2O_4$, Turnock and Eugster (1962) have shown that exsolution of hercynite begins between 600–700°C for a spinel containing 10–20 percent of $FeAl_2O_4$. This suggests a minimum temperature of about 700°C at which the St. Vincent material was quenched from a high temperature, but does not take into account the influence of other ions in solid solution.

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APPENDIX: *Analyses of Magnetites*

Various schemes have been published for the analysis of spinels. An outline of the method adopted here follows:

Total Fe_2O_3 10 mg samples were fused with 0.1 g of potassium pyrosulphate and dissolved in 1N HCl. The solution was passed through a silver reductor and titrated against N/40 ceric sulphate under a CO_2 atmosphere.

FeO Vanadate method used (Wilson, 1955).

TiO_2 10 mg samples were fused with 0.1 g potassium pyrosulphate and TiO_2 determined by the greenish yellow compound formed by the addition of hydrogen peroxide to an acid solution. Care was exercised to ensure that all readings were taken with the samples and standards at room temperature (approx. 18°C).

SiO_2, Al_2O_3, V_2O_3, *and* Cr_2O_3 80 mg samples were decomposed with a Seelye-Rafter frit. The sintered mass was leached with water and the oxides of iron, titanium and magnesium filtered off. The filtrate was neutralized with hydrochloric acid and made up to 25 ml. Suitable aliquots were taken.

SiO_2 Determined in the acidified solution by the molybdenum blue method (Riley, 1958).
Al_2O_3 5 ml aliquots were taken and the aluminium extracted with 8-hydroxyquinoline in chloroform and measured colorimetrically.
V_2O_3 Sandell (1959, p. 936).
Cr_2O_3 Sandell (1959, p. 398).

MgO 80 mg samples were decomposed with a Seelye-Rafter frit and the sintered mass dissolved in hydrochloric acid. A double ammonia precipitation for R_2O_3 was made. The filtrate was diluted to 100 ml and MgO determined by titration against EDTA using Eriochrome Black T as indicator. A correction was made for MnO.