The occurrence of magnesian pyroxenes and magnetite in porphyritic acid glasses.

By I. S. E. CARMICHAEL, M.A., Ph.D.

Department of Geology, Imperial College of Science and Technology, London S.W. 7.

Summary. The problem of magnesian pyroxenes in acid liquids is considered in the light of new analyses of pyroxene and magnetite phenocrysts. It is suggested that the early precipitation of titaniferous magnetite, which will strongly deplete the liquid in iron, will decrease the iron:magnesium ratio of the pyroxene components in the liquid. Accordingly the iron:magnesium ratio of a pyroxene precipitating from an acid liquid may vary over a wide range depending upon the presence or amount of early magnetite.

W AGER (1956) has defined various arbitrary stages of fractionation of basic igneous rocks using the normative molecular ratio Ab/(Ab+An) (albite-ratio) for the plagioclase feldspars and the atomic ratio $(Fe''+Mn)/(Fe''+Mn+Mg)$ (iron-ratio) for the ferromagnesian minerals. He showed that the normal course of crystallization of basic magma is to enrich successive liquids in the low-melting components of plagioclase and the ferro-magnesian minerals at broadly the same rate, so that there is a general correspondence between the increase in the albite-ratio and the increase in the iron-ratio in phenocryst mineral and liquid alike.

In some acid glasses, however, the occurrence of unusually magnesian pyroxene phenocrysts indicates a lack of concordance between their iron-ratios and those of their liquids, and this short account considers the cause of this discrepancy. The ferromagnesian phenocrysts in these glasses are not abundant (average volume per cent: 0·7 pyroxene, 0·3 iron ores, and 0·4 olivine (when present)), but nevertheless they satisfactorily illustrate the interdependence of ferromagnesian phases in natural liquids.

Pyroxene phenocrysts in acid glasses.

The pyroxene and olivine phenocrysts of some British and Icelandic pitchstones have already been described (Carmichael, 1960), and that account is supplemented here by two new analyses of the augite and the

coexisting hypersthene phenocrysts of an Icelandic acid pitchstone (table I). The variation in Ca, Mg, and Fe of these pitchstone pyroxene phenocrysts (table I; Carmichael, 1960) is shown in fig. 1, and the tie-lines of the calcium-rich and calcium-poor pyroxenes are parallel, or nearly so, to those of slowly cooled tholeiitic magma represented here by the Skaergaard intrusion (Brown, 1957, 1960; Brown, 1961).

TABLE I. Analyses, formulae, and optical properties of the augite and hypersthene phenocrysts of an Icelandic pitchstone (P. 946). Refractive indices ±0·002, 2V±2°

		11.	11A.				11.	11A.
SiO_2...	...	51·37	51·07	Si	...	...	1·950	1·963
TiO_2...	...	0·79	0·52	Al^{iv}	...	...	0·057	0·041
Al_2O_3	...	1·56	1·14	Al^{vi}	...	...	0·013	0·011
Fe_2O_3	...	1·62	0·62	Ti	...	...	0·022	0·015
FeO...	...	12·82	26·65	Fe'''	...	...	0·046	0·018
MnO	...	0·79	1·36	Fe''	...	...	0·407	0·857
MgO	...	12·28	16·82	Mn	...	...	0·025	0·044
CaO...	...	17·86	1·63	Mg	...	...	0·695	0·964
Na_2O	...	0·69	0·15	Ca	...	...	0·727	0·067
K_2O...	...	0·04	0·04	Na	...	...	0·051	0·013
Total	...	99·82	100·00	K	...	...	0·002	0·002

Atomic per cent:

		11.	11A.				11.	11A.
Ca	...	38·3	3·4	Z	...	...	2·007	2·004
Mg	...	36·6	49·5	WXY	...	...	1·988	1·991
Fe	...	25·1	47·1	% Al in Z	...	...	2·8	2·0
β	...	...	1·705	—
γ	...	...	—	1·728
2V	...	...	50° (+)	53° (−)

11, Augite phenocrysts; 11A, Orthopyroxene phenocrysts.
P. 946, top of rhyolite lava, Holmanes, Reydarfjordur, eastern Iceland.

This similarity of trend of the pyroxene tie-lines indicates that the calcium-poor and calcium-rich pyroxenes of these pitchstones are in equilibrium with one another (fig. 1, nos. 1, 1A; 2, 2A; 11, 11A) and the absence of marked zoning or evidence of dissolution of these phenocrysts together with the difficulty of providing a source for just these pairs of pyroxenes suggests that they are to be accepted as being in equilibrium with their enclosing liquids.

In slowly cooled basic magma (e.g. Skaergaard intrusion), the calcium-poor pyroxenes of similar Mg/Fe ratios to the pitchstone orthopyroxenes discussed here are pigeonites or inverted pigeonites (fig. 1) and indicate crystallization of the calcium-poor phase above the orthopyroxene–clinopyroxene inversion-temperature curve (Bowen and Schairer, 1935). It would seem then that the calcium-poor pyroxene crystallization curve of these acid liquids has been depressed towards lower temperatures

compared to the Skaergaard curve (Brown, 1957, fig. 5), so extending the range of iron-ratios over which orthopyroxene precipitated as a stable phase.

This depression of the calcium-poor pyroxene crystallization curve in relation to the orthopyroxene–clinopyroxene inversion curve necessitates that the co-existing calcium-rich pyroxenes also crystallized at lower temperatures than the corresponding Skaergaard calcium-rich pyroxenes;
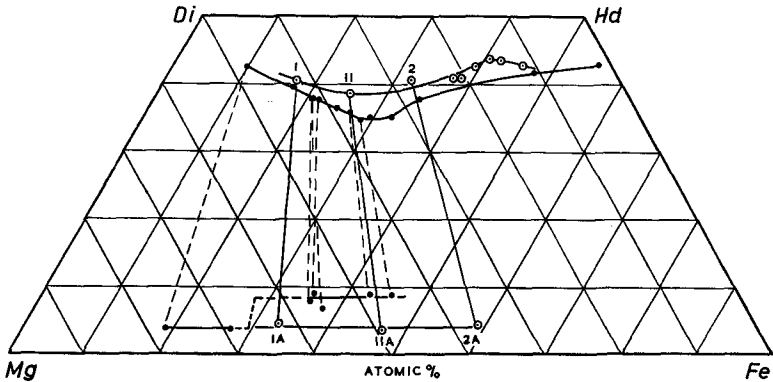

Fig. 1. Crystallization trend of pyroxene phenocrysts of British and Icelandic pitchstones ⊙—⊙—⊙ (Carmichael 1960, fig. 1) together with the new analyses 11–11A (table I). Coexisting pyroxenes are joined by solid tie-lines. The Skaergaard trend of pyroxene crystallization ●—●—● is taken from Brown (1957, 1960) and Brown (1961). Coexisting pyroxenes are joined by dashed tie-lines.

this temperature depression may give an indication of the slopes of the solvus limbs in the two-pyroxene field.

Muir (1954, fig. 4) has presented a series of hypothetical phase dia-grams to illustrate pyroxene crystallization particularly at the limit of the two-pyroxene field. In this field, the trends of crystallization of the calcium-rich and calcium-poor pyroxenes (fig. 1) represent the pro-jection of the traces of the intersections of the solidus with the solvus limbs of both series of pyroxenes. The orthopyroxenes of the slowly cooled Stillwater (Hess, 1960, p. 25) and Skaergaard (Brown, 1957) intrusions contain similar amounts of Ca (per cent of total Ca+Mg+Fe) to the orthopyroxenes of these pitchstones, so that the corresponding part of the solvus limb is likely to be very steep and is parallel to the enstatite–ferrosilite join. On the other hand, the trend of the calcium-rich pyroxene phenocrysts (fig. 1, nos. 1, 2, and 11) of these acid glasses shows that there is less replacement of the larger Ca ion by the smaller Fe'' and

Mg ions in these pyroxenes than in comparable pyroxenes of the Skaergaard intrusion, and accordingly the calcium-rich pyroxene solvus limb must dip towards the diopside–hedenbergite join, at least over the range $Ca_{40}Mg_{42}Fe_{18}$–$Ca_{40}Mg_{26}Fe_{34}$.

The trend of crystallization of the pitchstone calcium-rich pyroxenes shows that the Ca content (per cent of total $Ca+Mg+Fe$) only varies between 38 and 44 (fig. 1; table I; Carmichael, 1960) so that their variation may be almost completely expressed in terms of the replacement of Mg by Fe'', or more conveniently by the iron-ratio $(Fe'''+Fe''+Mn)/(Fe'''+Fe''+Mn+Mg)$. Accordingly, the iron-ratios of the calcium-rich and calcium-poor pyroxene phenocrysts have been plotted in fig. 2 together with the iron-ratios of their pitchstones and residual glasses.

The three pyroxene pairs nos. 1, 1A; 2, 2A; 11, 11A (fig. 1) are unusually magnesian for the environment in which they are found, as their composition is typical of pyroxenes crystallizing from basic or intermediate magma of considerably earlier fractionation stages.

Iron-ratios in the liquids.

The iron-ratios of the pitchstones and their residual glasses are given in fig. 2, although in view of possible oxidation after congelation of these glasses, the ratio $(Fe'''+Fe''+Mn)/(Fe'''+Fe''+Mn+Mg)$ has been used. As the concentration of iron and particularly magnesium is low in these rocks, a small error in the determination of magnesium will cause a relatively large difference to the iron-ratio, so that some spread of values is to be expected.

The iron-ratios of these pitchstones (with the exception of no. 1R, fig. 2) are of the same order of magnitude as those of the later liquids of the Skaergaard intrusion (UZb 91; UZc 93; Wager, 1960, table IV), and may therefore be taken as typical of late-stage liquids, so that the presence of magnesian pyroxene phenocrysts may not be ascribed to aberrant iron-ratios in the initial liquids (pitchstones).

A suggested origin of magnesian pyroxene phenocrysts in acid liquids.

The ferromagnesian silicate phenocrysts tend to form glomeroporphyritic aggregates in many pitchstones, and are frequently associated with feldspar and microphenocrysts of titaniferous magnetite and rarer ilmenite. The pyroxene phenocrysts almost invariably enclose small crystals of magnetite testifying to the early separation of iron-ore. Partial and complete analyses of many of the magnetite microphenocrysts

have been made (table II) and their iron-ratios have been plotted in fig. 2. In each case the magnetite microphenocrysts have higher iron-ratios than their pitchstones or their residual glasses, so that the early precipitation of magnetite (which is very much more abundant than ilmenite) will markedly impoverish these acid liquids in iron, and the
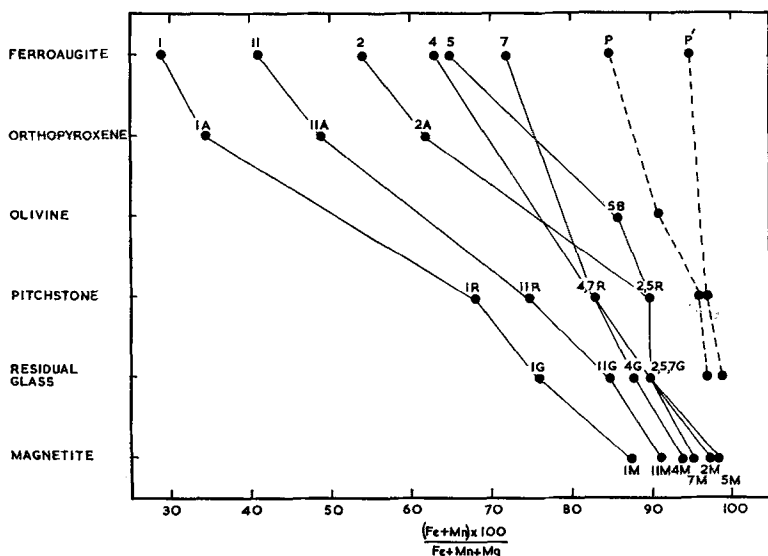

FIG. 2. The iron-ratios, $(Fe''' + Fe'' + Mn)100/(Fe''' + Fe'' + Mn + Mg)$, of the ferro-magnesian phenocrysts (calcium-rich and calcium-poor pyroxenes and olivines) are plotted together with those of the pitchstones and residual glasses (data taken from Carmichael, 1960 and table I). The iron-ratios, $(Fe'' + Mn)100/(Fe'' + Mn + Mg)$, of the titanomagnetite microphenocrysts have also been plotted (table II). Also shown are the relevant data of two porphyritic pantelleritic obsidians (P and P') (Carmichael, 1962).

pyroxene components in the liquids will become increasingly magnesian as magnetite continues to crystallize. It requires only a small precipitate of titanomagnetite (Carmichael, 1960, table I) to change the iron-ratios of the enclosing liquids, as these pitchstones contain only small total amounts of iron and magnesium (*op. cit.*, table 6).

Some confirmation of the suggested effect of the early precipitation of magnetite may be found in the porphyritic pantelleritic obsidians (Carmichael, 1962) in which microphenocrysts of magnetite are completely absent. These obsidians and their residual glasses have slightly higher iron-ratios (fig. 2, P and P') than the north Atlantic pitchstones, but the iron-ratios of the sodic ferrohedenbergite phenocrysts are considerably

higher than for the pitchstone pyroxene phenocrysts and illustrate the closer correspondence of liquid and pyroxene iron-ratios where the formation of magnetite is suppressed. It is likely that the calcium-rich pyroxenes form a solid-solution series of the plagioclase type, so that the iron-ratios of the liquids will always differ from those of the solid phases

TABLE II. Analyses and unit cell data of magnetite microphenocrysts.

	1M.	2M.	4M.	5M.	7M.	6M.	8M.	10M.	11M.
SiO_2 ...	2·80	4·82	3·94	3·46	4·23	—	—	—	—
TiO_2 ...	21·92	13·92	14·35	17·52	16·79	18·29	16·89	16·79	17·87
Al_2O_3 ...	0·87	1·79	1·25	1·19	1·65	—	—	—	—
Fe_2O_3 ...	33·05	39·77	38·25	38·81	35·06	—	—	—	—
FeO ...	34·23	37·71	35·58	36·42	37·04	—	—	—	34·80
MnO ...	1·20	0·63	1·98	0·69	1·68	0·97	0·86	0·66	2·97
ZnO ...	0·11	—	0·22	0·14	0·17	—	—	—	—
MgO ...	2·81	0·62	1·39	0·41	1·15	—	—	—	2·10
CaO ...	1·41	0·91	1·67	1·22	1·37	—	—	—	1·58
Insol. ...	1·27	nil	0·97	nil	0·90	—	—	—	—
Total ...	99·67	100·17	99·60	99·86	100·04				
a Å ...	8·424	8·43	8·444	8·452	8·447	8·47	—	—	8·419
$\frac{(Fe''+Mn)100}{Fe''+Mn+Mg}$	87·6	97·3	93·9	98·1	95·1	—	—	—	91·0

Recalculated analyses.

		1M.	2M.	4M.	5M.	7M.
TiO_2 ...	...	23·09	14·72	15·28	18·29	17·89
Al_2O_3 ...	...	0·32	1·08	0·62	0·69	0·94
Fe_2O_3 ...	...	34·79	42·08	40·72	40·50	37·34
FeO ...	...	36·04	39·87	37·82	37·98	39·29
MnO ...	...	1·26	0·67	2·11	0·72	1·78
ZnO ...	...	0·12	—	0·23	0·15	0·18
MgO ...	...	2·94	0·66	1·47	0·43	1·21
CaO ...	...	1·44	0·92	1·75	1·24	1·37
Total ...		100·00	100·00	100·00	100·00	100·00
% glass ...		4·0	6·5	5·5	4·7	6·3
Molecular proportions:						
MO ...	...	54·9	56·6	58·1	53·9	57·4
R_2O_3 ...	...	19·5	26·0	24·2	24·5	22·2
TO_2 ...	...	25·6	17·4	17·7	21·6	20·4

except for the two end-members. It is the contention of the author that this difference may be accentuated by the prior formation of magnetite.

If the partial pressure of oxygen controls the amount of Fe''' in the liquid, and hence the amount of early magnetite, then extreme variation of this pressure may cause extreme variation in the iron-ratios of the precipitating pyroxenes. In this way it may be possible to find the complete series of augite–ferroaugite–ferrohedenbergite pyroxenes (together with a calcium-poor pyroxene where appropriate) occurring as phenocrysts in acid liquids (fig. 1). However the magnesian pyroxenes

of acid liquids having similar iron-ratios to those found in basaltic or gabbroic environments preserve their individuality with their uniformly high contents of manganese (table I; Carmichael, 1960).

The titanomagnetite microphenocrysts.

Microphenocrysts of titanomagnetite[1] and rarer ilmenite are ubiquitous in all the porphyritic pitchstones of the North Atlantic Tertiary volcanic province. As noted above, the iron-ores are commonly associated with or enclosed by the pyroxene or olivine phenocrysts. Magnetite concentrates from eleven porphyritic pitchstones, the pyroxene and olivine phenocrysts of which have already been described (Carmichael, 1960), have been examined in reflected light. The enumeration of the magnetites described here is the same as that of the pyroxenes, olivines, pitchstones, and residual glasses. Thus, for example, 1M (table II) is the analysed magnetite, 1 and 1A the analysed pyroxenes (figs. 1 and 2), 1G the analysed residual glass, which together with feldspar make up the analysed pitchstone 1R (op. cit., 1960).

All the magnetite samples are similar under the microscope, there being no recognizable exsolution lamellae at ×950 magnification. The homogeneity of these titanomagnetites may, however, occasionally be disturbed by secondary irregular wisps of hematite, which are rarely oriented as lamellae parallel to the octahedral planes of the magnetite host. There is little or no secondary hematite in either 4M or 7M (table II), but small amounts occur in 1M, 2M, and 5M. Some grains in these latter samples may be fairly extensively replaced by hematite and the adjacent magnetite may show a distinct colour difference to unaltered magnetite, the whole intergrowth having a vermicular appearance. Rarely grains of magnetite may enclose little blebs of pyrite, and ilmenite grains may occasionally be moulded on the magnetite of 1M.

Mineral analyses.

The titanomagnetites were initially separated by a hand magnet, and then by repeated centrifuging in warm Clerici solution followed by separation in the Frantz isodynamic separator with the magnet switched off. In this way a concentration of magnetite free from ilmenite was obtained, the two principal contaminants being zircon and thin sheaths of glass enclosing or partially enclosing the magnetite grains.

The techniques used for chemical analysis were not unlike those

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[1] These iron-ores were mistakenly called ilmeno-magnetites in a previous publication (Carmichael and McDonald, 1961).

described by Vincent and Phillips (1954) except that titania was esti-
mated colorimetrically, ferrous iron was determined by the ammonium
vanadate method, and CaO and MgO were determined by titration with
EDTA. After the sodium peroxide frit of the magnetite samples for the
determination of SiO_2 and Al_2O_3 (V_2O_3 and Cr_2O_3 being below the limit
of sensitivity), a small insoluble residue of zircon was found in some
samples, and this was filtered off, weighed, and included in the summation
of the analyses (table II, nos. 1M, 4M, and 7M).

It has been assumed that the silica found in the analyses is not held in
the magnetite structure (cf. Vincent and Phillips, 1954; Vincent et al.,
1957; Phillips and Muan, 1959) but represents the amount in the
contaminating glass shards. By subtraction of the appropriate amount
of glass, whose analyses are also known (Carmichael, 1960), the analyses
of the titanomagnetites have been recalculated silica-free. The calculated
amount of contaminating glass has also been recorded (table II).

The molecular proportions of the five recalculated titanomagnetites
have been plotted in fig. 3, and show that all these iron-ores are mixtures
in varying proportions of the ilmenite, magnetite, and ulvöspinel mole-
cules; 4M lies close to the ulvöspinel–magnetite join and may be con-
sidered a member of this binary series.

The cell dimensions of the titanomagnetites.

The cell dimensions[1] of these titanomagnetites (table II) also suggest
that the ulvöspinel molecule is present in varying amounts. Basta (1957)
has determined the cell-edge of pure magnetite as 8·396 Å and he also
tabulates the lattice parameters of the various spinels formed by elements
that may enter the magnetite structure (op. cit., table III). Only Mn has
a larger ionic radius than Fe″, thus causing an increase in the cell size, and
Basta reports a cell-edge of 8·51 Å for $MnFe_2O_4$. The inclusion of Ca in
magnetite will have a similar but unknown effect; the amount found
(table II), although perhaps somewhat greater than in many existing
magnetite analyses, is less than the 2·5 wt. per cent of CaO that synthetic
magnetites can take into their structure (Phillips and Muan, 1959). As
the amounts of Ca and Mn in these analysed samples are only small, they
are unlikely to have any significant effect on the lattice parameters.

Ulvöspinel, however, has a larger unit cell than pure magnetite, the
average value for synthetic material being 8·495 Å (Vincent et al., 1957).
If the cell-edge of 4M, a member of the ulvöspinel–magnetite series, is

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[1] These determinations were made by Dr. Davis from powder photographs taken
in a Philips 11·46 cm camera using filtered Co-K_α radiation.

referred to the plot of the variation in the cell-size in this binary series (*op. cit.*, fig. 3), then the lattice parameters of 4M indicate that it contains about 50 % of the ulvöspinel molecule, in fair agreement with the results of the analysis (fig. 3). The presence of the ilmenite molecule in the
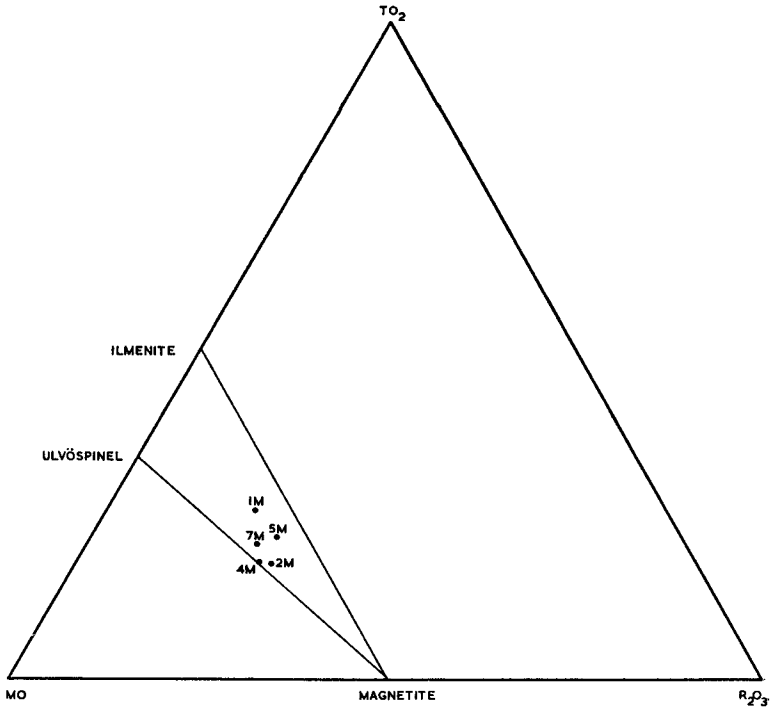

FIG. 3. Molecular composition of the recalculated analysed titanomagnetites. $MO = \mathrm{FeO + MgO + MnO + ZnO + CaO}$; $R_2O_3 = \mathrm{Fe_2O_3 + Al_2O_3}$; $TO_2 = \mathrm{TiO_2}$. The numbers refer to analyses in table II.

remaining homogeneous magnetites (fig. 3; 2M, 5M, 7M) is probably due to secondary oxidation to hematite in some grains giving a greater amount of $\mathrm{Fe_2O_3}$ in their analyses; the lattice parameters of these three specimens again indicate the presence of significant amounts of the ulvöspinel molecule. No detailed recalculation of any of these analyses into possible mineral molecules has been attempted in view of the impurity of the initial material.

Dr. Davis found that in the powder photographs of 2M and 5M two phases were present, the second, subordinate spinel phase having smaller

lattice parameters (8·39 and 8·364 Å respectively). This second phase (maghemite or purer magnetite) is presumably due to oxidation, as secondary hematite is most abundant in these two samples. The lattice parameters of the ilmenite of 1M are a 5·078 and c 13·99 Å which suggests that it may contain about 15 % (molecular) Fe_2O_3 (op. cit., fig. 6).

In conclusion, it is suggested that magnetite, which may later be joined by pyroxene and olivine phenocrysts rich in ferrous iron, may also reflect the reduced nature of the parent acid liquids, and accordingly varying but often considerable amounts of the ulvöspinel molecule may be held in solid solution in these early-crystallizing iron-ores.

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