Pantelleritic liquids and their phenocrysts.

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Summary: The phenocrysts of four porphyritic obsidians from Pantelleria have been analysed chemically, together with the residual glasses (liquids). Three new analyses of anorthoclase (one partial analysis), two of sodic ferrohedenbergite, one of fayalitic olivine, and two of cossyrite are presented together with their optical properties, and the relationship of these phenocrysts to their liquids is considered.

The experimental studies in the system $NaAlSi_3O_8-KAlSi_3O_8-SiO_2-H_2O$ show that for synthetic liquids of similar composition to the normative salic constituents of the pantelleritic liquids, a potassic alkali feldspar crystallizes, whereas in the pantelleritic liquids phenocrysts of anorthoclase ($Ab_{67}-Ab_{61}$) occur. It is suggested that sodium metasilicate, which appears in the norms of all the pantelleritic liquids, may be responsible for the divergence in trend between the synthetic feldspar–liquid tie-lines and the pantelleritic feldspar–liquid tie-lines.

THE Mediterranean volcanic island of Pantelleria has long been famous for its unusual peralkaline rhyolites and obsidians, which were first described and named pantellerite by Förstner (1881, 1884), the island becoming in consequence the type locality. Washington (1913) visited the island, and he has also given an account of its geology, together with many chemical analyses and detailed petrographic descriptions illustrating the pantellerites, which are associated with the closely related comendites (a silica-rich iron-poor pantellerite (Lacroix, 1930)), with trachytes, and with later alkali olivine-basalts that may contain normative nepheline (Washington, 1914). Similar associations are found, for example, in Kenya, where pantellerites, comendites, and trachytes occur with nepheline-bearing basalts, mugearites, phonolites, and kenytes (Campbell Smith, 1931).

Comendites and pantellerites, however, are of widespread distribution, being found in the deep oceanic areas (Broch, 1946; Tilley, 1950), in Sardinia (Johnsen, 1912), in the old French territories of West Africa and Equatorial Africa (Lacroix, 1934; Koch, 1955), in Nigeria (Jacobsen *et al.*, 1958), in Abyssinia (Lacroix, 1930), in Madagascar (Lacroix, 1923), and in Australia (Jensen, 1906) and New Zealand (Marshall, 1936). The Cenozoic alkaline province that surrounds the sea of Japan also includes comenditic and pantelleritic representatives (Aoki, 1959; Lacroix, 1927;

Nemoto, 1934; Tomita, 1935), and the paisanitic rhyolites of Texas (Cross, 1904) show close affinity to many comendites.

A typical pantellerite is porphyritic with phenocrysts of anorthoclase and sometimes quartz, together with cossyrite (believed to be synonymous with aenigmatite), a sodic pyroxene, and occasional olivine. The groundmass may be glassy (microlitic) or a finely crystalline intergrowth of feldspar and a silica mineral, together with needles of aegirine and cossyrite.

However, it is the chemical composition of pantellerites that has attracted the attention of petrologists since Washington published his analyses, for so great is the molecular excess of soda over alumina (which is characteristically low) that the CIPW norm requires the rare mineral molecule sodium metasilicate (ns) to be formed, the occurrence of which has been discussed by Chayes (1960) and Tuttle (1960). Since the re-analysis of two of Washington's specimens by Zies (1960) there can now be no doubt of the existence of this unusual normative molecule.

It is the purpose of this paper to present the results of a study of four porphyritic pantellerites from Pantelleria, their phenocrysts, and their residual glasses, and an attempt is made to compare the unusual chemical composition of the pantellerites with the relevant synthetic silicate systems in order to understand better these rather unusual and enigmatic natural liquids.

Petrography.

Washington (1913) has already published a detailed petrographic account of the pantelleritic obsidians (hyalopantellerites) and this is amplified here for the analysed specimens. The specimens available for examination (see key to tables, p. 90) were obtained from the collections of the Imperial College of Science, and were apparently purchased many years ago. In hand specimen, the black obsidians are vesicular, brightly lustrous, and apparently completely fresh.

One obsidian (1R) contains abundant phenocrysts of anorthoclase (1F) together with a sodic pyroxene (1) and a fayalitic olivine (1B), the last two tending to form clusters together with ilmenite. The pyroxene, which is distinctly pleochroic from bright emerald green to brown tinged with green, may be euhedral and is rarely twinned. Zoning is not detectable, and the pyroxene tends to enclose or be surrounded by crystals of ilmenite, which are invariably smaller than the silicate phenocrysts. Olivine, which is also a common phenocryst, may enclose or be surrounded by crystals of ilmenite. Cossyrite has not been found in thin

sections of this specimen, but is sparsely present in the heavy mineral concentrates. Anorthoclase is the commonest phenocryst mineral in all the obsidians, and may be of very variable size. The large subhedral phenocrysts may show patchy extinction, and are commonly twinned on the Carlsbad or Manebach laws. Small fragments of feldspar of all sizes suggest by their shape that they have formed by the mechanical breakdown of the larger phenocrysts, probably as a result of flow of the viscous obsidian.

The glass (1G) that encloses these phenocrysts contains microlites of feldspar ($Ab_{65}Or_{35}$)[1] that are larger and more abundant than in any of the other glasses. Microlites of aegirine are sparsely scattered throughout the pale-brown glass together with a few small stumpy crystals of cossyrite and minute crystals of zircon.

Several of the obsidians likewise contain numerous feldspar microlites in the glass, together with needles of aegirine, and in 2R the glass (2G) encloses large phenocrysts of cossyrite (2A), which show intense absorption from deep red-brown to black. Olivine and ilmenite phenocrysts are rare, and the glass also contains infrequent coarse patches of quartz and feldspar in granophyric intergrowth (Lacroix, 1930, p. 93), together with independent poorly shaped phenocrysts of quartz. The larger phenocrysts of anorthoclase (2F) often form clusters and also show considerable variation in size. The phenocrysts of pyroxene (2) may similarly form clusters with fayalite, ilmenite, and anorthoclase.

Quartz and cossyrite (3A) are common phenocrysts in 3R and are enclosed together with anorthoclase (3F) in a glassy groundmass (3G) almost free of feldspar microlites. Olivine and ilmenite are absent in the heavy mineral concentrates, and pyroxene seems unusually scarce. Phenocrysts of all minerals are rare in 4R, feldspar (4F) being the most abundant, and fayalite, pyroxene, ilmenite, and rarer cossyrite are enclosed in a glass (4G) that has rare feldspar microlites but common birefringent spiculites.

In 5R the glassy groundmass of the obsidians is replaced by a very fine-grained crystalline intergrowth of feldspar ($Ab_{53}Or_{47}$)[1] and a silica mineral, the groundmass also containing small needles of aegirine and small equant crystals of deep red cossyrite. The groundmass encloses phenocrysts of anorthoclase ($Ab_{62.5}Or_{37.5}$),[1] quartz, acicular pyroxene with a deep green outer zone, and cossyrite, the deep red core of which is enclosed by a deeper, almost black, outer zone of cossyrite. Near the

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[1] The compositions of these feldspars were determined by the $\bar{2}01$ method (Bowen and Tuttle, 1950).

phenocrysts the groundmass tends to be coarser and more completely crystalline, and may grade into less well-crystallized areas with little aegirine or cossyrite, but with abundant birefringent patches of pale yellow partially devitrified glass. In parts of the rock, the pale yellow colour of the less well-crystallized areas of the groundmass may grade to a reddish colour, which is presumably due to the oxidation of iron contained in these partially devitrified patches.

The trachyte obsidian from Pitcairn Island (6R) contains rare phenocrysts of alkali feldspar, rarer ferroaugite and iron-rich olivine, together with micro-phenocrysts of magnetite. The dark-brown glass, which contains a few scattered feldspar microlites, may also enclose xenoliths of olivine basalt, mugearite, or trachyte.

The modal analyses of the analysed specimens are given in table I, and although five or six thin sections of each specimen were counted, the ferromagnesian minerals are so unevenly distributed throughout the obsidians that the determined ferromagnesian modal content is perhaps best considered as an order of magnitude.

The ferromagnesian phenocrysts of these pantelleritic obsidians have many features in common. The olivine is usually the largest of the ferromagnesian phenocrysts, although it may show considerable variation in size: it is feebly idiomorphic and completely fresh with no visible alteration in the fracture cracks or the frequently well-developed cleavage. Microphenocrysts of ilmenite may be enclosed by the olivine phenocrysts or be associated with them in clusters with pyroxene. Microscopically the grains of olivine are coloured pale amber and show a pale yellow colour in thin section, with feeble but distinct pleochroism.

The pyroxenes, which are completely fresh, are a deep greenish-black under the binocular microscope, and unless the grains are small are easily mistaken for cossyrite. The distinctive pleochroism noted above is common to all the pyroxenes examined, and varies little, if at all, in intensity except in 5R. Simple twinning is not common, and there is no microscopic evidence of exsolution. The pyroxenes may be idiomorphic, but are commonly ill shaped, show a wide variation in size, and in those from the obsidians zoning cannot be detected.

The cossyrite phenocrysts are very distinctive with their intense absorption (deep red-brown to black) and moderately high birefringence. One well-developed cleavage is seen, and rare sections show a poorly defined second cleavage. Cossyrite usually forms large phenocrysts, which may be subidiomorphic with a shape (eight-sided polygon) not unlike a pyroxene, and it always appears completely fresh.

Magnetite as microphenocrysts is almost completely absent from all the pantellerites examined, but may occur as minute grains in the glasses. A small fraction was obtained by hand magnet from two samples, and the weight of sample so obtained indicates a magnetite concentration of 20 to 50 p.p.m.

TABLE I. Modal analyses (volume per cent.).

For the key to these analyses, see below.

	Glass.	Feldspar.	Quartz.	Pyroxene.	Olivine.	Cossyrite.	Iron oxides.
1R (5748)	88·2	10·7	—	0·5	0·4	trace	0·2
2R (3112)	80·6	18·0	0·1	0·3	trace	0·9	trace
3R (5749)	87·6	9·4	2·0	trace	—	0·9	—
4R (3114)	98·7	1·2	—	trace	trace	—	—
5R (5750)	85·0*	10·4	3·6	0·2	—	0·8	—
6R (12095)	99·3	0·6	—	0·1	trace	—	trace

* Microcrystalline groundmass.

KEY TO TABLES I–VII.

1 Sodic ferrohedenbergite from obsidian, Pantelleria. 5748.
1B Fayalite from 5748.
1F Anorthoclase from 5748.
1G Residual glass from 5748.
1R Porphyritic obsidian 5748.
2 Sodic ferrohedenbergite from obsidian, Pantelleria. 3112.
2A Cossyrite from 3112.
2F Anorthoclase from 3112 (Carmichael, 1960b, table III).
2G Residual glass from 3112 (Carmichael, 1960b, table V).
2R Porphyritic obsidian 3112.
3A Cossyrite from obsidian, Pantelleria. 5749.
3F Anorthoclase from 5749.
3G Residual glass from 5749.
3R Porphyritic obsidian 5749.

4F Anorthoclase from obsidian, Pantelleria, 3114.
4G Residual glass from 3114.
4R Porphyritic obsidian 3114.
5R Porphyritic micro-crystalline pantellerite, Pantelleria. 5750.
6R Trachyte obsidian, Pitcairn Island, 12095.
C Aegirine-hedenbergite from Skye alkali granite (Tilley, 1949).
D Ferroaugite from quartz-syenite (coexisting with olivine) (Hess, 1949, p. 654; Buddington, 1939, p. 120).
E Hyalopantellerite (P.R.C. 2000; Zies, 1960, p. 307).
F Hyalopantellerite (P.R.C. 2007; Zies, 1960, p. 307).

Analyses 1 to 6R by I. S. E. Carmichael.

Mineral analyses.

The ferromagnesian phenocrysts were separated on the Frantz isodynamic separator followed by repeated centrifuging in Clerici solution, and if necessary were then hand-picked under a binocular microscope. The elimination of cossyrite impurity from pyroxene was troublesome, as was the separation of fayalite from ilmenite, and effective separation on the small quantities of concentrates obtained could only be made by

hand-picking. The feldspars and residual glasses were initially separated on the Frantz separator followed by centrifuging in methylene iodide.

Whereas several grams of feldspar were separated and used for gravimetric analysis, only small quantities of the pyroxenes and olivine were obtained, and their chemical analyses were made on a semi-micro scale on a total sample of 100 mg or less. Ilmenite and magnetite are rare

TABLE II. Analyses and optical properties of the sodic ferrohedenbergite and fayalite phenocrysts.

For the key to these analyses, see p. 90.

	1.	2.	C.	D.	1B.
SiO_2	48·58	48·69	49·69	48·28	30·56
TiO_2	0·71	0·86	0·45	0·28	0·72
Al_2O_3	2·06	2·04	0·48	1·45	0·09
Fe_2O_3	5·69	5·60	8·79	3·96	0·10
FeO	20·15	21·96	18·23	27·02	60·81
MnO	1·31	1·25	0·25	0·76	3·43
MgO	2·67	0·89	1·98	0·32	3·47
CaO	16·93	16·36	16·87	16·18	1·13
Na_2O	2·31	2·86	3·79	1·51	—
K_2O	0·09	0·09	nil	0·14	—
Total	100·50	100·60	100·53	100·20*	100·31

* Includes H_2O^+ 0·15 %, H_2O^- 0·15 %

α	—	—	—	1·7355	1·809
β	1·740	1·747	—	1·7450	1·842
γ	—	—	—	1·7650	1·863
2V	65° (+)	66° (+)	—	$70\frac{1}{4}$° (+)	52° (−)
γ:[001]	54°	55°	—	$56\frac{1}{2}$°	—
Atomic percent.					
Ca	40·9	41·2	41·9	39·3	—
Mg	8·9	3·1	6·8	1·1	8·8
Fe	50·2	55·7	51·3	59·6	91·2

and only 20 to 30 mg of magnetite was obtained from approximately 1 kg of rock, and no attempt was made to analyse these iron-titanium oxides.

Pyroxene and olivine phenocrysts. Only two pyroxenes and one olivine were successfully separated in sufficient quantity for analysis, and the results are set down in table II (nos. 1, 2, and 1B). The two pyroxenes are sodic ferrohedenbergites and their analyses have been recalculated into the standard formula $(WXY)_2Z_2O_6$ (table III) by the method described by Hess (1949, p. 625). Thus instead of making $Z = 2$ by adding arbitrary amounts of Al, and where necessary Ti, to Si, the cations are allotted to groups in accordance with the balance of charge on a cation for cation basis.

The pyroxene formulae (table III, nos. 1 and 2) show that the incorporation of Na into the pyroxene structure is almost matched by the incorporation of an equivalent amount of Fe‴. There is, however, a small deficiency of Fe‴ in relation to Na+K, which is compensated for by Al to balance the structure. A small amount of Ti is found in tetrahedral coordination in the most iron-rich pyroxene (table III, no. 2) and also in a sodic ferrohedenbergite from the alkaline facies of a Tertiary Skye granite (Tilley, 1949) (table III, no. C). As Brown (1957,

TABLE III. Structural formulae of analysed pyroxenes and olivine. (Pyroxenes on the basis of 6 oxygens, fayalite on the basis of 4 oxygens.) For the key to these analyses, see p. 90.

			1.	2.	C.	D.	1B.
Si	...	...	1·934	1·950	1·973	1·976	0·996
Al	...	...	0·064	0·038	—	0·040	0·004
Ti	...	...	—	0·007	0·014	—	—
Ti	...	...	0·021	0·019	—	0·008	0·018
Al	...	...	0·032	0·058	0·026	0·029	—
Fe‴	...	...	0·172	0·168	0·262	0·123	0·004
Fe″	...	...	0·670	0·737	0·606	0·924	1·659
Mn	...	...	0·043	0·043	0·010	0·026	0·094
Mg	...	...	0·158	0·053	0·117	0·020	0·169
Ca	...	...	0·723	0·703	0·718	0·708	0·039
Na	...	...	0·177	0·221	0·291	0·120	—
K	...	...	0·005	0·005	—	0·007	—
Z	...	...	1·998	1·995	1·987	2·016	1·000
WXY	...	...	2·001	2·007	2·030	1·965	1·983
Percent. Al in Z			3·2	1·9	—	2·0	—
Percent. Ti in Z			—	0·3	0·7	—	—

p. 518) has pointed out, the inclusion of Ti in the Z group is not necessarily due to a high content of Ti, but rather to low Al and possibly a high content of Na+K. The concentration of Ti in these pantelleritic sodic ferrohedenbergites is higher than the average (0·56 %) found in a series of pitchstone ferroaugite phenocrysts (Carmichael, 1960a, table II), and Al is similarly higher than the ferroaugite average (1·4 %) although tetrahedrally coordinated Al in both groups is similar.

The variation of Ca, Mg, and Fe in these pyroxenes is shown in fig. 1 together with the composition (as Mg:(Fe+Mn)) of the associated fayalitic olivine. The pantelleritic pyroxenes and the Skye sodic ferrohedenbergite have similar Ca:(Mg+Fe) ratios to the ferroaugites and ferrohedenbergites of the Skaergaard intrusion (Muir, 1951; Brown, 1960) and to the ferroaugite phenocrysts of some North Atlantic Tertiary pitchstones (Carmichael, 1960a, fig. 1). If, as Muir (1954) suggests, pyroxenes on crossing the limit of the two-pyroxene field crystallize on

a liquidus minimum, then this minimum would seem to have a similar position with respect to Ca:(Mg+Fe) for pyroxenes crystallizing with notable amounts of Na (fig. 1, nos. 1, 2, and C) as for the tholeiitic pyroxenes that contain only negligible amounts of alkalis.

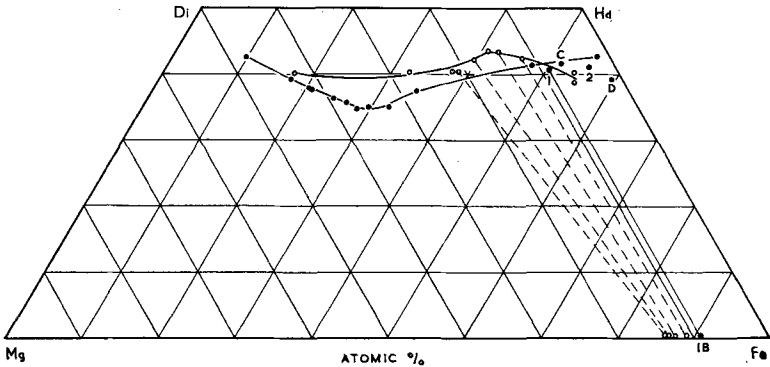The increase of Na that may occur with the progressive iron-enrichment

FIG. 1. The composition of sodic ferrohedenbergites plotted with respect to variation in Ca, Mg, and Fe. Solid circles Nos. 1 and 2 (table II) are pantellerite phenocrysts, and C and D are alkali-granite and quartz-syenite pyroxenes respectively (table II). The co-existing pantellerite pyroxene and olivine (plotted as Mg:(Fe+Mn)) are joined by a solid tie-line (Nos. 1 and 1B, table II). ●—●—● Skaergaard calcium-rich pyroxene trend (Brown, 1957, 1960); ○—○—○ pitchstone calcium-rich pyroxene trend, with the relevant pyroxene–olivine pairs joined by dashed tie-lines (Carmichael, 1960a, fig. 1).

of the calcium-rich pyroxenes cannot be seen in the conventional Ca, Mg, and Fe pyroxene diagram. Accordingly, in fig. 2 the alkali content of various series of calcium-rich pyroxenes has been plotted in order to illustrate such an increase of Na with progressive iron-enrichment. The formulae of the pyroxenes have been recalculated in terms of (Na+K), Mg, and (Fe''+Mn+(Fe''')), the last term (Fe''') being the excess, if any, of trivalent iron over Na+K. This procedure is more simple than that described by Yagi (1953), which necessitates the arbitrary formation of standard pyroxene molecules.

The tholeiitic trend represented by the calcium-rich pyroxenes of the Skaergaard intrusion (Brown, 1957, 1960) (fig. 2) shows a small decrease in Na as the early magnesian augites become progressively impoverished in Ca, and only in the latest stages of iron-enrichment does Na show a small increase. The ferroaugite phenocrysts of a series of pitchstones (Carmichael, 1960a) also show an increase in soda with progressive
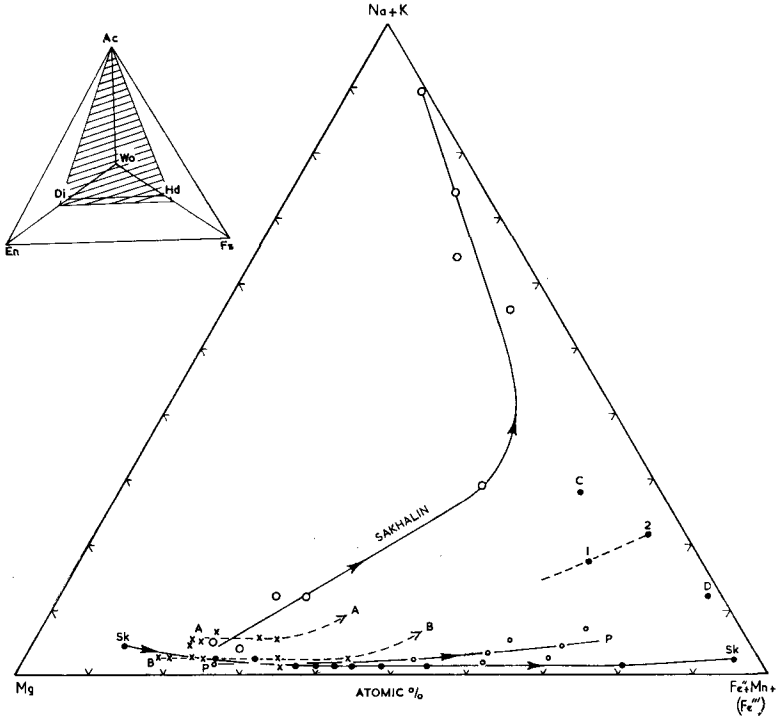
FIG. 2. The crystallization trends of various calcium-rich pyroxene series. Sk
●—●—● Sk represents the Skaergaard trend (Brown, 1957, 1960); P ○—○—○
P is the pitchstone pyroxene phenocryst trend (Carmichael, 1960a); A- - - - A and
B- - - - B (crosses) are the pyroxene trends of a differentiated teschenite sill (Wilkin-
son, 1957) and the Garbh Eilean sill, Shiant Isles (Murray, 1954) respectively; the
Sakhalin trend represents the pyroxenes from a differentiated dolerite–monzonite–
syenite series (Yagi, 1953). Solid circles are sodic ferrohedenbergites (Nos. 1 and 2,
pantellerite phenocrysts); C and D, alkali-granite and quartz-syenite pyroxenes,
(table II). (Fe''') is the excess of Fe''' over that required to combine with $Na+K$ in
the calcium-rich pyroxene formulae. The inset figure shows the generalized relation-
ship of the plane Mg, $Na+K$, and $Fe+Mn+(Fe''')$ for the calcium-rich pyroxenes
to the pyroxene tetrahedron enstatite (En), ferrosilite (Fs), wollastonite (Wo), and
acmite (Ac).

iron-enrichment, and are typically richer in soda than the Skaergaard fer-
roaugites. The two pantelleritic sodic ferrohedenbergites (nos. 1 and 2)
are considerably enriched in Na compared to the tholeiitic pyroxenes, and
their trend, which shows concomitant enrichment in Na, Fe''', and Fe'',
cannot be considered to be a continuation of the pitchstone ferroaugite
trend (cf. fig. 1), which, however, may continue to a pyroxene similar to

D (table II, figs. 1 and 2), a mildly-alkaline sodic ferrohedenbergite occurring with a fayalitic olivine in an Adirondack quartz-syenite (Hess, 1949, no. 19) (Buddington, 1939, p. 120). It is possible that the outermost zones of aegirine and aegirine-augite noted by Wilkinson (1957) in a series of Ti-rich sahlites (fig. 2) from a differentiated teschenite sill may generally correspond in composition to these pantelleritic sodic ferro-hedenbergites. In a similar way, the green outer zones of the pyroxenes in the picritic pegmatites of the Shiant Isles (Murray, 1954) may also show a trend in this direction (fig. 2).

The series of Ti-rich augites, sodion augites, aegirine-augites, and aegirines described and analysed by Yagi (1953) from a genetic series of dolerites, monzonites, and syenites illustrates a more extreme type of alkali enrichment (fig. 2). In a detailed discussion of the solid-solution relationships in pyroxenes, Yagi (op. cit., p. 798) suggests that acmite and diopside may form a complete solid-solution series with NaFe''' replacing CaMg in the pyroxene structure, and he later (Yagi, 1958) provides data on the synthesis of such pyroxenes. So far as is known to the writer, there is no experimental data on the existence of a solid-solution series between acmite and hedenbergite, but the calcium-rich pyroxene analyses plotted in fig. 2 suggest that this solid-solution series does exist and is more common in natural pyroxenes than that between diopside and acmite. Perhaps it may be taken that this solid-solution series does occur in natural calcium-rich pyroxenes, and in consequence it may be expected that pyroxene phenocrysts in equilibrium with acid or salic liquids will tend to be enriched in CaFe'' in relation to the pyroxene components (NaFe''') in the liquid. A similar conclusion was reached by Hytönen (1959, pp. 85–88) with regard to aegirine-augite occurring both as phenocrysts and in the groundmass of a natrolite tinguaite. It therefore seems unlikely that crystals of pure acmite will occur as phenocrysts in quickly cooled salic liquids, unless they are products of the synthetic reaction relationship of hematite (magnetite in nature)[1] to liquid (Bowen et al., 1930).

The analysis of the fayalitic olivine is given in table II (no. 1B) and its formula in table III (no. 1B). The olivine contains an unusually high content of Mn and Ca compared to the pitchstone ferrohortonolite phenocrysts (Carmichael, 1960a, table 4), and although the content of Mn may be related to the high content of Mn in the liquids (table VI,

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[1] J. Nolan (personal communication) has found that a reaction relationship exists between magnetite and liquid to give acmite in hydrothermal experiments in the system $NaAlSi_3O_8$–$NaFeSi_2O_6$.

nos. 1G–4G), there seems to be no good reason for the high Ca, and the writer cannot at the moment provide a solution. In relation to the coexisting pyroxene (table II, no. 1), the olivine is enriched in Mn and Fe, and the tie-line between the two (fig. 1) is parallel to those found for coexisting pitchstone ferroaugite–ferrohortonolite phenocryst pairs (fig.1).

Cossyrite phenocrysts. Phenocrysts of cossyrite occur in all the analysed rocks from Pantelleria, but in rather variable amounts (table I). It is

TABLE IV. Analyses and optical properties of the cossyrite phenocrysts. Refractive indices ±0·005.

For the key to these analyses, see p. 90.

			2A.	3A.	a.	b.
SiO_2	...	...	41·02	40·97	41·54	39·82
TiO_2	...	...	8·92	8·83	10·04	8·82
Al_2O_3	...	...	0·94	0·89	—	—
Fe_2O_3	...	...	1·31	1·19	—	8·82
FeO	...	...	38·84	38·86	40·63	35·70
MnO	...	...	1·16	1·08	—	—
MgO	...	...	0·07	0·54	—	—
CaO	...	...	0·45	0·55	—	—
Na_2O	...	...	7·36	6·93	7·79	6·84
K_2O	...	...	0·06	0·08	—	—
H_2O^+	...	...	—	nil	—	—
H_2O^-	...	...	—	0·07	—	—
Total		...	100·13	99·99	100·00	100·00
α	...	...	1·795	1·793		
β	...	...	1·805	1·804		
γ	...	...	1·87	1·87		

a Calc. for $2Na_2O.9FeO.2TiO_2.11SiO_2$.
b Calc. for $2Na_2O.9FeO.Fe_2O_3.2TiO_2.12SiO_2$ (Fleischer 1936).

commonly the most abundant ferromagnesian silicate, and as it is comparatively easy to separate it is not surprising that this occurrence of the mineral has long claimed the attention of mineralogists. Cossyrite is a mineral of intense absorption (deep red-brown to black), rather high birefringence (Bowen, 1937), and high refractive index (table IV).

Fleischer (1936) has collected the chemical and X-ray data of cossyrite (= aenigmatite) and has suggested a formula for this triclinic mineral. It is not, as was believed, related to the amphiboles, and does not contain essential water (table IV) although it is possible that small amounts of F or Cl may exist in the structure, as these two elements were not sought in the analyses. Fleischer's generalized formula is $X_4Y_{13}(Si_2O_7)_6$, which as a special case might become $Na_4Fe''_9Fe'''_2Ti_2Si_{12}O_{42}$, to which many of his analyses made a close approach. The two new analyses presented in table IV are very similar to one another, and not unlike many of the

analyses compiled by Fleischer (1936, table 1). However, the two new analyses contain much less Fe_2O_3 than many others, and would seem to approach more closely the formula $Na_4Fe''_9Ti_2 Si_{11}O_{37}$ than Fleischer's formula (table IV).

The paragenesis of cossyrite in these obsidians may give an indication of its thermal stability. As a result of comparing the heavy mineral concentrates obtained from these obsidians the author believes that the assemblage fayalite plus ilmenite is generally antipathetic to the existence of cossyrite. Certainly the amounts of fayalite and ilmenite are drastically reduced when cossyrite is in relative abundance, and this antipathetic relationship could suggest that cossyrite may form by the reaction of fayalite ($2FeO.SiO_2$) and ilmenite ($FeO.TiO_2$) (or possibly ulvöspinel, $2FeO.TiO_2$) with a sodium-rich liquid to give cossyrite. No petrographic evidence, however, has yet been found to suggest this reaction relationship, which, if it exists, may only be found in liquids having the unusual molecular excess of soda over ferric iron and alumina. Mere antipathy of the assemblages noted above does not necessarily imply a reaction relationship, and experimental investigation is clearly required.

Fleischer (1936) suggests that the mineral rhönite forms a solid solution series of the plagioclase type with cossyrite, CaAl replacing the NaSi of cossyrite. If this is so then the analyses presented in table IV show a close approach to the cossyrite end-member.

Iron-titanium oxides. Ilmenite is the more frequent representative of the iron-titanium oxides in the pantelleritic obsidians (especially 1R), although its concentration would seem to fall with an increase in that of cossyrite. Magnetite is extremely rare and only 25 mg or so were obtained from each of two specimens indicating that its concentration is of the order of 20 to 50 p.p.m. Under the microscope the magnetite is quite homogeneous, with no exsolution of ilmenite or ulvöspinel, and the ilmenite is similarly undistinctive optically. The magnetites are generally extremely fine-grained, and would seem to represent a quench product of the silicate liquid, whereas ilmenite may form much larger microphenocrysts, with a distinctive hexagonal or elongate habit easily seen under the petrographic microscope. Through the kindness of Dr. R. J. Davis, the lattice dimensions of two magnetites and an ilmenite have been determined, and the results are set down below.

Ilmenite from 1R (5748) a 5·091 ±0·001, c 14·083±0·003 Å, c/a 2·766±0·001
Magnetite from 2R (3112) a 8·503±0·001 Å
Magnetite from 4R (3114) a 8·479±0·001 Å

Vincent *et al.* (1957, fig. 6), using Basta's data, show the continuous decrease in the cell-dimensions of ilmenite with increasing solid solution of α-Fe_2O_3. They also record the cell-dimensions of ilmenite lamellae intergrown with magnetite (Skaergaard) before and after heating *in vacuo*, and show that the lattice parameters of the ilmenite decrease in response to the increasing entry of α-Fe_2O_3; the cell-dimensions of this ilmenite before heating are larger than those given by Basta (in Vincent *et al.*) for pure ilmenite without α-Fe_2O_3, and the similarity of the cell-dimensions of the pantelleritic ilmenite to the unheated (i.e. no α-Fe_2O_3) Skaergaard ilmenite lamellae (a 5·088, c 14·092 Å, $c/a = 2·770$) indicates that the underlying cause may be common to both. Vincent *et al.* (1957, p. 641) suggest that appreciable Mn in solid solution in the ilmenite (as $MnTiO_3$) will tend to increase the cell-dimensions as may $MgTiO_3$, but the paucity of Mg in the liquid compared to Mn (table VI, no. 1R) suggests that $MnTiO_3$ may be responsible for the larger cell-dimensions of the pantelleritic ilmenite (coexisting fayalite (1B) contains 3·43 % MnO), which like the Skaergaard ilmenite is unlikely to contain very much α-Fe_2O_3 in solid solution.

The cell-sizes of both the magnetites are unusually large and in view of the complexities of possible substitutions in the magnetite structure, and without a chemical analysis, it is only possible to speculate on the possible causes. Basta (1957) has determined the cell edge of pure magnetite as 8·396 Å and he also tabulates the cell-dimensions of the various spinels formed by elements that may enter the crystal structure of magnetite (op. cit., table III). Only Mn has a larger ionic radius than Fe'', thus causing a marked increase in the cell-dimensions, and Basta reports a cell edge of 8·51 Å for $MnFe_2O_4$.

Ulvöspinel, Fe_2TiO_4, similarly has a larger unit cell than pure magnetite, the value for synthetic material being 8·495 Å, a value closely approached by the more complex natural ulvöspinels (Vincent *et al.*, 1957). As these two combinations ($MnFe_2O_4$ and Fe_2TiO_4) seem to be the only ones capable of increasing the cell-size of magnetite, it can only be concluded that the pantelleritic magnetites contain considerable Mn or Ti or both.

The feldspar phenocrysts and the system $KAlSi_3O_8$–$NaAlSi_3O_8$–SiO_2–H_2O.

Only one feldspar, an anorthoclase, is found as phenocrysts in these pantellerites, and all the analysed specimens (table V) have generally similar optical properties. The anorthoclase phenocrysts of the analysed obsidians show only a small variation in composition, and are unusually

low in lime; iron, which is relatively high for sodium-rich feldspars, is taken to substitute for Al, and leads to a satisfactory formula balance (table V).

Before considering the pantelleritic feldspar–liquid relationships it is necessary to review the courses of equilibrium crystallization in the

TABLE V. Analyses, optical properties, and formulae (on the basis of 32 oxygens) of the feldspar phenocrysts. Refractive indices ± 0.002, $2V \pm 2°$.

For the key to these analyses, see p. 90.

	1F.	2F.	3F.	4F.		1F.	2F.	3F.
SiO_2	66·71	66·75	67·18	—	Si	11·936	11·924	11·977
Al_2O_3	18·86	18·84	18·54	—	Al	3·979	3·972	3·900
Fe_2O_3	0·74	0·88	0·90	0·78	Fe'''	0·107	0·129	0·128
CaO	0·03	0·06	0·04					
BaO	—	0·08	—	—	Ca	0·005	0·011	0·007
Na_2O	7·64	7·41	7·27	7·91	Ba	—	0·004	—
K_2O	5·92	6·12	6·46	5·59	Na	2·645	2·575	2·507
H_2O^+	0·15	0·18	0·15	—	K	1·355	1·395	1·478
H_2O^-	nil	0·09	nil	—				
Total	100·05	100·41	100·54	—	z	16·02	16·02	16·00
					xy	4·00	3·98	3·99

Composition (recalculated to 100 wt. per cent.)

Or	35·2	36·3	38·4	32·8
Ab	64·7	63·2	61·4	67·2
An	0·1	0·3	0·2	—
Cn	—	0·2	—	—
α	1·525	1·525	1·526	1·524
β	1·529	1·529	1·530	1·528
γ	1·530	1·530	1·532	1·529
$2V_\alpha$	43°	45°	43°	41°

Composition by X-ray, $\overline{2}01$ method
Or_{36} Or_{37} $Or_{37.5}$ $Or_{34.5}$

system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O, which have been discussed in detail by Tuttle and Bowen (1958). Equilibrium crystallization of a liquid whose composition is represented by X (fig. 3) will begin with the precipitation of a feldspar slightly more sodic than Y, and with continued crystallization (cooling) the liquid will move on a curved course to Y', at which point the feldspar crystals will have the composition Y. As quartz (or a silica mineral) will start to crystallize when the liquid has reached the quartz–feldspar boundary curve at Y', the join YY' is both a tie-line and a three-phase boundary. With further cooling, the liquid will move along the boundary curve towards the ternary minimum M, while the crystals of feldspar continuously react with the liquid and become more potassic than Y.

TABLE VI. Analyses of pantellerites and residual glasses. For the key to these analyses, .

	1R.	1G.	2R.	2G.	3R.	3G.	4R.	4G.	5R.	E.	F.	6R.
SiO_2	67·5	69·9	68·6	70·1	69·7	70·5	69·2	69·8	69·3	69·81	69·56	63·0
TiO_2	0·49	0·54	0·46	0·41	0·38	0·35	0·52	0·52	0·39	0·45	0·47	0·60
ZrO_2*	0·22	0·20	0·24	0·28	0·30	0·27	0·21	0·20	0·28	0·25	0·12	0·11
Al_2O_3	12·0	8·8	9·2	7·6	9·1	7·6	10·9	10·7	9·0	8·59	11·27	15·8
Fe_2O_3	1·8	2·1	2·7	2·9	2·2	2·0	2·0	2·0	5·1	2·28	1·87	2·6
FeO	4·0	5·9	5·3	5·6	4·9	6·3	4·0	4·0	2·3	5·76	4·18	3·3
MnO	0·21	0·30	0·31	0·34	0·26	0·32	0·29	0·30	0·28	0·28	0·28	0·18
MgO	0·13	0·13	0·11	0·04	0·07	0·03	0·24	0·23	0·49	0·10	0·23	0·42
CaO	0·50	0·52	0·54	0·53	0·39	0·39	0·44	0·43	0·78	0·42	0·44	1·9
Na_2O	6·9	6·5	6·8	7·1	6·9	7·0	6·5	6·5	4·8	6·46	6·28	6·4
K_2O	5·2	4·7	4·6	4·6	4·8	4·6	4·9	4·8	4·6	4·49	4·60	5·1
P_2O_5	0·04	0·04	0·04	0·05	0·04	0·04	0·04	0·05	0·03	0·13	0·10	0·12
H_2O+	0·38	0·04	0·32	0·23	0·33	0·05	0·22	0·17	1·0	0·14	0·13	0·24
H_2O-	0·02	nil	0·03	0·04	0·01	nil	0·02	0·01	1·2	0·05	0·02	0·03
Cl	(0·62)†	0·70	(0·56)	0·69	(0·72)	0·82	(0·30)	0·31	0·04	0·76	0·37	—
	100·0	100·4	99·8	100·5	100·1	100·3	99·8	100·0	99·6	100·06	99·99	—
Less $O \equiv Cl$	0·14	0·16	0·13	0·16	0·16	0·18	0·07	0·07	0·01	0·18	0·09	—
Total	99·9	100·2	99·7	100·4	99·9	100·1	99·7	100·0	99·6‡	99·88‖	99·90§	99·8

* Zr determined by X-ray fluorescence in 1R, 2R, 3R, 4R, 5R, and 6R; Zr(Hf)O₂ determined gravimetrically in 1G, 2G, 3G, and 4G.

† Cl content (in brackets) in the obsidian analyses is computed from the modal amount of glass (table I) assuming that none of the phenocryst minerals contain Cl.

‡ CO_2 present, not determined.

‖ Includes SO_3 0·06 and Cl (H_2O sol.) 0·03.

§ Includes SO_3 0·06 and Cl (H_2O sol.) 0·01.

TABLE VII. Norms of pantellerites and residual glasses, and refractive indices of the glasses.

For the key to these analyses see p. 90.

	1R.	1G.	2R.	2G.	3R.	3G.	4R.	4G.	5R.	6R.
qtz	16·6	27·5	24·2	29·6	26·7	30·8	21·4	22·6	26·0	2·6
or	30·6	27·8	27·2	27·2	28·4	27·2	28·9	28·4	27·2	30·0
ab	33·0	18·9	21·5	13·6	19·9	13·6	28·8	28·3	20·4	52·9
ac	5·1	6·0	7·8	8·3	6·5	6·0	6·0	6·0	14·8	0·9
wo	1·0	1·0	1·2	1·2	0·8	0·8	0·9	0·9	1·6	3·6
en	0·3	0·3	0·3	0·1	0·2	0·1	0·6	0·6	1·2	1·0
fs	7·0	10·4	9·5	10·3	8·8	11·5	7·1	7·1	4·1	3·6
ns	3·5	5·6	5·4	7·4	6·0	7·7	4·0	4·2	0·7	Mt. 3·2
il	0·9	1·1	0·9	0·8	0·8	0·8	0·9	0·9	0·8	1·2
hl	0·9	1·2	0·9	1·2	1·2	1·3	0·5	0·5	—	Ap. 0·3
z	0·4	0·4	0·4	0·4	0·4	0·4	0·4	0·4	0·4	0·2
Rest	0·4	0·1	0·4	0·3	0·4	0·1	0·3	0·2	2·3	0·3
Total	99·7	100·3	99·7	100·4	100·1	100·3	99·8	100·1	99·5	99·8
Σ salic minerals	80·2	74·2	72·9	70·4	75·0	71·6	79·1	79·3	73·6	85·5
n	—	1·516	—	1·523	—	1·517	—	1·512	—	1·531
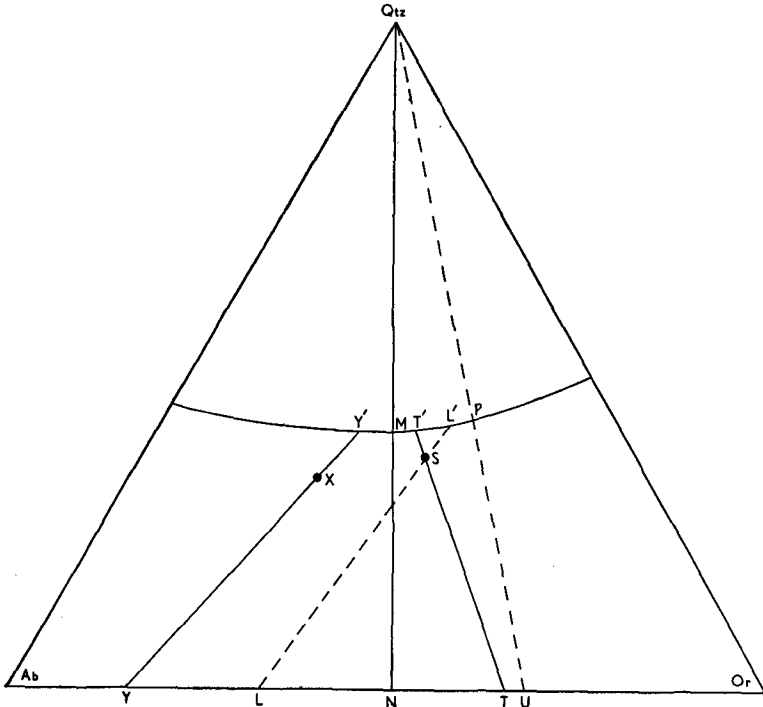
FIG. 3. Diagram showing the effect on the feldspar–liquid three-phase boundaries of a shift in the minimum in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O, due to the addition of other components. M is the experimentally determined minimum (Tuttle and Bowen, 1958) and P is a hypothetical minimum temperature produced by the addition of sodium silicate to the system.

In a similar way, a liquid having a composition represented by the point S will, on cooling, crystallize a feldspar slightly more potassic than T, and the liquid will move on a curved course to T', at which point the feldspar crystals will have a composition represented by T. At the point T', quartz will start to crystallize, and the liquid will move along the boundary curve towards the ternary minimum M. TT' is, like YY', both a tie-line and a three-phase boundary.

The 'thermal valley' (fig. 6) that extends from the alkali-feldspar minimum to the quartz–feldspar boundary curve (Tuttle and Bowen, 1958, fig. 30) may only rarely intersect this boundary curve at the ternary minimum, and in general the intersection is slightly displaced from the minimum. Consider now that the position of the minimum is moved to some position P by the addition of another component, so the composition of the feldspar at this minimum is represented by U. At the same time the position of the 'thermal valley' is also changed and may be considered to be near LL'.

The course of crystallization of a liquid having the composition S (fig. 3) now becomes quite different. On cooling, crystals of feldspar slightly more sodic than L will precipitate, and the liquid will move on a curved course to L', the feldspar crystals continuously reacting with the liquid so that they have the composition L when the liquid reaches L'. At L', quartz (or a silica mineral) will also crystallize and the liquid will move along the boundary curve towards P. By analogy with YY' and TT', LL' may also be a tie-line and a three-phase boundary. A change in the composition of the minimum therefore causes a considerable change in the course of crystallization of a liquid such as S, and the trend of the tie-lines and the three-phase boundaries for liquids whose compositions lie close to the boundary curve in the area $NMPU$ (fig. 3) will also change markedly in response to a change in the composition of the minimum and the position of the 'thermal valley'.

Natural feldspar-phenocryst–liquid (glass) assemblages have been plotted in fig. 4, and it may be seen that the Icelandic feldspar–liquid tie-lines have the same general trend as the experimental tie-lines represented by YY' in fig. 3. As quartz is not found as a phenocryst in the Icelandic pitchstones, the Icelandic tie-lines are not three-phase boundaries, the liquids having not yet reached the quartz–feldspar boundary curve.

The tie-line between the feldspar phenocrysts and the liquid of the Eigg sub-acid pitchstone (fig. 4) is also similar in trend to that found experimentally for liquids of similar composition. The feldspar–liquid
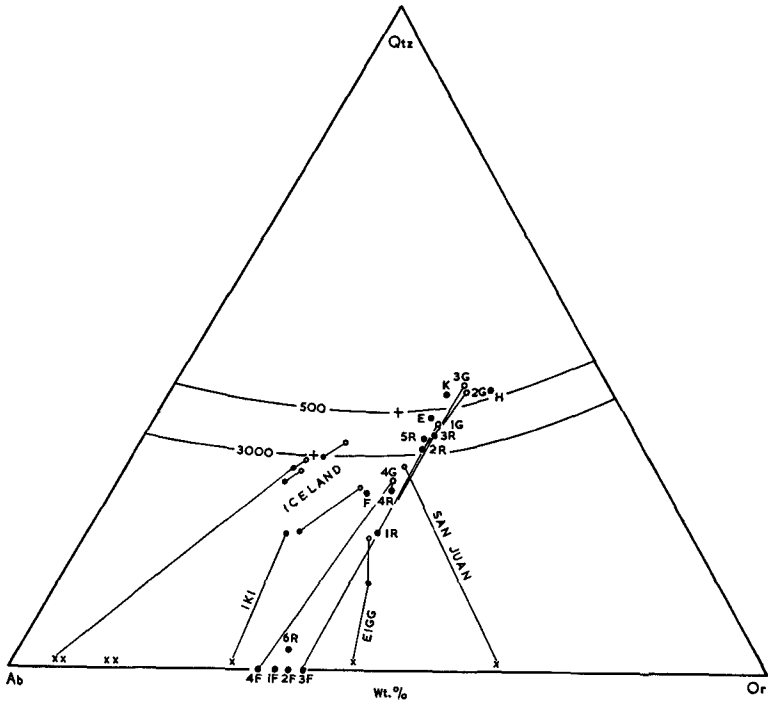
FIG. 4. Normative albite, orthoclase, and quartz of the enumerated analysed pantellerites (solid circles) (table VII) and their residual glasses (open circles) (table VII) are plotted in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2. The analysed pantelleritic feldspar phenocrysts (solid circles) (table V) are plotted on the alkali feldspar join. Only two complete pantelleritic-feldspar–residual-glass tie-lines are drawn for the sake of clarity. Analysed Icelandic pitchstones (solid circles) and residual glasses (open circles) and their analysed feldspar phenocrysts (crosses) are also plotted (Carmichael, 1960b), with only one complete feldspar–liquid tie-line shown. The Eigg (Scotland) subacid liquid is joined to its analysed feldspar phenocrysts (cross) (Carmichael, 1960b); the analysed anorthoclase phenocrysts are joined to the Iki (Japan) alkaline rhyolite (Aoki, 1959); and a San Juan, Colorado, residual glass is joined to its analysed sanidine phenocrysts (Larsen et al., 1938; Larsen and Cross, 1956). H and K represent the aegirine granites of Rockall (Sabine, 1960). The boundary curves at 500 kg/cm² and 3000 kg/cm² water-vapour pressure are plotted. + indicates the position of the minimum on the boundary curves (Tuttle and Bowen, 1958).

tie-line of the San Juan rhyolite (Larsen et al., 1938, p. 418, table 10, no. SCxx; Larsen and Cross, 1956, table 21, no. SCxx) is also closely parallel to that obtained experimentally (TT', fig. 3); although phenocrysts of another feldspar (Larsen et al., 1938, p. 235, table 5, no. 7), a strongly zoned plagioclase (Larsen and Cross, 1956, table 21, no. SCxx), are also

found, these may not be in equilibrium with the liquid (Larsen *et al.*, 1938, p. 256).

The normative salic constituents of the pantellerites and their residual glasses (liquids) have also been plotted in fig. 4: the trend of the pantelleritic feldspar–liquid tie-lines is in direct contrast to the synthetic tie-lines obtained for liquids of similar salic composition (cf. TT', fig. 3). This then is the problem of the pantelleritic liquids, namely the presence of phenocrysts of a relatively sodic feldspar (Ab_{61}–Ab_{67}, table V) in contrast to the relatively potassic feldspar that first crystallizes from synthetic melts of similar salic composition.

It is considered that if the composition of the minimum M (fig. 3) is changed for the pantelleritic liquids to a composition similar to P (fig. 3) and the 'thermal valley' is moved so as to more or less coincide with LL', then the presence of relatively sodic feldspar phenocrysts is readily understood. For the pantelleritic liquids, the tie-lines 2R–2F–2G and 3R–3F–3G are natural three-phase boundaries as quartz is present as phenocrysts in both these specimens (table I), and the composition of the minimum at P (fig. 3) may possibly be represented by the normative salic constituents of the liquids 2G and 3G (fig. 4, table VII). The cause of the change in the composition of the ternary minimum is not at the moment known, but it is suggested that Na_2SiO_3 (*ns*),[1] which is found in the norms of all these pantellerites (table VII), may be responsible.

If this hypothesis is correct, then analyses of comendites and pantellerites should show a progressive shift towards the Or–Qtz sideline with increase in the molecular excess of soda over alumina. All available analyses of these two rock types have been plotted in fig. 5 and show general conformity with the minimum in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O at low water-vapour pressure, and the average composition of pantellerites and comendites is given in table VIII. It is of interest that the analyses of Pantellerian rocks, which are unusually high in normative sodium metasilicate (*ns*), tend to be displaced towards the Or corner with respect to similar rocks from other localities. All the analyses plotted in fig. 5 were contoured with respect to the molecular ratio $(Na_2O + K_2O)/Al_2O_3$ and the results (fig. 6) indicate that there is a progressive and regular increase of the ratio towards the Or–Qtz sideline. This would seem to indicate that the addition of Na_2SiO_3 to the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O will progressively change the

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[1] The formation of normative acmite requires the presence of *ns*, and a molecular excess of soda over alumina is taken, in the sequel, to indicate the existence of *ns*.

position of the minimum towards the Or–Qtz sideline when projected down into the base Ab–Or–Qtz.

If the analyses of the Pantellerian rocks (fig. 5) may be taken to indicate the position of the 'thermal valley' extending from the alkali-
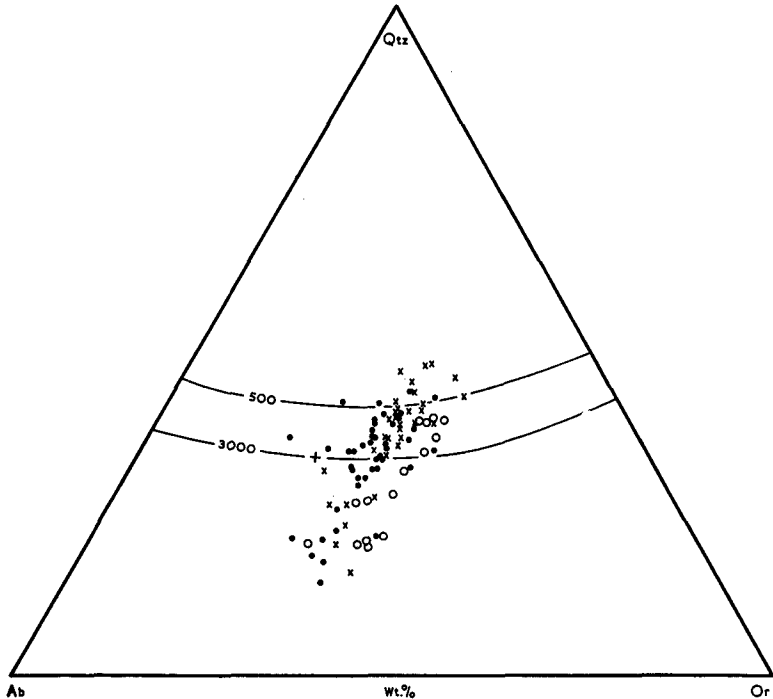

FIG. 5. Analyses of pantellerites and pantelleritic trachytes (crosses) and of comendites and comenditic trachytes (solid circles) taken from the literature are plotted in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2. The analyses of comendites and pantellerites from Pantelleria are represented by large open circles. The boundary curves at 500 and 3000 kg/cm² water-vapour pressure are plotted, and the minimum on the latter boundary curve is represented by + (Tuttle and Bowen, 1958).

feldspar minimum to the quartz–feldspar boundary curve, then this valley has quite a different position from that found in the system $NaAlSi_2O_8$–$KAlSi_3O_8$–SiO_2–H_2O.

The system FeO–Fe_2O_3–SiO_2–Na_2SiO_3.

It is now proposed to examine the ferromagnesian role of *ns* in silicate liquids, but it should be remembered, as Chayes (1960) has indicated,

H

TABLE VIII. Average analyses.

		A.	B.				A.	B.
SiO₂...	...	74·66	71·92					
TiO₂...	...	0·28	0·48	qtz	...	...	30·7	27·8
Al₂O₃	...	11·29	9·62	or	...	...	27·8	25·6
Fe₂O₃	...	2·35	3·81	ab	...	...	32·0	25·2
FeO	...	1·63	3·35	ac	...	...	4·6	11·1
MnO	...	0·07	0·23	ns	...	...	—	1·8
MgO	...	0·15	0·20	wo	...	...	0·9	1·3
CaO	...	0·45	0·63	en	...	...	0·4	0·5
Na₂O	...	4·42	5·38	fs	...	...	1·8	5·8
K₂O...	...	4·67	4·34	mt	...	...	1·2	—
P₂O₅	...	0·03	0·04	il	...	...	0·6	0·9
Total	...	100·00	100·00	Σ salic minerals			90·5	78·6

A. Average of 35 comendites, paisanites, and peralkaline granophyres.
B. Average of 40 pantellerites.
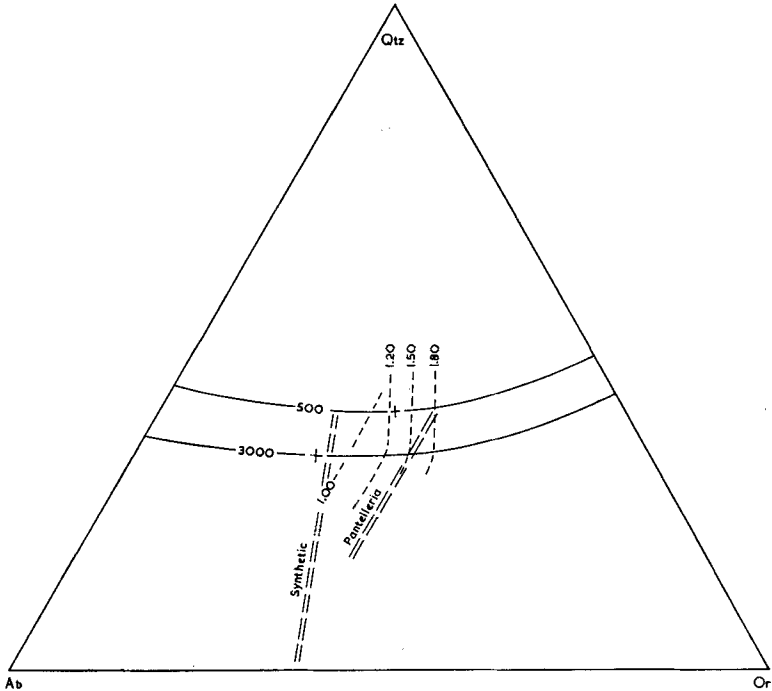
FIG. 6. The analyses of comendites and pantellerites plotted in fig. 5 are contoured (dashed line) with respect to their molecular ratios of $(Na_2O + K_2O)/Al_2O_3$. Also shown is the experimental 'thermal valley' extending from the alkali feldspar minimum to the quartz–feldspar boundary curve, and the trend of the Pantellerian analyses (fig. 5) is also represented by a double dashed line.

that normative ns is not confined to acid liquids, but may occur in undersaturated rocks, and the ferromagnesian assemblages noted above as characteristic of acid rocks may be found in trachytes and phonolites (Campbell Smith, 1931), with which pantellerites and comendites are frequently closely associated.

Of the experimental silicate systems which involve ns as a component, the most important for our purpose are $Na_2O.SiO_2–Fe_2O_3–SiO_2$ (Bowen et al., 1930), $Na_2O.SiO_2–FeO–SiO_2$ (Carter and Ibrahim, 1952; Schairer et al., 1953), which together with the system $FeO–Fe_2O_3–SiO_2$ (Muan, 1955) may be used to construct a four-component system $FeO–Fe_2O_3–SiO_2–Na_2O.SiO_2$.

This four-component system contains many of the ferromagnesian minerals found in pantellerites and their congeners, namely fayalite ($2FeO.SiO_2$), magnetite ($FeO.Fe_2O_3$), and acmite ($Na_2O.Fe_2O_3.4SiO_2$), together with quartz or a silica mineral. With the inclusion of TiO_2 as a fifth component, the ferromagnesian assemblages of these pantellerites are completely defined, with ilmenite ($FeO.TiO_2$) and cossyrite ($2Na_2O.9FeO.2TiO_2.11SiO_2$).

Before considering the relevance of this system to the pantelleritic liquids, the presence of SiO_2 in this system, and hence of quartz, requires amplification. It has been stated above that ferromagnesian assemblages similar to those found in the pantellerites may be found in trachytes and phonolites, so that the phase volume of SiO_2 in the four-component system would suggest that these assemblages could only be obtained in liquids containing uncombined silica. However, the system $FeO–SiO_2–NaAlSiO_4$ (Bowen and Schairer, 1938) indicates that nepheline occupies an equivalent position to the silica minerals, and the two ternary eutectics found in this system consist of albite+quartz+fayalite and nepheline+albite+fayalite. It does not seem unlikely then that in the system $FeO–Fe_2O_3–SiO_2–Na_2O.SiO_2$, the phase volume of the silica minerals will, in the undersaturated rocks, be represented by nepheline.

As the four-component system $FeO–Fe_2O_3–SiO_2–Na_2O.SiO_2$ contains two oxidation states of iron, it is to be expected that the partial pressure of oxygen prevailing at the time of crystallization and congelation of these pantelleritic liquids will influence the assemblage of the ferromagnesian minerals that precipitate. It is only possible, however, to indicate in a general way the ferromagnesian assemblages that may develop under varying partial pressures of oxygen.

Magnetite is virtually absent in the pantellerite, and it is considered that the partial pressure of oxygen was unusually low, as no mineral

containing essential ferric iron precipitated. Under more oxidizing conditions than those found in the pantellerites, fayalite may no longer be a potentially stable phase, its components forming magnetite and silica, and possibly cossyrite. However, as cossyrite may accept up to 10 % ferric iron in its structure (Fleischer, 1936), it is possible that it may be a stable phase over a relatively wide range of oxygen pressures, and it is assumed here that it is stable to higher partial pressures of oxygen than fayalite in liquids of pantelleritic composition. If, then, the conditions of oxidation are such that cossyrite is no longer a stable phase, its components may form magnetite and ilmenite, and its soda will be incorporated together with ferric iron to give a pyroxene composition nearer to the acmite end-member than the sodic ferrohedenbergite actually found with cossyrite.

So far as is known to the writer (cf. Lacroix, 1927, 1930), only pyroxenes similar in composition to sodic ferrohedenbergites are found to coexist with fayalite in pantellerites, and a pyroxene near the acmite end-member is never found with an iron-rich olivine. This indicates that the oxidation conditions necessary to form a highly sodic pyroxene are incompatible with the formation of an iron-rich olivine, and it further suggests that the green outermost zones of the titanium-rich sahlites that coexist with iron-rich olivine in the Shiant Isles crinanites (Murray, 1954) are unlikely to approach acmite in composition, but rather a sodic ferrohedenbergite (fig. 2).

It is suggested, then, that an increase of the partial pressure of oxygen in the pantelleritic liquids may increase the amount of the precipitating pyroxene and also its content of soda, and it may also increase the amount of magnetite and possibly ilmenite at the expense of fayalite and cossyrite. In a hydrous environment the alkali amphiboles riebeckite and arfvedsonite may be present in the ferromagnesian assemblages, but they have been neglected from consideration here as the presence of water inevitably makes the relationships more complex. Amphiboles are, however, frequently found in pantellerites (Jensen, 1906; Koch, 1955; Lacroix, 1923, 1927, 1930), but they have not been found in the specimens described here.

The chemistry of the pantellerites.

No detailed discussion will be presented here as a further geochemical study is being undertaken, the results of which will be presented elsewhere. There are, however, several unusual features of the chemical composition of the pantellerites that have not so far been mentioned, of

which perhaps the most unusual is the increase in iron (and manganese) in the residual glasses (liquids) compared to the rocks (obsidians) (table VI). As iron is predominantly in the reduced state, the concentration of iron in the liquid is possibly due to low partial pressures of oxygen preventing the precipitation of magnetite, the iron consequently being concentrated in the liquid in order to combine principally with ns to form cossyrite and a sodic pyroxene (groundmass of 5R).

The pantellerites are also unusually rich in Cl which is apparently expelled together with soda during crystallization of the liquid (table VI, no. 5R). Zies (1960) has already shown that Cl is unlikely to be a superficial contaminant, and it must be regarded as an original constituent of the liquid.

As Cl is very much more abundant than H_2O in the analyses of the residual glasses (1G–4G, table VI), it is possible that it may have some effect on the composition of the minimum in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O, and may modify or amplify the effect of Na_2SiO_3 suggested above. It would be interesting to know whether or not Cl is always present in pantelleritic liquids; Lacroix (1934) found notable quantities in the Tibesti pantellerites so that it may perhaps be regarded as a characteristic element. Zr is also unusually abundant in these obsidians, and must be concentrated in the liquid (table VI). In view of the very infrequent zircons found in the glasses, the solubility of Zr must greatly increase in acid liquids with increase in soda, as the North Atlantic Tertiary pitchstones, which contain very much less soda, indicate a solubility of Zr of only about 300 p.p.m. (Carmichael and McDonald, 1961).

The Agpaitic series.

The term agpaitic, which was originally used by Ussing (1912) to describe a series of peralkaline nepheline-syenites, has been reviewed in detail by Sørensen (1960), who concluded that agpaitic rocks may best be defined as follows '1. they are peralkaline nepheline syenites; 2. they contain aegirine, soda-amphibole and/or aenigmatite instead of biotite, diopsidic pyroxene and hornblende, that is they are low in Ca and Mg; 3. they contain complex Zr- and Ti-silicates instead of zircon and sphene; and 4. they are rich in F, Cl and H_2O which are present in complex silicates such as eudialyte and rinkolite.'

These agpaitic ferromagnesian assemblages characterize the pantellerites, and to deny their inclusion under the term agpaitic is to negate the close chemical and mineralogical affinities of the pantellerites to the

agpaitic nepheline-syenites. The underlying cause of these sodic ferro-magnesian assemblages is the presence of *ns*, and the author would like to widen the usage of the term agpaitic to include all salic rocks that develop these sodic ferromagnesian assemblages, and which may also concomitantly develop unusually high concentrations of Cl, F, and Zr. There is then a proposed agpaitic series, namely nepheline-syenites and phonolites, syenites and trachytes, and peralkaline granites, comendites, and pantellerites all of which are characterized by a molecular excess of soda over alumina. Representatives of this series are found in Pantel-leria (Washington, 1914), Kenya (Campbell Smith, 1931), and the Ili-maussaq batholith, SW. Greenland (Ussing, 1912), where, apart from Pantelleria, a complete range of oversaturated to undersaturated salic rocks, all of agpaitic type, may be seen.

Tilley (1958) has discussed the genetic problems of these complexes with reference to the thermal barrier that exists in the experimental system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 between the granite and the foyaite sinks. Perhaps the influence of *ns* in changing the composition of a feld-spar precipitating from oversaturated liquids discussed above will also obtain in undersaturated salic liquids and may also in some way mini-mize the thermal barrier in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 and so allow a natural liquid to progress from an undersaturated to an over-saturated condition. This suggestion is similar chemically to that pro-posed by Tilley (1958, p. 332) who sought in the incongruent melting of acmite a possible mechanism for traversing the experimental thermal saddle in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2.

Any explanation of the generation of *ns* in natural liquids must be applicable both to the oversaturated and undersaturated salic liquids and the formation of a molecular excess of soda over alumina and ferric iron provides one of petrogeny's greatest problems. No solution is offered here, and the author appreciates that until the conditions that govern the generation of *ns* are known and understood any account of the pantellerites must be incomplete.

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