

THE CHEMISTRY AND MINERALOGY OF SOME
EMERY-LIKE ROCKS FROM SITHEAN SLUAIGH,
STRACHUR, ARGYLLSHIRE

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ABSTRACT

A series of emery-like rocks occur adjacent to a dolerite plug at Sithean Sluaigh near Strachur, Argyllshire. They are made up of assemblages such as corundum-magnetite-spinel-pseudobrookite-sanidine, corundum-magnetite-spinel-mullite-pseudobrookite-sanidine and cordierite-mullite-spinel-magnetite-pseudobrookite. They represent the aluminous residues from banded pelitic/psammitic phyllites after a granitic fraction has been selectively refused and removed. Their mineralogy has been investigated in detail using optical, chemical, x-ray and other techniques. Twenty two new mineral analyses, including spinels, magnetites, mullites, pseudobrookites, corundums and cordierites are presented and used in conjunction with six new whole rock analyses to discuss the mineralogy in the system (Fe, Mg)O-Al₂O₃-Fe₂O₃-TiO₂.

INTRODUCTION

1.2 miles N. 138° from the croft of Stuckroech and at 2.8 miles N. 215° from the parish church, Strachur, Dalradian muscovite-chlorite quartz-albite phyllites are intruded by the dolerite plug known as Sithean Sluaigh (pronounced she-an-sluay). The plug which is kidney-shaped is only about 300^x long and 100^x in breadth, but despite its small size has a pronounced thermal aureole—in places in excess of 35 feet wide. The petrography, chemistry, mineralogy and petrogenesis of the rocks in the aureole will be dealt with in a paper at present in preparation. This account, however, is concerned mainly with the chemistry and mineralogy of an unusual group of emery-like rocks that are restricted to one part of the aureole (Fig. 1). Their genesis will be dealt with more fully in the subsequent paper, where it will be shown that they represent the residues from banded pelitic/psammitic phyllites after a granitic fraction has been selectively remobilized, and has migrated from its source.

A sequence of specimens was collected up to the contact in the emery locality and a petrographic account of these rocks follows. Throughout this paper specimen numbers refer to the Harker Rock Collection in the Department of Mineralogy and Petrology, Cambridge.

PETROGRAPHY

92427—6½ feet from the contact.¹ This specimen has a dark, massive and rather glassy appearance in the hand specimen. Thin sections show that it

¹ All the distances are approximate since the line of contact is somewhat irregular, and the vertical attitude is not known.

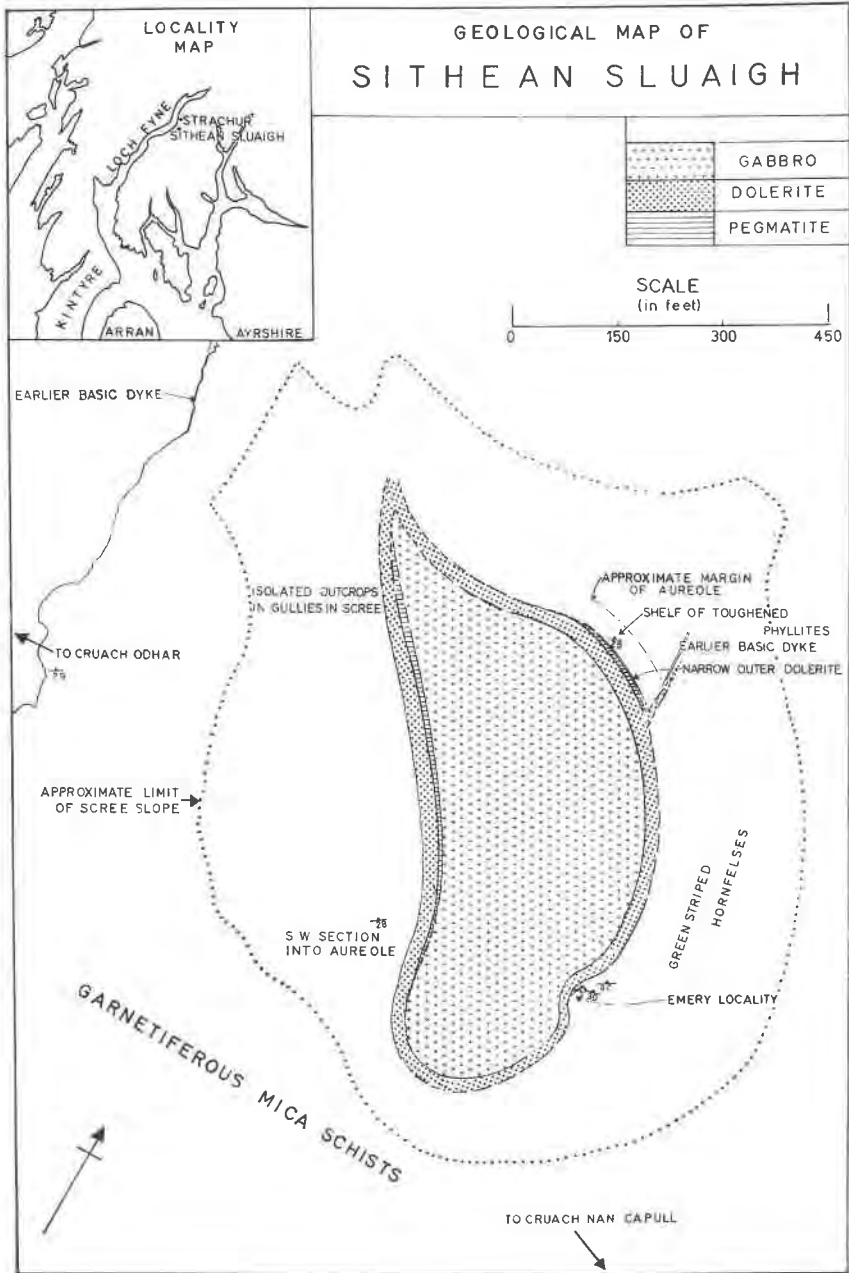


FIG. 1. Geological map of Sithean Sluaigh.

is made up of mullite, cordierite, magnetite, spinel,² pseudobrookite and very minor amounts of iron-corundum. Reflected light showed that the magnetite contains a few lamellae of spinel but, in general, the latter has been largely exsolved so that it occurs as rims around the magnetite. In transmitted light, these are seen as translucent green rims around opaque cores.

92426— $5\frac{1}{2}$ feet from the contact. The rock has a mottled gray and lilac color in hand specimen and faint traces of banding can be detected. The rock is made up of cordierite, magnetite, spinel and pseudobrookite plus a few small patches of granophyric material and partially devitrified glass.

The cordierite occurs as porphyroblasts often showing clearly, either the rectangular outline of the prism section or else the polygonal outline, with sector twinning, of the basal section. Almost invariably it has inclusions of mullite, magnetite, spinel, etc., and these are concentrated towards the cores of the grains and are generally much smaller than the grains of the same minerals outside the cordierite. Adjacent to granophyric material, the mineral has been partially pinitized, but elsewhere is fresh.

The few larger needles of mullite exhibit the lilac to colorless pleochromism in the prismatic section that is characteristic of the mineral when it contains iron and titanium.

The oxide phases are particularly interesting in this rock for they show very well-developed exsolution textures (Figs. 2, 3). The magnetite has well-formed lamellae of spinel which also occurs as discrete grains. The way in which these grains tend to surround the magnetite strongly suggests that they have been formed by complete exsolution from the latter. This is supported by the fact that the spinel grains never contain magnetite lamellae. If two homogeneous magnetite-spinel and spinel-magnetite solid solutions had coexisted on either side of a solvus, both would be expected to show exsolution textures. Pseudobrookite, which is readily distinguished in reflected light from other minerals present by its slight anisotropism, also occurs quite prolifically, and locally surrounds a very small, more anisotropic, core which is almost certainly ilmenite (Fig. 4). The shape of some of the pseudobrookite grains suggests that the ilmenite 'rods' of the original phyllites have been pseudomorphed due to changes of the P_{O_2} within the aureole. However, chemical data presented in the following section show that the process of formation is more complex than this.

² Throughout this paper the term "spinel" is used to mean any mineral approximating in composition to a member of the series $FeAl_2O_4$ - $MgAl_2O_4$.

92425— $4\frac{1}{2}$ feet from the contact. In hand specimen this most striking and unusual rock shows obvious but contorted banding due to the concentration in some layers of spinel and in others of a bright green corundum. Cleavage surfaces glisten due to the strong preferred orientation and the platy habit of the corundum, the basal pinacoid being very strongly developed relative to the prism and pyramid faces (Fig. 5). This habit is adopted by all the corundum that occurs in the altered phyllites around the plug, and contrasts strongly with the barrel-shaped habit that is common for example in corundum syenites. However, it appears to be normal in metamorphic rocks from the sanidine facies, and particularly so in certain aluminous xenoliths (*e.g.* Agrell and Langley, 1958, p. 106). The mineral is free of inclusions, except for the occasional spinel grain.

Magnetite, spinel and pseudobrookite (in places with small relict cores of ilmenite) are present. The magnetite contains well oriented lamellae of spinel, and some of the larger grains display a runic intergrowth of the two minerals (Fig. 3). In the largest grains there appears to have been almost complete unmixing, discrete grains of spinel and magnetite (with a few very fine spinel lamellae) making up the whole of a composite grain. The smallest grains have crypto-exsolution lamellae, recognizable under the microscope only by analogy with slightly coarser material and by the peculiar texture imparted to the surface of the mineral. The spinel, which is opaque in transmitted light, contains no exsolved magnetite, again suggesting that it is not a primary phase but an exsolution product.

The texture of this specimen is interesting. The preservation of relict schistosity shows clearly that the rock formed largely in the solid and not by the precipitation of excess alumina from the nearby basic magma, as was thought by Holmes (1926). At some period the rock was probably somewhat plastic in view of the contortion of the banding; this was doubtless a result of the lubricating effect of interstitial melt, which was subsequently largely squeezed out.

It is uncertain whether the very small amount of plagioclase present in this rock resulted from igneous contamination or from the breakdown of original clastic plagioclase grains and/or other lime-bearing minerals such as epidote and carbonates.

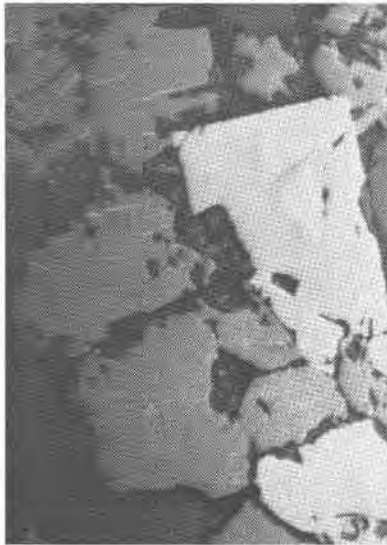
92424— $3\frac{1}{2}$ feet from the contact. In hand specimen the rock retains some of the characteristics of the previous specimen (92425), *e.g.*, the distinct but contorted foliation; but corundum is not as abundant and ferromagnesian oxides are much more prominent. The same assemblage of minerals is present as in 92425, except that a few bands contain mullite instead of corundum. Only in very few places are mullite and corundum seen in



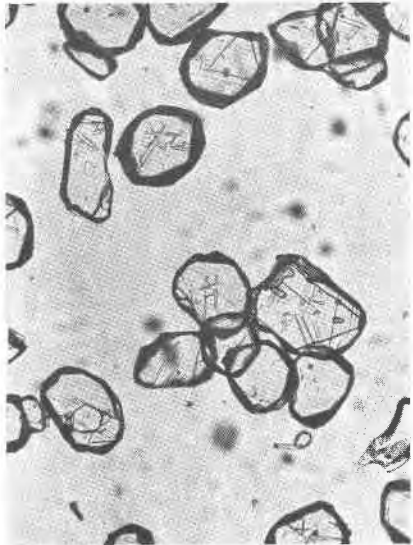
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FIG. 2. Magnetite (white) exsolving spinel (medium-gray) marginally and along $\{111\}$. Note that the spinel does not contain magnetite lamellae. The dark grey material is mullite and/or cordierite. Specimen no. 92427, reflected light. Magnification: $\times 100$.

FIG. 3. A large composite grain of magnetite and spinel showing runic intergrowth. The magnetite contains very fine spinel exsolution lamellae but the spinel which largely surrounds the magnetite, has no lamellae of the latter. The medium-gray, lath-like grains

juxtaposition, and there only where the different bands adjoin one another. The reason for the segregation of these two minerals is thought to be either a nucleation effect, or else, more probably, that mullite crystallized from a melt that was developed in the rock and which was segregated from the more solid parts. Many of the grains of mullite contain inclusions that are believed to be glass (Fig. 6).

Polished sections reveal that both magnetite and spinel are present, the latter far in excess of the former. Exsolution textures appear both in the spinel (poorly oriented, somewhat sinuous magnetite lamellae) and in the magnetite (thin spinel lamellae in some of the larger grains). There is some variation in the amounts of magnetite and spinel present in different parts of the rock. Pseudobrookite, a deep russet color in transmitted light, is a prominent constituent, but ilmenite cores to the grains were not observed. The corundum, which has the usual platy habit, is in the main free of inclusions and has a blue-green rather than a bright green color when separated and seen in bulk.

92423— $2\frac{1}{2}$ feet from the contact. This rock has a distinctly different appearance from any of the previous specimens. It is dark gray-black in color, but contains mauve bands. Relict schistosity is still clearly visible, but many bands are puckered and broken and appear to have flowed. Thin sections showed that the rock is composed of clots and layers of spinel (with interstitial devitrified glass) and bands of mullite set in a similar matrix.

The mullite shows distinct pleochroism from lilac to colorless in the prismatic sections, and the larger grains are full of inclusions of spinel and globules of an isotropic substance thought to be glass (Fig. 6). (X-ray photographs of a single crystal choked with such inclusions showed no pattern other than that of mullite. Furthermore the globules were observed protruding from the broken ends of the crystals during the separa-



are cross sections of platy corundums. Specimen no. 92425, reflected light. Magnification: $\times 100$.

FIG. 4. Fine sinuous magnetite lamellae have exsolved from spinel (medium-gray). The latter also shows in patches the peculiar texture due to crypto-exsolution lamellae of magnetite (best seen in grains near the bottom). At the right, a grain of pseudobrookite surrounds a relict core of ilmenite (white). Specimen no. 92420, reflected light. Magnification: $\times 320$.

FIG. 5. Crystals of corundum illustrating the platy habit. Note the blades of rutile arranged at 120° around the z axis in the (0001) plane, and the trigonal growth patterns on the (0001) faces. Specimen no. 92421, P.P.L. Magnification: $\times 100$.

tion of the mullite). If this included material is in fact glass, it indicates that the mullite crystallized from a liquid, presumably the matrix in which it is now found, and its preferred orientation must be a flow texture rather than a direct relic of the original foliation.

Reflected light shows that the spinel is a homogeneous phase. In transmitted light, the grains are a very deep green, being translucent only in the thinnest edges. Pseudobrookite grains, some with ilmenite relics at their cores are common (Fig. 4). Very thin laths of a deep brown mineral that may be an ilmenite-hematite s.s., frequently occur along the edges of spinel grains.

92421—1½ feet from the contact. The rock had a tendency to weather leaving a sandy mixture of corundum and spinel. Unweathered pieces are composed of a homogeneous green spinel, with small amounts of blue sapphire corundum, ? ilmenite-hematite s.s. (in extremely thin hexagonal plates), mullite, and an interstitial devitrified glass.

The corundum, which has exactly the same platy habit as the iron variety described above, is bright blue in bulk but only very pale blue in thin section. It contains extremely thin blades of rutile, perfectly oriented in three directions 120° apart within the (0001) plane (Fig. 5). These

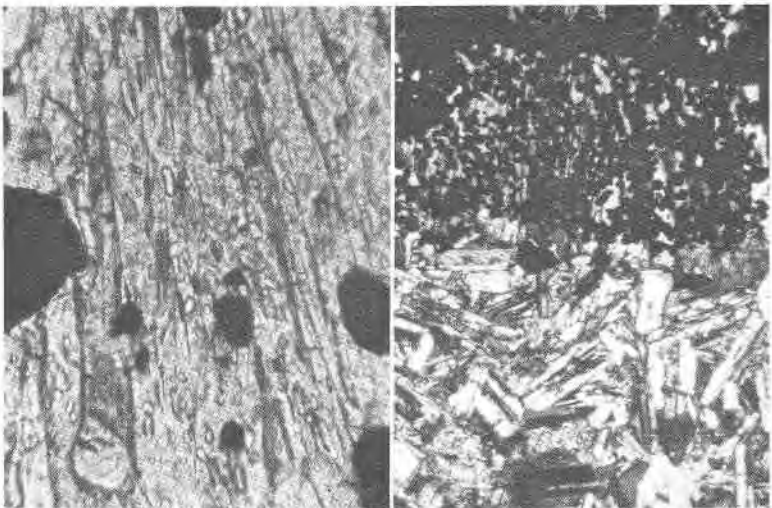


FIG. 6. Mullite crystals containing blebs of glass. Note the parallel arrangement of the mullite which is thought to be a flow texture due to the crystallisation of the mineral from a liquid. Specimen no. 92423, P.P.L. Magnification: $\times 320$.

FIG. 7. Contact between emery and the marginal dolerite. The former is made up almost entirely of spinel set in poikiloblastic plagioclase (decreasing sharply in amount away from the contact), while the dolerite is strongly depleted in mafic constituents. Specimen no. 92419, crossed polars. Magnification $\times 20$.

rutile crystals, the positive identification of which was finally made by means of the electron probe, are so thin that they give interference colors ranging down to first order gray. The crystals are sometimes seen protruding from the grains of corundum into the surrounding devitrified glass, where they tend to have greater thickness and thus more normal interference colors. Pseudobrookite does not appear to be present in this rock.

92420—2 feet from the contact. The specimen is a black, glassy rock, and occurs as a rather irregular vein-like body, one to two inches wide, cutting through 92421. In hand specimen it could easily be mistaken for a piece of chilled basic material. It is made up mainly of cordierite, with lesser amounts of spinel, magnetite and pseudobrookite. The magnetite occurs as fine, somewhat sinuous lamellae in the spinel, and the two were undoubtedly originally a single homogeneous phase. The cordierite is usually euhedral, commonly exhibiting the rectangular outline of the prismatic section or the sector twinning of the polygonal basal section. Most of the crystals have a knot of small inclusions concentrated at their cores, and whereas the majority of these are spinels, some are thought to be corundum. However, the minute size made positive optical identification impossible.

The origin of this rock, which contrasts strongly with that which it cuts, is not obvious. It was probably originally a quartz lens, and thus differed from the surrounding country rock in being more siliceous and without large amounts of albite, mica, etc. As a result its composition was altered by diffusion of Al, Fe and Mg into it from the adjacent decomposing bands, rather than by the melting-off of a granophyric fraction. The absence of appreciable amounts of interstitial melt may have prevented its deformation when the associated rocks were contorted; thus it now appears to be cross-cutting.

A little closer to the contact within the same band there seems to have been some igneous contamination, for labradoritic plagioclase is an important constituent at this point. Cordierite is absent, and the only other mineral present in appreciable amounts is a homogeneous green spinel.

92419—0—6 inches from the contact. The rock is made up very largely of a homogeneous green spinel. At the contact (Fig. 7) the spinels are set in large poikiloblastic crystals of basic plagioclase, which contrast strongly with the lath-shaped plagioclase of the adjacent igneous rock. The plagioclase persists only a few centimeters at the most into the aureole, after which the spinel grains are packed more tightly together with only a little interstitial devitrified glass. A few grains of corundum occur and increase in quantity away from the contact; near the contact these are unusually

large, but rather ragged as if in the process of being resorbed. Pseudo-brookite is absent, as is also magnetite. Fine hair-like blades or needles of rutile, identical to those described from 92421, again occur in the corundum, the spinel and the matrix. Only within the corundum has the direction of growth been controlled.

At the contact, the "dolerite" is made up almost entirely of plagioclase suggesting that the ferromagnesian components of the magma migrated into the metamorphic rock, along with a certain amount of lime, to contribute to the formation of the spinel and the plagioclase, respectively.

The series of rocks described above is considered to have formed by the effects of progressively changing physical conditions on banded phyllites as the igneous contact was approached. The initial composition of the phyllites probably varied considerably, and it must be emphasised that the sequence of specimens described does not represent the progressive metamorphism of *identical* material.

CHEMISTRY

Whole-rock analyses were carried out on six of the specimens in the sequence described above and are reported in Table 1.

The most striking feature of the analyses apart from the obviously unusual compositions as a whole, is the change in the oxidation ratio, (defined as $\text{mol. } 2\text{Fe}_2\text{O}_3 \times 100 / (2\text{Fe}_2\text{O}_3 + \text{FeO})$). This varies from about 14 at the contact to about 74 at 5 feet. Then, judging from the last analysis in the sequence, it starts to decrease again. This variation is also well displayed by the component minerals described in the subsequent section. Buddington and Lindsley (1964) showed by consideration of the stability curves for magnetite-ulvospinel and ilmenite-hematite solid solutions with respect to f_{O_2} and temperature, that in many igneous and some metamorphic rocks an oxidation of the magnetite-ulvospinel s.s. to magnetite s.s.+ilmenite s.s. will take place as the temperature falls. By analogy, we should expect to find an oxidation of the emery assemblages, moving away from the contact at Sithean Sluaigh—*i.e.* moving down the temperature gradient. Cann (unpubl. Ph.D. thesis, Department of Mineralogy and Petrology, Cambridge) has recently described the pyrometamorphism of basalts in the aureole of S'Airde Beinn, a plug on the Isle of Mull. In that case changes in the oxidation ratios within the lavas could be traced and correlated with the decomposition of olivine to give hypersthene+magnetite. Assuming a constant P_{O_2} superimposed by the magma in the vent, Cann pointed out that the effect of the decrease in temperature moving away from the plug will be for assemblages to become more and more oxidized. At a certain point a kinetic effect enters into consideration; the temperatures are too low for the oxidation reaction to take

TABLE 1. COMPOSITIONS OF THE EMERY ROCKS

	(1)	(2)	(3)	(4)	(5)	(6)
	92419	92420	92423	92424	92425	92427
SiO ₂	16.10	38.34	21.55	14.32	15.69	42.31
TiO ₂	0.74	0.89	1.19	1.35	1.65	1.83
Al ₂ O ₃	49.47	34.90	46.61	50.80	52.69	31.85
Fe ₂ O ₃	3.74	4.54	10.50	12.07	18.30	6.84
FeO	20.23	9.20	12.01	13.84	5.51	7.83
MnO	0.17	0.18	0.14	0.12	0.07	0.15
MgO	5.93	8.48	4.37	4.13	2.39	4.91
CaO	1.12	0.34	0.33	0.27	0.21	0.38
Na ₂ O	1.16	0.70	1.33	1.58	1.06	1.05
K ₂ O	0.88	0.75	0.57	1.01	0.96	1.31
H ₂ O ⁺	0.58	1.70	1.26	0.64	0.93	1.48
H ₂ O ⁻	0.00	0.28	0.39	0.28	0.43	0.32
P ₂ O ₅	0.05	0.08	0.06	0.03	0.05	0.11
	100.17	100.38	100.31	100.44	99.94	100.37
Oxidation Ratio	14.25	30.74	44.01	43.98	73.93	43.99
MgO:FeO (Wt.)	.293:1	.922:1	.364:1	.298:1	.434:1	.627:1
MgO:FeO+Fe ₂ O ₃ (Wt.)	.247:1	.617:1	.194:1	.159:1	.100:1	.355:1
Distance from assumed vertical contact	6"	2'	2'6"	3'6"	4'6"	6½'

Rocks corresponding to the "Harker" numbers are detailed in Table 3. Oxidation ratio = mol. 2Fe₂O₃ × 100 / (2Fe₂O₃ + FeO).

place so that the oxidation ratio gradually falls back to that in the unaltered basalt. A similar explanation may well account for the hump in the oxidation profile in the emery locality, although it is probable that the effect was modified somewhat by a P₀₂ gradient falling away towards the margins of the aureole.

Each of the analyses of Table 1 has been plotted in Fig. 8 after the alkalis and lime have been subtracted as feldspar. This is justified by the fact that feldspar appears as an accessory phase in most of these rocks. However, in some, devitrified glass occurs interstitially—either as well as the feldspar or instead of it. This "glass" apart from containing alkalis and lime also contains some excess silica. The composition of the material is strikingly similar, except in the ratio of alkalis, to the average composition of material removed from pelite xenoliths in the Cashel-Lough Wheelaun complex (Leake and Skirrow, 1960); both compositions are shown in Table 2. However, the amount of free silica is likely to vary from one rock to another and thus no attempt has been made to correct for it in

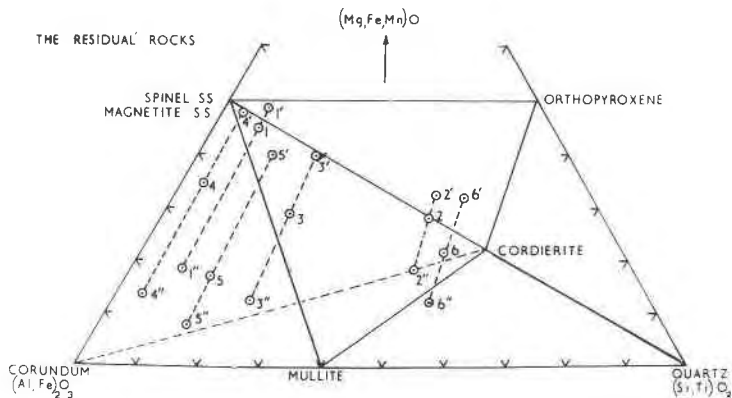


FIG. 8. A triangular plot of the emery rocks. Nos. refer to the analyses in Table 1. ' indicates the composition replotted with all the Fe reduced, and '' the composition with all the Fe oxidized, thus showing the range of assemblages that could have developed under different oxidation potentials. The mullite-spinellid join that operates close to contact is shown solid and the cordierite-corundum join, further from the contact, dotted.

TABLE 2

Analysis	I	II	CIPW norm	I	II
SiO ₂	64.01	63.4	Q	12.63	17.5
TiO ₂	0.52	0.5	C	5.39	5.7
Al ₂ O ₃	20.81	19.8	or	31.94	45.4
Fe ₂ O ₃	0.84	0.0	ab	42.50	21.0
FeO	0.34	0.9	an	4.65	6.6
MnO	trace	0.1	en } fs } hy	1.16	1.8
MgO	0.46	0.7	rt	0.14	—
CaO	0.92	1.3	il	0.72	1.0
Na ₂ O	4.93	2.0	hm	0.87	—
K ₂ O	5.30	7.4			
H ₂ O ⁺	2.06	3.7			
Total	100.19	99.8			

Rock descriptions:

I—88698 mullite-spinel-corundum buchite, in scree. (Probably formed about 1½–2' from the contact).

II—Average composition of material removed from pelitic xenoliths in the Cashel-Lough Wheelan complex (Leake and Skirrow, 1960).

TABLE 3. LIST OF THE EMERY ROCKS

No of Analysis (Table 1)		Approximate distance from contact ¹
—	88698—mullite-spinel-corundum-buchite	(in scree)
—	92394—Fe-corundum-magnetite-spinel-pseudobrookite-sanidine rock	5'
(1)	92419—spinel-plagioclase-(corundum) rock	6''
(2)	92420—cordierite-spinel-magnetite-pseudobrookite rock	2'
—	92421—corundum-spinel-mullite-buchite (with? ilmenite-hematite s.s.)	1½'
(3)	92423—mullite-spinel-pseudobrookite-buchite	2½'
(4)	92424—corundum-mullite-spinel-magnetite-pseudobrookite-sanidine rock	3½'
(5)	92425—corundum-magnetite-spinel-pseudobrookite-sanidine rock	4½'
(6)	92427—cordierite-mullite-magnetite-spinel-pseudobrookite-(Fe-corundum) rock	6½'
—	92431—cordierite-magnetite-mullite-pseudobrookite-(corundum) rock	9'

¹ Assuming vertical contact.

plotting the analyses on Fig. 8. In general it will mean that the plots should lie a little further away from the SiO₂ apex of the triangle than is shown. As the amount of the devitrified glass that is present is always relatively small, the discrepancy will be only very slight. TiO₂ has been included with SiO₂. However, in most of the rocks TiO₂ could not be completely accommodated by cordierite, mullite, corundum and the spinel-lids and a separate Ti-bearing phase—often pseudobrookite—crystallized. Again the amount of this phase was always relatively small and difficult to estimate accurately. No correction has been made for it as, again, only very minor discrepancies will be introduced by counting it as SiO₂. To make use of a triangular plot it is also necessary to include Fe₂O₃ with Al₂O₃ and MgO+MnO with FeO. The justification for doing this will be discussed below.

The assemblages that are present in the analyzed rocks are described in the section on petrography but are tabulated for convenience below (Table 3). All the assemblages that are present, with the exception of 92425, agree well with those to be expected from the triangular diagram—allowing for small discrepancies due to the presence of pseudobrookite and devitrified glass. The thin section of 92425 revealed no glass, but there is slight inhomogeneity in all the specimens and the rock that was

crushed for analysis probably contained patches of this somewhat siliceous material. Very minor amounts of corundum appear in the thin sections of 92427 and 92431, but are not thought to be in equilibrium with the rest of the minerals present. It is probable that they either result from the incomplete homogenization of original compositional differences in the phyllites or else that they are relics of an earlier stage of metamorphism when the join cordierite-corundum was operative (Tilley, 1923). In this respect it should be noted that nearby the emery locality, pelitic bands further from the contact are made up of cordierite-corundum-spinel-magnetite-pseudobrookite-sanidine assemblages.

Rock 92424 is made up of corundum, spinel, pseudobrookite, sanidine and small amounts of mullite. The position in which the specimen plots in Fig. 8 is in good agreement with this. 92423 is interesting in that only 4 phases (mullite, spinel, pseudobrookite and glass) are present, whereas the components in the system are FeO, MgO, Al_2O_3 , Fe_2O_3 , SiO_2 , TiO_2 , Na_2O and K_2O . The alkalis can doubtless be considered together and are present in the glass; the TiO_2 is largely held within the pseudobrookite. In view of the extensive or complete substitution of Fe and Mg in the spinel-lid structure at these temperatures, FeO and MgO can almost certainly be considered together as one component. Fe_2O_3 can substitute for Al_2O_3 in the spinel and to a lesser degree in the mullite and it also combines with TiO_2 to form pseudobrookite; in the quantities that it is present, it can therefore be considered with the Al_2O_3 . Thus we find that we have (Fe,Mg)O, (Al,Fe) $_2\text{O}_3$ and SiO_2 as the components and only mullite and spinel as the phases. The reason for this apparent deficiency in phases appears to be that the composition of this rock happens to lie very close to the mullite spinel join. Similar reasoning may be applied to 92420, which plots very close to the cordierite spinel join.

The rather variable ratio Mg:total iron in the rocks can be attributed to two interacting variables—the original proportions of muscovite and chlorite in the phyllites and the amount and composition of granophyric material fused and abstracted. The Mg:total iron ratio in all the analyzed muscovites is higher than in the co-existing chlorites. On the other hand, the ratio is even higher in some of the rheomorphic granophyres (but distinctly lower in others). Although the absolute percentages of total iron and of MgO in the granophyres are in general rather low, since it can be demonstrated that as much as 85 wt.% of granophyre may be formed from a normal pelitic phyllite by selective fusion, the ratio of Fe and Mg in the abstracted material is clearly going to be important in determining the ratio of these elements in the “residual” emery rocks. Thus the observed variations in the MgO:total iron ratio, are not anomalies, but rather are to be expected.

The analyses of 92420 and 92427 are clearly distinct from the other four in Table 1. This could be anticipated from the mineralogy of the rocks, which are made up largely of cordierite. Apart from the particularly high amounts of MgO present and relatively low iron contents, the SiO₂ content is much higher than for any of the other specimens. It is thought that these rocks have been formed by the diffusion of Al, Mg and Fe from the adjacent emery into a particularly siliceous band or lens, such as are common in the surrounding country rocks. Such a band, if it contained only very minor amounts of albite and muscovite would have had little tendency to melt during the extreme metamorphism, but on the other hand would have had a strong tendency to react with the adjacent highly desilicated material. The alkalis shown in the analyses of these rocks are almost certainly held very largely in the cordierites (Table 14); there are only traces of feldspar present and very little pinitisation of the mineral.

Apart from the normal plots of the emery rocks, their compositions have also been shown with all the iron present (a) unoxidized and (b) oxidized. This gives an idea of the assemblages that could have developed from the rocks had they been in different positions relative to the contact—and thus subjected to different oxidation potentials. The corrosion of corundum crystals very near the contact probably resulted from the change in oxidation ratio of the rock at a late stage in its development carrying the bulk composition across the mullite—spinel join out of the field of corundum and just into that of cordierite. The last mineral does not actually appear but is presumably a potential constituent of the interstitial matrix.

MINERALOGY

Spinel and magnetite. To avoid terminological confusion in this section, the usages of some names are first made clear. The term “spinelid” refers to any compound with the spinel structure. “Spinel” refers to any member of the series FeAl₂O₄-MgAl₂O₄ with or without small amounts of “magnetite” (FeFe₂O₄) in solid solution. “Spinel s.s.” refers to MgAl₂O₄ and “hercynite” to FeAl₂O₄. “Magnetite” as used includes those varieties containing small amounts of “magnesianoferrite” (MgFe₂O₄) and/or hercynite in solid solution.

The purification of the spinels and magnetites proved extremely difficult. Eventually most of the adhering siliceous material was removed by gentle grinding and repeated separation with heavy liquids. However, it proved impossible to separate completely intergrown spinel+magnetite from pseudobrookite. Furthermore, the exsolution of spinel from magnetite and vice versa, partially as narrow oriented lamellae, and partially marginally, meant that repeated grinding was undesirable if an approxi-

mation to the original bulk composition of this oxide phase was to be obtained.

The chemical analyses reported in Table 4 show the compositions of four homogeneous spinels, one spinel with a few fine sinuous lamellae of magnetite and three intergrowths of magnetite and spinel thought to approach, at least, the compositions of original homogeneous phases. The evidence for their original homogeneity comes from the reflected light examination described under "Petrography."

A check with the electron probe indicated that some, at least, of the SiO_2 shown by the chemical analyses is actually held within the spinel rather than resulting from siliceous impurities.

The TiO_2 contents of the analyses are difficult to interpret. In the case

TABLE 4. MAGNETITE AND SPINEL CHEMICAL ANALYSES

	92419	92421	88698	92423	92420	92424	92425	92427
SiO_2	0.28	0.25	0.29	0.04	0.06	0.08	—	—
TiO_2	0.69	0.76	0.95	0.62	0.85	0.71	1.63	2.06
Al_2O_3	57.71	54.34	54.03	51.52	50.28	45.55	31.68	25.61
Fe_2O_3	5.05	9.00	9.15	12.78	13.49	19.42	33.78	40.10
FeO	27.78	26.45	28.22	27.29	27.02	25.75	26.74	29.09
MnO	0.20	0.19	0.30	0.32	0.46	0.25	0.21	0.39
MgO	8.54	9.01	7.45	7.42	8.23	8.24	5.96	2.73
Total ¹	100.25	100.00	100.39	99.99	100.39	100.00	100.00	99.98
Numbers of cations on the basis of 32 oxygen anions								
Si	0.062	0.056	0.065	0.009	0.014	0.019	—	—
Ti	0.114	0.127	0.160	0.106	0.145	0.124	0.306	0.413
Al	14.964	14.274	14.269	13.813	13.472	12.476	9.334	7.895
Fe^{3+}	0.836	1.509	1.543	2.188	2.308	3.396	6.354	7.892
Fe^{2+}	5.111	4.930	5.288	5.192	5.137	5.004	5.590	6.362
Mn	0.037	0.036	0.057	0.062	0.089	0.049	0.044	0.086
Mg	2.800	2.993	2.488	2.515	2.788	2.854	2.220	1.064
Total	23.924	23.925	23.870	23.885	23.953	23.922	23.848	23.712

¹ Totals of 99.98%, 99.99% and 100.00% result from the way in which the analyses were carried out—the sample being taken up by a pyrosulphate fusion and R_2O_3 's not being precipitated (for a further description of this method of analysing oxide phases, see the section on corundums). In other cases, protracted sodium carbonate fusions were used.

Rock descriptions as for Table 3.

92419–92421, 92423 and 88698 are homogeneous spinels; 92420 is a spinel with fine sinuous lamellae of magnetite; 92424, 92425 and 92427 are all exsolution intergrowths of spinel and magnetite.

of the reduced rocks such as 92419 and 88698, much of the TiO_2 may be present as needles of rutile, these being observed in thin section within the spinels. In the more oxidized rocks, where magnetite appears, an appreciable amount of the TiO_2 is certainly held within that mineral. Thus, checks with the electron probe showed that the magnetite phase of 92425 contained approximately 2% of TiO_2 (and the co-existing spinel phase only about 0.1%). 92423 showed about 0.5% of TiO_2 within the spinel—in good agreement with the chemical analyses. On the other hand, 92420 (a spinel with exsolution lamellae of magnetite) contains only about 0.25% of TiO_2 , according to the probe. Since ulvöspinel is considered to have the inversed spinel structure, if one is concerned with separating cations into groups according to the sites they occupy, Ti should be considered together with the trivalent cations, and an equal amount of divalent ions should be added to the trivalent ions. Certainly, the presence of Ti should increase the ratio of divalent to trivalent + tetravalent ions from the normal ratio of 1:2. Apart from the Ti which is actually held within the structure, it is very probable that small amounts of pseudobrookite intergrown with the other phases remain in some of the samples. As noted above this was virtually impossible to eliminate during separation without fractionating the magnetite-spinel exsolutions considerably.

These possibilities make it difficult to interpret precisely the analyses of the spinels and magnetites in terms of end-members. There is, however, a tendency towards an excess of trivalent + tetravalent over divalent ions, although the reverse would be expected with the substitution of the ulvöspinel molecule. The tendency is particularly marked in the analysis of 92427, and strongly suggests the presence of pseudobrookite as a contaminant. Appreciable solid solution from magnetite towards pseudobrookite is unlikely (see MacChesney and Muan, 1959).

Certain trends within the analyses to be correlated with distance from the contact, and thus with changes in temperature and the redox potential are clear. Thus, there is a progressive decrease in the Al_2O_3 contents accompanied by a corresponding increase in Fe_2O_3 . FeO remains more or less constant and in the most magnetiferous specimens MgO decreases sharply.

Ignoring the contents of Ti and Si, the ratios of $\text{Fe}^{3+}:\text{Al}$ and $\text{Mg}:(\text{Fe}+\text{Mn})$ allow the analyses to be plotted on a square diagram with hercynite, spinel s.s., magnetite and magnesioferrite as end-members. On the assumption of little fractionation of the spinel-magnetite exsolution intergrowths during separation, the indicated compositions approximate to that of an original homogeneous spinellid phase. Figure 9 shows the Strachur spinels and magnetite-spinel intergrowths plotted on the square diagram. The progressive change in the compositions from the reduced

rocks near the contact to the more oxidised ones further away is clearly seen in the plot. The large drop in the MgO content in 92427 is very apparent, and since the whole-rock analysis indicated a high MgO content relative to other rocks in the sequence (Table 1), most of this oxide must be contained in the cordierite.

Turnock and Eugster (1962) have shown that complete solid solution exists in the magnetite-hercynite series above $860 \pm 15^\circ \text{C}$. The composition of the magnetite-spinel exsolution 92427 indicates a minimum temperature of formation of approximately 860°C . if it can be assumed that the substitution of Mg for Fe^{2+} has little effect on the position of the solvus. Even allowing that quite a large amount of marginally exsolved spinel could have been lost from the sample during separation (and this is not thought to be likely) the temperature would not have been below about 800°C . On the other hand, higher temperatures may have obtained, since the composition of a spinel-magnetite solid solution gives only the minimum temperature of formation. Thus, although the rocks nearest to the contact were almost certainly at higher temperatures, their spinels show less magnetite in solid solution. This is undoubtedly a compositional effect reflecting the lower oxidation ratios in the higher temperature rocks.

The cell dimensions of the analyzed spinellids were obtained by computation from 2θ values measured for (220), (311), (400), (242), (511) and (440) peaks on diffractometer traces. The results are presented in Table 5. Deer *et al.* (1962) give a diagram showing the variation of the unit cell dimension with composition, which is based on the assumption that

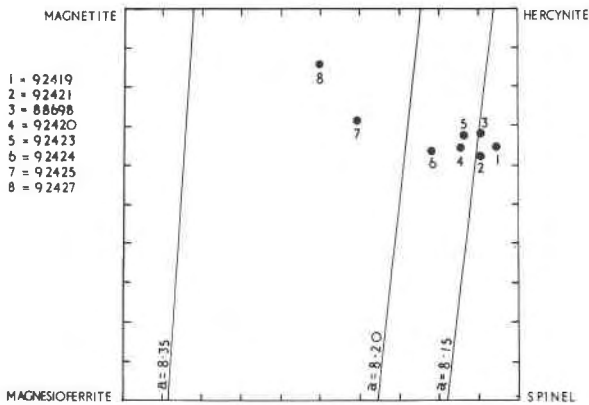


FIG. 9. Square plot of the spinellids from the Sithean Sluaigh emery locality. The dots represent the compositions of originally homogeneous phases that have subsequently exsolved spinel or magnetite. The cell dimensions of the exsolved phases are given in Table 5.

TABLE 5. CELL DIMENSIONS OF THE SPINELS AND MAGNETITES

Specimen No.	a(in Å)	Specimen Descriptions
92419	8.150±0.001	spinel—single homogeneous phase
92421	8.160±0.001	spinel—single homogeneous phase
88698	8.169±0.003	spinel—single homogeneous phase
92423	8.167±0.001	spinel—single homogeneous phase
92420	8.168±0.002	spinel with sinuous magnetite exsolution lamellae
92424	8.168±0.001	spinel from magnetite-spinel exsolution intergrowth
92424	8.384±0.002	magnetite exsolved from spinel
92425	8.154±0.011	spinel exsolved from magnetite
92425	8.376±0.011	magnetite from magnetite-spinel exsolution intergrowth
92427	8.163±0.001	spinel exsolved from magnetite
92427	8.382±0.015	magnetite from magnetite-spinel exsolution intergrowth
92431	8.388±0.001	magnetite from magnetite-spinel exsolution intergrowth
	8.396	magnetite (Deer <i>et al.</i> , 1962)
	8.135	hercynite (Deer <i>et al.</i> , 1962)
	8.103	spinel ss. (Deer <i>et al.</i> , 1962)
	8.385	magnesioferrite (Deer <i>et al.</i> , 1962)

Rock descriptions as for Table 3.

Diffractometer traces were obtained using either FeK α or CuK α radiation and a Si internal standard.

Vegard's Law holds true (see Zen, 1956; Turnock and Eugster, 1962). By this diagram, the observed cell dimensions indicate that exsolution from an original homogeneous phase has approached completion in the cases of 92424, 92425 and 92427. Thus, from Fig. 9, it appears that only 10–15 mol.% of magnetite remains in the spinels, and somewhat less spinel (5–10 mol.%) in the magnetite. The compositions of the exsolved spinels seem, on the basis of the cell dimensions, to be very comparable to those of the homogeneous spinel phases nearer the contact. Turnock (1959) notes that exsolution of magnetite from hercynite and vice versa is sluggish particularly at lower temperatures, and thus it is likely that these homogeneous spinels did not exsolve magnetite because of a kinetic factor. It is interesting to note, in this respect, that 92420, which contains slightly more ferric iron than specimens rather nearer the contact, has exsolved a little magnetite. The poorly developed, sinuous exsolution lamellae (Fig. 4) testify to the sluggishness of the process at temperatures which, using Turnock and Eugster's (1962) solvus curve, must have been around 600° C.

Corundums. Several of the emery rocks contain large amounts of gem-quality corundum. The mineral always has the same platy habit and

varies in the largest dimension from 1 mm downwards. The color changes from typical sapphire-blue in the reduced rocks near the contact, through blue-green to green and yellow-green in the most oxidised rocks at about five feet from the contact. The sapphire corundum often contains needles of rutile arranged with their long axes in three directions at 120° , normal

TABLE 6. CHEMICAL ANALYSES OF CORUNDUMS

	92419	92421	92424	92425	92394
SiO ₂	0.72	0.00	0.05	1.86	2.34
TiO ₂	0.30	0.31	0.24	0.32	0.30
Al ₂ O ₃ ¹	97.07	97.45	94.91	90.53	90.75
Fe ₂ O ₃	1.71	2.10	4.57	6.98	6.41
MnO	—	trace	—	—	trace
CaO	0.20	0.14	0.23	0.31	0.20
Total	100.00	100.00	100.00	100.00	100.00
Trace element determinations (in p.p.m.)					
Ca	55	45	65	45	100
Cr	450	450	450	450	900
V	45	45	22	22	22
Sn ²	100	100	100	10	0
Ni	4	4	10	4	10
Cu	25	22	10	46	14
distance from contact	6"	1'6"	3'6"	4'6"	4'9" (estimated)
oxidation ratio of rock	14	not known	44	74	not known
Electron probe determinations on corundums					
	92424	92425	estimated limit of error		
SiO ₂	0.21	0.56	(± 0.1)		
TiO ₂	0.17	0.12	(± 0.1)		
Al ₂ O ₃ ¹	98.35	93.65	(± 4.0)		
Fe ₂ O ₃	4.53	6.38	(± 0.3)		
	103.26	100.71			

¹ Errors in the analysis are likely to be concentrated in this oxide because of the rather large absorption corrections. Corrections have not been made for atomic number effect since this should be low in view of the amount of Al present. Rock description as for Table 3.

² May result from contamination during separation with heavy liquids.

to the z axis of the corundum host (Fig. 5); in contrast, the iron-corundum (*i.e.* the green variety), never contains them. The yellow-green variety is reminiscent of the iron-corundum described by Agrell and Langley (1958) from a porcellanite near its contact with an olivine dolerite plug at Tievebulliagh, Co. Antrim.

A series of specimens were separated from the Strachur emery rocks and analyzed chemically (Table 6).¹

Because of the appreciable amounts of silica indicated by three of the analyses, it was decided to check to see if it really was contained in the corundum or whether it was an impurity. Two of the corundums (92425, 92424) were therefore examined by the electron probe; the semi-quantitative analyses obtained, are also reported in Table 6. It is clear that much of the SiO_2 found by chemical analysis in 92425 must be due to contamination from adhering particles (probably the feldspathic matrix of the rock)—and the same doubtless applies to the other specimens. However, the amounts of iron indicated by the probe are in fair agreement with those determined volumetrically by chemical analysis.

Another method exists for the determination of iron in corundum. This was developed as a by-product of experimental work on the system iron-oxide— Al_2O_3 by Muan and Gee (1956). It is based on the variation of $d(12.4)$ with the solid solution of hematite in corundum. It is obvious from Table 7 that there are large discrepancies between the amounts of iron indicated chemically and by the x -ray method. Since the Fe_2O_3 contents of two specimens were checked by the electron probe, there can be little doubt that the curve of Muan and Gee can give erroneous results when applied to natural corundums. As a further check, a corundum from

¹ The separation of pure concentrates of corundum is rather difficult. Because of the hardness, it cannot be ground in the normal way in an agate mortar, and adhering particles are hard to remove completely. Corundum is purported to be insoluble even in HF , but treatment of some of the material with this acid, in an attempt to free it of impurities, produced etch-pits on the surfaces of the grains. Consequently, this treatment was not used subsequently, and recourse was made to repeated gentle grinding followed by separation with heavy liquids. Subsequent analyses made it clear that this procedure did not entirely eliminate impurities.

The chemical analysis of corundum also presented problems. The highly refractory nature of the mineral, inhibited the normal sodium carbonate fusion and the mineral had to be taken up directly in pyrosulfate. The cake was dissolved and any insoluble residue filtered off and silica determined on it. TiO_2 and Fe_2O_3 measurements were made colorimetrically and by titration with ceric sulfate solution, respectively. CaO , found to be present in small quantities, was determined on separate samples using a standard versene titration; Al_2O_3 was determined by difference. This procedure inevitably gives totals of precisely 100% because R_2O_3 s are not precipitated—although there is no reason why they cannot be. However, the large amounts of Al_2O_3 would result in very bulky precipitates and make adequate washing difficult. The method adopted here is probably the more accurate.

Siberia, used as a standard in the *x*-ray laboratory of the Department of Mineralogy and Petrology, Cambridge, was examined by the *x*-ray technique and also by the probe. The latter indicated that certainly no more, and probably somewhat less, than 0.5% Fe₂O₃ was present in the sample; the *x*-ray method indicated 2.9% Fe₂O₃. Finally the iron-corundum from Tievebulliagh analyzed by Agrell and Langley (1958) was also checked by Muan and Gee's method. This indicated 10.9 wt.% Fe₂O₃, whereas the chemical analysis showed only 9.5 wt.%.

Figure 10 shows the curve of Muan and Gee re-plotted after conversion from molecular to weight percent Fe₂O₃. The best curve is also drawn through the series of points obtained from chemical and electron probe analyses.

Oscillation photographs were taken of several single crystals of the high-iron corundum to see if any ordering of Fe³⁺ ions might be indicated by weak or diffuse interlayer reflections; none was observed. No explanation can be offered at the moment for the discrepancies between the natural and synthetic data—more detailed *x*-ray work may need to be carried out. It seems unlikely that the small amounts of TiO₂, SiO₂ and CaO present, can be responsible; it is more probable that some order/disorder relationship amongst the trivalent ions, which fill only two-thirds of the available sites, is indicated.

TABLE 7. X-RAY AND OTHER DATA ON Fe₂O₃ CONTENT OF CORUNDUM

	d(12.4)	indicated % Fe ₂ O ₃	% Fe ₂ O ₃ from chem. analysis	% Fe ₂ O ₃ indicated by probe	% Fe ₂ O ₃ by new curve
92419	1.4055	3.40	1.71	—	1.50
92421	1.4063	5.10	2.10	—	2.40
88698	1.4065	5.40	—	—	2.65
92423	1.4068	5.85	—	—	3.00
92424	1.4079	7.50	4.57	4.53	4.40
92425	1.4091	9.15	6.98	6.38	6.35
92394	1.4093	9.55	6.41	—	6.60
92431	1.4080	7.60	—	—	4.45
Tievebulliagh	1.4102	10.90	9.50	—	8.95
Standard	1.4049	2.90	—	0.30	0.70

CuK α radiation was used throughout, and all measurements are based on the position of the (12.4) peak for CuK α ₁ radiation, relative to a silicon internal standard.

Identity of rocks:—see Table 3, except:

Tievebulliagh—porcellanite, (Agrell and Langley, 1958, Anal. 1a, Table 2, p. 104).

Standard—a lilac-coloured prismatic crystal with well-developed terminal faces, from Siberia (from the Brooke Collection, Department of Mineralogy and Petrology, Cambridge).

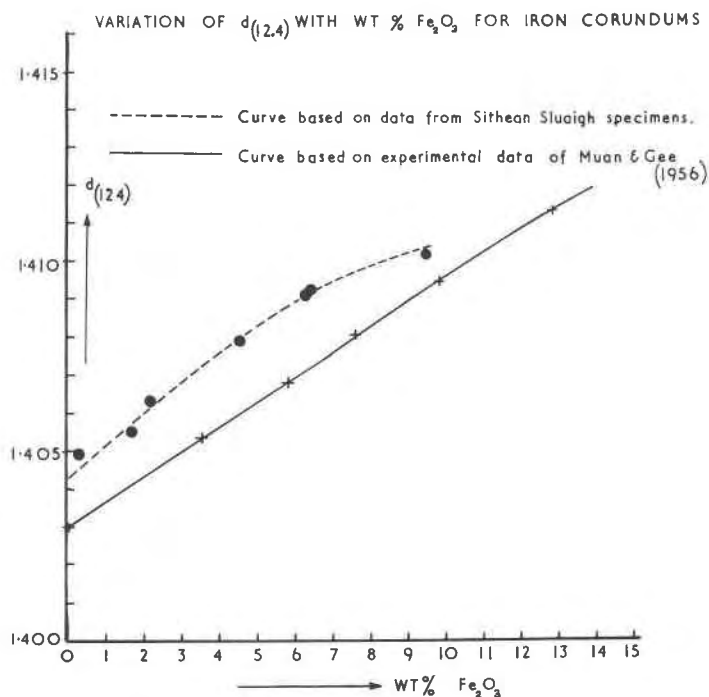


FIG. 10. A comparison of the curves obtained from experimental work of Muan and Gee (1956), and from natural corundums from Sithean Sluaigh, etc.

Whatever the precise values for the iron in the corundums, there can be no doubt at all about the trend. The steady increase in the amount of Fe_2O_3 away from the contact, reaching a peak at about 5 feet, agrees well with the increasing oxidation away from the contact observed in the whole rocks (Table 1).

With regard to the color of the corundums, Deer *et al.* (1962), consider that the blue of the sapphire variety is due to the presence of Ti and Fe^{2+} , while green corundum results from the substitution of V, Co, Ni and Fe^{2+} , and yellow from Fe^{3+} or Ni. The trace element determinations (Table 6) show that only Cr is present in more than trace quantities—and that even this is always less than 0.1% (*cf.* 2–3% in ruby corundum). The sequence of colors, blue—blue-green—green—yellowish-green, observed in specimens from Strachur seems to be accounted for by the interfering effects of the Ti and Fe^{3+} contents. Agrell and Langley (1958) also found sapphire corundum at Tievebulligh—associated with mullite, spinel and magnetite (a paragenesis very similar to that at Sithean Sluaigh). They believed that the blue variety appeared as a result of a greater $\text{FeO}:\text{Fe}_2\text{O}_3$ ratio, the larger cooling range near the contact, and

the influence of magmatic volatiles. The first of these conclusions, at least, is borne out by the present study.

Mullites. Much literature has appeared on this comparatively rare mineral—largely because of its interest to ceramists. Recently Shears and Archibald (1954) and Agrell and Smith (1960) have reviewed the present state of knowledge of this mineral. Two aspects which are now receiving particular attention are the experimental distinction of the mineral from sillimanite, and the extent of solid solution towards sillimanite on the one hand, and corundum on the other.

Bárta and Bárta (1956), using the flame fusion method of synthesis, claimed to have obtained mullite ranging in composition between $5\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ and $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, and suggested that possible compositions vary between $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. Other workers consider the possible range in composition is much smaller (*e.g.* Trömel, 1956, reported in Agrell and Smith, 1960). Two other substitutions are common in mullite—those of Fe^{3+} and Ti; Cr can also enter the structure. Murthy and Hummel (1960), found that 2–4% TiO_2 can enter at 1600°C ., 10–12% Fe_2O_3 at 1300°C ., and 8–10% Cr_2O_3 at 1600°C . They suggested that temperatures of 1200°C . were required to initiate appreciable solid solution of Fe^{3+} .

Two mullites¹ both from spinel-mullite buchites were analyzed in the course of the present study (Table 8). Great attention was paid to the purification of the minerals. However, as Shears and Archibald (1954) note, mullite commonly contains small inclusions of the liquid in which it grows, and it was shown previously that this is the case in the Strachur mullites (Fig. 6). By grinding to $-300 + 350$ U.S. Standard Sieve sizes, after preliminary treatment with heavy liquids, the magnetic separator, and dilute HF, and then further separation by heavy liquids, quite pure concentrates were eventually obtained. It was estimated that impurities (pockets of glass and included spinel grains) did not exceed 2% in the material finally analyzed. The small amounts of MgO present in the analyses may be partly due to such contamination.

Within the limits of accuracy imposed by such impurities, the analyses show no indication of deviating appreciably from $3\text{R}_2\text{O}_3 \cdot 2\text{SiO}_2$ towards either $2\text{R}_2\text{O}_3 \cdot \text{SiO}_2$ or $\text{R}_2\text{O}_3 \cdot \text{SiO}_2$. The extent of solid solution of iron is rather small but shows that the lower temperature limit for the substitu-

¹ A new technique for distinguishing mullite and sillimanite and perhaps of illuminating differences in composition and ordering among mullites themselves, has been described by Smith and McConnell (1966, in press). The technique, which uses the electron microscope, has been applied to the Strachur mullites and their identification by optical criteria confirmed.

TABLE 8. COMPOSITIONS AND CELL DIMENSIONS OF MULLITES

	88698		92423	
SiO ₂		27.77		27.38
TiO ₂		0.90		0.69
Al ₂ O ₃		69.37		68.59
Fe ₂ O ₃		1.87		3.18
MnO		0.00		0.00
MgO		0.30		0.31
		100.21		100.15
Molecular percentages of the oxides				
	88698	92423	sillimanite	mullite
			(Al ₂ O ₃ ·SiO ₂)	(3Al ₂ O ₃ ·2SiO ₂) (2Al ₂ O ₃ ·SiO ₂)
SiO ₂	39.34	39.12	50.00	40.00 33.33
TiO ₂	0.96	0.74		
Al ₂ O ₃	58.06	57.77	50.00	60.00 66.67
Fe ₂ O ₃	1.00	1.71		
MgO	0.63	0.66		
Unit cell dimensions				
	<i>a</i> (in Å)		<i>b</i> (in Å)	<i>c</i> (in Å)
88698	7.5468±0.0006		7.6957±0.0007	2.8907±0.0003
92423	7.5461±0.0014		7.6976±0.0016	2.8912±0.0006

Cell dimensions were obtained by the diffractometer method outlined by Agrell and Smith (1960).

Identity of rocks: See Table 3.

tion must be much less than that indicated by Murthy and Hummel (1960).

In general the mullites fall well within the range of compositions previously reported for natural mullites, *e.g.* by Agrell and Smith (1960) and Agrell and Langley (1958). When the cell dimensions are plotted on the diagrams of Agrell and Smith (1960), they fall between the synthetic mullite and the natural Fe,Ti-bearing curves, very close to another mullite from Sithean Sluaigh analysed by them. No simple relationship between the variation in cell dimensions and the contents of Ti and Fe is apparent, and it seems probable that an effect due to variations of ordering of Al and Si (suggested by Smith and McConnell, 1966, in press) is superimposed upon and may mask compositional effects.

Pseudobrookites. The presence of pseudobrookite in the emery rocks of Sithean Sluaigh was not immediately apparent. The mineral is usually deep red-brown to black in thin section and translucent only in the thinnest edges or under intense illumination. However, in the more reduced rocks it is a lighter honey brown color. In polished mounts it can readily be distinguished from ilmenite by its lower reflectivity and lesser anisotropism. While many of the crystals have a granular habit, some form perfect laths. In reflected light small cores of ilmenite can be seen in a few grains, suggesting that the mineral owes its origin, in part, to oxidation of the ilmenite frequently present in the unaltered phyllites. Some of the material was separated and positive identification made by x -ray techniques.

The composition that has generally been ascribed to pseudobrookite in recent years is Fe_2TiO_5 , this being based largely on the work of Pauling (1930), who determined its structure. Pauling noted that in the few available analyses, there was usually an excess of TiO_2 over that required by the formula Fe_2TiO_5 , but claimed that in the case of the pseudobrookite from Aranyer Berg, used for his work, there was x -ray evidence to suggest the presence of rutile. Further, he remarked that in the space group to which the mineral belongs, there are places for atoms in groups of four or multiples of four, only; if it were assumed with earlier workers that the formula was $\text{Fe}_4\text{Ti}_3\text{O}_{12}$, at least four molecules would have to be present in the unit cell, giving a density in excess of ten (*cf.* 4.4 to 4.6, observed). On these grounds, Pauling excluded this formula and recommended $4\text{Fe}_2\text{TiO}_5$, the only composition compatible with the x -ray data. Palache *et al.* (1944), give three analyses of pseudobrookite, but all are of inferior quality in that only Fe_2O_3 , TiO_2 and MgO are reported. The analysis of the type material from Aranyer Berg shows 42.35% TiO_2 , and although Pauling ascribed this to the presence of rutile, the new analyses of pseudobrookites presented below, suggest that the type-material ought to be re-examined.

A pseudobrookite from Sithean Sluaigh was analyzed chemically, (Table 9, Anal. I). There is no possibility that the divergence of the composition from the theoretical Fe_2TiO_5 results either from the presence of rutile or of spinel; rutile was not observed in any of the pseudobrookite-bearing rocks, and the subtraction of Fe^{2+} , Mg and Al to form pleonaste would result in an even larger excess of Ti than is apparent.

The observed composition can be explained if part of the Ti is held in the sites normally occupied by Fe^{3+} , the excess charge being balanced by simultaneous substitution of Fe^{2+} for Fe^{3+} . The slight charge deficiency that still remains due to an excess of divalent ions over the amount of Ti available for the position appears to be compensated by an excess in the

TABLE 9. COMPOSITIONS OF "PSEUDO BROOKITE" MINERALS

	I	II	III	IV
SiO ₂	0.21			
TiO ₂	41.18	33.35	68.99	60.33
Al ₂ O ₃	7.22			2.15
Fe ₂ O ₃	46.21	66.65		28.77
Cr ₂ O ₃				0.37
FeO	4.70		28.57	2.00
MnO	trace		1.41	0.07
MgO	0.95		0.32	6.45
CaO	trace			trace
Nb ₂ O ₅ } Ta ₂ O ₅ }			0.44	
	100.47	100.00	99.73	100.14

Numbers of cations on the basis of 5 oxygens for Analysis I				
Si	0.008	} 1.176	Si	} 1.000
Ti	1.168		Ti	
Al	0.321	} 1.632	Ti	} 1.809
Fe ³⁺	1.311		Al	
			Fe ³⁺	
Fe ²⁺	0.148	} 0.201	Fe ²⁺	} 0.201
Mg	0.053		Mg	

I. Pseudobrookite (92427) from Sithean Sluaigh, Strachur, Argyllshire.

II. Theoretical composition of Fe₂TiO₅.

III. "Iserite" from Bohemia (Analyst: W. T. Schaller).

IV. "Kennedyite" from S.E. Southern Rhodesia (Analyst: O. von Knorring).

The analysis of the mineral was carried out in the standard way, except that "grade A" glassware was used throughout. TiO₂ was determined colorimetrically, several times on two separate aliquots, and the average of all results taken. FeO was determined by the vanadate method, the mineral dissolving completely in a surprisingly short time.

number of divalent ions. This could result from the presence of small amounts of spinel, which, having a cation to anion ratio of 3:4 instead of 3:5, would result in there being apparently too many cations present. 1.2% (mol.) of spinel would bring about this excess—an amount of impurity entirely possible in view of the difficulty of separation, intergrowth and small amount of raw material available.

A rather different way of looking at the analysis is in terms of the solid solution of four end-members—FeTi₂O₅, MgTi₂O₅, Al₂TiO₅ and Fe₂TiO₅.

The last of these is the mineral pseudobrookite, and the others are all known as synthetic compounds. On this basis, after the small excess of divalent and trivalent ions have been removed as hercynite, the mineral has the composition:

MgTi ₂ O ₅	5.37%
FeTi ₂ O ₅	13.57%
Al ₂ TiO ₅	14.69%
Fe ₂ TiO ₅	66.37%

Figure 11 shows the composition of this pseudobrookite (92427) plotted on the triangular diagram (Si,Ti)O₂-(Fe,Al)₂O₃-(Fe,Mg,Mn)O. It lies very close to the tie-line between Fe₂TiO₅, and just on the spinel side of it again reflecting the presence of very small amounts of spinel contamination.

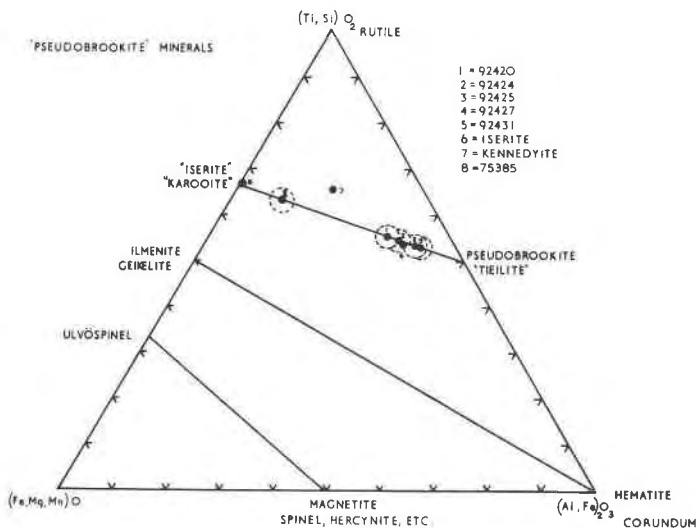


FIG. 11. Triangular plot of pseudobrookite minerals.

In view of the interesting composition indicated by the chemical analysis, further analyses were desirable. The small amounts of the mineral present in most rocks and difficulties of separation, precluded further chemical work, and therefore use was made of the electron probe. Although this instrument cannot yet give the same accuracy as a classical chemical analysis, errors can be greatly reduced if sufficient measurements are made. Unfortunately, the instrument cannot distinguish between valence states, and as this is important in the case of pseudobrookite, because of the iron content, an assumption must be made: since

TABLE 10. ELECTRON PROBE ANALYSES OF PSEUDOBROOKITES

	75385	92420	92424	92425	92431	
1. Results corrected for fluorescence, mass absorption, and atomic number effects:						
SiO ₂	—	0.13	0.43	0.13	0.15	
TiO ₂	64.13	44.35	43.31	39.50	38.62	
Al ₂ O ₃	5.18	7.22	7.88	7.48	6.37	
Fe ₂ O ₃	22.38	47.16	48.21	49.70	52.11	
MgO	8.31	1.82	1.97	1.11	0.96	
2. Final results with calculated Fe ₂ O ₃ and FeO, corrected to 100%:						
SiO ₂	—	0.1	0.4	0.1	0.1	±0.05
TiO ₂	64.9	44.2	42.7	40.5	39.5	±1.0
Al ₂ O ₃	5.3	7.2	7.8	7.7	6.5	±0.5
Fe ₂ O ₃	11.7	41.8	43.8	48.0	50.3	±1.5
FeO	9.7	4.9	3.4	2.6	2.6	±1.0
MgO	8.4	1.8	1.9	1.2	1.0	±0.2
Totals	100.0	100.0	100.0	100.1	100.0	
Distance from contact in feet.	2	3½	4½	9		
Oxidation ratio of parent rock.	14	44	74	unknown		

Identity of rocks: See Table 3, except for:

75385—a bytownite-spinel-ilmenite-pseudobrookite rock from Tievebulliagh, near Cushendall, Co. Antrim, N. Ireland. (Analyzed for S. O. Agrell by S. J. B. Reed.)

analysis I of Table 8 showed that the mineral has a composition lying very close to the (Fe,Al)₂TiO₅-(Fe,Mg)Ti₂O₅ join, it has been assumed that other samples of the mineral have compositions lying on this line. This permits the Fe³⁺:Fe²⁺ ratio to be determined from the data obtained from the electron probe and the problem of valence states to be overcome. Four further pseudobrookite analyses carried out in this way are reported in Table 10. The apparent concentrations were corrected for fluorescence, mass absorption and atomic number effects. The four analyses have been plotted on Fig. 11 along with the chemical analysis; the large circle represents the estimated maximum limit of error, and the center spot the best position. In all probability, the errors fall well inside the large circle.

These analyses bear out all the features of the chemical analysis, and suggest even greater solid solution towards (Fe,Mg)Ti₂O₅. Fe₂O₃ increases steadily as the oxidation ratio of the parent rock rises, and the temperature falls. The increase in Fe₂O₃ is not matched by an increase in Al₂O₃, which instead remains reasonably constant. As would be expected,

there is a fall in TiO_2 , FeO and MgO as Fe_2O_3 increases. SiO_2 is low, although one specimen (92424) contains appreciably more of this oxide than the rest.

The presence of significant amounts of Al and Mg in the analyzed pseudobrookites indicates that the mineral cannot have formed simply by the oxidation of ilmenite, but that the latter must have entered into reaction with its highly aluminous, ferromagnesian environment.

Akimoto *et al.* (1957) have shown experimentally that there is complete solid solution in the series FeTi_2O_5 - Fe_2TiO_5 above 1150°C ., and it is therefore not surprising that appreciable solid solution can exist several hundred degrees lower. Further, one might anticipate that the compound $(\text{Fe,Mg})\text{Ti}_2\text{O}_5$ would be found occurring naturally. However, Taylor (1964) has found that FeTi_2O_5 is not stable with respect to ilmenite and rutile at 1000°C . and at least some of the examples of the intergrowth of the latter two minerals, described for instance by Edwards (1954), may have originated by the breakdown of "pseudobrookite." The proposition might be tested by carrying out chemical analyses of the bulk material (*i.e.* ilmenite+rutile). If this mixture frequently had exactly the composition of $(\text{Fe,Mg})\text{Ti}_2\text{O}_5$, there could be little doubt that the intergrowth had been formed in the way suggested. However, the possibility of the oxidation of iron would have also to be considered.

Von Knorring and Cox (1961) described a mineral of the pseudobrookite family from an olivine-augite-alkali felspar rock in the Karroo succession of southeastern Southern Rhodesia. They presented chemical and x-ray data and named the mineral "kennedyite." Their analysis is reproduced in Table 9. Further, they called the hitherto unnamed end-member MgTi_2O_5 "karrooite" because of the amount of this molecule in their analyzed specimen. It seems to the present writer unnecessary to name the intermediate members of "pseudobrookite" solid solution series, at least until some particular significance is attached to their compositions, and further, that the name "karrooite" has undesirable petrological implications. If the chemical analysis of "kennedyite" given by von Knorring and Cox is plotted on Fig. 11, it is immediately apparent that the mineral actually lies well away from the $(\text{Fe,Mg})\text{Ti}_2\text{O}_5$ - $(\text{Fe,Al})_2\text{TiO}_5$ join. In a description of the mineral the writers say, "An examination of polished sections showed the new mineral in well defined laths. In some grains marginal patches of secondary hematite were observed and with high magnification ($\times 500$) lamellar intergrowths were seen. The lamellae are believed to be exsolved rutile." Once again, it seems undesirable that a mineral should be named on the basis of chemical data from material that is manifestly impure. The observations of von Knorring and Cox (1961) regarding the lamellar "exsolution" of rutile and the marginal

appearance of "hematite" from their "kennedyite," might be construed as further evidence for the breakdown of the "pseudobrookite" minerals with falling temperature. One wonders, however, if this is the case, what has happened to the MgO.

Janovsky (1880) described a mineral "iserite," the chemical analysis of which is shown in Table 9, but Schaller (1912) considered that this mineral (and also "nigrine") is only iron-rutile. He quoted seven partial analyses of minerals ranging in composition from 5% to 64% ilmenite and 95% to 36% rutile, and suggested that they were part of an isomorphous series. Janovsky's "iserite" analysis is plotted in Fig. 11 and it lies very close to the "unnamed" end-member of the "pseudobrookite" series. This may be fortuitous, but MacChesney and Muan (1959), in an experimental study of the system iron oxide-titanium oxide, show only very limited solid solution between the ilmenite-hematite series and the "pseudobrookite" series, and between the latter and rutile, at temperatures around 1500° C.

Palache *et al.* (1944) say of iserite, "Supposedly contains Fe²⁺ without significant amounts of (Ta,Cb) in substitution for Ti. Highly ferroan material has been reported. The validity of this variety is doubtful." No reason for their doubt is given.

Agrell and Long (1960) referred to "ferropseudobrookite" from a metasomatised porcellanite at Tievebulliagh, Northern Ireland. In view of the data from Sithean Sluaigh, they have recently re-examined this mineral and the new complete electron probe analysis is given in Table 10. The composition of the mineral lies quite close to (Fe,Mg)Ti₂O₅ and is the only natural occurrence known to the writer of material approximating in composition to this end of the "pseudobrookite" series—with the exception of Janovsky's iserite. The name iserite might thus in future be used for FeTi₂O₅, unless it is definitely established that the mineral described by Janovsky was an intergrowth of two or more minerals. The seven analyses presented by Schaller (1912), mentioned above, range between iserite and rutile and do not extend over the whole range between ilmenite and the latter. Even accepting for the sake of argument that limited solid solution exists between iserite and rutile, the data suggests that iserite is an end-member of the series, and is thus a distinct mineral species. If there were indeed solid solution between these two compounds, one might reasonably expect it to exist between rutile and pseudobrookite proper, or rutile and any member of the "pseudobrookite" series. There is little to suggest that such compounds exist in nature, unless the mineral crichtonite, which, from the scanty data available, appears to have a composition lying in the field TiO₂-FeTi₂O₅-Fe₂TiO₅, and the "kennedyite" of von Knorring and Cox (1961) are examples.

Pauling's structure for pseudobrookite (Pauling, 1930, p. 104), shows

the Fe^{3+} in very distorted octahedral coordination, and the Ti in the more regular octahedral positions, there being twice as many "distorted" as "regular" sites. This structure, it was claimed, would satisfactorily explain both the observed cell dimensions and the intensities of the reflections. Now, according to Akimoto *et al.* (1957), the compound FeTi_2O_5 has the same structure as pseudobrookite, with slightly different cell dimensions. If this is the case it seems likely that there will be a switch in the positions occupied by the titanium atoms, the appreciably larger Fe^{2+} going into the "regular" sites and the Ti into the "distorted" sites.

The cell dimensions of the four end-members used above and of the chemically analysed pseudobrookite from Strachur are given below (Table 11).

TABLE 11. CELL DIMENSIONS OF MINERALS IN THE PSEUDOBROOKITE FAMILY

	a (in Å)	b (in Å)	c (in Å)	Cell vol. (in Å ³)
MgTi_2O_5	9.774	9.980	3.732	364.0
FeTi_2O_5	9.798	10.041	3.741	368.0
Fe_2TiO_5	9.767	9.947	3.717	361.1
Al_2TiO_5	9.436	9.648	3.557	323.8
Strachur pseudo- brookite 92427	9.738	9.954	3.715	360.1

The cell dimensions for FeTi_2O_5 and Fe_2TiO_5 were taken from Akimoto *et al.* (1957), for Al_2TiO_5 from Austin and Schwartz (1953), and those for MgTi_2O_5 were computed from data given in the A.S.T.M. index (card no. 9-16).

The variations are all in the directions to be expected from a consideration of the ionic radii. Thus the Mg end-member has a slightly smaller cell than the Fe end-member, and the Al analogue is considerably smaller than pseudobrookite proper. The experimental data of Akimoto *et al.* (1957) show that for the series FeTi_2O_5 - Fe_2TiO_5 , Vegard's Law is definitely not obeyed, the variations in cell dimensions being far from linear. This deviation from ideal behavior may result from the distribution of the Ti ions over two different sites. In naturally occurring pseudobrookites made up of several end-members, the distribution of Fe^{3+} , Fe^{2+} , Mg, Al and Ti over the two alternative sites must be complex, and it seems unlikely that it would be possible to use cell dimensions of such specimens as an aid to obtaining quantitative information on their compositions. Clearly, however, the cell edges and the cell volume of the Strachur pseudobrookite reflect the contracting effect of the 14% or so of the Al_2TiO_5 molecule present. Thus measurement of cell dimensions may indicate that a particular specimen is an aluminous variety.

TABLE 12. DISTORTION INDEXES OF CORDIERITES

Cordierite	Distortion Index	Definition after Schreyer and Schairer (1961)
92420	0.24	low-cordierite
92427	0.26	low-cordierite

Cordierites. Cordierite from Sithean Sluaigh always appears to be the common orthorhombic variety, as, even when it occurs amongst the high-temperature emery rocks, sector and polysynthetic twinning is ubiquitous. Nevertheless, diffractometer traces of two analysed cordierites were run to determine the distortion indices (defined by Miyashiro (1957), as $\Delta = 2\theta_{131} - (2\theta_{511} + 2\theta_{421})/2$). The results are given in Table 12. In neither case does the distortion index reach the maximum observed in natural cordierites (0.31), nor even the maximum of 0.28 achieved experimentally by Schreyer and Schairer (1961) after ten months heating. These investigators arbitrarily divided cordierite into groups, dependent on the structural state, as follows:

- $\Delta < 0.01$ — high-cordierites
- $\Delta = 0.01 - 0.20$ — intermediate-cordierites
- $\Delta > 0.20$ — low-cordierites

On this basis, both of the analyzed specimens are low-cordierites, probably reflecting the rather slow cooling of the aureole (Schreyer and Schairer, 1961). However, far too few data are available on the rates of transition in various chemical environments for any meaningful estimates to be made of the actual period of cooling.

Two cordierites were analyzed chemically (Table 13), and both show several interesting features. The Fe^{2+} contents are not particularly large considering the iron-rich environments in which they formed. However, the increased oxidation of the parent-rock 92427 relative to 92420, is not shown up by an increase in the Fe^{3+} content of the cordierite which, in each case, is low. Despite the fact that in thin section the specimens appear rather fresh, with only patches of pinitite (which were virtually eliminated during separation), the alkalis are remarkably high. This is particularly so for 92427 which has a higher total alkali content than any of the 18 analyses quoted by Deer *et al.* (1962), with the exception of an Fe-rich cordierite from a pegmatitic quartz-cordierite intergrowth (which contains 3.53% Na_2O and 0.90% K_2O). If this alkali content is not due to pinitization, it shows the remarkable extent to which the hexagonal holes in the cordierite structure can be stuffed with K and Na ions.

A large amount of water is also present. If this is assumed to occur as

the H_2O molecule, and also to be held in the hexagonal holes, the number of alkali ions + H_2O molecules exceeds the number of holes available. Folinsbee (1941) has suggested that Na may replace Be in the closely related beryl structure, and it seems possible that in cordierites Na may substitute in the equivalent positions taking the place of a divalent ion (Mg, Fe or Mn). In this respect it should be noted that both the analyses show deficiencies of divalent cations when compared with the theoretical value of two. Even allowing for such a substitution of Na, the K ions + water molecules still exceed the number of available sites. Kleeman (1944) suggested that in beryl hydrogen may replace Si as it does in the hydrogrossular series, and possibly a limited amount of this type of substitution may take place in the cordierites, although the bulk of the "water" may be still situated as molecules in the ring-channels. On the other hand, in the analyses of 92427, there is an appreciable excess of Si over the theoretical value of five, and a smaller deficiency in Al. There may be here an attempt to balance the charge deficiencies introduced by the substitution of the Na ion, by a substitution of Si for tetrahedral Al. Several other substitutions must also occur for, in 92427, there is approximately a 25% deficiency in divalent ions.

TABLE 13. CORDIERITE ANALYSES

	92420	92427	Numbers of cations on the basis of 18 oxygens ¹		
				92420	92427
SiO_2	48.32	51.61	Si	4.978	5.623
TiO_2	0.16	0.17	Al	1.022	0.377
Al_2O_3	32.47	30.08	Al	2.921	3.486
Fe_2O_3	0.89	0.75	Ti	0.021	0.014
FeO	4.84	4.54	Fe^{3+}	0.069	0.061
MnO	0.14	0.13	Fe^{2+}	0.417	0.414
MgO	9.29	6.67	Mn	0.012	0.011
CaO	0.25	0.33	Mg	1.426	1.083
Na_2O	0.71	1.27	Ca	0.028	0.038
K_2O	0.74	1.92	Na	0.142	0.268
H_2O^+	1.95	2.03	K	0.097	0.267
H_2O^-	0.28	0.40			
			Totals	11.133	11.642
	100.04	99.90	No. of molecules	0.766	0.883

¹ Water contents ignored for the purpose of this calculation, being assumed to be present as the H_2O molecule.

Identity of rocks: See Table 3.

Finally, although the cordierite appeared fresh under the microscope, and gave a perfectly normal x -ray diffraction pattern, the possibility of incipient pinitization cannot be completely dismissed. The separated mineral looks to be quite free of yellowish pinite, although small amounts of the minute inclusions of magnetite and mullite remain; but these will tend to reverse the observed high Si, low Al and low divalent ions, and neither can affect significantly the alkali or water contents.

The fact that there is such latitude in the compositions of cordierite, be it due to substitutions or subsequent incipient pinitization, accounts, in part, for the fact that the rocks 92420 and 92427 have such simple mineralogy. In 92420, the ratios of Na:K and also the amounts of these ions, in the whole rock and in the cordierite, are very nearly identical. However, in 92427, there is a significant difference in both the ratios and the amounts, and this must be ascribed to the presence of some small pockets of granophyric material and devitrified glass observed in one of the thin sections.

In Table 14 the compositions of the coexisting minerals cordierite, magnetite-spinel s.s. and pseudobrookite, and the composition of the parent rocks are brought together. No other phases are present in significant amounts in 92420, but in 92427 an appreciable amount of rather finely crystalline mullite appears. This mullite could not be purified sufficiently to give a satisfactory chemical analysis, as it contained inclusions of glass and magnetite etc., and adhering particles of cordierite. However, the inferior incomplete analysis obtained is given mainly to show the distribution of Fe and Ti, which are probably not greatly in error.

Despite the high amount of Fe in the rock, the well known preferential entry of Mg into the cordierite is maintained, most of the Fe^{2+} entering magnetite in 92427 and spinel and 92420. Since these two rocks are thought to have originated largely from the metasomatic introduction of material from the adjacent emery rocks into a quartz-rich segregation in the phyllites, the observed concentrations of the various elements must largely reflect the availability of the components, and the ability of the band to fix them. Thus the higher concentrations of Mg relative to Fe^{2+} in 92420 illustrates the greater ability of the spinel in that rock to accommodate Mg relative to the more magnetiferous spinel solid solution in 92427. In turn, this is a reflection of the greater availability of Al relative to Fe^{3+} in the less oxidised rock (92420).

DISCUSSION OF RESULTS

Apart from the generally unusual nature of the Sithean Sluaigh emery rocks, one of the more interesting aspects of the occurrence is the coexistence of spinel-magnetite s.s.+pseudobrookite s.s. rather than other

TABLE 14. COMPOSITIONS OF THE COEXISTING MINERALS AND OF THE WHOLE ROCK

1. 92420—A cordierite-spinel-(magnetite)-pseudobrookite rock about 2 feet from the contact with the plug.

	Cordierite	Spinel-magnetite solid solution	Pseudo- brookite ¹	Whole rock
SiO ₂	48.32	0.06	0.1	38.34
TiO ₂	0.16	0.85	43.8	0.89
Al ₂ O ₃	32.47	50.28	7.1	34.90
Fe ₂ O ₃	0.89	13.49	42.3	4.54
FeO	4.84	27.02	5.0	9.20
MnO	0.14	0.46	—	0.18
MgO	9.29	8.23	1.8	8.48
CaO	0.25	—	—	0.34
Na ₂ O	0.71	—	—	0.70
K ₂ O	0.74	—	—	0.75
H ₂ O ⁺	1.95	—	—	1.70
H ₂ O ⁻	0.28	—	—	0.28
P ₂ O ₅	—	—	—	0.08
Total	100.04	100.39	100.1	100.38

2. 92427—A cordierite-magnetite-spinel-pseudobrookite-mullite rock with traces of iron corundum, about 7 feet from the contact.

	Cordierite	Magnetite- spinel solid solution	Mullite	Pseudo- brookite	Whole rock
SiO ₂	51.61	—	26.63	0.21	42.31
TiO ₂	0.17	2.06	0.61	41.18	1.83
Al ₂ O ₃	30.08	25.61	64.73	7.22	31.85
Fe ₂ O ₃	0.75	40.10	4.24	46.21	6.84
FeO	4.54	29.09	—	4.70	7.83
MnO	0.13	0.39	trace	trace	0.15
MgO	6.67	2.73	1.10	0.95	4.91
CaO	0.33	—	—	trace	0.38
Na ₂ O	1.27	—	—	—	1.05
K ₂ O	1.92	—	—	—	1.31
K ₂ O ⁺	2.03	—	—	—	1.48
H ₂ O ⁻	0.40	—	—	—	0.32
P ₂ O ₅	—	—	—	—	0.08
Total	99.90	99.98	97.31	100.47	100.34

¹ Determined on the electron probe.

assemblages such as spinel-magnetite s.s.+ilmenite-hematite s.s. or spinel-magnetite-ulvöspinel s.s.+ilmenite-hematite s.s. It must be remembered that these emeries are highly aluminous rocks and thus the spinel molecule appears where it would be absent in igneous rocks. In the latter it seems that magnetite-ulvöspinel s.s.+ilmenite-hematite s.s. are a common pair (*e.g.* Buddington and Lindsley, 1964). Other highly aluminous pyrometamorphic assemblages were described by Agrell and Langley (1958) and these included magnetite+ilmenite+pseudobrookite and magnetite+hematite+pseudobrookite. Two factors in particular are significant in understanding the assemblages that can crystallize: (1) the presence of a considerable excess of alumina and (2) the effects of temperature on the various solid solution series in the system. In the first case it has been demonstrated above that appreciable amounts of the Al_2TiO_5 molecule can be incorporated in pseudobrookite and this fact will favor the crystallization of spinel-magnetite s.s.+pseudobrookite s.s. rather than spinel-magnetite s.s.+ilmenite-hematite s.s. This can be demonstrated most clearly if the tetrahedron $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-Fe}_2\text{O}_3\text{-FeO}$ is constructed. Tie lines drawn between the hercynite-magnetite s.s. series and the pseudobrookite s.s. plane (justified by the assemblages observed at Sithean Sluaigh) define a surface separating the field of corundum+hercynite-magnetite s.s.+pseudobrookite s.s. from the field of hercynite-magnetite s.s.+pseudobrookite s.s.+ilmenite-hematite s.s. The latter field is separated by another surface defined by ilmenite-hematite—hercynite-magnetite tie lines from one in which the last two phases coexist with a magnetite-ulvöspinel s.s. Thus there are several large three-phase volumes within this 4-component system because of the possibilities for substitution within the mineral series concerned. In particular, the pseudobrookite series with its demonstrated ability to incorporate variable amounts of FeO, TiO_2 , Al_2O_3 and Fe_2O_3 (thus being represented by a plane in the tetrahedron) is important in simplifying the mineralogy. In fact the substitutional possibilities within the pseudobrookite series should give rise to a number of 2-phase volumes—for example between the pseudobrookite plane and part of the ilmenite-hematite series. The addition of moderate amounts of MgO to the system is unlikely to complicate the picture appreciably in view of the fact that at these temperatures it can substitute extensively in the hercynite-magnetite series and can also be incorporated to a lesser extent in the pseudobrookite and to a small extent in the ilmenite-hematite series. The existence of the planar and linear solid solutions of the various minerals within the tetrahedron make 2-dimensional representation of the various 2, 3 and 4 phase volumes, difficult. However, in Fig. 12 an attempt has been made to represent the more important planes and lines of solid solution and the tielines

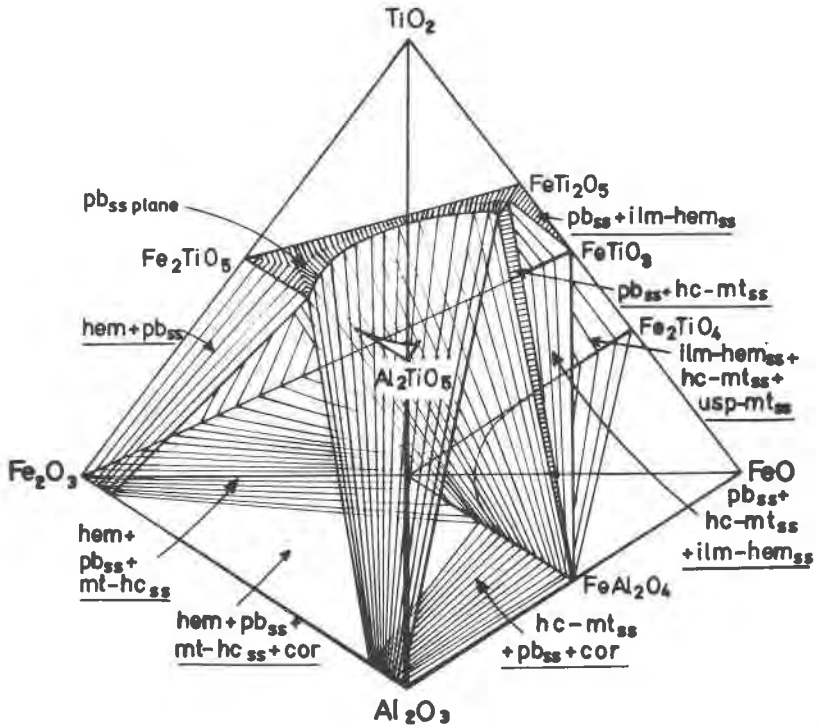


FIG. 12. A view of the tetrahedron TiO_2 - FeO - Fe_2O_3 - Al_2O_3 showing the suggested form of some of the principal sets of tie-lines at high (magmatic) temperatures.

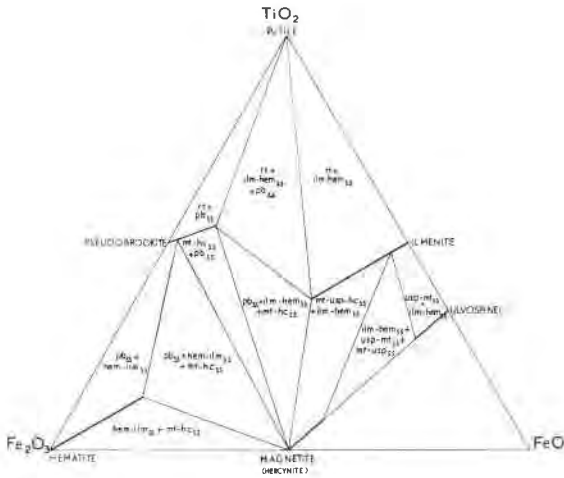


FIG. 13. A diagram showing suggested joins in the system FeO - Fe_2O_3 - TiO_2 in a somewhat aluminous environment and at temperatures well below magmatic.

between them at high (magmatic) temperatures, so that the positions of the phase volumes can be appreciated.

Although at magmatic temperatures there is complete solid solution in the ilmenite-hematite, pseudobrookite and spinel-magnetite solid solution series, at lower temperatures with less extensive substitutions the phase relations will be further complicated. Thus in somewhat aluminous environments the type of situation indicated in a simplified way in Fig. 13 may obtain.

The compositions of some of the analyzed minerals from the Sithean Sluaigh emeries are shown in Fig. 14—a projection onto the base of the tetrahedron $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-FeO}$.

A further final complication to the phase relations in the system is introduced by the exsolution of spinel and magnetite, hematite and ilmenite and by the possible instability of pseudobrookite minerals at lower temperatures mentioned earlier.

There is little doubt, as will be shown in a subsequent paper, that the

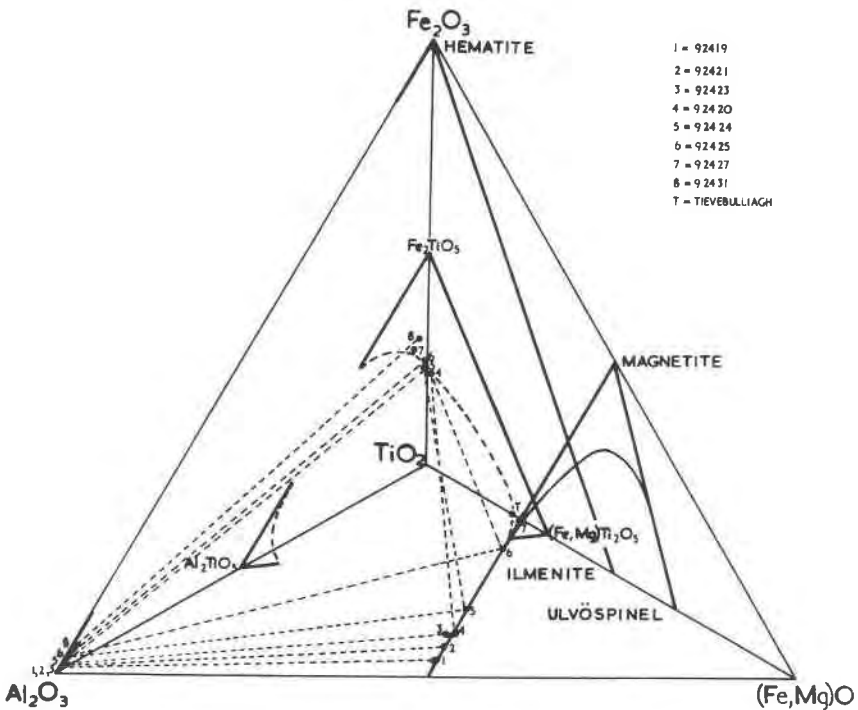


FIG. 14. The compositions of some of the analysed minerals from the Sithean Sluaigh emeries, plotted on a projection onto the base of the tetrahedron $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-FeO}$. Analyses from Tables 4, 6, 7 and 9.

emery rocks from Sithean Sluaigh are the aluminous residues from banded pelitic, semipelitic and psammitic phyllites after a granitic fraction has been selectively remobilized. Aluminous xenoliths described by Read (1931) from Haddo House, and some of the famous mullite and spinel-bearing xenoliths of the Scridain sill on the Isle of Mull (Thomas, 1922; Bailey *et al.*, 1924; Buist, 1961) may have had a similar origin. Bowen (1922) believed that the emery deposits associated with the Cortlandt Complex of Peekskill, N. Y., are perfect examples of the reaction of basic magma with aluminous metasedimentary material, and Read (1931) favored a similar explanation for the Haddo House emery xenoliths. Barker (1964) has reinvestigated the Peekskill rocks and believes that reaction between the basic magma and the pelitic xenoliths took place via "an aqueous intergranular phase." It seems to the present writer that selective fusion of a part of the original pelitic and semi-pelitic material following a preliminary heating to near magmatic temperatures by passing magma, may have been important in the Haddo House and Peekskill localities as it was at Sithean Sluaigh. However the presence at Peekskill of assemblages containing sapphirine, almandiferous garnet and sillimanite (rather than mullite) indicates that final recrystallization must have taken place at rather lower temperatures than at Sithean Sluaigh.

Read (1931) pointed out that the Haddo House xenoliths had far too large MgO contents to be simply reconstituted lumps of laterite or bole. There can be no possibility that the Sithean Sluaigh emeries have been derived from this material and it is certainly true that they have high MgO contents. Furthermore, definite pyrometamorphic derivatives of laterites were described by Agrell and Langley (1958) and in these rocks the MgO content is always low.

The Strachur emery assemblages are thought to have formed at near magmatic temperatures. This is indicated by mineralogical features such as the extent of the solid solution between magnetite and spinel, the presence of iron corundum and the Fe,Ti-bearing mullites; also the occurrence of quartz paramorphs after tridymite in siliceous rocks further from the contact than the emeries. It remains impossible however, to fix any precise temperature limits because of lack of experimental data on the more complex oxide minerals and also the fact that, in general, the extent of solid solution gives only the minimum temperature of formation.

The restricted development of the emeries in the aureole of Sithean Sluaigh may have been due to gas-streaming in the pipe adjacent to this particular locality or else to the restriction of heat flow from the rocks—due perhaps to the presence of a now eroded small sill or dyke above the

present exposure. Particularly rapid heating of this small area of rocks, so that selective refusion took place before reaction, may also have played an important part.

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