The kyanite isograd in Glen Clova, Angus, Scotland

By G. A. CHINNER

Department of Mineralogy and Petrology, Cambridge University

Summary. Mineral data from Glen Clova, Angus, suggest that the development of kyanite in graphite-bearing staurolite mica-schists, treated in terms of a Ca-free system, involved decrease of staurolite and a decrease in biotite MgO:FeO ratio. A kyanite isograd may be defined in Glen Clova as the locality where kyanite joins the assemblage staurolite–garnet–biotite–muscovite–plagioclase–quartz–graphite, the biotite having mol. $\dfrac{MgO \times 100}{MgO + FeO} = 51\cdot7$, although the persistence of this identical assemblage over some 600 metres introduces some uncertainty of interpretation. It is suggested that the reaction staurolite + quartz → garnet + kyanite is unlikely to be a common reaction in nature and that its use to subdivide the amphibolite facies is unjustified.

Introduction

THE term 'isograd' was introduced by Tilley (1924) as a refinement of the 'lines joining the points of first entry' of index minerals defining the metamorphic zones mapped by Barrow thirty years before. The isograd, marked by the incoming of a new mineral in rocks of the same composition, is a trace of the 'fossil' surface of P, T and n along which a reaction occurred during metamorphism; as such it holds a key to understanding the physical conditions that prevailed during a metamorphic episode.

One approach to a determination of the gradients of pressure and temperature that existed during the metamorphism of the Scottish Dalradian, utilizes the relationship between the inversion isograd of kyanite to andalusite, and the dehydration isograds along which andalusite and kyanite developed from hydrous minerals (Chinner, 1961). The dehydration isograds as yet lack adequate definition. While the presence of kyanite is of itself sufficient to differentiate between a kyanite zone and an andalusite zone, it is not sufficient to differentiate between a meaningful kyanite zone and lower-grade zones.[1] The

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[1] Cf. Francis (1956) who suggested examples of kyanite in the staurolite zone. The occurrence of Greenschist and Glaucophane schist facies kyanite is seen in the Alps (Niggli, 1960) and in the Piedmont of the Eastern United States (Hurst, 1957).

presence of kyanite in pegmatites, segregations, or ferrous-poor rocks may suggest that such rocks were metamorphosed within the kyanite P, T field; but the 'line joining the points of first entry' of such kyanite is not necessarily an isograd.

Both the recognition of a unique kyanite isograd in the field, and its specification in the laboratory, will require a definition of the precise reaction involved. The most common occurrence of kyanite in the Grampians is in garnet–mica–graphite schists of pelitic composition, with or without staurolite. It is clearly for such rocks that one should define the isograd; as a step towards such definition this paper presents data on the development of kyanite in Glen Clova, Angus.

Petrology and mineralogy

The 'outer limit' of kyanite occurrence in Glen Clova lies in the Craigs of Inchdowrie, to the south-east of Clova village (fig. 1). The schists involved belong to the staurolite schist group of Harry (1958, p. 406); the pelitic members are medium-grained relatively homogeneous schists with none of the marked disequilibrium textures that characterize the coarsely crystalline sillimanite-zone gneisses outcropping to the north-west of Clova (Chinner, 1960).

The fundamental assemblage of the staurolite schists is staurolite–garnet–biotite–muscovite–plagioclase (An_{0-10})–quartz, with tourmaline, apatite, ilmenite, magnetite, and graphite. At the kyanite isograd kyanite joins this assemblage, and kyanite–staurolite–bearing rocks form a belt extending for some 600 metres until pelitic outcrops are terminated by (*premetamorphic*) orthoamphibolite in the Cadham Crags, at which locality a few staurolite-free kyanite schists may be found. Modal proportions of minerals for staurolite- and kyanite-bearing rocks are typically 30–50 % micas; 20–30 % staurolite+kyanite; 1–3 % garnet; 1–3 % tourmaline; 1–10 % quartz+plagioclase. Regression analysis of forty modal analyses of kyanite–staurolite schists revealed no correlation between staurolite/kyanite ratios and the proportion of other minerals in the rocks, and so the main effort for determining the kyanite-isograd reaction was concentrated on the mineral compositions.

The ferromagnesian silicates of several slides were checked for inhomogeneity by Dr. J. V. P. Long on the X-ray microanalyser. Despite the occasional occurrence of garnets with poeciloblastic cores and inclusion-free rims, none showed any zoning for Fe or Mn. Biotites were similarly zoneless to less than 0·3 % total Fe. Tourmaline, how-ever, is strongly zoned, showing under transmitted light cores of

ω = blue-green and rims of ω = yellow-brown. The bluish tint cor-
responds to a higher Fe-content: one crystal examined had a core 35 μ
in diameter with 6·0±0·2 % Fe, and a rim varying from 6–14 μ
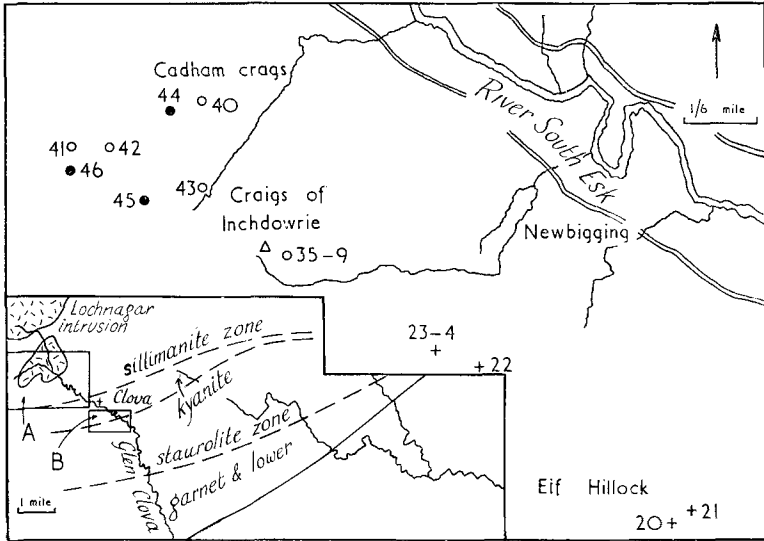with 3·8±0·2 % Fe. A transition zone between core and rim was
2–5 μ wide.

FIG. 1. Localities of analysed specimens in Glen Clova.

Cross: Staurolite-bearing (kyanite-free) assemblages.
Open circles: Staurolite–kyanite-bearing assemblages.
Solid circles: Kyanite-bearing (staurolite-free) assemblages.

Inset shows the relation of this map (rectangle B) to fig. 1 of Chinner (1960) (rect-
angle A) and the metamorphic zones of Angus and south Kincardineshire. (Adapted
from Barrow.)

The mineral assemblages are thus disequilibrium assemblages in that
tourmaline has failed to recrystallize completely during the main
metamorphic phase. None the less the homogeneity of garnet and
biotite suggests that they approached equilibrium within their im-
mediate neighbourhood.

The minerals analysed were separated from cubes of approximately
1·5 cm edge cut from the more modally-homogeneous specimens to
minimize the risk of individual separations representing more than one
compositional system (Phinney, 1963); biotites were checked for absence
of chloritic alteration products by X-ray powder photography. Although

abundant specimens of assemblages containing both staurolite and
kyanite fulfilled the twin requirements of homogeneity and freshness,
only two specimens of staurolite-free kyanite schists appeared to be
adequate. In the search for data from more kyanite schists, biotite
from a coarse-grained kyanite rich garnet–biotite–apatite rock (no. 46)
occurring as a 4–10 cm thick vein in normal schist was analysed; this

TABLE I. Chemical analysis of staurolite

| | Weight % | | Cations to 48 (O, OH) | |
	A	B		
SiO_2	30·13	28·89	Si	8·00
Al_2O_3	51·64	52·61	Al	17·16
TiO_2	0·80	0·81	Ti	0·17
Fe_2O_3	2·90	2·95	Fe^{3+}	0·61
FeO	10·58	10·78	Fe^{2+}	2·49
MnO	0·09	0·09	Mn	0·02
MgO	2·06	2·09	Mg	0·85
CaO	0·00	0·00	Ca	0·00
H_2O	1·75	1·78	OH	3·28
	99·95	100·00		

Refractive indices: $\alpha = 1·741$, $\beta = 1·747$, $\gamma = 1·755$.

A. Staurolite with quartz impurity from rock no. 20, Elf Hillock, Glen Clova.
    Analyst: G. A. Chinner.
B. Analysis A recalculated to 8 Si atoms per unit cell.

proved, however, inconsistent with the remainder of the data and was
ignored. The lack of a wide variety of kyanite schists is the most serious
drawback to the interpretation later proposed.

Chemical data on staurolites, garnets, and biotites are presented in
tables I–III. Only the staurolite analysis requires comment. Ferrous
iron was determined by the fluoborate method, which gave consistent
if not necessarily accurate results. Unfortunately, most Glen Clova
staurolites contain variable amounts (up to 30 %) of fine graphite dust
which, at the high temperatures of fluoborate fusion, reduces the ferric-
iron content. The staurolite of table I was graphite-free, but the purest
concentrate obtainable contained an inseparable quantity of included
quartz. Recalculation of the analysis to 8 atoms per unit cell shows the
deficiency in divalent ions and excess of hydroxyl over the Naray Szabo
formula $H_2Fe_4Al_{18}Si_8O_{48}$ discussed by Deer et al. (1962, p. 152).

Interpretation

If the remote possibility of substantial alumina metasomatism is
neglected, it is obvious that the kyanite-producing reaction chiefly

involved release, as kyanite, of aluminium previously contained in
staurolite. The main problem is thus to discover how the iron and
magnesium of the staurolite are redistributed amongst the other ferro-
magnesian silicates, notably garnet, tourmaline, and biotite. Oxidation
or reduction will have been controlled by the ubiquitous graphite, and
hence the role of iron oxides was probably small.

TABLE II. Garnet analyses (localities on fig. 1)

	Elf Hillock	Cadham Crags			
	20G	41G	44G	45G	46G
SiO_2	37·29	37·10	37·08	37·16	36·46
TiO_2	0·41	0·86	0·36	0·14	0·54
Al_2O_3	22·17	22·87	21·53	21·91	22·23
Fe_2O_3	0·29	0·49	0·91	0·83	1·61
FeO	30·10	31·36	30·00	30·30	31·55
MnO	2·48	1·83	2·13	1·27	1·53
MgO	2·80	3·23	2·36	2·60	3·30
CaO	5·01	2·83	5·99	6·04	3·11
	100·55	100·57	100·36	100·25	100·33

Cations to 12 oxygens

Si	2·953	2·926	2·954	2·954	2·902
Ti	0·024	0·051	0·022	0·008	0·032
Al	2·069	2·126	2·022	2·053	2·085
Fe^{3+}	0·017	0·029	0·055	0·050	0·096
Fe^{2+}	1·993	2·069	1·999	2·014	2·100
Mn	0·166	0·122	0·144	0·086	0·103
Mg	0·330	0·380	0·280	0·308	0·391
Ca	0·425	0·239	0·511	0·514	0·265

Partial garnet analyses

		37G	38G	39G
	CaO	4·27	4·97	5·42
	MnO	n.d.	1·19	1·02

Analyses 37–39, 44–46 by J. H. Scoon, 20, 41 by G. A. Chinner.

The Fe/Mg contents of garnet (table II) are strongly affected by the
variable contents of Mn and Ca substituting for them; while the strong
zonation of tourmaline shows that it has not fully reacted with the
system. However, biotite is both unzoned and contains insufficient
interfering atoms to affect the Fe/Mg ratio. By neglecting garnet and
tourmaline, the reaction may be treated in terms of the system K_2O–
Al_2O_3–FeO–MgO–SiO_2–H_2O, with the relevant phases staurolite,
kyanite, muscovite, biotite, and quartz. This differs from Thompson's
(1957) treatment only in that here the high garnet grossular contents
permit the occurrence of garnet with biotite–Al_2SiO_5 assemblages.

The type of reaction one may expect is very well illustrated by the sub-solidus relations of the system $MgO–FeO–SiO_2$ (Bowen and Schairer, 1935) shown in fig. 2. At 1150° C (fig. 2a) the composition (+) is represented by the assemblage pyroxene $a(En_{36.2}Fs_{63.8})$–olivine $x(Fo_{22.7}Fa_{77.3})$. At 1250° (fig. 2b) the pyroxene solid-solution range has retreated to b, and the three-phase triangle has migrated towards the join $MgO–SiO_2$; the composition (+) is now represented by the assemblage
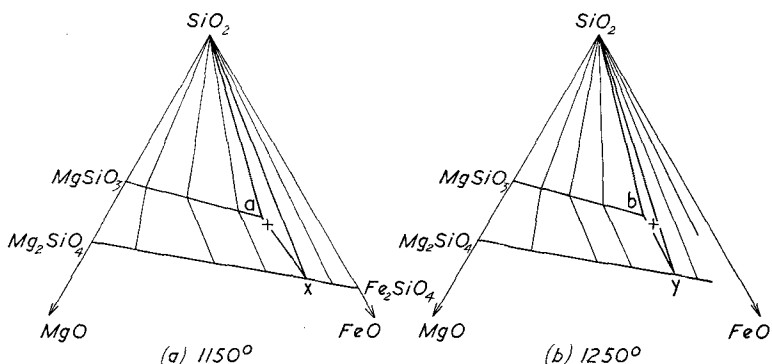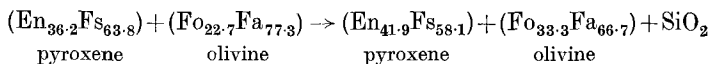

Fig. 2. The system $MgO–FeO–SiO_2$ at one atmosphere pressure (wt. %) showing migration of the three-phase field olivine–pyroxene–SiO_2 as the temperature is raised from (a) 1150° C to (b) 1250° C. On (b) a field of liquid in the vicinity of the fayalite composition has been omitted. (After Bowen and Schairer, 1935.)

pyroxene $b(En_{41.9}Fs_{58.1})$–olivine $y(Fo_{33.3}Fa_{66.7})$–tridymite. Migration of the three-phase triangle has been effected by the reaction:

$$(En_{36.2}Fs_{63.8}) + (Fo_{22.7}Fa_{77.3}) \rightarrow (En_{41.9}Fs_{58.1}) + (Fo_{33.3}Fa_{66.7}) + SiO_2$$

$$\text{pyroxene} \qquad \text{olivine} \qquad \text{pyroxene} \qquad \text{olivine}$$

The proportions depend on the original proportion of pyroxene to olivine.

In Glen Clova it is the solid-solution range of staurolite that is being reduced. Analytical difficulties prevent estimation either of the solid-solution range of staurolite or of the effect of increasing grade on its composition. However, the biotite compositions (table IV) show a consistent pattern which may be summarized, using the cypher

$$M/FM = mol.[MgO \times 100]/[MgO + FeO].$$

Lower grade, Elf Hillock, Inchdowrie:

(i) staurolite assemblages: biotite $M/FM = 54.2 – 55.8$.

Higher grade, Cadham, Inchdowrie:

   (ii) staurolite–kyanite assemblages: biotite $M/FM = 51.7 \pm 0.5$.

   (iii) kyanite assemblages: biotite $M/FM = 50.3–55.5$.

In contrast to the wide range of the few analyses of (i) and (iii), the narrow range of M/FM of (ii) suggests that the staurolite–kyanite assemblages have no more degrees of freedom than a three-phase triangle on fig. 3a.[1]

M/FM values of staurolite-free kyanite schist biotites (iii) straddle the value of (ii). However, since the low value (50.3) corresponds to a biotite separated from a kyanite vein which may have crystallized at a slightly different time and under conditions different from those of the schists surrounding it (page 135), there is some justification for ignoring rock 46 and concluding that kyanite schist biotites have higher M/FM than staurolite–kyanite schist biotites. In this case, at the metamorphic grade corresponding to (ii) and (iii), kyanite-free staurolite schists would contain biotites of M/FM lower than (ii) and (iii), as shown in fig. 3a.

At the lower grade represented by assemblages (i) from Elf Hillock, staurolites of varying $MgO:FeO$ ratio coexist with biotites of a solid solution range for which the maximum M/FM is greater than 55.8. The minimum M/FM is unknown, but from a staurolite–garnet–biotite–muscovite–quartz assemblage of equivalent grade in the West Water, 6 miles east-north-east of Clova, Snelling (1957) records a biotite of $M/FM = 46.2$; the minimum is therefore probably less than this.

From the foregoing data, it follows that the maximum M/FM of kyanite-free staurolite schist biotites is greater at low grades than at high grades. One may then conclude that as the metamorphic grade increases, the volume occupied by the staurolite–biotite–muscovite assemblage is progressively modified as the kyanite–staurolite–biotite–muscovite assemblage moves across from the Mg-rich side. This contention is to some extent supported by the fact that five biotites from graphite-bearing kyanite- or sillimanite-gneisses in the higher-grade Glen Clova sillimanite zone have M/FM varying from 45 to 48 (Chinner, 1960); but since these are not all maximum-phase assemblages, and show strong signs of disequilibrium, too much weight cannot be placed on the fact.

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[1] Garnets from staurolite–kyanite assemblages have, however, widely varying compositions (table 11). This may be rationalized by assuming that the larger system to which garnet belongs has a greater variance than the subsystem involving staurolite–kyanite–biotite–muscovite–quartz.

Movement of the three-phase triangle of fig. 3a is presumably accomplished by successive reactions of the type:
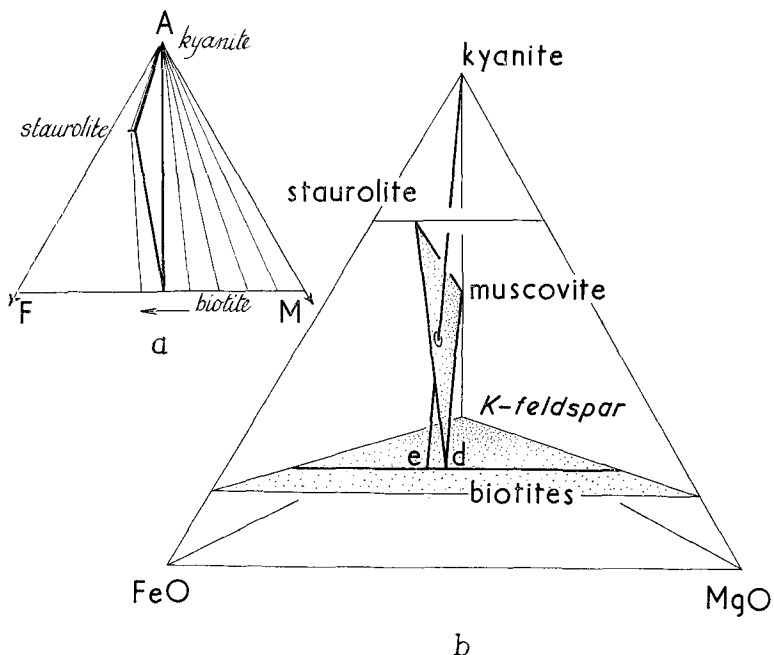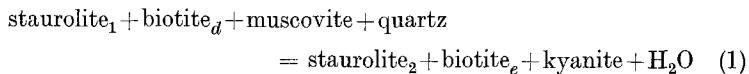
staurolite$_1$+biotite$_d$+muscovite+quartz

$$= \text{staurolite}_2 + \text{biotite}_e + \text{kyanite} + H_2O \quad (1)$$

FIG. 3. (a) Migration of the kyanite–staurolite–biotite (muscovite) field towards more iron-rich compositions illustrated on an $A(Al_2O_3-K_2O)$-$F(FeO)$-$M(MgO)$ diagram (mol. %). Almandine is presumably a phase on the join $A-F$: its phase relations with staurolite and biotite will be similar to those figured by Thompson (1957).

(b) The tetrahedron Al_2SiO_5–$KAlSi_3O_8$–FeO–MgO (mol. %), showing piercing of the plane staurolite–muscovite–biotite$_d$ by the join kyanite–biotite$_e$, quartz in excess.

In this, staurolite$_1$ and biotite$_d$ have MgO:FeO respectively higher than staurolite$_2$ and biotite$_c$. Garnet and tourmaline will adjust their MgO:FeO ratios sympathetically, and their involvement must include feldspar as well. The reaction is shown diagrammatically in fig. 3b where the plane muscovite–staurolite–biotite$_d$ is cut by the join kyanite–biotite$_e$. The P, T interval over which the reaction (1) occurs is primarily a function of the unknown, though probably small, solid solution range of

staurolite. However, for any one rock composition, chemical potential of water being arbitrarily set, the first appearance of kyanite would be univariant, and for a specified M/FM of the minerals the assemblage staurolite–kyanite–biotite–muscovite–quartz would be univariant. In the case of reaction (1) in Glen Clova, the 'univariant' assemblage may be specified by the composition of the biotite M/FM = 51·7.

TABLE III. Chemical analyses of biotites (localities on fig. 1)

	20B	41B	44B	Cations to 24 (O, OH, F)		
SiO_2	35·79	n.d.	35·49	Si	5·292	—	5·298
TiO_2	1·71	n.d.	1·78	Ti	0·190	—	0·200
Al_2O_3	19·44	n.d.	19·78	Al	3·387	—	3·479
Fe_2O_3	1·50	0·76	1·25	Fe^{3+}	0·167	—	0·139
FeO	16·49	17·76	17·35	Fe^{2+}	2·038	—	2·166
MnO	0·03	0·02	0·02	Mn	0·004	—	0·004
MgO	11·45	10·72	10·63	Mg	2·522	—	2·364
CaO	0·00	0·00	0·00	Ca	0·000	—	0·000
Na_2O	0·26	n.d.	0·29	Na	0·075	—	0·084
K_2O	8·51	n.d.	8·64	K	1·605	—	1·647
BaO	0·07	n.d.	0·08	Ba	0·004	—	0·004
H_2O^+	4·36	n.d.	4·09	OH	4·298	—	4·071
F	0·32	n.d.	0·29	F	0·142	—	0·137
H_2O^+	0·01	n.d.	0·06				
C	0·16*	n.d.	0·09*				
	99·97*		99·72*				

* C = graphite impurity; totals less O for F.

Analyst: J. H. Scoon.

Assemblages containing both staurolite and kyanite persist for an interval of some 600 metres after the first appearance of kyanite. The obvious interpretation is that this interval reflects the P, T interval over which reaction (1) sweeps across the composition range of the pelites.[1]

However, if this were so, the biotites should decrease in M/FM as the metamorphic grade increases; and the eight analyses of table IV suggest that biotite compositions over this interval remain constant. Several explanations of this apparent inconsistency follow:

[1] M/FM ratios of pelites with sufficient Al/K to develop staurolite and kyanite are surprisingly constant. Fifty analyses of haematite-free Dalradian pelites with CaO less than 1·5 % culled from the literature had an average M/FM of 28·5 with a standard deviation of 4·0. This, combined with the presumed narrow solid-solution range of staurolite, accounts for the restricted development of kyanite–staurolite assemblages in the Dalradian. Regions in which the kyanite–staurolite assemblage is developed over wide areas were presumably metamorphosed under lower spatial thermal gradients, or else contain rocks of much wider compositional range.

(*a*) A change in biotite composition occurs, but is too small to be detected by the analytical techniques used.

(*b*) The interval represents disequilibrium—the univariant *P*, *T* surface expanded into a volume by fluctuations in physical conditions during recrystallization.

(*c*) Reaction (2) for specified M/FM ratios has greater variance than the univariance suggested. This would be so if the composition of the fluid phase deviated markedly from the system H–O (Wyllie, 1962). An obvious contaminant is CO_2 produced by the reaction of graphite with water released from hydrous minerals, although at high fluid pressures the ratio of $CO_2:(H_2O+H_2)$ would be small. Greater variance might also result if additional components (e.g. Na in muscovite) vitiate the foregoing arguments.

Whatever the precise interpretation, however, it seems possible that the 600-metre uncertainty may prove to be the limit of precision with which the *P*, *T* surface may be identified. At first sight, 600 metres does not seem a serious uncertainty when one is considering the distribution of *P* and *T* over several hundred square miles of terrain; but at high geothermal gradients the temperature variation involved might be considerable—with vertical isograd surfaces and 50° C/km gradient, 600 metres represents 30° C. This is a question which only more data can resolve.

The reaction staurolite+quartz = garnet+kyanite

For many years it has been customary to attribute the disappearance of staurolite with increasing metamorphic grade to the reaction staurolite + quartz = garnet + kyanite. The frequency of its invocation seems to be due more to the elegance of its simplicity than to any indications of its occurrence. Some authors (e.g. Hietanen, 1941) have claimed that the operation of this reaction can be detected visually by an increase in the proportion of garnet; but in this equation the volume increase in garnet is so small that it would be undetectable without detailed modal analysis.[1] Although the reaction is undoubtedly a feasible one, rocks with staurolite as the sole ferromagnesian mineral are rare, and hence it is likely that in most terrains (as in the Scottish Dalradian), staurolite disappears by reaction with other phases long before it becomes incompatible with quartz. The subdivision of the amphibolite facies on the basis of this

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[1] Unless the rocks were originally garnet-free. In another paper Hietanen (1961) records aggregates of kyanite, garnet, and muscovite resembling pseudomorphs after staurolite, but no figures are given.

TABLE IV. Ferromagnesian contents of biotites (wt. %)

(i) Staurolite schists, Elf Hillock

	20†	21	22	23	24
FeO	16·49	15·14	16·84	15·89	16·59
MgO	11·45	10·22	11·59	11·25	11·05
M/FM*	55·3	54·5	55·1	55·8	54·2

(ii) Staurolite-kyanite schists, Cadham Inchdowrie

	35	36	37	38	39	40	41†	42	43
FeO	17·81	17·64	17·21	17·35	17·38	17·78	17·76	17·77	17·75
MgO	10·62	10·66	10·20	10·54	10·64	10·66	10·72	10·57	10·73
M/FM*	51·5	52·1	51·4	51·9	52·1	51·5	51·8	51·5	51·8

(iii) Kyanite schists, Cadham

	44†	45	46
FeO	17·35	16·81	17·34
MgO	10·78	11·76	9·83
M/FM*	52·1	55·5	50·3

Analyst. G. A. Chinner. † By J. H. Scoon (table III).

$$*M/FM = \text{mol.} \ \frac{MgO \times 100}{FeO+MgO}.$$

reaction (Francis, 1956; Fyfe, Turner, and Verhoogen, 1958, p. 230) is thus ill-founded, if not illusory.

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