A former association of enstatite and kyanite

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Summary. An enstatite–cordierite–sillimanite–quartz rock from a pyroxene-granulite facies terrain in southern Rhodesia gives evidence of at least two stages of recrystallization: an early, high-pressure recrystallization to form the assemblage enstatite–kyanite–quartz, and a later, 'retrogressive' recrystallization during which kyanite inverted to sillimanite, and cordierite was formed by reaction. The rock itself has ratios of R^{2+}: Al: Si that are virtually those of cordierite; the recent data of Schreyer (1967) may thus be applied to the occurrence. The early kyanite–enstatite recrystallization occurred under pressures in excess of 10 kb, corresponding to depths greater than those of the continental Moho.

THE coexistence of enstatite and aluminium silicate is precluded at moderate pressures by joins between cordierite and spinel, sapphirine, corundum; at very high pressures, the join pyrope–SiO_2 intervenes (Boyd and England, 1963; Schreyer, 1967). In the presence of water, many more joins occur. Within an intermediate range of pressure and temperature, however, enstatite–sillimanite or enstatite–kyanite form stable assemblages. Although this range appears to be quite extensive— from at least 12 kb to 25 kb at 900 °C (W. Schreyer, pers. comm.)— enstatite–aluminium-silicate associations are but rarely encountered. This rarity reflects the rarity of highly magnesian argillaceous rocks, and possibly also the infrequency with which rocks crystallized at pressures greater than 10 kb are exposed or preserved at the earth's surface.

A collection of basement gneisses from Rhodesia sent to Cambridge by Mr. R. Tyndale-Biscoe of the National Museum, Bulawayo, included samples of a disequilibrium enstatite–sillimanite–corundum–cordierite–quartz rock, which appears at one stage of its history to have been composed of kyanite, enstatite, and quartz. Although no detailed description of its field occurrence is available, the unusual character of this assemblage justifies its description.

The samples described were collected from a locality[2] north-east of Beitbridge on the southern border of Rhodesia. Predominantly grani-

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[2] '2 miles north of the Limpopo River and 250–300 yards east of the Beitbridge Bulawayo road'—R. Tyndale-Biscoe, pers. comm.

toid gneisses of the area appear to form part of a pyroxene-granulite facies terrain belonging to the Limpopo orogenic belt, which bounds the Rhodesian Craton to the south (*ca.* 2900 Myr, Swift, 1961) and contiguous with the Messina series of the Swaziland system in the neighbouring Transvaal (Söhnge, 1946).

Petrography

The rock is white and massive, bearing a superficial resemblance to quartzite, but with colourless plates of enstatite plainly visible on the surface.
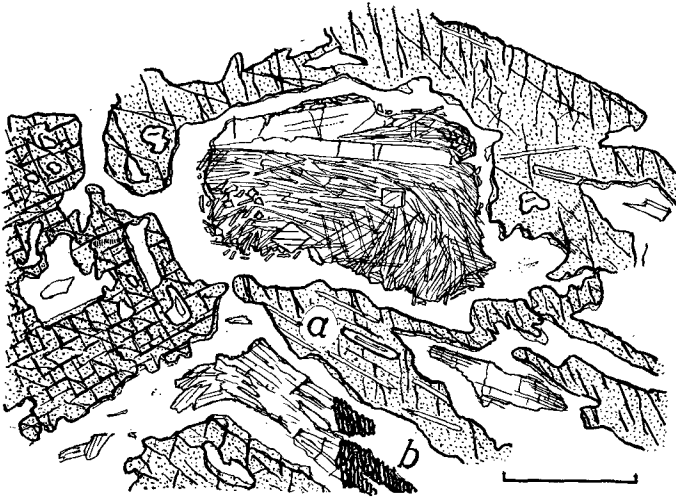

FIG. 1. Micro-drawing of the enstatite–sillimanite–cordierite rock No. 93543. Sillimanite aggregates presumed to be pseudomorphing kyanite are separated from enstatite (stippled) by volumes of cordierite (unornamented): (*a*), enstatite grain with elongate inclusions of cordierite, sometimes containing a sillimanite prism; (*b*), sillimanite has been partly desilicated to form aggregates of corundum (heavily accented). Scale line denotes 750 μ.

The microscopic texture of the rock is dominated by enstatite crystals several millimetres in length, and crystalline sillimanite aggregates of similar size, set in a cordierite ground. *Sillimanite* aggregates are composed of prisms in varying orientation and size; they are almost certainly pseudomorphous after some pre-existing mineral (fig. 1). Isolated rods of sillimanite are occasionally found, usually included in cordierite. *Enstatite* plates shew {210}, {010}, and {100} cleavages, and are

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considerably embayed by cordierite. Many crystals include swarms of cordierite rods, presumably derived by the reaction of original aluminium silicate inclusions with the host enstatite; occasional relicts of sillimanite are preserved within a rod.

Sillimanite and enstatite are invariably separated by rims of *cordierite*. Cordierite is generally unaltered, although in places pinitic or micaceous alteration products occur. Occasional cordierite may form larger granular volumes, and in such may be associated with quartz in almost micrographic intergrowth. Monazite inclusions in cordierite show no pleochroic haloes.

The distribution of quartz is very irregular—portions of the rock may be quartz-free, and in these corundum may appear, usually as compact aggregations of rods pseudomorphing sillimanite grains. The possibility that some such fine-grained corundum might in fact be sapphirine was tested by the electron probe, but no crystals examined contained magnesium. Yoderite, kyanite, gedrite, and magnesium staurolite were also sought for but not found. Opaque minerals are absent.

Mineral chemistry

Electron-probe analyses of minerals given in Table I were made using the Cambridge Instrument Company Geoscan. The instrument, which has an X-ray take-off angle of 75°, was operated at a beam accelerating voltage of 15 kV and a probe current of 0·3 μA.

Pure metals were used as standards for titanium, manganese, and iron, synthetic periclase for magnesium, and natural corundum, quartz, and wollastonite for aluminium, silicon, and calcium respectively.

Analyses were made at a minimum of three positions on each of five enstatite, three cordierite, and three sillimanite grains. Following the correction of the X-ray intensities for background and resolving time losses, 'apparent percentages' were obtained by comparison of the counting rates from standards with those from the unknown. These 'apparent percentages' were corrected for absorption, fluorescence, and atomic number effects: absorption correction utilized the modified form of Philibert's equation (Duncumb and Shields, 1966) with σ value calculated from Heinrich's (1967) expression for voltage dependence, and mass absorption coefficients compiled by the same author (Heinrich, 1966); fluorescence correction, procedure proposed by Reed (1965); atomic number correction, Duncumb and Reed (1967).

Counting times were such that errors due to counting statistics would be less than 1 % for magnesium, aluminium, silicon, and iron in all cases. While it is difficult to determine precisely the magnitude of errors resulting from the correction procedures used, comparison with the analysis of a number of standard minerals of similar composition to those involved in the study suggests that the relative error for these elements, when present as major constituents, would be less than 2 %.

For the minor elements calcium, manganese, titanium, and (in the case of cordierite and sillimanite) iron, counting times of 200 seconds on both peak and background were used. Defining the 'limit of detection' as the concentration that

corresponds to a net line count of three times the standard deviation of the background count the limits would be of the order of 30 ppm for titanium and manganese and 100 ppm for calcium. These limits are not exceeded in cordierite and sillimanite.

TABLE I. Chemical composition of minerals from enstatite–sillimanite–cordierite rock 93543, and of the rock. Minerals by electron-probe, rock by X-ray fluorescence.

	1	2	3	4	5
SiO_2	55·79	55·59	37·05	50·65	51·71
TiO_2	0·045	0·045	0·00	0·00	0·04
Al_2O_3	5·56	5·69	62·33	33·49	32·49
Fe_2O_3	—	—	0·60†	—	0·12
FeO	2·25*	2·19*	—	0·31*	0·58‡
MnO	0·015	0·020	0·00	0·00	0·01
MgO	35·81	35·90	0·00	13·35	14·26
CaO	0·065	0·070	0·00	0·00	0·05
H_2O^+	n.d.	n.d.	n.d.	2·00	0·87§
Sum	99·54	99·51	99·98	99·80	100·26‖

Atomic ratios to N oxygen

	N	*6*	*6*	*5*	*18*	*18*
Si		1·89	1·89	1·00	4·98	5·07
Al^{iv}		0·11	0·11	1·00	1·02 ⎱	3·77
Al^{vi}		0·11	0·11	0·98	2·86 ⎰	
Fe		0·06	0·06	0·01	0·25	0·05
Mg		1·81	1·82	—	1·96	2·09
Ca		0·002	0·003	—	—	—

1 and 2. Enstatite.   5. Enstatite–cordierite–sillimanite rock. Beitbridge,
3. Sillimanite.   Rhodesia. (Anal. K. Norrish, method of Norrish and
4. Cordierite.   Chappell, 1967)

* Total iron as FeO.   † Total iron as Fe_2O_3.
‡ $KMnO_4$ titration by J. H. Scoon.   § Loss on ignition.
‖ Also 0·09 % Na_2O, 0·04 % K_2O.

Enstatites, with only 3 % Fe in (Fe+Mg), show a close approach to the system $MgO–Al_2O_3–SiO_2$. Measurements of Fe:Mg on other grains did not show significant variation from this figure. Aluminium contents, however, were variable from grain to grain. The median of 12 measurements was 5·81 wt. % Al_2O_3, but values ranged from 4·76 to 8·35. The differential in R.I. between cordierite and enstatite being considerable, it was not always possible to correlate values with position in a grain, but the maximum value (8·35) was certainly measured from the centre of a grain that showed decreasing Al_2O_3 contents (to 5·56) at the margin. The lowest value, corresponding to 0·2 Al per

$R_2Si_2O_6$ formula unit, probably represents that of pyroxene in equi-
librium with cordierite. The *cordierite* is virtually the magnesian end-
member; a number of measurements showed no significant variation of
the Fe/Mg ratio within or between cordierite grains. The *sillimanite*
iron content—0·60 % as Fe_2O_3—is by no means exceptional for silli-
manites in granulite facies environments (Chinner, Smith, and Knowles,
1968).

Interpretation

It is apparent that the cordierite now occurring is a 'retrogressive'
reaction product, and that prior to its formation the rock had been
crystallized, at pressures above the appropriate maximum for cordierite,
to the assemblage enstatite–Al_2SiO_5–quartz. The sillimanite now present
in the rock appearing pseudomorphous, it seems likely that the Al_2SiO_5
mineral present in the high-pressure assemblage was the high-pressure
polymorph kyanite.

Boyd and England (1963) have demonstrated that, below the mini-
mum pressures of pyrope stability, increasing pressure promotes the
formation of aluminous orthopyroxenes by the coupled substitution of
$Al^{[6]}Al^{[4]}$ for $Mg^{[6]}Si^{[4]}$. Maximum Al contents at any pressure will,
however, only be shown by enstatites from assemblages such as en-
statite–sapphirine–Al_2SiO_5 or sapphirine–enstatite (fig. 2); enstatites
from quartz-bearing assemblages would show Al contents less than the
maximum. The moderate Al_2O_3 contents of table I are thus not sur-
prising. These, however, do represent the composition of pyroxenes that
have partly adjusted to equilibrium with cordierite during the 'retro-
gressive' recrystallization. The preservation, in some cores, of Al_2O_3
contents as high as 8·35 wt. % (p. 1055) gives a minimum figure for the
Al content at the pressures of kyanite–enstatite crystallization; the
actual figure may have been higher. The maze of cleavages and partings
in most pyroxene crystals presumably aided relatively rapid loss of Al
by grain-boundary diffusion. The possibility that the swarms of
cordierite rods included within some enstatites represent reaction be-
tween host enstatite and alumina exsolved from it seems small, for the
rods are rarely oriented parallel to any specific crystallographic direction,
and the relict mineral within some of them is not corundum, but silli-
manite.

The reaction of enstatite and Al_2SiO_5 to produce cordierite consumes
silica:

$$2MgSiO_3 + 2Al_2SiO_5 + SiO_2 \rightarrow Mg_2Al_4Si_5O_{18}$$
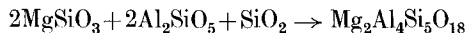
Irregularity in the initial distribution of quartz resulted in local desilication—not of cordierite to spinel or to sapphirine, but of sillimanite to corundum. Thus under the physical conditions of the 'retrogressive' recrystallization, the join cordierite–corundum, rather than the alternatives sillimanite–spinel or sillimanite–sapphirine, was stable.
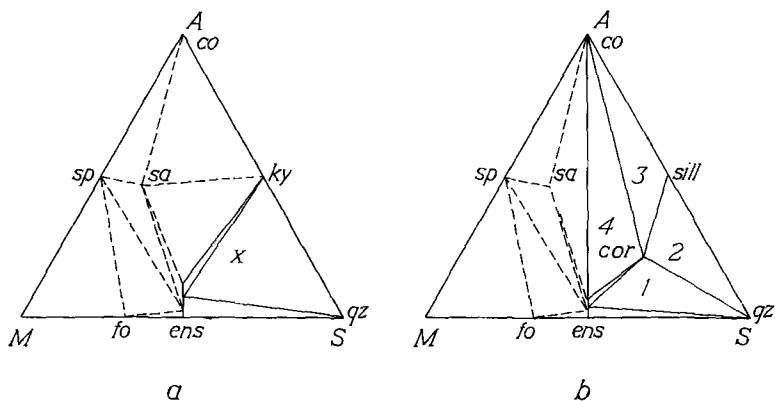

Fig. 2. The system MgO (M)–Al$_2$O$_3$ (A)–SiO$_2$ (S) at: (a) higher pressures of kyanite–enstatite equilibrium; and (b) the lower pressures of 'retrogressive' recrystallization. Dashed joins putative. X marks the cordierite composition. In (b) Nos. 1–4 refer to the assemblages deduced in the text. Possible hydrous minerals (yoderite, talc, gedrite, Mg-staurolite) omitted. co, corundum; cor, cordierite; ens, enstatite; fo, forsterite; ky, kyanite; qz, quartz; sa, sapphirine; sill, sillimanite; sp, spinel.

Another desilicated local 'retrogressive' assemblage is indicated by the absence of sapphirine and the close association of cordierite, enstatite, and corundum, suggesting the stability of the join enstatite–corundum rather than cordierite–sapphirine.

The constancy in cordierite Fe/Mg ratios, however, indicates that Fe and Mg diffused more rapidly than Si and Al, and were able to achieve an approach to chemical equilibrium. The three-phase assemblages stable during the retrogressive metamorphism are thus likely to have been:

enstatite–cordierite–SiO$_2$; sillimanite–cordierite–SiO$_2$; corundum–cordierite–sillimanite; enstatite–cordierite–corundum; these form the fields numbered 1 to 4 respectively of fig. 2.

P–T conditions of formation

The Al content of enstatite in specific assemblages will no doubt in the future prove a reliable indicator of pressure and temperature, but as yet insufficient experimental data are available for it to be used.

The unusual composition of the rock, however, lying very close to the join $MgO-Al_2O_3-SiO_2$, makes recent experimental work directly relevant to its occurrence. A chemical analysis of the rock (table I) shows that not only is 98 % of the rock composed of the three oxides MgO, Al_2O_3, and SiO_2, but also the three element groupings (Fe+Mg), Al, and Si occur in the ratio 2·13:3·77:5·07—virtually those of cordierite. The likelihood that any fortuitous aggregation of sedimentary materials would produce the $Mg_2Al_4Si_5O_{18}$ ratio seems to be so small that it is tempting to consider the rock, prior to its enstatite–kyanite crystalliza-tion, to have been a metamorphic segregation of cordierite. One is, however, given pause by the occurrence in other high-grade terrains of undoubted metasediments showing the unusual combination of high Al and Mg with a virtual absence of alkalis. The yoderite–talc schist of Mautia Hill, Tanzania (McKie, 1959) is a good example. Given that no metasomatic process is assumed to have operated, such rocks must represent original bentonitic sediments; in view of the wide range of possible montmorillonite compositions, (cf. Schreyer and Yoder, 1964, p.284) it cannot perhaps be said that the probability of producing the $Mg_2Al_4Si_5$ ratio in a bentonite is any less than that of producing any other combination of Mg, Al, and Si. Nonetheless, the coincidence between the R^{2+}:Al:Si of this rock and that of cordierite is remarkable, and it is regrettable that no field data bearing on the point are available.

Whatever the origin of the present chemistry, however, it is possible to regard the rock as essentially Mg-cordierite and to apply the recent experimental data of Schreyer (1967) to its occurrence. Fig. 3 indicates that, for $P_{H_2O} = P_{tot}$, the kyanite–enstatite–quartz assemblage occupies a narrow field between 825 and 950 °C, at pressures in excess of 10 kb. For $P_{H_2O} < P_{tot}$, the kyanite–enstatite–quartz field would be extended to lower and higher temperatures; pressures would however, still be in excess of those of the extension of the curve representing the reaction kyanite + enstatite + quartz → cordierite, i.e., the line AB on fig. 3. Given that granulite facies temperatures are likely to be in excess of 700 °C, (cf. Winkler, 1964), the Beitbridge kyanite–enstatite–quartz assemblage would appear to have crystallized at pressures above 10 kb, corresponding on the load-pressure assumption to depths greater than those of the continental Moho.

The 'retrogressive' recrystallization doubtless occurred under con-ditions of decreasing pressure. The P/T conditions of retrogression lay within the field of sillimanite stability and also within those of the stability of the assemblages *cordierite–corundum* and *corundum–enstatite*.
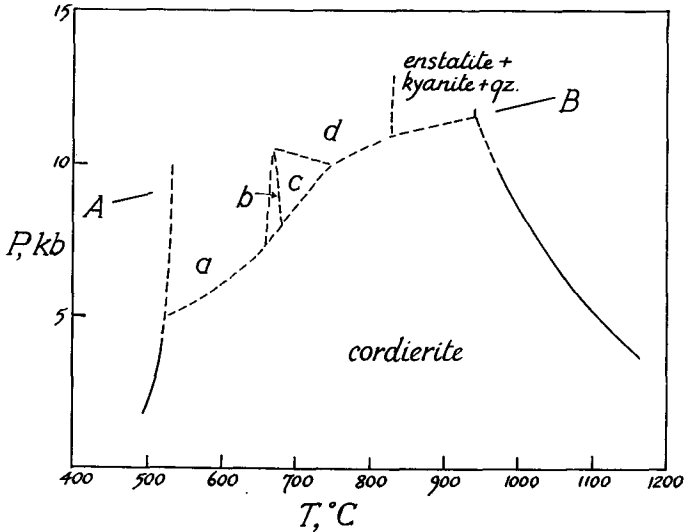
Fig. 3. Preliminary P/T stability field of Mg-cordierite, $P_{H_2O} = P_{tot}$, after Schreyer (1967). Letters refer to unlabelled stability fields: (a), Al_2SiO_5-chlorite-quartz; (b), yoderite-chlorite-quartz; (c), yoderite-talc-quartz; (d), talc-kyanite-quartz. The line AB is the extension of the curve for the reaction cordierite $\rightarrow$ enstatite + kyanite + quartz.

The association *cordierite–corundum* rather than the equivalent sapphirine–sillimanite is recorded by Yoder and Fawcett at 10 kb and 900 °C, and by Schreyer (pers. comm.) between 8 and 9 kb, 800–50 °C. Similarly *corundum–enstatite* appears to be an intermediate, rather than a low-pressure join. The reaction

cordierite + sapphirine $\rightarrow$ enstatite + corundum,
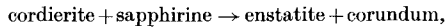
proceeds to the right at pressures between 8 and 10 kb and temperatures *ca.* 850 °C. The 'retrogressive' metamorphism is thus unlikely to have been associated with any substantial diminution of depth.

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