Chemical study of pyroxenes from the charnockitic rocks of Kondapalli (Andhra Pradesh), India, with emphasis on the distribution of elements in coexisting pyroxenes

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Summary. The chemical analyses, structural formulae, and trace element data are presented for 18 orthopyroxenes and 9 clinopyroxenes from the charnockitic rocks of Kondapalli, Andhra Pradesh, India. The chemistry of these pyroxenes is discussed and conclusions are drawn. The data are compared with the similar data available for the pyroxenes of the charnockites of the type area near Madras, some 200 miles south of Kondapalli. The element-distributional relationships between the coexisting pyroxenes are discussed and inferences are made regarding the temperature of crystallization of charnockite pyroxenes.

THE hill ranges of Kondapalli (16° 37′ N., 80° 32½′ E.), Krishna district, Andhra Pradesh State, form a part of the Eastern Ghats belt of the charnockitic region of peninsular India and are known for the occurrence of charnockites in their full variety in association with the basement complex of the khondalitic suite of rocks. The bulk of the hill ranges consist of rocks of the different divisions of the charnockite series, while the khondalites (quartz–feldspar–biotite–garnet–sillimanite gneisses), leptynites (reconstituted khondalites), granitic gneisses, and anorthosites have a restricted distribution. A large number of pegmatites, a few aplitic veins, and rare dolerite dykes also occur in the area. The ultrabasic charnockites occur as dykes or lenses in basic or intermediate charnockites. The basic charnockites, in addition to the intermediate and acid varieties, occur as hill masses; they also occur as dykes, bands, or lenses, occasionally in khondalites and rarely in less basic charnockites. The terms 'ultrabasic charnockite', 'basic charnockite', 'intermediate charnockite', and 'acid charnockite' are employed here corresponding to the ultrabasic, basic, intermediate, and acid

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divisions of the charnockite series of Holland (1900), without any signi-
ficance to the genetic relationship or otherwise among the different
divisions (see discussion on the paper by Cooray, 1962). A detailed
discussion on the nomenclature, the exact field relationships of the
Kondapalli charnockites, and a petrographic account are deferred to
a later publication, while in this paper an attempt is made to present the
chemical data obtained on the pyroxenes from the charnockitic and
associated ultrabasic rocks of Kondapalli, to make direct comparisons
with the excellent data available for the type area near Madras, some
200 miles south of Kondapalli, and to evaluate the element distribu-
tional relationships in coexisting ortho- and clino-pyroxenes of the
Indian charnockites.

The Kondapalli orthopyroxenes show rare schiller structure, wavy
extinction, and bent cleavage. They occasionally contain (100) lamellae
of clinopyroxene, reddish brown ilmenite plates, opaque needles, and
rarely plagioclase lamellae. Preliminary single-crystal X-ray work in-
dicated that a few orthopyroxenes contain 'twinned' augite lamellae
parallel to (100). The lamellae of clinopyroxene, plagioclase, and
ilmenite were confirmed, in some examples, by the use of the electron
microprobe X-ray analyser. The Kondapalli clinopyroxenes exhibit
rare wavy extinction and poorly defined (100) or (010) parting. They
occasionally contain (100) lamellae of orthopyroxene. Single-crystal
X-ray work revealed that a few clinopyroxenes contain (100) ortho-
pyroxene lamellae and also spinel (? hercynite, with cell-size less than
that of magnetite, Dr. M. G. Bown, *pers. comm.*). Whether there is
any systematic relationship between the incidence of the lamellae
and bending of the host grains is not quite clear, though it appears
that bent crystals exhibit lamellae that broaden at the maximum
curvature of the bend. A few exhibit severe cataclastic effects and the
lamellae are then markedly bent.

The pyroxenes were separated and purified by using an isodynamic
separator and centrifuging in Clerici's solution; the purity of the samples
was finally checked by two independent workers. It is estimated that
all the samples were not less than 99·5% pure. Classical chemical
methods were followed for the analysis of the minerals; Ti and Mn were
determined colorimetrically and the alkalis by flame photometry. Total
iron was determined by titration with standard ceric sulphate, and
ferrous iron was determined against standard permanganate solution;
the FeO of all the analysed pyroxenes was determined in duplicate, and
often in triplicate or quadruplicate.

Orthopyroxenes

The analyses of 18 Kondapalli orthopyroxenes, arranged in the increasing order of Fe^{2+}/Mg ratio, are presented in table I, together with their trace element contents and their structural formulae calculated on the basis of 6 oxygens. The orthopyroxenes display a considerable range in composition, and the ratio $100Mg/(Mg+Fe^{3+}+Fe^{2+}+Mn)$ varies from 91·6 to 41·9. The orthopyroxenes 48 and 323 are more magnesian than the orthopyroxenes from the ultrabasic chronockites of the type area (Howie, 1955). As far as the author is aware, the orthopyroxene 48 (En_{92}) is more magnesian than any analysed orthopyroxenes reported from other granulitic terraines of the world; but Fuchs (1965) recently reported an orthopyroxene (En_{97}, determined from optical data) from Kondapalli more magnesian than the orthopyroxene 48. It is difficult to decide whether the host rock 48 (enstatite) belongs to the charnockitic group or whether it represents a different suite of ultrabasics. Table II shows the comparison of the variation in different constituents between the Kondapalli and Madras orthopyroxenes.

The amount of Al in the Z group is generally much greater than the Al in the Y group. The Al content is variable and there is no systematic decrease with increase in Fe. The orthopyroxenes from the Kondapalli ultrabasic charnockites all contain more than 2·5 % Al_2O_3 compared with an upper limit of about 2 % in orthopyroxenes of igneous rocks (Muir, 1951). The highest amount, Al_2O_3 5·4 %, occurs in the orthopyroxene from the ultrabasic lens J22, which is very rich in Al_2O_3 and which contains an alumina-rich spinel. The basic charnockite orthopyroxenes, as a group, have less Al_2O_3 than the ultrabasic charnockite orthopyroxenes. The orthopyroxenes from acid charnockite (M12) and enderbites (B4 and 322) contain slightly less than 4 % Al_2O_3. The highest amount of Al_2O_3 (5·76 %) for a hypersthene from a garnetiferous enderbite from the type area is reported by Howie (1963), while the lowest value, 0·96 %, for a eulite from non-garnetiferous enderbite is given by Subramaniam (1962). It appears that the orthopyroxenes of garnetiferous enderbites have higher Al_2O_3 content than those of non-garnetiferous enderbites. The garnet-bearing granulites of Lapland (Eskola, 1952) also contain orthopyroxenes with high amounts of Al_2O_3 (8·26 and 4·51 %) and these are inferred by Boyd and MacGregor (1964) to have been formed approximately at 700° C and 10 Kb.

The cause of the high and variable nature of the Al_2O_3 content in the granulite orthopyroxenes is not properly understood. Eskola (1957)

TABLE I. Orthopyroxene Analyses. Analyst: C. Leelanandam

	48 UBC	323 UBC(L)	J22 UBC(L)	D14 UBC	431 UBC	28 BC(L)	61 Ans	G17 BC	220 BC(L)
SiO_2	56·46	54·24	50·69	51·69	51·01	50·81	51·24	51·42	50·79
TiO_2	0·10	0·27	0·33	0·43	0·20	0·38	0·26	0·24	0·27
Al_2O_3	3·24	3·33	5·40	2·51	3·66	3·20	2·16	1·34	2·18
Fe_2O_3	0·48	0·31	1·86	1·29	1·06	0·14	1·14	1·19	1·01
FeO	5·20	11·67	15·33	21·41	22·22	24·36	24·75	25·25	26·25
MnO	0·11	0·24	0·63	0·38	0·48	0·60	0·45	0·61	0·84
MgO	34·80	29·71	24·99	22·29	21·69	19·51	19·64	18·68	18·87
CaO	0·18	0·51	0·47	0·53	0·26	0·64	0·60	1·02	0·18
Na_2O	—	0·03	0·13	0·02	0·04	0·11	0·02	0·06	0·02
K_2O	—	—	0·02	—	0·04	0·02	0·02	0·04	0·02
H_2O^+	0·10	—	—	n.d.	n.d.	0·10	n.d.	0·08	n.d.
H_2O^-	0·03	0·03	0·05	0·03	0·08	0·05	0·02	0·01	0·04
Total	100·70	100·34	99·90	100·58	100·74	99·92	100·30	99·94	100·47

Numbers of metal atoms on the basis of 6 oxygens:

Si	1·927	1·915	1·846	1·915	1·893	1·920	1·934	1·958	1·929
Al $\begin{cases} \\ \end{cases}$	0·073	0·085	0·154	0·085	0·107	0·080	0·066	0·042	0·071
	0·057	0·054	0·078	0·025	0·053	0·063	0·030	0·018	0·027
Ti	0·003	0·007	0·009	0·012	0·006	0·011	0·007	0·007	0·008
Fe^{3+}	0·012	0·008	0·051	0·036	0·030	0·004	0·032	0·034	0·029
Fe^{2+}	0·148	0·345	0·467	0·663	0·690	0·770	0·781	0·804	0·834
Mn	0·003	0·007	0·019	0·012	0·015	0·019	0·014	0·020	0·027
Mg	1·770	1·563	1·356	1·231	1·200	1·099	1·105	1·060	1·068
Ca	0·007	0·019	0·018	0·021	0·010	0·026	0·024	0·042	0·007
Na	—	0·002	0·009	0·001	0·003	0·008	0·001	0·004	0·001
K	—	—	0·001	—	0·002	0·001	0·001	0·002	0·001
$X + Y$	2·000	2·005	2·008	2·001	2·009	2·001	1·995	1·991	2·002
R^*	91·57	81·28	71·63	63·39	62·02	58·09	57·19	55·27	54·55
Fe^{2+}/Mg	0·08	0·22	0·34	0·54	0·58	0·70	0·71	0·76	0·78
Ca	0·36	0·98	0·94	1·07	0·51	1·36	1·23	2·14	0·36
Mg	91·24	80·48	70·96	62·71	61·70	57·30	56·49	54·08	54·35
$\Sigma\dagger$	8·40	18·54	28·10	36·22	37·79	41·34	42·28	43·78	45·29

Trace elements$\ddagger$ (in ppm.):

Ga	2	3	3	11	11	11	8	11	11
Cr	3200	2500	22	465	465	100	125	46	125
Ni	1200	700	35	350	700	125	350	125	200
Co	45	125	28	125	125	125	125	125	80
V	18	100	100	100	42	100	100	42	6
Zr	—	28	56	70	100	100	70	100	160
Sc	—	—	22	—	—	45	—	18	—
Yt	—	—	—	—	—	—	—	—	—
Pb	—	—	—	—	—	—	—	—	—
Ba	—	—	—	—	—	—	—	—	—
Cu	—	—	—	10	220	—	22	10	—
Sn	—	—	—	—	—	220	—	—	100

* $100Mg/(Mg + Fe^{3+} + Fe^{2+} + Mn)$.
$\dagger$ $Fe^{3+} + Fe^{2+} + Mn$.
$\ddagger$ Determined by Mr. R. S. Allen.

TABLE I (*cont.*)

	474 BC	P45 BC(D)	382 AC(L)	62 AC	A18 BC	M12 AC	B4 AC	S1 AC	322 AC
SiO_2	50·97	50·45	49·84	50·07	50·50	49·07	48·33	48·81	47·46
TiO_2	0·28	0·33	0·35	0·38	0·30	0·40	0·41	0·42	0·30
Al_2O_3	2·49	1·67	2·75	2·51	1·92	3·95	3·96	2·07	3·82
Fe_2O_3	0·34	0·70	0·36	0·60	1·02	0·47	0·47	1·10	1·29
FeO	26·12	27·31	28·91	28·39	28·89	29·88	31·23	31·89	31·91
MnO	0·65	0·52	0·54	0·57	0·98	0·12	0·53	0·40	0·62
MgO	18·18	17·94	17·23	16·78	16·17	15·99	14·95	14·18	13·61
CaO	0·75	0·68	0·39	0·64	0·57	0·38	0·14	0·66	0·85
Na_2O	0·06	0·06	0·06	0·11	0·03	n.d.	0·03	0·01	0·02
K_2O	0·02	0·06	0·04	0·05	0·02	n.d.	0·01	0·02	0·01
H_2O^+	0·09	0·16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H_2O^-	0·03	0·03	0·08	0·04	0·02	n.d.	0·02	0·14	0·11
Total	99·98	99·91	100·55	100·14	100·42	100·26	100·08	99·70	100·00

Numbers of metal atoms on the basis of 6 oxygens

	474	P45	382	62	A18	M12	B4	S1	322
Si	1·942	1·941	1·913	1·927	1·946	1·892	1·885	1·926	1·873
Al	{0·058	0·059	0·087	0·073	0·054	0·108	0·115	0·074	0·127
	{0·054	0·017	0·037	0·041	0·033	0·072	0·067	0·022	0·051
Ti	0·008	0·010	0·010	0·011	0·009	0·012	0·012	0·012	0·009
Fe^{3+}	0·010	0·020	0·010	0·017	0·030	0·014	0·014	0·033	0·033
Fe^{2+}	0·832	0·879	0·928	0·914	0·931	0·964	1·019	1·053	1·053
Mn	0·021	0·017	0·018	0·019	0·032	0·004	0·018	0·013	0·021
Mg	1·032	1·028	0·986	0·963	0·928	0·919	0·869	0·834	0·801
Ca	0·031	0·028	0·016	0·026	0·024	0·016	0·006	0·028	0·036
Na	0·004	0·004	0·004	0·008	0·002	—	0·002	0·001	0·002
K	0·001	0·003	0·002	0·002	0·001	—	—	0·001	0·001
$X+Y$	1·993	2·006	2·011	2·001	1·990	2·001	2·007	1·997	2·007

	474	P45	382	62	A18	M12	B4	S1	322
R^*	54·46	52·88	50·77	50·34	48·31	48·34	45·26	43·15	41·87
Fe^{2+}/Mg	0·81	0·86	0·94	0·95	1·00	1·05	1·17	1·26	1·32
Ca	1·61	1·42	0·82	1·34	1·23	0·83	0·31	1·43	1·85
Mg	53·58	52·13	50·36	49·66	47·71	47·94	45·12	42·53	41·10
$\Sigma\dagger$	44·81	46·45	48·82	48·99	51·05	51·22	54·57	56·04	57·05

Trace elements (in ppm):

	474	P45	382	62	A18	M12	B4	S1	322
Ga	11	11	16	8	22	—	16	16	11
Cr	46	70	260	46	180	—	125	28	—
Ni	125	38	160	65	100	—	65	35	28
Co	125	45	80	45	100	—	65	65	45
V	54	100	140	42	140	—	180	54	—
Zr	100	100	125	100	125	—	125	125	100
Sc	22	45	70	18	40	—	56	70	450
Yt	—	—	25	—	—	—	25	12	45
Pb	—	—	—	—	—	—	—	55	—
Ba	—	22	—	—	—	—	—	—	—
Cu	—	60	22	10	—	—	—	18	—
Sn	45	270	55	—	100	—	—	270	220

* $100Mg/(Mg+Fe^{3+}+Fe^{2+}+Mn)$.   † $Fe^{3+}+Fe^{2+}+Mn$.

Key to Tables I and III

UBC = ultrabasic charnockite, BC = basic charnockite, AC = acid or intermediate charnockite, Ans = anorthosite.
D = dyke, L = lens; Opx = orthopyroxene, Cpx = clinopyroxene, Hb = hornblende, Bi = biotite, Gt = garnet, Qtz = quartz, Kf = potassium feldspar (orthoclase perthite); specimens contain traces of apatite, zircon, secondary calcite and scapolite, and the five-digit numbers apply to the collection in the Department of Mineralogy and Petrology, Cambridge. The mineral assemblages of the host rocks and localities are given below:

48. Opx; Ore, Cpx, Plag (96243); south of the hill .766.
323. Opx; Cpx, Plg (96245); top of Nakkal Banda.
J22. Opx, Hb; green spinel, Plag, Ore (96247); south of Hyder Banda.
D14. Cpx; Hb, Plag, Opx (96242), near the Binny chromite quarry.
431. Hb, Bi; Opx, Plag (96250); hill west of Erra Burju.
28. Plg; Opx, Hb, Cpx; Bi, Qtz, Ore, Gt (96256); hill .472.
61. Plag; Opx, Cpx; Hb, Bi (96265); east of Koyya Gutta .1003.
G17. Plag, Cpx, Opx; Hb, Ore, Bi (96258); southern tip of the hill .305.
220. Plag, Hb, Bi; Opx, Ore, Qtz, Gt (96252); southern flank of Ontimanu Gutta Δ 1406.
474. Plag, Cpx, Opx; Ore, Hb (96257); northern flank of the hill .305.
P45. Plag, Bi, Opx; Qtz, Cpx, Kf, Ore (96259); southern fringe of Balija Gutta .707.
382. Plag, Opx; Qtz, Bi; Gt, Ore, Kf (96273); north-east of Sudda Bodu.
62. Plag, Qtz; Kf, Opx; Ore, Cpx, Hb, Bi (96275); hill .317.
A18. Plag, Opx, Hb, Bi; Cpx, Qtz, Gt, Ore (96251); north-western portion of the mound west of Toll near Kondapalli R.S.
M12. Qtz, Kf; Plag, Gt; Opx, Ore, Bi (96281); north-west of Edlakonda .1482.
B4. Plag, Qtz; Opx, Kf; Gt, Bi (96282); northern face of the hill west of Toll.
S1. Kf, Qtz, Plag; Gt, Bi, Ore, Opx (96280); quarry west of Toll.
322. Qtz, Plag; Ore, Opx; Gt (96293); eastern face of Nakkal Banda.
472. Cpx; Opx, Plag (96249); hill north of Kotta Ibrahimpatnam village (table III).

attributed the high alumina in the pyroxenes to high pressures. Though the experimental work of Boyd and England (1960) suggests that higher Al_2O_3 is favoured by higher pressures, it does not seem to be valid universally. Parras (1958) reported two analyses of charnockite orthopyroxenes from south-western Finland and aluminium is absent from both of them. Howie (1964) reported a hypersthene with 7·21 % Al_2O_3 from a thermally metamorphosed silica-poor argillaceous rock that was not formed under high pressures, while O'Hara and Mercy (1963) have demonstrated that orthopyroxenes from garnet-peridotites, formed in an alumina-bearing high-pressure environment, have a low Al_2O_3 content in comparison with the alumina contents of orthopyroxenes in peridotite nodules in basalts. The recent work of Boyd and England (1964), MacGregor and Ringwood (1964), and Skinner and Boyd (1964) shows that the Al_2O_3 in enstatite drops markedly when pyrope appears

as a stable phase, though pressure is increased. Binns (1965) indicated that Al contents of isogradic pyroxenes from the Broken Hill area depend very much upon host-rock chemistry and the nature of coexisting phases; he also suggested that the more aluminous pyroxenes coexist with more sodic plagioclases and that the low Al contents of Broken Hill pyroxenes, compared to those from certain other metamorphic terraines, may reflect the relatively low sodium contents of their host rocks rather than differences in pressure conditions. Murty (1965)

TABLE II. Comparison of the variation in composition
of 18 Kondapalli and 19 Madras orthopyroxenes

	Kondapalli	Madras
SiO_2	47·46–56·46%	46·17–52·54%
TiO_2	0·10–0·43	0·10–1·78
Al_2O_3	1·34–5·40	0·96–5·76
Fe_2O_3	0·10–1·86	0·54–1·98
FeO	5·20–31·91	15·28–38·06
MnO	0·11–0·98	0·17–1·03
MgO	13·61–34·80	7·86–26·65
CaO	0·14–1·02	0·06–2·24
Na_2O	< 0·1	< 0·5
K_2O	< 0·06	< 0·5
Cr	22–3200 ppm	25–300 ppm
Ni	28–1200	8–650
Ga	2–22	5–30
Co	28–125	25–100
V	6–180	100–200

attributed the aluminous nature of the hypersthene from the Visakhapatnam (India) charnockite to its formation from aluminium-bearing minerals like hornblende, biotite, and garnet. The available analytical data suggest that the Al_2O_3 content of the orthopyroxenes from the rocks of granulite facies is controlled by a variety of factors such as the host-rock chemistry, presence and amounts of alumina-bearing minerals in the rock, and nature of the environment, especially with reference to its enrichment or impoverishment in Al_2O_3. If these conditions are nearly the same for a set of rock types, then pressure seems to favour the formation of high-alumina orthopyroxenes.

The Kondapalli orthopyroxenes always contain less than 0·5 % TiO_2, while in those of Madras acid charnockites the value goes up to 1·8 %. Murty (1964a, 1964b) has concluded that the Ti content can be correlated with the strength of pleochroism in the orthopyroxenes of the Visakhapatnam charnockites. Howie (1963) has established that the pleochroism in charnockite orthopyroxenes is largely a 'physical effect' of

contraction in their cell parameters by incorporation of increasing amounts of Al in the structure. Subramaniam (1962) related the intensity and colours of the pleochroism to the presence of minor amounts of Ni or Cr. Binns (1965) found no correlation between depth of pleochroism of Broken Hill orthopyroxenes and content of Fe, Mn, or Ti, or of the trace elements Ni and Cr. None of these postulates, however, explain systematically the observed variations in strength and intensity of the pleochroism in the large number of Kondapalli orthopyroxenes and exceptions from any or all of the above explanations are not uncommon. It is likely that the pleochroism may not be directly related to any one particular element, but a combination of chemical factors may possibly have some influence. Recently Burns (1966) concluded that the necessary conditions for optical pleochroism in orthopyroxenes are: ordering of Fe^{2+} ions in the crystal structure, with preferential occupation of M_2 positions; entry of small, high valence cations (Al^{3+}, Fe^{3+}, Ti^{3+}, Ti^{4+}) into M_1 positions; replacement of Si by Al; and a sufficient Fe^{2+} content—more than 15 mole % ferrosilite.

The Kondapalli orthopyroxenes have variable Fe_2O_3 content; the amount is generally less than 1·5 %, though J22 shows a slightly higher value. MnO is generally lower in the magnesian orthopyroxenes, though again J22 is exceptional. The orthopyroxenes show a wide range in the Fe^{2+}/Mg ratio from 0·08 to 1·32, and this ratio is not systematically related to either the SiO_2 content or the Fe^{2+}/Mg ratio of the host rock. This independence of the composition of the orthopyroxenes from the acidity of the host rocks is precisely the fundamental petrological problem that makes charnockites charnockites (Parras, 1958).

CaO is generally less than 1 % in the Kondapalli orthopyroxenes while the amount exceeds 2 % in some Madras orthopyroxenes. The maximum number of Ca atoms that can be accommodated in enstatite at different temperatures was given by Atlas (1952) and the recent work of Boyd and Schairer (1964) shows that the solid solution along the join $MgSiO_3$–$CaMgSi_2O_6$ is even more restricted than was found by Atlas. No estimates for the temperatures of formation of natural pyroxenes can be made from these data, as the orthopyroxenes in the granulites show a wide range in composition and as some of them coexist with garnet, hornblende, or clinopyroxene. The variable amounts of CaO in the orthopyroxenes of the Madras 'charnockite suite' are explained by Subramaniam (1962) as due to the differences in the degree of recrystallization of the host—the greater the deformation, the fewer the exsolution lamellae of clinopyroxene and hence the smaller the amount

of CaO. He also considered that the lamellar structure in the ortho-pyroxenes of the 'basic granulites' was due to translation gliding (Henry, 1942), and not to the presence of exsolution lamellae of clinopyroxene. As has been stated earlier, single crystal X-ray work and electron
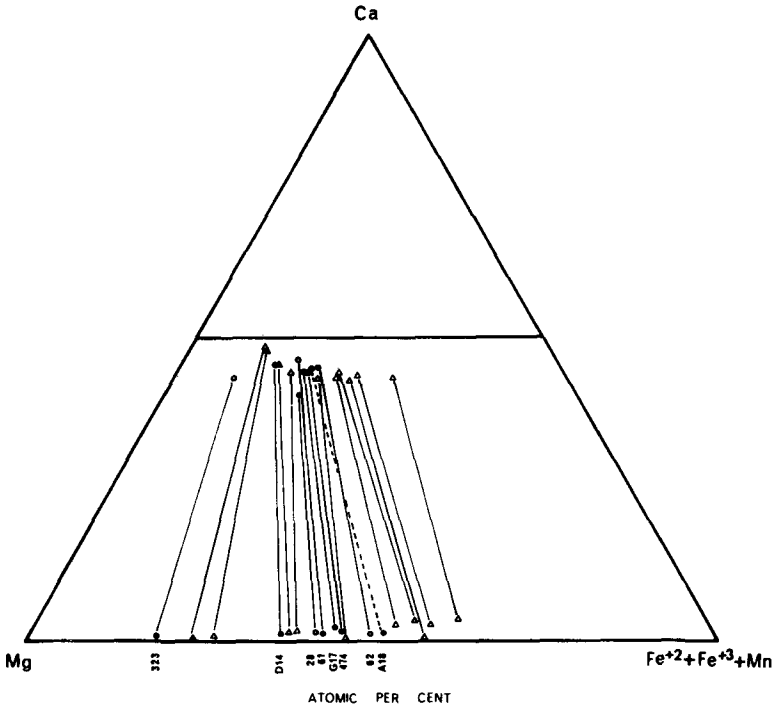

FIG. 1. Triangular compositional plot of coexisting pyroxenes from the Kondapalli (numbered circles) and Madras (triangles) charnockites. Note that the tie lines do not intersect, except for the pair A18; for details see the text.

microprobe measurements on the pyroxenes from the Kondapalli basic charnockites prove that the exsolution lamellae are clinopyroxene. The available analyses of the Kondapalli and Madras orthopyroxenes reveal that the content of CaO in general increases as Mg is substituted by Fe^{2+} (fig. 1). This is in conformity with the findings of Binns (1962b, 1965) and of Howie and Smith (1966). The alkalis in the orthopyroxenes are very small, Na usually being more abundant than K.

The distribution of the trace elements is very similar to that described by Howie (1955) for the Madras orthopyroxenes. It is noticed that Cr

and Ni, as expected, are generally more abundant in the more magnesian members. But the interesting feature is the occurrence of Cr and Ni in much greater amounts compared to the Madras orthopyroxenes (table II).

Out of 17 Kondapalli orthopyroxenes whose trace elements are determined, 9 have Co < Ni, 5 have Co = Ni, and only 3 have Co > Ni; *per contra*, out of 13 Madras orthopyroxenes whose trace element data are reported by Howie (1955), only 2 have Co < Ni, 1 has Co = Ni, and 10 have Co > Ni. Thus the marked excess of Ni over Co in the majority of the Kondapalli orthopyroxenes (table I) is just the opposite of what has been observed for the majority of the Madras orthopyroxenes and for the orthopyroxenes from calc-alkaline rocks (Sen, Nockolds, and Allen, 1959), with which the charnockites are so often compared (Groves, 1935; Howie, 1955; Parras, 1958). This feature is further reflected in the clinopyroxenes from the Kondapalli charnockites.

The orthopyroxene J22 from the ultrabasic lens shows abnormal features in having the lowest Cr content and very small amounts of Ni and Co; it is also unusual for a magnesian orthopyroxene to have a high content of Sc (table I). It has been noted earlier that the minor elements too behave differently in this pyroxene from the rest of the series, and it is suggested that this ultrabasic charnockite J22 may not be related to other members of the ultrabasic division; the trace elements of the coexistent amphibole and spinel, and also of the host rock point to the same conclusion (Leelanandam, 1965).

The constant presence of Ga in small amounts in the Kondapalli and Madras orthopyroxenes suggests that it is a characteristic property, obviously camouflaged in Al, of the charnockite orthopyroxenes. Mo is totally absent in all the Kondapalli orthopyroxenes, while its presence is reported in some of the iron-rich members from the Madras area. Among the enderbite orthopyroxenes, 322 is exceptional for the absence of Cr and V, and for the unusual enrichment of Sc; the orthopyroxene B4 has more Cr than some of the more magnesian minerals and has the highest V content of the entire series. Yt is present only in some iron-rich orthopyroxenes and its amount is small and variable. The orthopyroxenes from the lenses also behave differently: most of them have higher Cr and Ni compared with the orthopyroxenes of similar Mg content, while the individual minerals are enriched in particular elements such as V, Zr, or Sc. The orthopyroxene from the dyke P45 is exceptional in being the only orthopyroxene in the series that contains appreciable Ba (22 ppm).

Clinopyroxenes

Nine clinopyroxenes from the Kondapalli charnockites have been analysed and the formulae calculated on the basis of 6 oxygens are seen to fit the theoretical structural formulae fairly closely (table III). The number of Si together with Al atoms is always sufficient to make the Z group equal to 2. Al in Z is always greater than Al in the Y group with the exception of the clinopyroxene 472. The highest amount of tetrahedral Al is present in the clinopyroxene 323 from the ultrabasic charnockite lens. The high Al_2O_3 in clinopyroxene 62 should be treated with caution as the main fusion for the analysis was done on less than 0·2 g. Alumina contents of more than 5 % have been reported in the clinopyroxenes from the ultrabasic and basic charnockites of the type area (Howie, 1955).

In a Ca–Mg–ΣFe triangular compositional plot (fig. 1), the Kondapalli clinopyroxenes are seen to fall in the fields of endiopside (323), diopside (472, not shown), sahlite (61 and D14), and augite (28, G17, 474, 62, and A18). The variation in the weight per cent oxides and trace elements of the Kondapalli clinopyroxenes are compared with those of the Madras clinopyroxenes in table IV. The clinopyroxene 472, from a clinopyroxenite dyke, is distinct from the rest of the series, having the lowest contents of Na, Fe^{3+}, Ti, and Al and the highest Ca content with 0·93 atom per formula unit. As will be seen later, the trace elements also behave in an exceptional way in this pyroxene.

Ti is variable and the clinopyroxene 323 contains the highest amount at 0·019 per formula unit. Fe_2O_3 is usually higher than 1 %, but always lower than 2 %; in general, the value is lower in the clinopyroxenes of the ultrabasic charnockites than in those of the basic charnockites. Mn is small and variable but shows a tendency to increase with the increase in Fe^{2+}. The clinopyroxene 323 is more magnesian than the most magnesian clinopyroxene reported from the Madras area. The Fe^{2+}/Mg ratio of the Kondapalli clinopyroxenes varies from 0·12 to 0·48; but this ratio, as in the case of orthopyroxenes, cannot be correlated with the Fe^{2+}/Mg ratio of the host rock.

The Ca content of the clinopyroxenes in equilibrium with orthopyroxenes from the Kondapalli and Madras charnockites is greater than that of similar clinopyroxenes from igneous rocks (Brown, 1957), but is of the same order as that of the Scourie gneisses (O'Hara, 1961) and Broken Hill granulites (Binns, 1965). The sudden decrease in Ca content in the clinopyroxenes of the basic charnockites when compared to those

TABLE III. Clinopyroxene analyses. For key to the rocks and localities, see p. 158.
Analyst: C. Leelanandam.

	323 UBC(L)	472 UBC(D)	D14 UBC	61 Ans	28 BC(L)	G17 BC	474 BC	A18 BC	62* AC
SiO_2	50·80	53·71	51·75	51·07	51·95	50·95	51·10	50·35	49·74
TiO_2	0·69	0·11	0·43	0·48	0·41	0·35	0·43	0·43	0·40
Al_2O_3	4·96	1·15	3·45	2·87	3·15	3·24	3·12	3·80	5·79
Fe_2O_3	1·97	0·70	1·52	0·92	1·89	1·97	1·77	1·88	1·63
FeO	3·53	5·15	6·65	8·90	9·62	9·23	9·51	9·61	10·17†
MnO	0·10	0·16	0·15	0·19	0·29	0·30	0·30	0·38	0·28
MgO	16·67	14·59	13·90	13·04	13·63	12·50	12·54	12·47	11·95
CaO	20·81	23·49	21·65	22·26	19·16	20·77	20·92	21·71	21·44
Na_2O	0·78	0·23	0·59	0·41	0·46	0·49	0·67	n.d.	n.d.
K_2O	0·05	0·01	0·01	0·02	0·06	0·06	0·11	n.d.	n.d.
H_2O^+	0·17	0·13	0·20	n.d.	n.d.	0·09	0·18	n.d.	n.d.
H_2O^-	0·02	0·04	0·05	0·06	0·03	0·01	0·01	n.d.	n.d.
Total	100·55	99·47	100·35	100·22	100·65	99·96	100·66	100·63	'101·40'

Numbers of metal atoms on the basis of 6 oxygens:

Si	1·852	1·989	1·915	1·912	1·926	1·914	1·912	1·883	1·846
Al	⎰0·148	0·011	0·085	0·088	0·074	0·086	0·088	0·117	0·154
	⎱0·065	0·039	0·065	0·039	0·064	0·057	0·050	0·051	0·099
Ti	0·019	0·003	0·012	0·014	0·011	0·010	0·012	0·012	0·011
Fe^{3+}	0·054	0·020	0·042	0·026	0·053	0·056	0·050	0·053	0·046
Fe^{2+}	0·108	0·160	0·206	0·279	0·298	0·290	0·298	0·301	0·316
Mn	0·003	0·005	0·005	0·006	0·009	0·010	0·010	0·012	0·009
Mg	0·906	0·805	0·767	0·728	0·753	0·700	0·699	0·695	0·661
Ca	0·813	0·932	0·858	0·893	0·761	0·836	0·839	0·870	0·853
Na	0·055	0·017	0·042	0·030	0·033	0·036	0·049	—	—
K	0·002	—	—	0·001	0·003	0·003	0·005	—	—
$X + Y$	2·025	1·981	1·997	2·016	1·985	1·998	2·012	1·994	1·995
$R\ddagger$	84·593	81·313	75·196	70·067	67·654	66·287	66·130	65·504	64·050
Fe^{2+}/Mg	0·119	0·199	0·269	0·383	0·396	0·414	0·426	0·433	0·478
Ca	43·15	48·49	45·69	46·22	40·61	44·19	44·25	45·05	45·25
Mg	48·09	41·88	40·84	37·68	40·18	37·00	36·87	35·99	35·07
$\Sigma\S$	8·76	9·63	13·47	16·10	19·21	18·82	18·88	18·95	19·68

Trace elements (in ppm):‖

Ga	2	2	11	2	5	5	3	—	
Cr	5600	18	1000	220	125	100	125	680	
Ni	300	22	200	300	125	45	80	100	
Co	28	14	45	45	45	45	65	70	
V	220	100	320	320	260	180	220	380	
Zr	56	28	28	70	40	56	40	—	
Sc	45	—	70	100	220	150	125	150	
Yt	22	—	12	25	45	45	40	55	
Sr	—	5	—	—	—	—	—	—	
Pb	22	—	—	22	—	—	—	—	
Ba	—	18	—	—	5	5	10	—	
Cu	—	—	—	28	—	—	—	45	
Sn	32	—	—	—	100	—	55	—	

* The main fusion was done on 0·2 gm sample.   § = $Fe^{3+} + Fe^{2+} + Mn$.
† Determined by Mr. J. H. Scoon.   ‖ Determined by Mr. R. S. Allen.
‡ = $100Mg/(Mg + Fe^{3+} + Fe^{2+} + Mn)$.

of the ultrabasic charnockites is evident from fig. 1. The clinopyroxenes 323 and 28 from the ultrabasic and basic charnockite lenses (respectively) are distinctly less calcic, and clinopyroxene 28 is the least calcic of all. It is likely that the mode of occurrence of the host rock, in addition to

the bulk chemistry of the rock and its mineralogy, might have had some influence in yielding these low Ca values. It is suggested that the localized special conditions attending the formation of these lenses might have facilitated the greater solid solution of $(Mg,Fe)SiO_3$ in these two clinopyroxenes (see Shido, 1958).

The solubility gap between the calcium-rich and calcium-poor pyroxenes is greater at the crystallization temperatures of the granulite

TABLE IV. Comparison of the variation in composition
of 8 Kondapalli and 10 Madras clinopyroxenes. The
clinopyroxene 472 from Kondapalli is excluded

	Kondapalli	Madras
SiO_2	49·74–51·95 %	48·52–52·04 %
TiO_2	0·35–0·69	0·24–0·85
Al_2O_3	2·87–5·79	2·00–5·94
Fe_2O_3	0·92–1·97	0·72–3·21
FeO	3·53–10·17	4·48–15·05
MnO	0·10–0·38	0·08–0·48
MgO	11·95–16·67	8·21–14·42
CaO	19·16–22·26	19·66–23·67
Na_2O	0·41–0·78	0·11–1·04
K_2O	< 0·11	< 0·19
Ga	2–11 ppm	5–10 ppm
Cr	100–5600	10–800
Ni	45–300	10–650
Co	25–65	25–65
V	180–320	25–400
Zr	28–70	100–200
Sc	45–220	40–200
Yt	12–45	35–150
Ba	5–10	5–10

facies than at magmatic temperatures (Bartholomé, 1962; Binns, 1965). From experimental studies in the system $MgSiO_3$–$CaMgSi_2O_6$, Boyd and Schairer (1964) estimated the limits of composition of the two-pyroxene field for various temperatures, but since the natural pyroxene assemblages contain FeO and Al_2O_3 as important constituents, no direct inferences may be drawn from their values. The recent work of O'Hara and Schairer (1963) shows that the $Ca/(Ca+Mg+Fe)$ ratios of natural coexisting pyroxenes precipitated from complex liquids in the presence of other crystalline phases cannot be used directly to obtain an estimate of the temperatures of crystallization. Binns (1962a) has constructed a Ca–Mg–ΣFe triangular diagram showing the generalized fields of clinopyroxenes coexisting with orthopyroxenes for various environments together with the stylized isothermal sections through the pyroxene

solvus. Extrapolations of the data for the Kondapalli and Madras clinopyroxenes on this diagram yielded approximate temperatures over 700° C.

The alkali contents in the clinopyroxenes are not negligible. The amount of Na_2O is always less than 1 %, though two Madras clinopyroxenes reported by Howie (1955) contain slightly more than 1 %. The amount of K_2O is far less than that of Na_2O in all the clinopyroxenes of the charnockites.

Turning to a consideration of the trace elements, the behaviour of clinopyroxene 472 is quite exceptional (table III). Though this pyroxene is highly magnesian, it has lowest Cr, Ni, Co, V, and Zr and highest Ba among all the Kondapalli clinopyroxenes; it contains Sr and is devoid of Sc and Yt, while the reverse is true for the rest of the series. These features and the minor elements in this clinopyroxene indicate that the host rock, like the rock J22, does not belong to the same suite as the other members of the ultrabasic division; the relationship between some of the ultrabasic rocks 48, 472, J22, etc., anorthosites represented by the rock 61, and charnockites will be discussed in a later publication. The clinopyroxene 28 from the basic charnockite lens has highest Sc, while only the clinopyroxene 61 from anorthosite contains Cu and has high Ni, V, and Zr. Gallium is present in small amounts in almost all the samples. Cr and Ni are enriched in the magnesian members and the clinopyroxene 323 has an abnormally high amount of Cr (5600 ppm). Out of 8 Kondapalli clinopyroxenes whose trace elements are determined, 7 have Co less than Ni and only 1 has Co equal to Ni; out of 6 Madras clinopyroxenes, 3 have Co less than Ni while the other 3 have Co greater than Ni. The comments made on the significance of the preponderance of Ni over Co in the Kondapalli orthopyroxenes will also hold good for the clinopyroxenes. Mo is absent in all the Kondapalli clinopyroxenes, though its presence is noted from iron-rich clinopyroxenes of the Madras area. Yt is slightly enriched in the iron-rich varieties and its amount is lower than that present in the clinopyroxenes of the type area (table IV).

Coexisting pyroxenes

Analyses of paired pyroxenes for eight Kondapalli charnockites were obtained during the present study; in addition, ten coexisting pairs are available from the charnockites of Madras State from the work of Howie (1955), Howie and Subramaniam (1957), and Subramaniam (1962). The compositions of these pyroxenes are represented on a Ca–Mg–ΣFe triangular compositional plot and tie lines are drawn for the coexisting

ortho- and clinopyroxenes (fig. 1). The importance of the intersection points of the projected tie lines on the Ca–Mg side line has been discussed by Hess (1941), Muir and Tilley (1958), Brown (1961), and Howie (1965). Attempts have been made by Wilson (1960) and Subramaniam (1962) to evaluate the significance of these intersection points in relation to the host-rock petrogenesis. Kretz (1961a; 1961b) has criticized the projecting of tie lines as a 'meaningless operation' and concluded that the tie lines, on theoretical grounds, should not intersect at a point except when the distribution constant is unity, in which case the apex of the triangle forms the intersection point.

From an observation of the 18 pyroxene pairs from Indian charnockites, it can be generalized that the amounts of Al^{iv}, Al^{vi} (and hence total Al), TiO_2, Fe_2O_3, CaO, Na_2O, K_2O, Cr, V, and Sc are greater and the amounts of FeO, MnO, MgO, Ni, Ga, Co, and Zr are less in a clinopyroxene than in the coexisting orthopyroxene; the $Mg/(Mg+Fe^{3+}+Fe^{2+}+Mn)$ ratio is greater in the clinopyroxene. Very similar features are shown by coexisting pyroxenes from the calc-alkaline rocks (Sen, Nockolds, and Allen, 1959). The distribution of Fe^{2+}, Mg, Mn, Ti, Cr, Ni, Co, and V only are discussed in the following pages.

The first thermodynamic approach to the problem of the distribution of the Fe and Mg in the coexisting pyroxenes was made by Mueller (1960). Later on a more rigorous and systematic treatment was given independently by Kretz (1961b) and Bartholomé (1962). Bartholomé has shown that for equilibrium conditions, $(Fe^{2+}/Mg)_{Opx} = (Fe^{2+}/Mg)_{Cpx} \times K_p(T)$, where K_p is the partition coefficient and equal to 1·8 for high grade metamorphic assemblages. The K_p values for the Indian charnockites are given in table V, and the relationship between Fe^{2+}/Mg ratios of the coexisting pyroxenes is shown in fig. 2. The values are highly consistent and indicate a close approach to equilibrium. The single aberrant K_p value obtained for the pair A18 is not surprising, as the rock sample (deliberately chosen) is not homogeneous and consists of two portions with varied mineralogical assemblages, one portion being rich in hornblende and biotite, while the other is impoverished in these constituents and separated from the former by a local shear plane. The purpose of selecting this specimen was to ascertain whether its K_p value would be different from any other in the present study. An added proof of the non-attainment of equilibrium in this rock is the occurrence of plagioclase strongly zoned from An_{55} to An_{72}; the zoning is of reversed type and was confirmed by the use of the electron probe.

Binns (1962b) has given an equation to represent the empirical

distributional relationship of Fe and Mg in coexisting pyroxenes of different metamorphic grades: $(Fe^{2+}/Mg)_{Opx} = P+Q$. $(Fe^{2+}/Mg)_{Cpx}$ where Q is a constant (equal to 1·48) for the equilibrium conditions and defined by the slope of line on an Fe^{2+}/Mg plot, and P is a function of metamorphic grade measured by the intercept of the distribution line with the orthopyroxene axis. He showed that P varies from 0·35 to 0·17 for the Broken

TABLE V. Coexisting pyroxenes

No.	Orthopyroxene $\dfrac{Fe^{2+}}{Mg}$	Orthopyroxene $\dfrac{Mn}{Mg+Fe^{2+}+Mn}$	Clinopyroxene $\dfrac{Fe^{2+}}{Mg}$	Clinopyroxene $\dfrac{Mn}{Mg+Fe^{2+}+Mn}$	K_p*	K_D†
Kondapalli						
323	0·22	0·0037	0·12	0·0029	1·9	1·2
D14	0·54	0·0063	0·27	0·0051	2·0	1·2
28	0·70	0·0101	0·40	0·0085	1·8	1·2
61	0·71	0·0074	0·38	0·0059	1·8	1·2
G17	0·76	0·0106	0·41	0·0100	1·8	1·1
474	0·81	0·0111	0·43	0·0099	1·9	1·1
62	0·95	0·0100	0·48	0·0091	2·0	1·1
A18	1·00	0·0169	0·43	0·0119	2·3	1·4
Madras						
3709	0·32	0·0045	0·18	0·0027	1·8	1·7
4645	0·36	0·0044	0·18	0·0043	2·0	1·0
Ch. 114	0·60	0·0069	0·33	0·0069	1·8	1·0
2270	0·62	0·0145	0·33	0·0078	1·9	1·8
2941	0·83	0·0056	0·47	0·0066	1·8	0·8
Ch. 132	1·27	0·0132	0·71	0·0088	1·8	1·5
Ch. 199	1·28	0·0094	0·68	0·0079	1·9	1·2
4642A	1·32	0·0103	0·75	0·0073	1·8	1·4
Ch. 207	1·41	0·0139	0·80	0·0157	1·8	0·9
115	1·71	0·0169	1·02	0·0163	1·7	1·0

* $K_p = (Fe^{2+}/Mg)_{Opx} \div (Fe^{2+}/Mg)_{Cpx}$.
† $K_D = Mn/(Mg+Fe^{2+}+Mn)_{Opx} \div Mn/(Mg+Fe^{2+}+Mn)_{Cpx}$.

Hill granulites of lower and higher grades respectively. Howie (1965) has estimated P to be approximately equal to 0·12 for the Madras charnockites and this implies that the Madras charnockites represent a higher grade of metamorphism than the highest grade assemblages of the Broken Hill area. For the Kondapalli charnockites, the value of P is not consistent; it is 0·05 for the ultrabasic lens 323, 0·11 for the basic lens 28, and the value varies from 0·14 to 0·18 for others. Though these values on the whole suggest a very high grade of metamorphism for the Kondapalli charnockites, the variation of P is not held to indicate different intensities of metamorphism for the different rock types; on
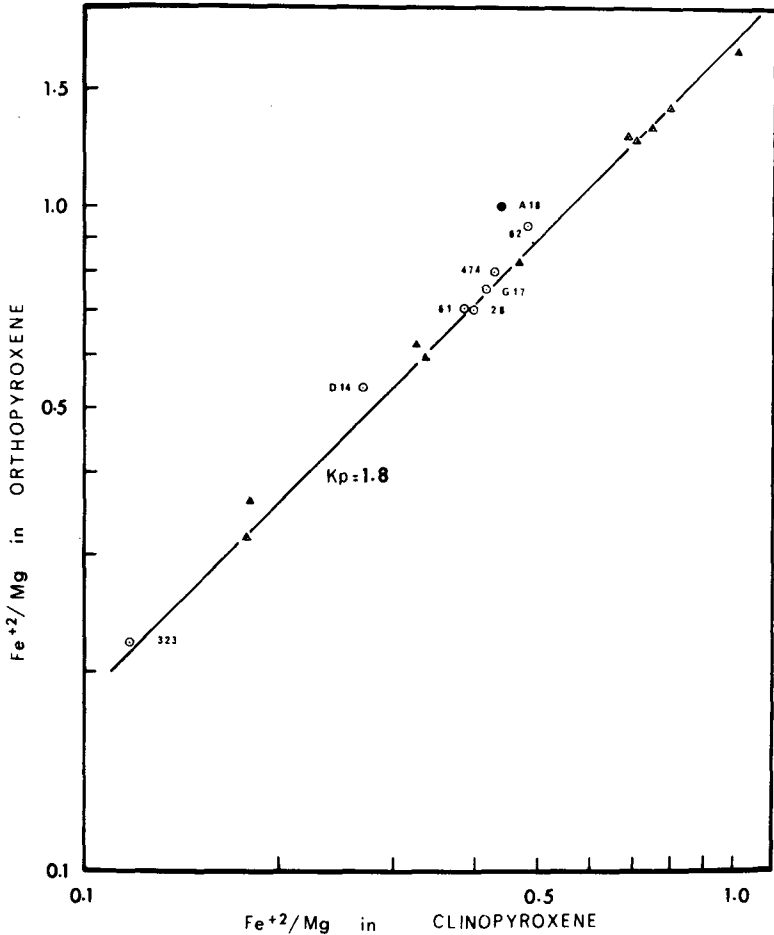
FIG. 2. Graphical log-log plot indicating the distribution of Fe^{2+}/Mg in coexisting pyroxenes from the Kondapalli (numbered circles) and Madras (triangles) charnockites. Note that A18 is away from the line representing K_p value of 1·8.

the contrary, it is suggested that all the charnockites of Kondapalli have been subjected to a uniformly high grade of metamorphism. The equation given by Binns cannot be used for the Indian charnockites (which contain pyroxenes of a wide range of composition); he himself stated that the equation will be valid, for the areas other than Broken Hill, only when the magnesian assemblages with coexisting pyroxenes represent, as a whole, higher grades of metamorphism than iron-rich assemblages.

M
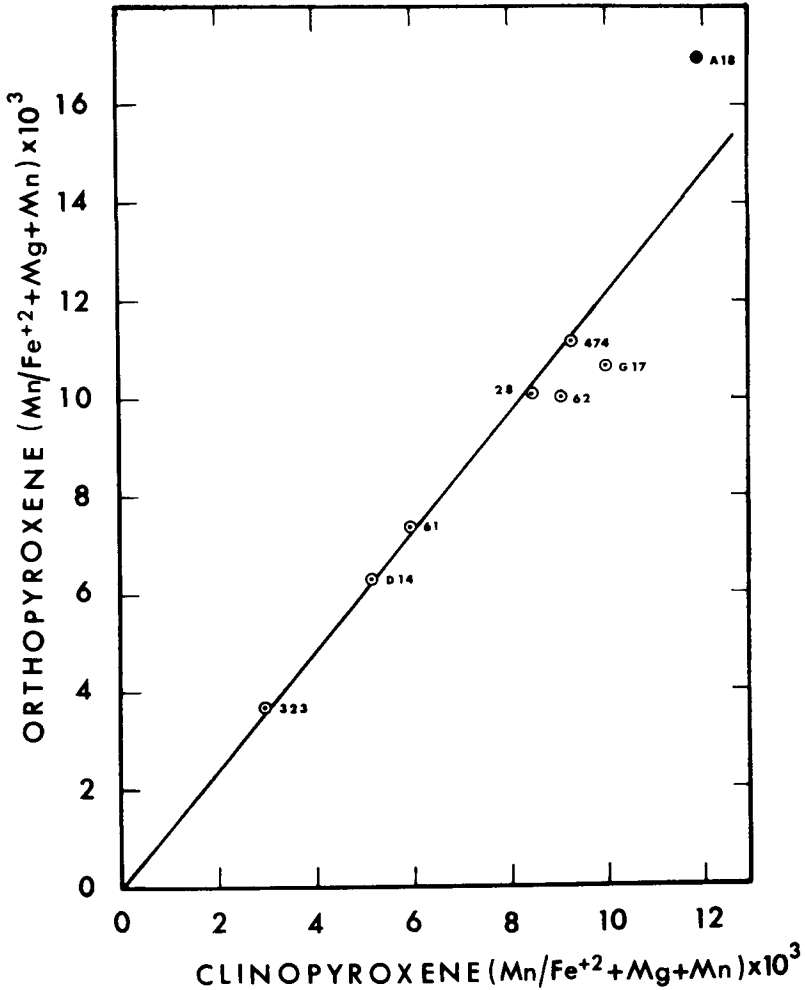
FIG. 3. Distribution of manganese between coexisting pyroxenes from Kondapalli charnockites. Note that A18 is away from the distribution line representing $K_D \simeq 1\cdot2$; for details see the text.

Attempts to find such differences in the grade of metamorphism between magnesium-rich and magnesium-poor members have not met with success in the Kondapalli area and this could be the same for the type area as well.

Bartholomé (1962), Kretz (1963), and Engel, Engel, and Havens

(1964) have constructed diagrams showing K_p as a function of temperature of crystallization. The exact estimation of the temperature from these diagrams for each K_p value may not be of great significance, though an over-all estimate for a family of K_p values will give a general indication of the temperature of crystallization. Thus temperatures above 600° C are suggested for the Kondapalli charnockites and similar temperatures are inferred to have prevailed during the formation of the Madras charnockites.

Mueller (1962) indicated that the systematic variation of $Mn/(Mg + Fe + Mn)$ in the pyroxenes suggests that Mn replaces Mg and Fe^{2+}. Recently Kretz (1963) has discussed the distribution of Mn in the coexisting pyroxenes and indicated that the distribution coefficient K_D expressed as the ratio $Mn/(Mg + Fe^{2+} + Mn)_{Opx} : Mn/(Mg + Fe^{2+} + Mn)_{Cpx}$ is about 1·2 for rocks of the granulite facies. The K_D is nearly constant (1·1–1·2) for the Kondapalli pyroxene pairs with the exception of A18 (fig. 3), while it is discouragingly variable (0·8–1·8) for the Madras pyroxene pairs, as can be seen in table V. The high value of K_D for the pair A18 is not unexpected for the reasons given earlier. The erratic K_D values of the Madras pyroxenes suggest various degrees of departure from equilibrium and this is surprising because the highly uniform K_p values indicate that perfect equilibrium was attained in the host rocks. Kretz (1963) did not give an adequate explanation to account for the large variation in these K_D values and the problem still remains; analytical error alone may account for much of the observed variation (Howie, *pers. comm.*). It is perhaps pertinent to note that the mean of the 10 values of the Madras pyroxenes is exactly 1·2.[1] Calculation of the analytical data provided by Sen and Rege (1966) shows that the K_D values for 4 pyroxene pairs from the basic granulites of Saltora (India) are 0·5, 1·0, 1·2, and 1·3, while that of the data given by Binns (1962b) shows K_D to vary only from 1·2 to 1·7 for 6 pyroxene pairs from the Broken Hill granulites.

Mueller (1963) posed the interesting question whether or not equilibrium can be established with respect to Fe^{2+} and Mg when at the same time the coexistent plagioclase exhibits compositional zoning indicating that the kinetic situation is unfavourable for equilibrium in the latter. Goldsmith (1952) discussed the kinetic problem of plagioclase in terms of

---

[1] A diagram (similar to fig. 3) drawn by Mueller (1961, fig. 15) for 6 pyroxen pairs from Quebec and for 7 pyroxene pairs from Pennsylvania and Delaware, suggests that the distribution of Mn is highly regular and that the K_D values are nearly uniform ($\simeq$ 1·2).

the Al/Si ratio and Si–O bond strengths and the difficulties in overcoming these kinetic barriers. The present study reveals that equilibrium was established with respect to Fe^{2+}, Mg, and Mn in coexisting pyroxenes, even when the plagioclase in the host rock shows moderate zoning as in D14, 28, G17, and 62; but in the rock A18 described earlier, equilibrium was not established in coexisting pyroxenes and the plagioclase shows intense zoning. The chemical equilibrium attained in the Kondapalli charnockites suggests that chemical communication was maintained during the period of crystallization of the coexisting pyroxenes.

Theoretical conclusions on the distribution of Fe and Mg between coexisting pyroxenes, arrived at on the basis of a thermodynamical approach from ideal solid solution theory (Kretz, 1961b; Bartholomé, 1962; Mueller, 1961, 1962), are challenged by O'Hara and Mercy (1963), Binns (1962b) and others. Their main objections include the assumption that the two pyroxenes are essentially ideal solid solutions of their Mg and Fe end members, the variation of Ca with respect to iron in the coexisting phases and the dependence of K_p on Ca content, the preferential acceptance of iron in the Ca site of the clinopyroxene as a result of 'orthopyroxene solid solution', the ordering of Fe and Mg in the pyroxene structure and the temperature dependence of the degree of this order, the variation of K_p with respect to change in composition at constant temperature and pressure conditions, the influence of the grade of metamorphism on K_p, the possible effect of pressure on K_p, and, finally, the lack of adequate reasoning to explain the inconsistent K_p values for the ultramafic (peridotite) assemblages.

As far as the Indian charnockites are concerned, the study of the pyroxene pairs reveals that there is no evidence to support the above mentioned objections. On the other hand, it can be deduced that the distribution functions are independent of the compositional variation and also of the presence or absence of other phases such as hornblende, biotite, or garnet. Though pressure can theoretically have an effect on the K_p value, it has been shown by calculation that this effect is negligible (Kretz, 1963). Constituents such as Al, Ca, Ti, Fe^{3+}, etc., which are present in variable amounts in the charnockite pyroxenes, seem to exert no appreciable influence on equilibrium relations and hence introduce very little scatter in the distribution constant. Though theoretically one expects that the distribution coefficients are affected by the variety of factors mentioned above, the present analytical techniques could not detect these effects.

The weight per cent TiO_2 in orthopyroxene was plotted against the

weight per cent TiO_2 in clinopyroxene on a graphical log-log plot (not shown here) for all the eight pyroxene pairs from Kondapalli char-nockites and the six pyroxene pairs from Madras charnockites; the distribution points are scattered. The presence of Ti-bearing minerals occurring as lamellae in some of the analysed pyroxenes will not permit a serious discussion of the distributional relationships of the element. It is likely that the amount of Ti now present in the analysed grains of purified pyroxene concentrates may not be the same as that present at the time of crystallization. Kretz (1959) and Albee (1965) have

TABLE VI. Partition of TiO_2, Ti(O = 6), $[Al]^6 + Fe^{3+} + Ti$, and $Ti/(Fe^{2+} + Fe^{3+} + Mg + Mn + Ti)$ in the Kondapalli coexisting pyroxenes

	TiO_2		Ti(O = 6)		$[Al]^6 + Fe^{3+} + Ti$		$Ti/(Fe^{2+} + Fe^{3+} + Mg + Mn + Ti)$	
	OPX	CPX	OPX	CPX	OPX	CPX	OPX	CPX
323	0·27	0·69	0·007	0·019	0·069	0·138	0·0036	0·0174
D14	0·43	0·43	0·012	0·012	0·073	0·119	0·0061	0·0116
28	0·38	0·41	0·011	0·011	0·078	0·128	0·0058	0·0098
61	0·26	0·48	0·007	0·014	0·069	0·079	0·0036	0·0133
G17	0·24	0·35	0·007	0·010	0·059	0·123	0·0036	0·0094
474	0·28	0·43	0·008	0·012	0·072	0·112	0·0042	0·0112
62	0·38	0·40	0·011	0·011	0·069	0·156	0·0057	0·0105
A18	0·30	0·43	0·009	0·012	0·072	0·116	0·0047	0·0112

noticed that the elements Ti and Zr show the most erratic distribution between coexistent phases, as the concentrations of these elements are dependent on the abundance of rutile, ilmenite, and zircon inclusions in the minerals.

Deer, Howie, and Zussman (1963) observed that no apparent relation-ship exists between the amount of Ti and the replacement of Mg by Fe^{2+} in clinopyroxenes. The total concentration of the Y group ($[Al]^6 + Fe^{3+} + Ti$) of the pyroxenes appears to be more important than the concentration of a single member of the group, as $[Al]^6$, Fe^{3+}, and Ti are more closely related to one another by size, charge, and ionization potential than they are to the other major constituents (DeVore, 1957). Yet it has been found that the distribution diagrams drawn (not shown here) on the basis of Ti(O = 6) or $[Al]^6 + Fe^{3+} + Ti$ or $Ti/(Mg + Fe^{2+} + Fe^{3+} + Mn + Ti)$ values for the coexisting pyroxenes of Kondapalli charnockites (table VI) exhibit no less scatter of the distribution points than that observed for the TiO_2 values.

Turning to a consideration of the distribution of trace elements in coexisting pyroxene phases, a rigorous treatment for the calculation of distribution coefficients was not attempted, as the accuracy of the

spectrographic determinations is rather poor and as there are too many complications that can be introduced by differences in rock composition and mineralogy and by variations in the major-element composition of the pyroxenes (DeVore, 1955; Turekian and Phinney, 1962; McIntire, 1963).

The partition of Cr, Ni, Co, and V between the seven pyroxene pairs from the Kondapalli charnockites and six pyroxene pairs from the

TABLE VII. Distribution of Cr, Ni, Co, and V in the coexisting pyroxenes

	Cr		Ni		Co		V	
	OPX	CPX	OPX	CPX	OPX	CPX	OPX	CPX
Kondapalli								
323	2500	5600	700	300	125	28	100	220
D14	465	1000	350	200	125	45	100	320
28	100	125	125	125	125	45	100	260
61	125	220	350	300	125	45	100	320
G17	46	100	125	45	125	45	42	180
474	46	125	125	80	125	65	54	220
A18	180	680	100	100	100	70	140	380
*Madras**								
3709	100	100	650	650	60	60	25	25
4645	300	800	450	500	100	40	40	150
2270	15	75	30	30	80	40	40	150
2941	125	300	65	70	100	50	50	400
4642A	25	75	65	50	100	65	125	400
115	—	10	30	10	40	25	20	50

* Data from Howie (1955)

Madras charnockites (table VII) is presented in figs. 4, 5, 6, and 7; the diagrams are plotted on a log-log graph, and lines of equal K_D have a 45° slope on such a graph. If distribution coefficients are unaffected by compositional differences, then 'equilibrium distributions will be reflected in clusters of points elongated parallel to the 45° lines, and non-equilibrium distributions will be reflected in scatter perpendicular to the 45° lines' (Albee, 1965). According to this principle, and taking into cognizance the accuracy of the data, it is inferred that the Cr partition shows the closest approach to equilibrium and V a slightly poorer approach; Ni distribution implies near-equilibrium conditions, while Co distribution is not entirely erratic. Diagrams showing the partitions of Cr/Fe^{3+}, Ni/Mg, Ni/Fe^{2+}, Co/Mg, Co/Fe^{2+}, and V/Fe^{3+} in both the sets of Kondapalli and the Madras pyroxene pairs were also drawn on graphical log-log plots, but they are not given here and only the data are presented in table VIII.
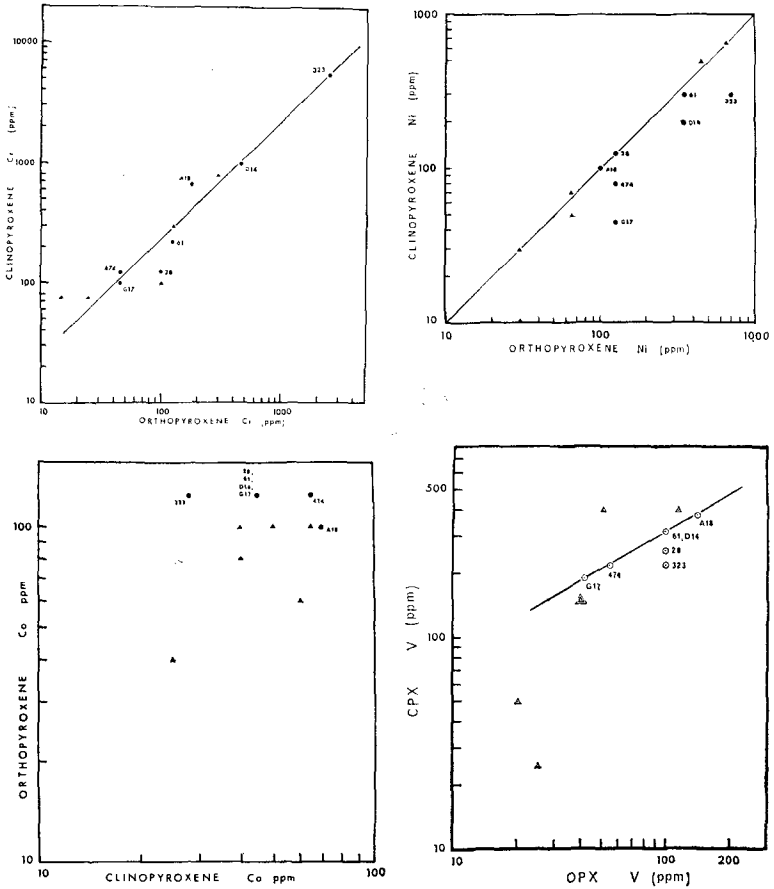
FIGS. 4 to 7: FIG. 4 (top left). Distribution of Cr between coexisting pyroxenes from Kondapalli (numbered circles) and Madras charnockites (triangles); the distribution line is drawn for the Kondapalli pairs. FIG. 5 (top right). Distribution of Ni between coexisting pyroxenes from Kondapalli (numbered circles) and Madras charnockites (triangles): the distribution line drawn has a slope of 45°; for details see the text. FIG. 6 (bottom left). Distribution of Co between coexisting pyroxenes from Kondapalli (numbered circles) and Madras charnockites (triangles); note that 4 Kondapalli pairs are represented by one point. FIG. 7 (bottom right). Distribution of V between coexisting pyroxenes from Kondapalli (numbered circles) and Madras charnockites (triangles); the distribution line is drawn for the Kondapalli pairs and is not of 45° slope.

TABLE VIII. Ratios between the trace elements ($\times 1000$) and associated major elements of the coexisting pyroxenes

	Cr/Fe^{3+}		Ni/Mg		Ni/Fe^{2+}		Co/Mg		Co/Fe^{2+}		V/Fe^{3+}	
	OPX	CPX	OPX	CPX	OPX	CPX	OPX	CPX	OPX	CPX	OPX	CPX
Kondapalli												
323	1152·0	407·0	3·91	2·98	7·72	10·94	0·70	0·28	1·38	1·02	46·08	15·98
D14	51·6	94·2	2·60	2·39	2·10	3·87	0·93	0·54	0·75	0·87	11·09	30·13
28	102·0	9·5	1·06	1·52	0·66	1·67	1·06	0·55	0·66	0·60	102·0	19·68
61	15·7	34·2	2·96	3·82	1·82	4·34	1·06	0·57	0·65	0·65	12·55	49·77
G17	5·5	7·3	1·11	0·60	0·64	0·63	1·11	0·60	0·64	0·63	5·05	13·07
474	19·3	10·1	1·14	1·06	0·62	1·08	1·14	0·86	0·62	0·88	22·69	17·78
A18	25·2	51·8	1·03	1·33	0·45	1·34	1·03	0·93	0·45	0·94	19·64	28·92
Madras*												
3709	10·0	7·0	4·0	7·7	5·5	18·8	0·4	0·7	0·5	1·7	2·6	2·0
4645	60·0	58·0	2·9	5·8	3·5	13·7	0·6	0·5	0·8	1·1	8·1	11·0
2270	3·7	5·0	0·2	0·4	0·2	0·5	0·6	0·5	0·4	0·7	9·7	9·0
2941	9·3	17·0	0·6	1·0	0·3	0·9	0·9	0·7	0·5	0·7	15·0	22·0
4642A	2·6	0·8	0·8	0·8	0·3	0·4	1·2	1·0	0·4	0·6	13·0	43·0
115	—	0·1	0·1	0·2	0·03	0·08	0·6	0·5	0·1	0·2	0·9	2·0

* Data from Howie (1955).

It is noticed that Cr distribution is highly systematic for pyroxenes of both the areas and the linear relationship is excellently maintained, but its distribution is definitely more regular in the pyroxene pairs from Kondapalli than those from Madras (fig. 4). The distribution of Ni (fig. 5), Ni/Mg, or Ni/Fe^{2+} is far more regular in the coexisting pyroxenes from Madras than those from Kondapalli; it is also observed that Ni/Fe^{2+} values provide a better correlation than Ni or Ni/Mg distribution in the pyroxene pairs of both the areas. Co is more uniformly distributed than Co/Mg in the Kondapalli pyroxene pairs, while the reverse is true for the Madras pyroxene pairs; as four out of seven Kondapalli pyroxene pairs are represented by one point in fig. 6, no distribution line is drawn on the diagram. The V distribution diagram (fig. 7) exhibits a better correlation than the V/Fe^{3+} diagram for both the Kondapalli and Madras pyroxene pairs. What is interesting to observe in all these diagrams is that the pyroxene pair A18 does not behave in any erratic manner, though it is earlier noticed that the distribution of Fe^{2+}, Mg, and Mn is not normal in this particular pair. Though the accuracy of the trace element data does not permit of any definite conclusion, it seems not unlikely that the distribution coefficients for the trace elements are less sensitive to departure from equilibrium than are the distribution coefficients for Fe^{2+}, Mg, and Mn.

Summarizing, it is concluded that the major element data indicate that the coexisting pyroxenes from the Kondapalli and from the Madras charnockites experienced a time of chemical communication and approached a state of perfect chemical equilibrium; the trace element data indicate that these pyroxenes attained more than a rudimentary equilibrium and a very high degree of equilibrium cannot be discounted. Both the sets of data suggest that the equilibrium (or near equilibrium) conditions once attained are subsequently retained. The trace-element studies also suggest that further intensive and more accurate data for the pyroxene pairs from known igneous and metamorphic assemblages, found in different parts of the world, may yield fruitful results. One obvious function of such data will be to provide a guide as to which elements or which distribution coefficients are most likely to serve as useful parameters of temperature, the like of which has been demonstrated by the contrasting distribution of Fe^{2+} and Mg in coexisting pyroxenes of igneous and metamorphic paragenesis.

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