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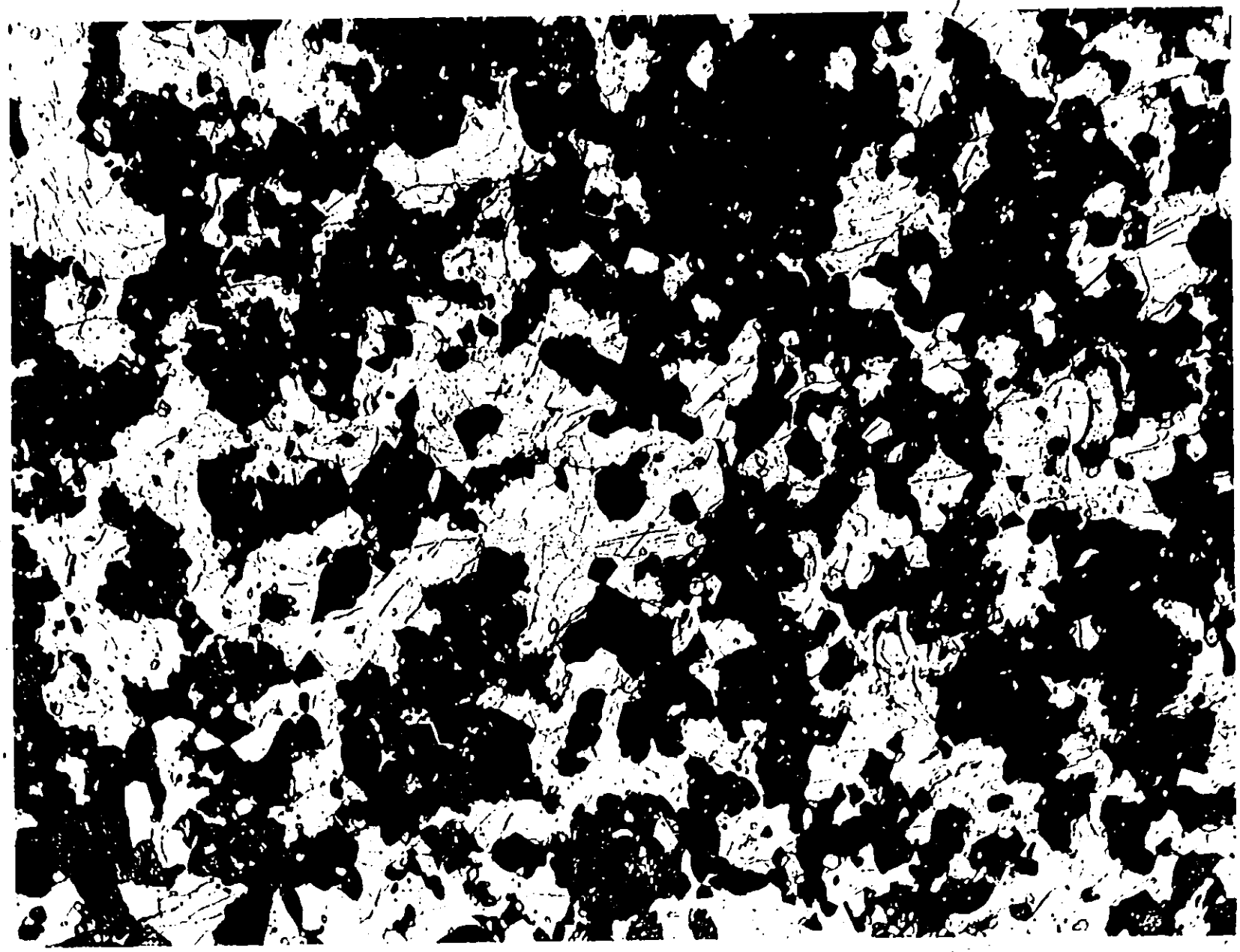

FRONTISPIECE

Photomicrograph of a mafic charnockite (J-35) from the Adirondack Mts., N.Y.

(x17) Plane polarized light

White: plagioclase (andesine)
Dark green: amphibole (ferrohastingsite)
Bluish green and granular: clinopyroxene (ferrosalite)
" " " prismatic (lower right corner): orthopyroxene (eulite)
Dark beige: garnet (almandine)
Brown (centre left): biotite
Black: Fe-Ti oxides and Fe sulphides

BACK PAGE

Photomicrograph in partially polarized light

SPATIAL DISTRIBUTION OF CRYSTALS AND PHASE EQUILIBRIA IN CHARNOCKITIC GRANULITES FROM THE ADIRONDACK MOUNTAINS, NEW YORK

by

Lo-Sun Jen

A thesis

Submitted in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

in geology

to the

School of Graduate Studies

University of Ottawa

May 1975

Abstract

Twelve specimens of charnockitic granulites from the Adirondack Mountains in New York were investigated in detail with an aim to increasing our understanding of chemical processes that take place during high-grade metamorphism. Data were obtained on the chemical composition of the rocks, the spatial distribution of the contained crystals, the distribution of Mg and Fe^{2+} between non-equivalent sites in some of the ferromagnesian minerals, the distribution of Mg, Fe^{2+}, and Mn among coexisting orthopyroxene, clinopyroxene, amphibole, and garnet, and the composition of coexisting magnetite and ilmenite.

The spatial distribution of orthopyroxene, clinopyroxene, amphibole and feldspar was investigated by measuring the frequency of the different kinds of contacts between like and unlike crystals, and by comparing the results with those expected for a random mingling of the crystals. The results show that some aspects of the distributions are random, while others represent a departure from randomness towards a distribution which favours the occurrence of contacts between unlike grains. These results are interpreted in relation to a rearrangement of matter during metamorphism to bring about a reduction in interfacial free energy.

By use of Mössbauer spectroscopy, the distribution of Mg and Fe^{2+} in the M_1 and M_2 sites of orthopyroxene was determined for four crystals of different Fe/Mg ratio. The resulting distribution agrees very closely with that obtained experimentally by Saxena and Ghose (1971) at 700°C.

The distribution of Mg, Fe^{2+}, and Mn among orthopyroxene, clinopyroxene, amphibole, and garnet, produces the following sequence of decreasing affinity for Fe and Mn:

Fe: garnet orthopyroxene amphibole clinopyroxene

Mn: garnet orthopyroxene clinopyroxene amphibole

Moreover, for any mineral pair, the distribution points define exactly or very nearly a linear or curvilinear pattern, which may be taken to indicate that exchange equilibrium was very closely established during metamorphism.

The distribution of Mg and Fe^{2+} between orthopyroxene and clinopyroxene is examined from a thermodynamic viewpoint. Data from the present study provide needed information on the iron-rich end of the 'exchange isotherm', and when combined with the magnesium-rich data from India produce a well defined isotherm. A good 'fit' to these data points can be obtained by assuming that both mineral phases are simple mixtures (Guggenheim, 1967), with small departures from ideal behaviour.

The composition of coexisting magnetite and ilmenite, when compared with the experimental data of Buddington and Lindsley (1964) indicate a temperature of less than 600°C and an oxygen fugacity less than 10^{-18} atm. Reaction and re-equilibration are thought to have taken place, to some extent during cooling of the rocks.

The rocks evidently represent a suite of cogenetic mafic igneous rocks of calc-alkaline type, that was metamorphosed at about 735°C. Metamorphic pressures are more difficult to estimate, but a confining pressure of 6 Kbs and a water vapour pressure of about 4.8 Kbs are not in conflict with experimental results on phase equilibrium studies.

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PART 1

GEOLOGY AND PETROGRAPHY

I INTRODUCTION

Statement of Problem

This thesis presents the results of a study of the spatial distribution of crystals, and a study of phase equilibrium in some charnockitic granulites from the Adirondack Mountains in New York. These studies were undertaken in an attempt to increase our understanding of the processes that take place during the crystallization of high-grade metamorphic rocks. The spatial distribution of crystals in a rock may give information on nucleation sites and the role of interfacial free energy in metamorphic crystallization, and data on the association of minerals and their chemical composition may provide information on the equilibrium characteristics of complex silicate and oxide systems containing minerals of variable composition.

General Statement

The term charnockite was proposed by Holland (1893, p162) for a hypersthene-bearing granite found near Madras, India. Later, Holland (1900, p125, 128) described a charnockite series which consists of acid, intermediate, basic and ultrabasic orthopyroxene-bearing plutonic and metamorphic rocks. More recently Subramanian (1959, p328) attempted to redefine charnockite as a hypersthene-bearing

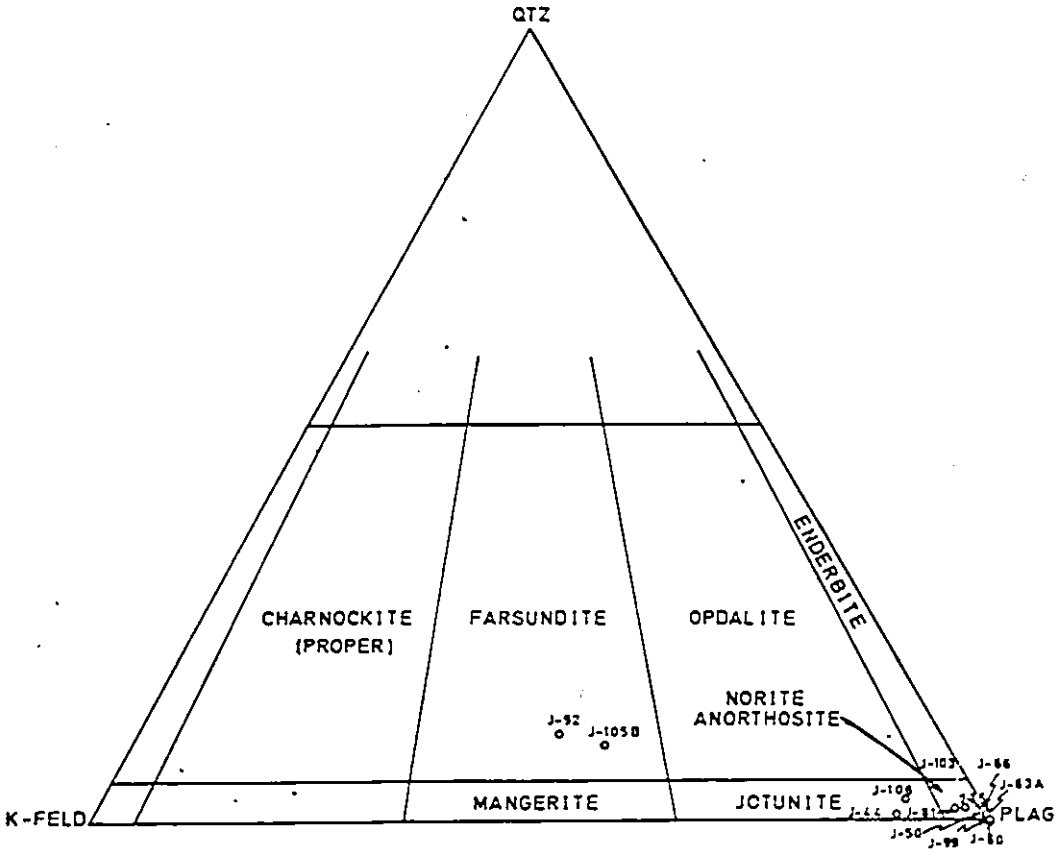
rock with or without garnet, characterized by greenish-blue feldspars and greyish-blue quartz, the dominant feldspar being a microperthite. This has restricted the term charnockite to the acid charnockites of Holland (1900).

The rock suite under investigation has close similarities to intermediate and basic charnockites from India and other parts of the world. In the present thesis the terms charnockite and charnockitic granulites will be used in a broad sense intended by Holland (1900). Two samples, J-50 and J-99, without orthopyroxene, are also included because of close association and similarity in chemical composition to the other charnockitic rocks. More specific terms will be used locally, and these follow the nomenclature used by Philpotts (1966, p13) and de Waard (1969, p78) as shown in Fig. 1.

The modal proportion of quartz, K feldspar and plagioclase in some rocks that will be described in detail below are shown in Fig. 1. Most of these fall in the field of norite and anorthosite, two in the field of jotunite and two in farsundite. In addition, the rocks contain 10-50 per cent ferromagnesian minerals. Thus the rocks of the present study belong to the intermediate and basic divisions of the charnockite series.

Since the original work of Holland, charnockites from the type area near Madras have been studied extensively by Howie (1955), Pichamuthu (1953), Howie and Subramaniam

Figure 1. Qtz-K feld-Plag modal compositional plot of twelve charnockitic granulites from the Adirondack Mts., N.Y.


QTZ
CHARNOCKITE
(PROPER)
FARSUNDITE
OPDALITE
ENDERBITE
NORITE
ANORTHOSITE
MANGERITE
JCTUNITE
K-FELD
PLAG
J-92
J-105B
J-103
J-66
J-63A
J-109
J-50
J-99
J-80

(1957), Subramaniam (1962) and Sen and Sahu (1970). According to Subramaniam (1962) these rocks resulted from the emplacement of a charnockitic magma into a sequence of metasediments and mafic granulites.

The best known group of charnockites in North America occurs in the Adirondack Highlands, within the Grenville Province of the Canadian Shield. The field relation and petrology of these rocks have been described in detail by Buddington (1939, 1952, 1963, 1965, 1966, 1969) and de Waard (1964, 1965a, 1965b, 1967, 1969). The present study provides additional information on these interesting rocks particularly on the chemical composition of the minerals and on the spatial distribution of the contained crystals.

General Geology

The Precambrian rocks of the Adirondack Mountains form part of the Grenville Province of the Canadian Shield and comprise igneous and metamorphic rocks of various compositions (Buddington, 1939). According to Stockwell (1972, p2), the most recent orogeny in this part of the Shield (the Grenvillian Orogeny) occurred about 1,000 m.y. ago.

The nature and sequence of intrusion and deformations in the Adirondack area were described by Buddington (1952, p39) and are summarized in the following paragraphs.

Following the deposition of a sequence of limestones, sandstones, shales, etc. (the Grenville Series), three major orogenic events took place in the Adirondack region. During the earliest event the Grenville Series was folded, and anorthosite, olivine diabase or gabbro, and the quartz syenitic and charnockitic series were emplaced in sequence, as is indicated by the presence of intrusive contacts.

During the second period of orogeny, deformation and metamorphism occurred on a regional scale. Garnet crystallized in many of the rocks that were affected by this metamorphism. At this time, the quartz syenitic and charnockitic series were invaded by dikes of hypersthene diabase.

The third and last period of orogenic deformation and metamorphism was marked by the emplacement of various granitic rocks, particularly granite and subordinate alaskite, microcline granite and soda-granite.

Unmetamorphosed basaltic dikes marked the end of the history of intrusions and deformations in the area.

Successive metamorphism and deformation has produced in the Adirondack region a variety of medium to high grade metamorphic and plutonic rocks. Nearly all of these rocks have been affected to some extent by deformation and metamorphism, and may be described as being gneisses and granulites. The charnockitic granulites of the present study are

largely orthogneisses (Buddington, personal communication, 1969) and are closely associated with anorthosites, olivine gabbros, migmatites, and hornblende- and pyroxene-bearing granitic and syenitic gneisses. They occur as small plutons, dike-like bodies and as layered rocks of possible sedimentary or volcanic origin. All of these are situated in and around the main anorthosite massif of the central and eastern Adirondack Mountains (de Waard, 1969, p221, and also Fig. 2). Most of these rocks are homogeneous but in some, a small scale layering is discernible. A foliation, marked by the preferred orientation of crystals is probably present in all of these rocks, but is not conspicuous. The rocks are fine to medium-grained, i.e. mean grain size normally is 0.2 to 1.5 mm.

Small apophyses into anorthosite have been observed, indicating that some of the charnockitic granulites may be of magmatic origin.

Field Sampling

Valuable information regarding the charnockite localities in the Adirondacks was kindly provided by Professor A.F. Buddington of Princeton University. An area measuring 30 miles by 20 miles, situated immediately west of Lake Champlain, was chosen as the sample area for the present

study (Fig. 2). A few mineral and bulk rock chemical analyses from this area were previously reported by Buddington (1952). These data together with some information from him through personal communications have greatly assisted the writer in locating favourable sites for obtaining samples. Altogether, one hundred and twenty rock samples were collected during a period of 15 days early in August and in October, 1969. The locations of those rocks that were selected for detailed study are shown in Fig. 2.

Laboratory Work

One hundred standard-size thin-sections were examined and 12 rocks containing different mineral assemblages, and little alteration were chosen for further study. These rock samples are J-35, J-44, J-50, J-63A, J-66, J-80, J-81, J-92, J-99, J-103, J-105B, and J-106.

Each of the above mentioned rock samples, except J-92,was first crushed into small fragments (less than two inches in diameter) in a chipmunk crusher. Several representative fragments were hand-picked and ground to fine powders (<200 mesh) by use of a porcelain mortar and pestle: this material was used for bulk-rock chemical analysis. The remaining fragments were passed through a disc grinder several times, and the resulting powders then sieved with Cu-wire metal sieves. About 100 to 150 grams of this material, between 170 and 230 mesh, was used for mineral separation.

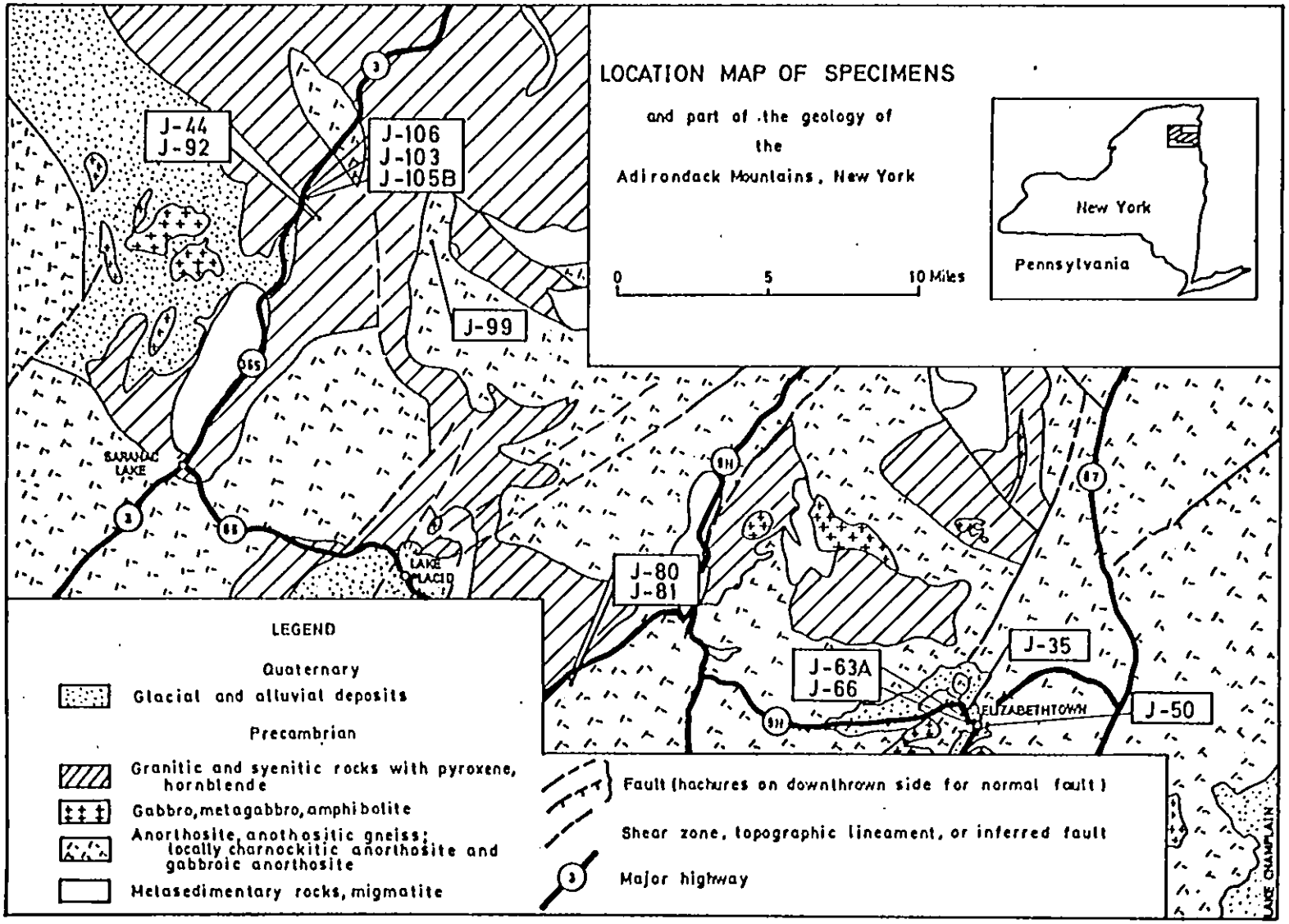


Figure 2. Sample location map with geology After Geological Map of New York, 1961, Adirondack Sheet (J. G. Broughton et al)

These powders were first washed and rinsed with distilled water and acetone. The samples were then dried in an electric oven at temperatures of about 105°C. After cooling, the powders were spread on a piece of clean paper and the strongly magnetic minerals together with iron contamination were removed with a hand magnet.

Pyroxenes, amphiboles and garnets in the eleven rocks chosen for detailed chemical study were separated and purified to >99%, with many >99.9% pure, using combinations of the Frantz isodynamic separator and various dilutions of heavy liquids, mainly methylene iodide and Clerici solution (thallium malonate-formate).

The mineral and rock samples (approximately 100 mg of each) were taken into solution employing the perchloric acid method. They were then analyzed for total Fe, MgO, CaO, Na_2O, K_2O and MnO by means of atomic absorption spectrometry in the Geochemical Laboratory, Department of Geology, University of Ottawa. A Techtron model AA4 atomic absorption spectrophotometer was used following a procedure similar to that described by Kretz (1970).

FeO was analyzed by a rapid wet chemical method that was developed by the writer (Jen, 1973). Fe_2O_3 was then calculated from the determined FeO and total Fe as Fe_2O_3 obtained by atomic absorption, using the equation

$$\text{wt\% } Fe_2O_3 = \text{wt\% total Fe as } Fe_2O_3 - 1.1 \text{ wt\% FeO}$$

SiO_2, Al_2O_3 and TiO_2 in the silicate minerals, and total Fe and TiO_2 in magnetites and ilmenites were analyzed by use of an electron microprobe, located at Carleton University. SiO_2, Al_2O_3 and TiO_2 in the rocks were determined, through Dr. I. Ermanovics at the Geological Survey of Canada; SiO_2 and TiO_2 were determined colorimetrically and Al_2O_3 by use of a Perkin-Elmer model 303 atomic absorption spectrophotometer.

The USGS BCR-1 basalt standard was used as a check on accuracy for all the wet chemical analyses. An analyzed ilmenite standard and a NASA pyroxene standard were used in the probe analysis. The computer program by Rucklidge and Gasparrini (1969) was used for the probe data reduction.

Analyses, excepting the probe analyses were measured in duplicate. In the probe analysis, 2 to 4 measurements were made per mineral grain, and 2 to 5 mineral grains of the same mineral were analyzed per rock section (polished-thin section). For each measurement spot, counts were recorded for 5 time intervals of 10 seconds each.

The precision of the analyses, expressed in terms of standard deviation (s) and percentage relative deviation (c) were determined by analyzing standard USGS BCR-1 ten times, and NASA pyroxene standard (LUD) fifteen times. Standard and relative deviations were calculated by use of the equations

$$s = \sqrt{\frac{\Sigma (x-\bar{x})^2}{n}}$$

$$c = 100s/\bar{x}$$ (Ahrens and Taylor, 1961, p116)

where x = determination or measurement per sample
$\bar{x}$ = sample mean
n = number of sample measurements

Results are shown in the following table, which also provides indication of the accuracy that was achieved.

Analytical precision and accuracy

USGS BCR-1 by AA (FeO by titration) NASA Pyroxene by Electron Microprobe

NASA Pyroxene	(Furnished by N.D. MacRae, 1971)	$\bar{x}$	s	c
SiO_2	51.61	50.59	0.96	1.90
Al_2O_3	5.92	5.90	0.16	2.71
TiO_2	0.27	0.21	0.046	21.90
BCR-1	(Flanagan, 1967*, 1973)			
Fe_2O_3	3.20*	3.17	0.18	5.67
FeO	9.08*	9.10	0.16	1.75
MgO	3.46	3.58	0.14	3.91
MnO	0.18	0.19	0.01	5.26
CaO	6.92	6.81	0.40	5.87
Na_2O	3.27	3.47	0.19	5.47
K_2O	1.70	1.70	0.06	3.52

Formula calculations and ionic ratios for the minerals were obtained by use of a Fortran IV computer program (Appendix I) using an IBM 360/65 computer installed at the Computing Centre, University of Ottawa.

Methods used to obtain information on cation distribution within crystals (the Mössbauer experiment) and on the spatial distribution of crystals will be described in subsequent chapters.

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The writer is grateful to Dr. Ralph Kretz for his continued interest, encouragement and guidance during the course of this research and for his critical reading of the manuscript. Drs. F.P. Agterberg and Donald D. Hogarth have also offered many valuable discussions and suggestions regarding the statistical analysis and the mineralogical aspects of the thesis, respectively. Dr. William K. Fyson made some valuable editorial comments.

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The writer also wishes to thank Dr. Edgar Froese of the Geological Survey of Canada for critically reading the manuscript. His valuable discussions regarding chemical reactions, petrogenesis, and the pyroxene equilibria were

appreciated. Drs. Donald H. Lindsley of the State University of New York at Stony Brook, and A.R. Philpotts of the University of Connecticut have critically reviewed the entire thesis which has been greatly improved through their comments and suggestions.

Thanks must also be extended to Drs. Ingo Ermanovics and A.G. Plant of the Geological Survey of Canada for their assistance in obtaining some chemical analyses and electron microprobe analysis of a biotite sample respectively. The analysis of minerals by electron microprobe was done by Mr. Paul Mainwaring under the supervision of Dr. David Watkinson of the Department of Geology, Carleton University.

Dr. S.K. Saxena of the City University of New York kindly provided a computer run on the least square solution of an equation for co-existing pyroxenes based on a simple mixture solution model. Mass balance of five chemical reactions by Dr. T.M. Gordon of the Geological Survey of Canada was also appreciated.

The writer is particularly indebted to Dr. A.F. Buddington of Princeton University, who kindly provided advice concerning the collection of rock samples. Also appreciated are the many valuable discussions and encouragement he offered during the initial phases of the study.

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the laboratory work and development of a rapid ferrous iron analytical technique. Mr. Edward Hearn prepared the photomicrographs.

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II MINERALOGY, PETROGRAPHY AND BULK-ROCK CHEMICAL ANALYSES

The mineral assemblages and modal analyses of the twelve charnockitic granulites that were selected for detailed study are shown in Table 1. Bulk-rock chemical analyses of eleven of these rocks are shown in Table 2. These data will be discussed in a later chapter.

A brief description of the minerals present in the rocks is given in the following sections. Chemical analyses of orthopyroxene, clinopyroxene, amphibole, garnet, magnetite, and ilmenite will be presented in Part 3 of this thesis, which deals with exchange equilibrium.

Feldspars

The feldspars are fine to medium grained and granoblastic. K-feldspar is commonly perthitic and locally may be microperthitic. Potash feldspar, some showing microcline twinning, occurs in trace amounts in only a few samples. The perthitic feldspars are mostly blebby and rod perthite. String perthite and mesoperthite have also been observed. Plagioclase commonly occurs as two types, well twinned and clear crystals as well as antiperthitic crystals. They may be optically positive or negative. 2V determined for J-35 plagioclase is $2V_x=83.5^\circ$ and for J-66 $2V_x=85^\circ$. Grain shapes vary from xenoblastic to hypidioblastic, and are more hypidioblastic than K-feldspars. Compositions of plagioclase

Table 1 Mineral Assemblages and Modal Analysis of Charnockitic Granulites from the Adirondack Mountains, N.Y. (in %)

Specimen No. / Mineral	J-35	J-44	J-50	J-63a	J-66	J-80	J-81	J-92	J-99	J-103	J-105b	J-106	Av
Plagioclase	45.4	45.1	59.1	50.8	48.6	22.8	30.0	36.9	43.1	51.7	33.6	51.8	43.3
Perthitic Feldspar	-	7.6	-	-	-	-	1.1	35.7	-	1.5	25.3	5.0	6.4
Antiperthitic Feldspar	Trace	21.6	7.2	Trace	-	1.0	2.0	2.8	-	15.1	1.5	3.5	4.6
Microcline	-	-	0.4	-	-	-	-	-	-	Trace	-	Or 1.2	Trace
Orthopyroxene	3.7	7.8	-	2.2	5.3	23.6	15.8	6.2	-	10.3	9.2	10.8	7.9
Clinopyroxene	17.9	6.2	15.3	15.7	15.6	13.5	20.0	1.9	28.2	9.0	3.4	8.7	13.0
Amphibole	7.1	7.9	4.8	0.1	2.7	8.3	-	4.0	11.1	4.5	2.5	9.6	5.2
Biotite	0.3	Trace	-	Trace	Trace	0.1	Trace	0.3	0.4	Trace	1.4	Trace	0.2
Garnet	13.2	-	9.1	20.9	15.8	8.5	16.0	Trace	7.8	-	8.3	-	8.3
Quartz	0.6	0.5	0.5	0.4	0.7	-	0.5	9.2	0.1	1.0	6.5	1.6	1.8
Myrmekite	-	Trace	-	-	-	-	-	†Trace	-	-	Trace	-	Trace
Opaques**	10.5	2.0	3.2[V]	6.8	8.1	14.2	8.5	1.3	6.8*	4.8	3.3	5.0	6.2
Apatite	1.2	0.9	0.2	2.8	2.6	8.0	5.9	1.1	2.4	1.8	2.4	2.8	2.7
Zircon	Trace	0.4	-	-	Trace	-	-	<0.1	-	Trace	0.3	-	Trace
Calcite	Trace	Trace	0.1	0.4	0.4	-	0.2	0.5	0.1	0.2	2.3	Trace	0.4
Total	99.9	100.0	99.9	100.1	99.8	100.0	100.0	100.0	100.0	99.9	100.0	100.0	100.0

Trace - <0.1%
† - Myrmekite with unmeasurable mixed quartz and feldspar
** - Opaques consist of magnetite, ilmenite, pyrrhotite and pyrite
* - No magnetite; V no pyrrhotite; magnetite grains in J-50 and J-105b are too tiny to be focused by electron beam of microprobe
Av. No. of point counts = 2500

Table 2 Bulk rock chemical compositions of eleven charnockitic granulites from the Adirondack Mts., N.Y.

BULK ROCKS
CHARNOCKITIC GRANULITES

Oxides \ Sp.No.	J-35	J-44	J-50	J-63A	J-66	J-80	J-81	J-99	J-103	J-105B	J-106	Av.
SiO_2	40.80	60.55	49.50	47.70	45.50	41.05	42.10	46.40	53.00	57.50	53.30	48.86
Al_2O_3	13.20	12.85	19.20	14.50	14.40	8.70	11.80	14.20	13.60	13.40	13.30	13.56
TiO_2	5.35	1.35	2.60	3.65	4.25	4.75	4.65	3.75	2.85	2.30	2.80	3.48
Fe_2O_3	1.80	1.46	1.77	2.05	2.05	5.24	2.81	1.66	1.38	1.84	2.10	2.20
FeO	19.16	8.81	9.31	14.38	17.18	21.49	19.53	14.09	11.62	10.03	11.09	14.24
MgO	3.21	1.26	2.58	3.59	3.43	5.20	5.27	3.63	2.35	2.03	2.33	3.17
MnO	0.32	0.21	0.13	0.24	0.27	0.36	0.35	0.25	0.26	0.18	0.23	0.25
CaO	12.31	4.76	10.47	8.90	7.62	10.47	10.20	11.02	7.08	4.16	6.74	8.52
Na_2O	2.49	3.69	2.76	2.98	2.97	1.72	1.99	3.01	4.06	3.72	3.86	3.02
K_2O	0.68	4.93	1.05	1.28	0.69	0.46	0.71	0.96	2.97	3.77	2.98	1.86
Total	99.32	99.87	99.37	99.27	98.36	99.44	99.41	98.97	99.17	98.93	98.73	99.16
Atomic or ionic %												
$Fe^{2+}+Fe^{3+}$	68.64	47.91	54.05	58.57	64.22	67.26	62.97	58.14	52.29	50.15	52.46	63.08
Mg	19.67	11.40	24.61	24.47	21.71	26.12	28.43	25.34	17.91	16.67	18.13	24.62
Na+K	11.69	40.69	21.34	16.96	14.07	6.62	8.60	16.52	29.80	33.18	29.41	12.30
Ca	82.24	43.15	77.07	72.02	71.12	85.10	82.14	76.99	56.55	42.58	56.15	78.95
Na	15.05	30.23	18.37	21.82	25.08	12.69	14.49	19.04	29.35	34.42	29.12	15.79
K	2.71	26.62	4.56	6.16	3.80	2.21	3.37	3.97	14.10	23.00	14.73	5.26

range from An_{23} (oligoclase) to An_{42} (calcic andesine). Table 3 shows the compositions of plagioclases in the 12 rocks studied as determined by the maximum extinction angle method (synthesized by Wynne-Edwards, 1959, unpublished). Plagioclases may show wavy extinction and vague zoning (normal zoning: core-rim=An_5). Some myrmekitic texture has been observed in samples J-105B and J-44.

Orthopyroxene

Orthopyroxene crystals are fine grained, granoblastic to short prismatic granoblastic in shape, commonly hypidioblastic. Pleochroism varies from pale green or pale grey to light pink. Prismatic cleavage is often well developed. The crystals are optically biaxial (-), and are closely associated with clinopyroxene and biotite where they occur, less frequently with garnet, amphibole and opaques. The orthopyroxene grains occur as two types, (1) with well-defined grain boundaries, and (2) with vaguely defined grain boundaries with clinopyroxene. Occasionally they may show exsolution lamellae of clinopyroxene in some of the rocks (J-44, J-92, J-103). Commonly they are inclusion-free. However, apatite and opaques may be included in very small amounts and biotite may occur as an alteration product along cleavages. For J-35, $2V_x$=60.5°.

Table 3 Plagioclase compositions in terms of %An content of the twelve charnockitic granulites from the Adirondack Mountains, N.Y.

Sp.No.	J-35	J-44	J-50	J-63A	J-66	J-80	J-81	J-92	J-99	J-103	J-105B	J-106
%An	An_{32}	An_{23}	An_{42}	An_{32}	An_{32}	An_{29}	An_{32}	An_{28}	An_{35}	An_{26}	An_{28}	An_{28}

Clinopyroxene

Clinopyroxene crystals are fine to medium grained pale green to greenish in colour. Most grains are granoblastic; very few grains show prismatic habit probably due to the orientation of the thin sections (perpendicular or at an angle to the foliation). Xenoblastic to hypidioblastic in shape, most grains show moderate to strong birefringence. Some grains may be partially or entirely surrounded by amphibole, but with no reaction rim. The clinopyroxene grains are commonly closely associated with amphibole, orthopyroxene, garnet, opaques and biotite. Apatite and opaques are common inclusions. All crystals are optically biaxial (+). Grains show slight pinkish pleochroism in J-99. Multiple twinning occurs in J-103. Minor amounts of fine exsolution lamellae of a second clinopyroxene (less calcic?) occur in some grains of a few samples (J-103, J-105B and J-106). For clinopyroxene J-35, $2V_z=58°$, and $c\wedge z=41°$.

Amphibole

Amphibole crystals are fine to medium grained, granoblastic to short prismatic, pale brownish green, and xenoblastic to hypidioblastic. Apatite and opaques are common inclusions. The amphibole grains may show myrmekitic texture with quartz (e.g. locally in J-66). 2V determined for J-35 amphibole is $2V_x=74.5°$. The optic angle is consistent with an intermediate member of the hornblende series

which is determined by the chemical analyses. A generalized pleochroism is

X = light yellow-green to light greenish yellow

Y = dark green, dark to light brownish green or greenish brown to brownish red

Z = dark green, brownish green to light reddish brown

Absorption: X<Y>Z

Locally some porphyroblastic grains have been observed in some rocks. Smaller grains often are inclusion-free or contain fewer inclusions than the larger grains. Some large grains are poikiloblastic.

Garnet

Garnet crystals are pinkish in colour and are fine grained in all rocks except J-105B. The garnet grains are xenoblastic to idioblastic in shape and may be inclusion-free to poikiloblastic, with opaques, quartz, clinopyroxene, feldspars and apatite as inclusions. They may show corrosive or embayment texture with quartz and plagioclase (J-66, J-105B), may be myrmekitic with quartz (symplektite) (J-99), and may also be clustered as in most of the rocks as well as random under the microscope.

Biotite

Biotite crystals are reddish brown to reddish in colour; they are very fine grained, xenoblastic to hypidioblastic, and are associated with pyroxenes, amphibole, opaques and garnet. The biotites occur as traces of poorly defined grains along cleavages of orthopyroxene in some rocks (e.g. J-80). They appear to be a disappearing phase (relic primary phase) in some rocks but appearing phase (secondary) in the others as an alteration product. Generally, they are inclusion-free.

Quartz

Quartz crystals are fine to very fine grained and xenoblastic. They may be associated with all minerals but appear to occur commonly as inclusions in amphibole and garnet (e.g. J-105B) probably as a reaction product. They show undulose extinction, and are usually inclusion-free.

Opaques

Opaque minerals are fine grained and often appear as aggregates of crystals. By use of an ore microscope, four different types of opaque phases were identified in the charnockitic granulites, but in the less mafic (intermediate) rocks, only two to three types of opaque phases are present. These opaque phases are magnetite, ilmenite, pyrite, and pyrrhotite. The iron oxides are of major concern

in the present study. Most rocks contain magnetite except J-50 and J-105B, and all rocks contain ilmenite. Ore microscopic study has also revealed that ilmenite is the major iron oxide and magnetite commonly occurs as very fine-grained crystals in and/or closely associated with ilmenite. Magnetite or titanomagnetite lamellae are sometimes also present within ilmenite crystals.

Apatite

Apatite is very fine grained and commonly idioblastic. It occurs commonly as inclusion in all minerals except quartz and zircon.

Carbonate

Carbonate is fine-grained and xenoblastic to hypidioblastic. It is closely associated with clinopyroxene (J-66), amphibole, biotite and quartz (J-105B) probably as an alteration product.

Zircon

Zircon is very fine grained, usually occurs as idioblastic prismatic crystals, and is inclusion-free. It is commonly associated with mafic minerals especially pyroxenes.

PART 2

SPATIAL DISTRIBUTION OF CRYSTALS IN ROCKS

III GENERAL PRINCIPLES

Definitions

Like phase: A like-phase contact is a contact between two crystals of the same mineral

Unlike phase: An unlike-phase contact is a contact between two crystals of different minerals

Transition: A sequence of two crystals along a linear traverse, for example AA AB BA where A and B are minerals

Transition matrix: A matrix composed of all the different kinds of transitions observed in a rock or defined by a particular model

Transition series: A series of transition matrices derived from a particular transition matrix. For example from a matrix for minerals A, B, and C, another could be derived by considering minerals B and C together denoting them as Q, giving an AQ matrix

Background and Methods

Although studies on spatial distributions in the field of ecology (e.g. Gleason, 1920; Neyman, 1939; Clark and Evans, 1954; Moore, 1954; Pielou, 1959) and in metallurgy (e.g. Smith, 1948, 1952; Gurland, 1967) have been underway

for some time, comprehensive studies of spatial distributions of crystals in rock began little more than a decade ago.

Harker (1939) and others had long ago presented some information on the distribution of minerals in small volumes of rock, as seen in thin-section, but Ramberg (1952, p220-229), DeVore (1956, 1959), Laffitte (1957,p328), Rogers and Bogy (1958) and Lafeber (1963, 1966) were among the first to examine the subject in greater detail or to consider the subject in terms of interfacial energy. Ramberg, DeVore, and Laffitte suggested that recrystallization may produce a rearrangement of the minerals so as to reduce the total interfacial free energy of the rock.

Rogers and Bogy (1958) and Mahan and Rogers (1968) observed and recorded the kind and frequency of crystal contacts in some granitic and metamorphic rocks. Observations were made along linear traverses across thin-section of the rocks. They found more K-feldspar to K-feldspar contacts in metamorphic rocks than in granitic rocks, and attributed the tendency for K-feldspar crystals to be separated from each other (in granitic rocks) to magmatic crystallization.

Lafeber (1963) used two methods for the analysis of randomness in the distribution of crystals in some granitic rocks. The line sampling method, is similar to that used by Rogers and Bogy (1958) and records all grain

boundaries encountered along a group of parallel lines through a rock. Allowance is made for grains or grain boundaries that are intersected more than once. The area sampling method involves counting all the grains and boundaries in a selected area of a thin-section. He realized that the first method may be biased in favour of minerals that occur as coarser grains, while the second method is difficult to use unless a drawing is made of the rock section.

Agterberg (1967) described a method which may be used to characterize the spatial distribution of minerals in crystalline rocks. The method, which makes use of power spectrum analysis, was applied to two specimens of gabbro from the Muskox Intrusion, and appears to be especially useful in detecting faint layering or other types of periodicity in the arrangement of minerals in rocks.

Vistelius (1966) considered the problem of the origin of the Mt. Belaya granodiorite by examining the distribution of minerals within samples of the rock body. His method of obtaining data is similar to the line-sampling method described above, and his observations were presented in matrix form (transition matrix). Vistelius considered the sequence of crystals recorded along a line through the rocks in terms of the theory of Markov chains; and he concluded from his study that the observed patterns of crystals in the Mt. Belaya granodiorite are consistent with patterns

expected to be produced by magmatic crystallization. In a recent study (1972, p518-519) he defined ideal granites as those in which the sequence of crystal contacts have simple markovian properties, and suggested that metasomatism will produce grain contact sequences which are Markov chains of the second and higher orders. This was supported by Romanova (1972, p517) in a study of the effect of greisenization on the grain sequence in granitic rocks.

Kretz in 1969 (p39-65) carried out tests for homogeneity and randomness in the spatial distribution of crystals in a metamorphic rock and described various methods that may be used for minerals present in major and minor amounts. An area of a thin-section of a pyroxene-scapolite-sphene granulite from Quebec was tested for homogeneity by dividing the area into quarters and determining the mineral proportions in each quarter. The line sampling (line-transect) method, similar to that used by Vistelius (1966) was applied to a homogeneous portion of the thin-section. This study showed that pyroxene and scapolite are evidently distributed at random; and led to the conclusion that the nucleation sites for the minerals were randomly determined and were independent of other crystals in the neighbourhood.

From the study of a suite of gneisses from Shetland and Siberia, Flinn (1969) concluded that the minerals are not randomly distributed but are arranged so that grain contacts between unlike phases occur more frequently than

expected on the basis of randomness. He suggested that interfacial energy between unlike crystals is less than that between like crystals, and that interfacial energy has been responsible for the observed distribution.

R. Kretz and his students have found many such distributions; the results have not been published.

In the present study the method of Vistelius is applied to a suite of rocks from the Adirondacks. This will be referred to as the "line transect method". According to this method, the sequence of crystals encountered along a linear traverse through a rock is considered in relation to the theory of Markov chains. In a random arrangement of crystals, the probability of encountering a crystal of mineral A will depend only on the frequency of occurrence of crystals of A in the traverse as a whole, and will be independent of the nature of the preceding crystal, whether A or some other mineral. Thus in an aggregate of crystals of A and B:

$$p(A/B) = p(A)$$

$$p(A/A) = p(A)$$

where p(A/B) is the probability of moving from a crystal of B to one of A, and p(A/A) is the probability of moving from a crystal of A to another of A. Also, p(A) is the probability of encountering A in the whole traverse, for example if, altogether, the traverse passed over 400 crystals of A and 600 of B, p(A) would be 400/1000=0.4. The above is the model

of randomness that will be employed in the present study. A two-dimensional picture of this model was illustrated by Kretz (1969).

Two kinds of departure from the random model are immediately apparent. Firstly, if $p(A/A)>p(A)$, a tendency toward clustering of A, beyond that expected in a random distribution, would be anticipated, and secondly, if $p(A/B)>p(A)$, crystals of A and B would be inferred to be more strongly associated than in a random distribution.

The chi square test may be used to decide if the random model is accepted or rejected.

The rocks of the present study appear to be homogeneous in hand specimens. In the majority of the thin-sections, grain apparent diameters vary between 0.2 and 1.5 mm, excluding some very fine-grained inclusions. In sample J-92, which is somewhat coarser, grain size ranges from 0.2 to 3 mm.

A standard thin-section was cut from each of the rocks, in a random direction. Modal analyses and mineral assemblages of the rocks are shown in Table 1. The phases considered are total feldspar (F=plagioclase ± K-feldspar), orthopyroxene (H), clinopyroxene (C), amphibole (A), garnet (G), opaque minerals (D=ilmenite ± magnetite ± pyrite ± pyrrhotite), and all other minor phases (O=biotite ± quartz ± apatite ± zircon ± calcite).

The present study will concentrate on the spatial distribution of total feldspar, the two pyroxenes and amphibole. The distribution of garnet and opaque minerals will not be considered in detail, for grain boundaries between two garnet crystals and two crystals of opaque minerals could not be seen under the polarizing microscope and were not recorded. Also, the distribution of biotite, quartz, apatite, zircon and calcite will not be considered.

Measurements were carried out with a Zeiss research microscope equipped with a moving stage. The number of transitions measured ranged from 500 to 987, averaging 768.5 measurements per thin-section. Analysis of grain transitions based on chi square test was performed by a Fortran IV computer program (Appendix II) using an IBM 360/65 computer at the Computing Centre, University of Ottawa.

Spatial Distribution as a Function of Interfacial Free Energy

The role of interfacial free energy (f) in aggregates of crystals has been discussed by Smith (1948), DeVore (1956, 1959), Kretz (1966b), Swalin (1962, p180-213), Gurland (1968), Spry (1969, p25-29) and Flinn (1969). Smith (1948, p18-21), Sinnot (1958, p272-273) and Swalin (1962, p213) report that in annealed metals, the interface between like phases (i.e. two crystals of the same metal) have a higher interfacial free energy than those between unlike

phases, and DeVore (1959, p216-217) and Flinn (1969) suggested that this may also be true for silicates. Thus a rock in which the crystals are randomly distributed may tend to recrystallize to increase the proportion of unlike grain contacts and decrease the proportion of like grain contacts, thereby decreasing its total interfacial free energy.

The specific interfacial free energy for an interface between phases α and β is the Helmholtz free energy associated with unit area of interface and was defined by Johnson (1959) as follows:

$$f = \frac{F^S}{\Omega} = \frac{F - F^\alpha - F^\beta}{\Omega} \qquad (1)$$

where F is the total Helmholtz free energy of a system that contains phase α, phase β, and an α-β interface.

F^α is the bulk Helmholtz free energy of phase α.

F^β is the bulk Helmholtz free energy of phase β.

F^S is the total interfacial free energy.

Ω is the interfacial area.

Similarly, interfacial free energy may be defined as the Gibb's free energy (G) associated with interface:

$$f = \frac{G^S}{\Omega} = \frac{G - G^\alpha - G^\beta}{\Omega} \qquad (2)$$

Thus

$$F^S = \Sigma(f^{\alpha\alpha}\Omega^{\alpha\alpha}) + \Sigma(f^{\beta\beta}\Omega^{\beta\beta}) + \Sigma(f^{\alpha\beta}\Omega^{\alpha\beta}) \qquad (3)$$

Notice that the total interfacial free energy in unit volume of rock may decrease by decreasing one or all of the terms in Ω, i.e. by increasing grain size. Also, it may decrease by decreasing $(\Omega^{\alpha\alpha} + \Omega^{\beta\beta})$ and increasing $\Omega^{\alpha\beta}$, by the same amount, provided $2f^{\alpha\beta} < (f^{\alpha\alpha} + f^{\beta\beta})$ or by decreasing $\Omega^{\alpha\beta}$, and increasing $(\Omega^{\alpha\alpha} + \Omega^{\beta\beta})$ by the same amount, provided $2f^{\alpha\beta} > (f^{\alpha\alpha} + f^{\beta\beta})$. This latter decrease in energy, although small in magnitude could be achieved by a rearrangement of crystals in the rock, or by the initial nucleation and growth of crystals, during metamorphism, at sites which would produce, preferentially, interfaces of relatively low energy.

Other factors that are likely to affect the spatial distribution of crystals in rocks insofar as they affect interfacial free energy are: temperature, pressure, composition, partial pressure of vapour phase and compressional or shear stress. While the effects of temperature (Bonie and Derge, 1956; Smith, 1948) and composition (DeVore, 1955, 1956, 1959; Johnson, 1959) are small, the roles of the other factors are relatively unknown. However, their effects on the relatively dry and high grade rocks studied are unlikely to be large.

Effect of Chemical Reactions on Spatial Distribution

Metamorphic crystallization of rocks is brought about by one or more chemical reactions, leading to the formation of new phases. Consider for example a reaction

$$A + B = C + D$$

where A, B, C, and D are minerals. If the reaction between crystals A and B has gone to completion, crystals of the stable products, C and D, may show tendency to occur close to each other in the rock. At univariant equilibrium one may find all four minerals closely associated in a rock. Therefore, the position occupied by crystals of one mineral may depend on the distribution of crystals of other minerals, and this dependence may show up, even if weakly developed, by a statistical study of the kind and frequency of grain contacts found in the rock. Thus mineral associations may appear for reasons other than those involving interfacial free energy.

Procedure

The mineral assemblage of a rock is a list of all the minerals present, and the first order transition ideally records the frequency of transitions or grain contacts for all of these minerals. The data may be expressed in matrix form (a transition matrix) and may be discussed in relation to the theory of Markov chains (Anderson and Goodman, 1957, p89-99; Agterberg, 1966, p764-765; Kretz, 1969, p58-59; Vistelius, 1966, p48-50). From this first order transition matrix a series of other transition matrices may be obtained through a procedure of combining two or more 'phases' at a time. This procedure is similar to the combining or lumping of states by Kemeny and Snell (1960, p123-125). The group of matrices will be referred to, in short, as a 'transition series'.

In the following the term 'order' is employed to designate one of a group of transition matrices derived from an original transition matrix. It bears no relation to 'powering', which is commonly used in the study of stochastic processes (e.g. Anderson and Goodman, 1957, p89-110; Parzen, 1962, p191-192; Vistelius, 1966, p48-50).

The first order transition matrix need not contain all the minerals of a rock, and one may lump together several minerals that occur in small amounts, thus arriving at a number of 'phases' in the first order transition matrix that will be less than the number of minerals in the rock. The set of transition matrices derived therefrom will be called the 2nd order transition matrix, the 3rd order transition matrix, and so on.

Several types of spatial distribution studies may be carried out, namely:

1. The spatial distribution of all mineral phases - the gross pattern.
2. The spatial distribution of all major phases in the rock.
3. The spatial distribution of minor phases in the rock.
4. The preferred associations of two unlike phases.
5. The preferred associations of three or more different kinds of phases, here called a 'complex'.

6. The clustering of crystals of a phase.
7. The spatial distribution of units consisting of two unlike crystals in the rock.
8. The spatial distribution of complexes.

For the distribution of minor phases the nearest-neighbour method (Clark and Evans, 1954; Kretz, 1966a, 1969) and the random-point method (Moore, 1954; Kendall and Moran, 1963; Kretz, 1969) would be more appropriate than the line-transect method (Vistelius, 1966; Kretz, 1969) used in the present study.

The present study will focus on types 4, 6 and 7 above with brief consideration of 1 and 2.

Models for Spatial Distribution of Minerals in Rocks

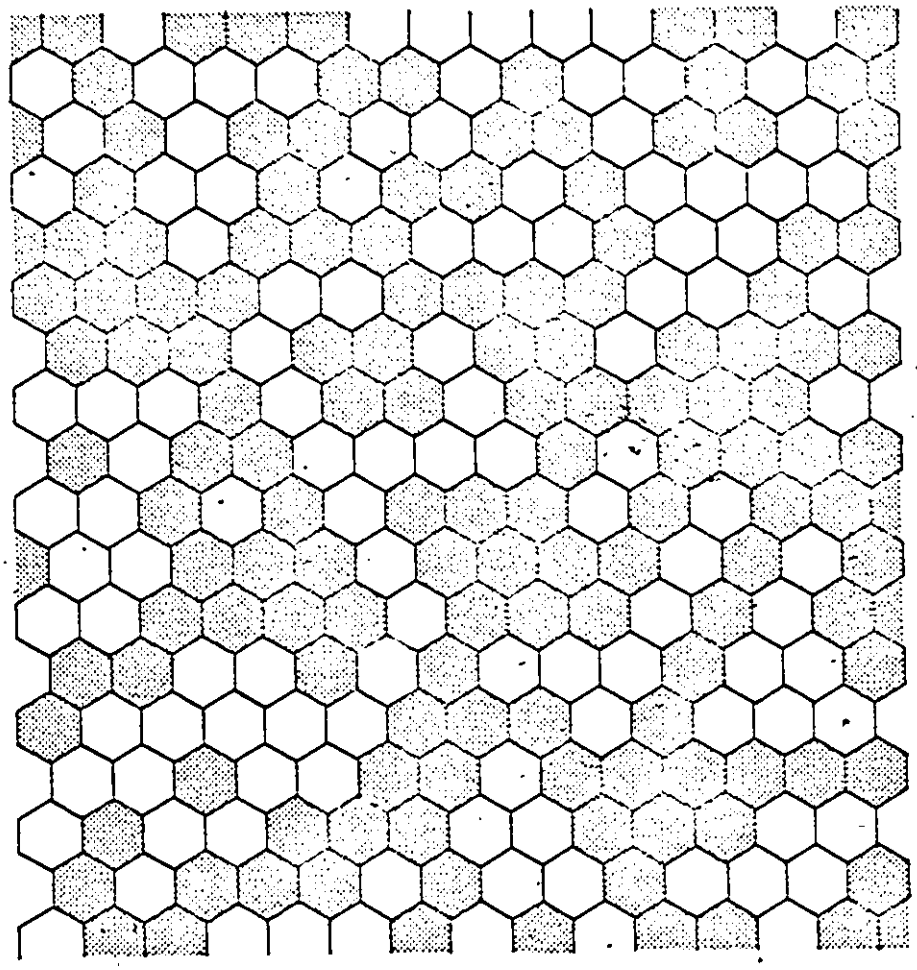
In a rock composed of several minerals, a nearly infinite number of possibilities exist for the arrangement of crystals in the rock, provided that the volume is sufficiently large to contain several thousands of crystals. In a consideration of this problem, a random distribution of crystals would appear to offer a convenient point of departure. Although a random distribution of points in space may be readily characterized, and utilized in the study of 'minor' minerals in a rock (Kretz, 1969) no adequate definition appears to exist for the distribution of many small volumes (crystals) in space. The best one can do at present is to

construct a model in which all the small volumes have the same size and shape. These can then be arranged in a random sequence, thus building up a 'rock' in which the crystals are randomly distributed. A two-dimensional analogue of such a model is shown in Fig. 3. Notice that a certain amount of clustering of crystals is an integral part of a random distribution. Notice also that the distribution may be described in terms of like and unlike contacts. A traverse across this model would produce a random sequence of crystals and crystal transitions, in agreement with the 'line-transect method' of testing for randomness.

A regular distribution may be defined as a distribution in which the crystals are more uniformly or widely distributed than in a random distribution. In terms of the simple model of Fig. 3, this would result in a larger number of unlike contacts, i.e. a greater tendency for unlike crystals to be associated with each other. In a traverse through such a distribution, the probability of encountering a crystal of a particular mineral would depend on the nature of the preceding crystal, and the 'chain' of observations would possess Markovian properties.

In a rock composed of several minerals, a great variation is possible, such that some may be apparently random while others are non-random. For example in a rock composed of minerals A, B, C, and D, A and B may be associated more frequently than expected, i.e. A and B form a two-

Figure 3. A two-dimensional analogue of randomness model in the form of a random mosaic (After Kretz, 1969)



phase association while C and D may be distributed randomly. Should A, B, and C be associated, i.e. form a complex, the distribution may nevertheless be dealt with in terms of a number of two-phase associations. Additional variation may be introduced by the possibility that a particular two-phase association may itself be regular or randomly distributed in the rock volume.

A clustered distribution is here defined as an aggregation of crystals of the same phase, beyond that found in a random distribution (Fig. 3). It also possesses Markovian properties. Several possibilities arise, for example, clusters of crystals of mineral A may be regularly associated with those of another mineral B, thus producing many A-A contacts and many A-B contacts. The clusters themselves may or may not be randomly distributed. The case in which clusters are dispersed will not be considered since it would require an entirely different method of assessing the degree of dispersion (Grucer, 1965; Gurland, 1968, p281).

The present study attempts to obtain information on the distribution of crystals in rocks by use of the line-transect method and with the help of the above models. After observing and recording all crystal-crystal transitions, the number of all kinds of transitions expected (based on the model of randomness) are compared with the number observed by use of the chi square test. If the calculated or measured chi square exceeds the chi square at the 95% level of signifi-

cance and with the appropriate degrees of freedom (the expected chi square) the model of randomness is rejected.

Initially, two questions may be added: (i) How are crystals of a particular mineral (e.g. A) distributed, and (ii) is there any preferred association between any two minerals (e.g. A and B).

(i) Spatial distribution of crystals of a particular phase

The spatial distribution of crystals of phase A in a rock composed of A and other minerals (B, C, D), where these are designated O, is evaluated as follows. If the measured chi square is less than the expected chi square the distribution of crystals of A is considered to be random (R), regardless if the observed transitions of AA are greater than, equal to, or less than the expected values (the probability of the observed transitions of AA for these three cases is the same* - Agterberg, 1973, personal communication). If the measured chi square is greater than the expected value, the distribution of A is considered to be non-random. If the number of AA transitions is less than expected, A is anti-clustered (AC), and if the number of AA transitions is greater than expected, A is clustered (C). Distributions of crystals of B, C and D may be determined in the same way.

(ii) Association of unlike phases

The association of two unlike phases (e.g. A and B) in a rock composed of A, B and O = (C + D) is evaluated as

* Two equal probabilities, both 0.5, are for the cases (1) greater than, and (2) less than.

follows. If the measured chi square is less than the expected value, regardless if the measured transitions of AB are greater, equal, or less than expected, the distribution of A and B in the rock is taken to be random. If the measured chi square is greater than expected, the distribution of A and B is not random. Now, if the number of AB transitions is less than expected, the distribution with regard to A and B is referred to as anti-regular (ARg), and if the number of AB transitions is greater than expected, i.e. A and B are preferentially associated, the distribution with regard to A and B is referred to as regular (Rg). Distributions of AC, AD, BC, BD and CD in the rock may be determined in the same way.

The above may be summarized as follows:

(i) Distribution of a particular phase (A-O Type)

1.	$\Sigma\chi^2_m < \chi^2_{0.95}$	T<E or T>E (e.g. $T_{AA} < E_{AA}$)	Random (R)
2.	$\Sigma\chi^2_m > \chi^2_{0.95}$	T<E (e.g. $T_{AA} < E_{AA}$)	Anti-clustered (AC)
3.	$\Sigma\chi^2_m > \chi^2_{0.95}$	T>E (e.g. $T_{AA} > E_{AA}$)	Clustered (C)

(ii) Association of unlike phases

(A-B-O Type)

4. $\Sigma\chi^2_m < \chi^2_{0.95}$ — $T<E$ or $T>E$ — Random (R)

(e.g. $T_{AB}<E_{AB}$)

5. $\Sigma\chi^2_m > \chi^2_{0.95}$ — $T<E$ — Anti-Regular (ARg)

(e.g. $T_{AB}<E_{AB}$)

6. $\Sigma\chi^2_m > \chi^2_{0.95}$ — $T>E$ — Regular (Rg)

(e.g. $T_{AB}>E_{AB}$)

where T = observed transition

E = expected transition

A,B = minerals of interest

O = all other minerals, considered collectively

χ^2_m = 'measured' chi square

$\chi^2_{0.95}$ = chi square at the 95% confidence level

IV SPATIAL DISTRIBUTION OF CRYSTALS IN CHARNOCKITIC GRANULITES FROM THE ADIRONDACK MOUNTAINS

General Statement

In the rocks of the present study, crystals are nearly equidimensional, retrograde effects are minimal, and grain contacts are clearly defined. However, contacts between grains of garnet and opaque minerals could not be recognized, and the distribution of these minerals was therefore not studied in detail. All minor phases are grouped as 'others'.

The following sections deal first with the question of homogeneity, and then with details in the distribution of pyroxenes, amphibole and feldspar.

Homogeneity

Since all of the eleven specimens studied appear to be homogeneous in hand specimens and under the microscope, tests for homogeneity were carried out on only five samples. These samples, which were chosen at random are J-35, J-44, J-50, J-92 and J-106. Standard-size thin-sections were cut for each rock in a random plane where foliation is lacking and perpendicular to the foliation where it is present. The point-sample method described by Kretz (1969, p45-47) was used to test for homogeneity. The crystal density method (Kretz, 1969, p41-42) was used on J-35 and J-44 to check the results.

Using the point-sample method, a rectangular area measuring 15mm x 20mm on each thin section was divided into four quarters, and the mineral proportion in each quarter were determined by the point-count method. The points were distributed as shown in Fig. 4. The chi square test was then used to determine if the variation found may or may not be attributed to chance, i.e. whether or not the model of homogeneity may be accepted. For the homogeneity test, 252 to 337 points and an average of 307 points were counted per thin-section. Results for the distribution of feldspar(F), orthopyroxene(H), clinopyroxene(C), amphibole(A), garnet(G), opaque minerals(D) and remaining minerals(O), in these rocks are as follows:

J-35 Homogeneous, since $\Sigma\chi_m^2 = 5.04 < \chi_{0.95}^2(\nu=12) = 21.03$

J-44 " " $\Sigma\chi_m^2 = 16.38 < \chi_{0.95}^2(\nu=12) = 21.03$

J-50 Not homogeneous, since $\Sigma\chi_m^2 = 27.79 > \chi_{0.95}^2(\nu=15) = 25.00$

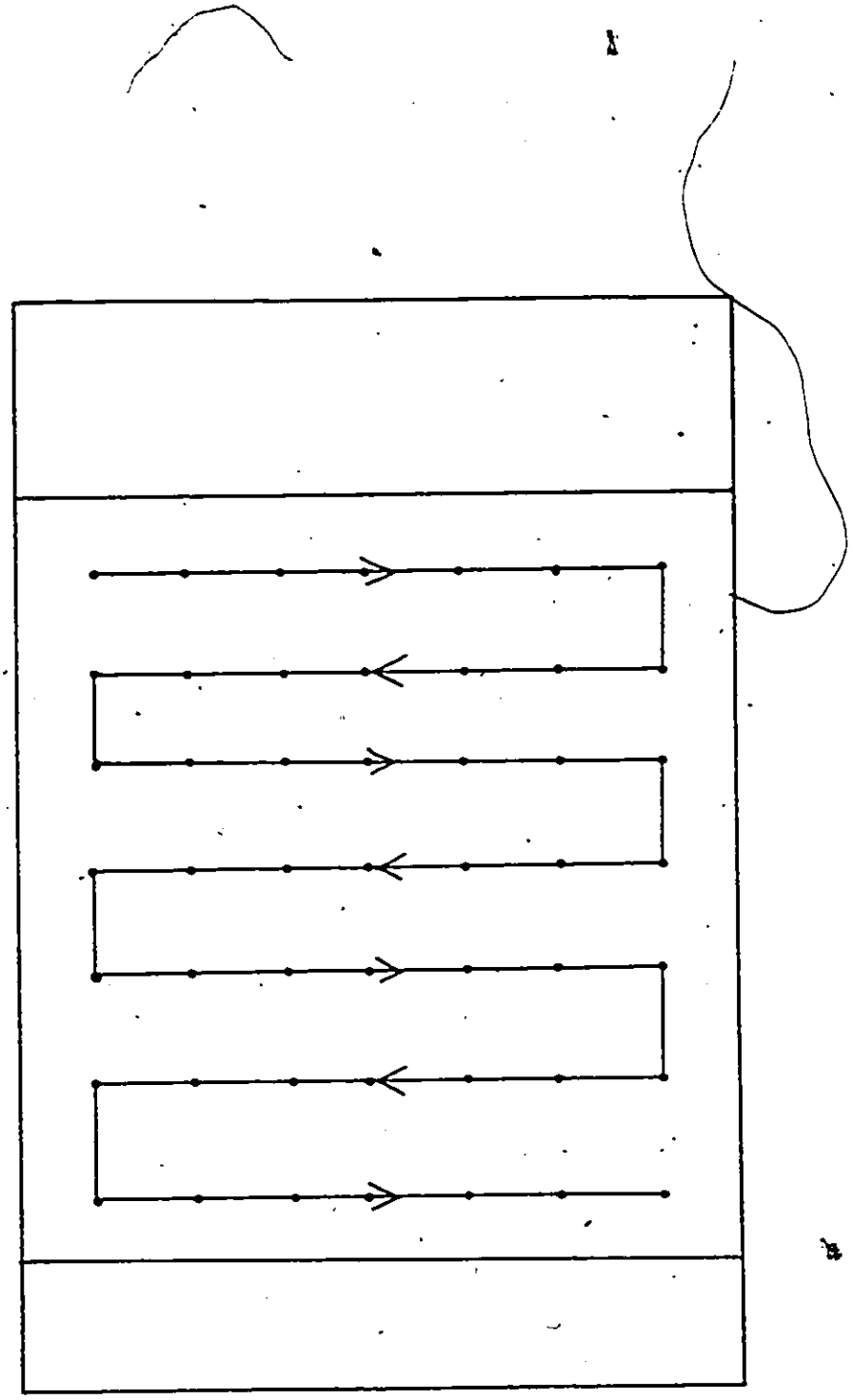
J-92 Homogeneous, since $\Sigma\chi_m^2 = 12.13 < \chi_{0.95}^2(\nu=9) = 16.92$

J-106 " " $\Sigma\chi_m^2 = 16.28 < \chi_{0.95}^2(\nu=15) = 25.00$

where χ_m^2 is the calculated chi square and ν is the number of degrees of freedom.

Evidently sample J-50 is nearly homogeneous, or slightly heterogeneous, since χ_m^2 is very close to $\chi_{0.95}^2$. The results show that the rocks examined and probably the others as well are homogeneous or very nearly so with respect to all the minerals for which measurements were obtained.

Figure 4. A sketch to show the point-sample and line-transect methods of spatial distribution measurements of crystals in thin-sections. The point-sample method locates grains under a point system whereas the line-transect method measures the grain contacts along parallel lines.



Spatial Distribution - The Overall Pattern

Tests for randomness in the distribution of crystals in the set of samples described above were carried out by use of the line-transect method (Kretz, 1969, p58-61). All crystal-crystal contacts that were encountered along a linear traverse of the kind shown in Fig. 4 were recorded, and an average of 770 such measurements were made per thin-section. An example is given in Appendix III and the data are shown in Appendix IV. The frequency of the different kind of contacts was then compared to the frequencies that would be expected if the crystals were randomly distributed, by use of the chi square test, giving the following results

J-35 Not random, since $\Sigma\chi^2_m = 62.36 > \chi^2_{0.95}(\nu=25) = 37.65$

J-44 " " " $\Sigma\chi^2_m = 133.83 > \chi^2_{0.95}(\nu=25) = 37.65$

J-50 " " " $\Sigma\chi^2_m = 118.84 > \chi^2_{0.95}(\nu=36) = 51.00$

J-92 " " " $\Sigma\chi^2_m = 60.83 > \chi^2_{0.95}(\nu=25) = 37.65$

J-106 " " " $\Sigma\chi^2_m = 44.18 > \chi^2_{0.95}(\nu=25) = 37.65$

The above results indicate that with reference to all the minerals that were considered, none of the rocks has passed the particular test for randomness that was adopted.

The above information refers only to the 1st order transition matrix. The transition series must be considered before the distribution of crystals in a rock can be char-

acterized in detail. These aspects of the spatial distribution of crystals in rocks are now considered.

Spatial Distribution of Pyroxenes, Amphibole and Feldspar

The 1st order observed and expected transition matrices together with the condensed transition series of the eleven rocks under investigation are shown in Appendices IV and V. χ^2 values were taken from Owen (1962). The spatial distribution of crystals in each of the rocks is represented by two transition series. Transition series I is composed of multiphase and two-phase transitions in matrix form, whereas transition series II consists mainly of two-phase transitions, also in matrix form.

These data show that in rocks containing garnet(G) and opaque minerals(D) the low-order transitions (1st, 2nd and 3rd orders) invariably show non-random distributions. By successively eliminating garnet and opaque minerals, as shown by series I, it is found that garnet and opaques consistently cause other minerals to appear to depart from a random distribution. A similar effect, produced by feldspar and pyroxenes was noticed in some rocks (e.g. samples J-44, J-50, J-66 and J-99 of transition series I, Appendix V). A careful examination of the results has revealed that minerals that are not distributed at random may affect the distribution of other minerals in the direction of departing from randomness, as shown in Appendices IV and V.

In view of a more recently developed chi square test (Anderson and Goodman, 1957, p97-101; Krumbein, 1967, p8) and the possibility that it may take the place of the conventional chi square test when class expectations are small (Fisher, 1950, p24; Kullback, 1959, p119), chi square values for two by two transition matrices of some of the present samples were recalculated using this newer method. The new chi square test gives a set of statistics of the form

$$\chi^2(m-1)^2 = 2\sum_{ij}^{m} n_{ij} \log_e(\hat{P}_{ij}/\hat{P}_j) \qquad (4)$$

where n_{ij} is the component value of the ij-th cell in the transition matrix,

$\hat{P}_{ij}$ is the transition probability in the same cell,

$\hat{P}_j$ is the marginal probability for the column of the matrix,

m is the number of states

$(m-1)^2$ is the degrees of freedom.

Using equation (4), it is found that when the expected number of transitions between two crystals in a matrix is less than 3 or 4, the chi square value obtained by the new method differs considerably from that of the conventional chi square test (by more than 2 orders of magnitude). However, when expected transitions are greater than 3 or 4, results by the two chi square methods are similar.

The spatial distributions of pyroxenes, amphibole and feldspar in the examined charnockitic granulites may be summarized from the data given in Appendices IV and V in the form of a table (Table 4). It is evident from Table 4 that crystals of pyroxenes, amphibole and feldspar are generally distributed in a random, anti-regular or regular manner, and feldspar is commonly clustered. Crystals of clinopyroxene are anti-clustered in two rocks; crystals of orthopyroxene are clustered in one rock, and crystals of feldspar in seven. The observed patterns of spatial distribution are more complex than was expected when the study was initiated. An interpretation of the data will now be presented.

Interpretation

The data of the present study, as presented in Appendices IV and V, show that all the 1st order transition matrices of the rocks studied indicate a gross pattern of non-random distribution. Although this implies the existence of some regular and/or clustered crystals, the 1st order transition is certainly not sensitive enough to detect details in the spatial distribution pattern. Detailed information can be obtained by studying the transition series.

As noted above, grain boundaries between two garnet crystals and between two crystals of opaque minerals are not readily detectable by use of the petrographic microscope.

Table 4 Summary of spatial distribution of orthopyroxenes (H), clinopyroxenes (C), amphiboles (A) and feldspars (F) in charnockitic granulites from the Adirondack Mts., N.Y.

Spatial Distribution / Sp.No.	Random	Regular	Anti-regular	Cluster	Anti-cluster
J-35	H^1,A^1,F FH,HA^1	FC,FA, HC^1	CA^1		C
J-44	H,A^1,C^1 HC^1,HA^1, CA^1		FH,FC,FA	F	
J-50	H^1,A,C^1 HC^1,HA^1, CA^s		FH^s,FC,FA	F	
J-63A	H^1,C HC		FH,FC	F^s	
J-66	H,C,F^s FH,FC^s	HC			
J-80	H,A,C HA^s,CA	HC	FH,FC,FA^s,	F	
J-81	C	HC^s	FH,FC	H,F	
J-92	H^1,A^1,C^1 HC^1,HA^1, CA^1		FH,FC^s,FA^1	F	
J-99	A,F, CA	FA	FC^s		C
J-103	H,A^1,C HC^1,HA^1, CA^1	FA^s	FH,FC	F	
J-106	H,A^1,C^s, F FH,FC, FA,HC, HA^1,CA				

Superscripts s = similar values of chi squares and/or observed and expected transitions
1 = very low values of observed and expected transitions e.g. less than 4 or 5

Determination of whether such minerals are clustered or not is impossible without the aid of other techniques such as ore microscopy. Like transitions of such minerals, as a result, are always zero while the expected frequencies are always greater than zero. Therefore, the presence of such minerals in a matrix would invariably increase the total chi square of the matrix and cause the spatial distribution of all the minerals to appear to depart from randomness. Since the amount of garnet and opaque minerals is small, the above effect is assumed to be negligibly small.

From Table 4 it is obvious that the majority of the spatial distributions are of the random type, while the anti-clustered type is the least common. An order in terms of decreasing frequency of occurrence may be established as follows:

$$R > ARg > C > Rg > AC$$

where R = random, ARg = anti-regular, Rg = regular, C = clustered, and AC = anti-clustered.

Furthermore Table 4 indicates that while transitions or contacts between like phases of amphibole (A), clinopyroxene (C), and orthopyroxene (H) occur as frequently as expected, transitions between crystals of feldspar (F) occur more frequently than expected. This is clearly shown in Table 4a. This table also shows that transitions between unlike phases H and C in about half of the rocks occur more frequently than expected, and transitions between H and F

Table 4a. Type and frequency of spatial distribution of feldspar (F), amphibole (A), orthopyroxene (H) and clinopyroxene (C) in the charnockitic granulites from the Adirondack Mts., N.Y.

	Number of Rock Specimens			
	Fewer than expected Anti-cluster	As many as expected Random	More than expected Cluster	Interpretation
HH	0	9	1	-
CC	2	9	0	-
AA	0	8	0	-
FF	0	4	7	f^{FF} small
	Anti-regular	Random	Regular	
HC	0	6	4	f^{HC} small
HA	0	7	0	-
HF	7	3	0	f^{HF} large
CA	1	7	0	-
CF	8	1	1	f^{CF} large
AF	4	1	3	-

where f is the interfacial free energy

and, between C and F in most of the rocks occur less frequently than expected. These results suggest to the writer that during metamorphism crystals of feldspar, amphibole and pyroxenes took up positions in the rock such that grain boundaries of like crystals of feldspar (which are mostly plagioclase) and unlike crystals of pyroxenes increased in proportion while those of unlike crystals of orthopyroxene and feldspar and, clinopyroxene and feldspar decreased in proportion, thereby reducing the interfacial free energy of the rock as a whole. This interpretation is based on the fundamental concept of interfacial free energy and on the assumption that such energy may play a part in determining the distribution of crystals in multi-phase systems. Although in metals, interfacial free energy between unlike crystals is generally lower than between like crystals (Bonie and Derge, 1956; Sinnott, 1958; Smith, 1948, 1952; Swalin, 1962; Gurland, 1968), no experimental information is available for silicates, and these may behave differently.

The results of the present study suggest that the interfacial free energy of grain contacts vary with type of phases. In the case of AA, HH and CC, although the interfacial free energies f^{AA}, f^{HH} and f^{CC} may not all be the same, they are generally higher than that of f^{AH}, f^{AC} and f^{HC} whereas in the case of FF or HC, the interfacial free energy f^{FF} would be less than f^{FA}, f^{FH}, f^{FC}, and that f^{HC} less than f^{HA}, f^{CA}, f^{CF} and f^{AF}. The following scheme may be derived from Table 4a:

$$(f^{CF}, f^{HF}) > (f^{HA}, f^{CA}, f^{AF}) > f^{HC}$$
$$(f^{HH}, f^{CC}, f^{AA}) > f^{FF}$$

and possibly

$$(f^{HH}, f^{CC}, f^{AA}) > (f^{FA}, f^{FH}, f^{FC}) > f^{FF}$$

Alternatively, the following relationships may be established in a rock with regard to the types of spatial distribution:

(1) For like crystals of feldspar

$$(\Sigma f)^{AC} > (\Sigma f)^{R} > (\Sigma f)^{C}$$

(2) For unlike crystals of feldspar, amphibole and pyroxenes

$$(\Sigma f)^{ARg} > (\Sigma f)^{R} > (\Sigma f)^{Rg}$$

We may define the condition for equilibrium in a system as follows:

$$\Delta F^{total} = \Delta F + \Delta(\Sigma f) + \Delta F_s = 0 \qquad (5)$$

$$\Delta G^{total} = \Delta G + \Delta(\Sigma f) + \Delta F_s = 0 \qquad (6)$$

where ΔF and ΔG are Helmholtz and Gibb's free energy change respectively, $\Delta(\Sigma f)$ is the interfacial free energy change and ΔF_s the strain energy change of solids. Thus defined, Σf and F_s of the solids cannot be ignored. However, under high temperature, pressure, and very low shear stress conditions as in high grade metamorphism, the strain energy of solids (Bikerman, 1959, p1658) may be negligible. This leaves two important terms ΔF (or ΔG) and $\Delta(\Sigma f)$.

Surface or interfacial free energy is usually a small portion of the total free energy of the system. "From the data of Jura and Gurland (1952, p6033-6044) the surface free energy of MgO is 1000 ergs/cm^2 at 298°K, as determined by the heat of solution difference between fine and coarse particles. For an area of $3.48 \times 10^7 cm^2$/mole, for the fine particles, the surface free energy results in an additional energy of 0.831 Kcal/mole and additional entropy of 70 cal $deg^{-1} mole^{-1}$. These values when compared to the heat of formation of MgO of 145.76 Kcal/mole and entropy of 1.952 Kcal $deg^{-1} mole^{-1}$ at 298°K, are small contributions to the total free energy" (DeVore, 1959, p212-213). However, such small values of surface or interfacial free energy could nevertheless play a dominant role during nucleation, crystal growth, exsolution, replacement, and diffusion transfer - processes that largely involve surfaces and interfacial phenomena (DeVore, 1959) and therefore should not be ignored when total equilibrium in a system is considered.

Now, if different types of spatial distributions occur in a system, for example clustered and random, or random and regular, the system is not in total equilibrium even when ΔG or $\Delta F = 0$, since $\Delta(\Sigma f) \neq 0$.

Results of the present study have demonstrated that all three major types of spatial distribution may occur in a rock. Since this occurs frequently, although in most of the rocks there are two instead of all three types, such

mixing of different kinds of spatial distribution is evidently the rule rather than the exception. This implies that ideal cases of random, regular or clustered distribution of crystals in natural rocks is rare, and that in these rocks total interfacial free energy is rarely minimized.

Plutonic and high grade regional metamorphic rocks that crystallize slowly, and in the absence of shear stress may be expected to reduce their interfacial free energy and acquire particular distribution of crystals. Low grade metamorphic rocks, which may be subjected to high stress, might be expected to show more variation. Extreme clustering might be produced for example by breaking up a large crystal into a number of small crystals, due to the application of shear stress. In rocks that depart from equilibrium with regard to bulk free energy, the probability of encountering clustered distribution of phases might also be greater.

It is difficult to determine if the observed distribution of minerals was formed while the mineral-forming reaction took place, as the result of preferred nucleation and growth, or whether they are largely a consequence of readjustments and rearrangements that took place during the subsequent annealing of the rocks. The selection of a nucleation site may itself be dependent on interfacial free energy, and some two-phase association may be the result of the preferred nucleation of one phase on another. Regardless of the mechanism involved, it appears that some

of the study rocks represent a lower energy level (with regard to interfacial free energy) than others. Another, entirely different interpretation of the results is possible. This supposes that the present crystal distribution is a consequence of the particular mineral-forming chemical reaction that took place. For instance a two-phase association involving minerals A and B may have formed in a rock because A and B are both products of a particular reaction. However, since crystals of feldspar, garnet, and opaque minerals were not distinguished under the microscope, evaluation of this aspect would be rather premature.

PART 3

ION EXCHANGE EQUILIBRIA

V CHEMICAL COMPOSITION OF COEXISTING FERROMAGNESIAN MINERALS

General Statement

In order to understand the chemical processes that take place during the crystallization of multi-phase high-grade metamorphic rocks such as the charnockitic granulites of the present study, information on the equilibrium characteristics of the rocks must be determined. Such information may be obtained by careful study of the chemical composition of the constituent mineral phases.

In Part 3 of this thesis, the chemical composition of the phases orthopyroxene, clinopyroxene, amphibole, garnet, biotite, magnetite, and ilmenite are presented. These data are then used for the detailed consideration of ion exchange equilibrium between coexisting phases. In Part 4, the overall phase equilibrium and petrogenesis of the study rocks are examined.

Chemical Composition of Pyroxenes, Amphibole, Garnet, Biotite, Magnetite, and Ilmenite

Chemical analyses of orthopyroxene, clinopyroxene, amphibole, garnet, and one biotite from the rocks that were selected for detailed study are shown in Tables 5 to 9 respectively. The orthopyroxenes vary between ferrohypersthene and orthoferrosilite and are mostly eulite in

composition (cf. Deer et al., 1962, V2, p19-22). The clinopyroxenes are mainly ferrosalite (cf. Deer et al., 1962, V2, p52-53). The amphiboles vary in composition between hornblende and ferrohastingsite and are mostly hastingsite (cf. Deer et al., 1962, V2, p278-291). Since H_2O was not determined, the amphibole formulae have been calculated on the basis of 23 oxygen ions. The garnets are all iron-rich almandines (cf. Deer et al., 1962, V1, p86-87) and the biotite appears to be a high TiO_2 and low Al_2O_3 and CaO variety (cf. Deer et al., 1962, V3, p58-60). Since H_2O was not analyzed, the biotite formula has been calculated on the basis of 22 oxygen ions. Chemical composition (major elements only) of magnetites and ilmenites are shown in Table 10. These iron oxides are mainly present as ilmenite and magnetite solid solutions.

Table 5 Chemical compositions of Orthopyroxene from charnockitic granulites from the Adirondack Hts., N.Y. together with calculated formulae.

ORTHOPYROXENES

SP NO / OXIDES	J-35	J-44	J-66	J-80	J-81	J-103	J-105B	J-106	Av
SiO_2	48.92	46.50	48.14	46.80	47.75	47.82	46.56	47.13	47.45
Al_2O_3	0.67	0.44	0.64	0.91	0.89	0.57	0.51	0.67	0.66
TiO_2	0.09	0.11	0.00	0.06	0.12	0.10	0.08	0.09	0.08
Fe_2O_3	0.43	0.92	3.25	1.35	0.24	0.80	2.30	2.10	1.51
FeO	36.00	42.05	33.44	33.89	33.87	39.70	39.37	38.36	37.09
MgO	11.53	6.57	14.71	13.81	14.59	9.41	9.21	9.23	11.13
MnO	0.49	1.16	0.32	0.49	0.38	1.04	0.90	0.99	0.72
CaO	1.53	1.58	1.03	1.15	1.54	1.69	1.70	1.70	1.49
Na_2O	0.06	0.05	0.07	0.03	0.06	0.07	0.07	0.07	0.06
K_2O	0.04	0.03	0.05	0.01	0.03	0.08	0.06	0.09	0.05
Total	99.76	99.41	101.65	98.50	99.47	101.28	100.76	100.43	100.24
$Fs = (X_{Fe^{2+}}) \times 100$ =	63.7	78.2	56.1	57.3	56.6	70.3	70.6	70.0	

Number of ions on the basis of 6 oxygens

	J-35	J-44	J-66	J-80	J-81	J-103	J-105B	J-106
Si	1.969	1.955	1.895	1.900	1.915	1.942	1.912	1.929
$(Al)^T$	0.031	0.022	0.030	0.044	0.042	0.027	0.025	0.032
$(Ti)^T$	0.0	0.004	0.0	0.002	0.004	0.003	0.003	0.003
$(Fe^{3+})^T$	0.0	0.019	0.076	0.041	0.007	0.025	0.061	0.036
Z	2.00	2.00	2.00	1.99	1.97	2.00	2.00	2.00
$(Al)^O$	0.001	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$(Ti)^O$	0.003	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$(Fe^{3+})^O$	0.013	0.010	0.021	0.0	0.0	0.0	0.011	0.029
Fe^{2+}	1.212	1.479	1.101	1.153	1.136	1.348	1.352	1.313
Mg	0.692	0.442	0.863	0.838	0.872	0.570	0.564	0.563
Mn	0.017	0.041	0.011	0.017	0.013	0.036	0.031	0.034
Ca	0.066	0.071	0.043	0.050	0.066	0.074	0.075	0.075
Na	0.005	0.004	0.005	0.002	0.005	0.006	0.006	0.006
K	0.002	0.002	0.003	0.001	0.002	0.004	0.003	0.005
XY	2.01	2.02	2.05	2.06	2.09	2.04	2.04	2.03
X_{Mg}	0.363	0.218	0.439	0.421	0.434	0.297	0.294	0.300
X_{Fe}	0.637	0.782	0.561	0.579	0.566	0.703	0.706	0.700

Superscripts

T = tetrahedral

O = octahedral

Table 6 Chemical composition of clinopyroxenes from charnockitic granulites from the Adirondack Mts., N.Y. together with calculated formulae

CLINOPYROXENES

Oxides \ Sp.No.	J-35	J-44	J-50	J-63A	J-66	J-80	J-81	J-99	J-103	J-105B	J-106	Av.
SiO_2	48.35	48.71	48.38	49.76	51.57	46.88	47.58	51.27	49.04	51.45	49.02	49.27
Al_2O_3	1.64	1.23	2.55	2.09	2.20	2.03	2.11	1.31	1.60	1.80	1.63	1.84
TiO_2	0.10	0.19	0.27	0.13	0.14	0.19	0.23	0.17	0.17	0.19	0.17	0.18
Fe_2O_3	1.02	2.53	3.59	2.60	2.15	3.86	2.38	1.04	1.56	1.39	2.47	2.24
FeO	16.62	22.10	12.07	13.88	13.25	13.33	13.56	15.95	18.54	18.88	18.76	16.11
MgO	8.85	5.38	10.49	10.94	10.67	10.49	10.47	9.57	7.53	7.66	7.57	9.06
MnO	0.22	0.60	0.13	0.16	0.15	0.25	0.21	0.24	0.49	0.50	0.48	0.31
CaO	22.54	16.76	20.01	17.85	17.55	22.54	19.89	18.57	19.79	16.00	19.39	19.17
Na_2O	0.55	0.57	0.52	0.74	0.72	0.63	0.62	0.40	0.67	0.61	0.54	0.60
K_2O	0.06	0.03	0.06	0.05	0.07	0.02	0.08	0.04	0.17	0.09	0.13	0.07
Total	99.95	98.40	98.07	98.20	98.47	100.22	97.13	98.56	99.56	98.57	100.16	98.85

Numbers of ions on the basis of 6 oxygens

	J-35	J-44	J-50	J-63A	J-66	J-80	J-81	J-99	J-103	J-105B	J-106	
Si	1.897	1.968	1.891	1.935	1.979	1.829	1.891	1.992	1.935	2.013	1.926	
$(Al)^T$	0.076	0.032	0.110	0.065	0.021	0.093	0.099	0.008	0.065	0.0	0.074	
$(Ti)^T$	0.003	0.0	0.0	0.0	0.0	0.006	0.007	0.0	0.0	0.0	0.0	
$(Fe^{3+})^T$	0.024	0.0	0.0	0.0	0.0	0.072	0.004	0.0	0.0	0.0	0.0	
	Z=2.00	Z=2.00	Z=2.00	Z=2.00	Z=2.00	Z=2.00	Z=2.00	Z=2.00	Z=2.00	X=2.00	Z=2.013	Z=2.00
$(Al)^o$	0.0	0.026	0.008	0.031	0.079	0.0	0.0	0.052	0.010	0.083	0.001	
$(Ti)^o$	0.0	0.006	0.008	0.004	0.004	0.0	0.0	0.005	0.005	0.006	0.005	
$(Fe^{3+})^o$	0.006	0.077	0.106	0.076	0.062	0.042	0.067	0.030	0.046	0.041	0.073	
Fe^{2+}	0.545	0.757	0.395	0.452	0.425	0.435	0.451	0.518	0.612	0.618	0.616	
Mg	0.518	0.324	0.611	0.634	0.610	0.610	0.620	0.554	0.443	0.447	0.443	
Mn	0.007	0.021	0.004	0.005	0.005	0.008	0.007	0.008	0.016	0.017	0.016	
Ca	0.948	0.726	0.838	0.744	0.722	0.942	0.847	0.773	0.831	0.671	0.816	
Na	0.042	0.045	0.039	0.056	0.054	0.048	0.048	0.030	0.051	0.046	0.041	
K	0.003	0.002	0.003	0.003	0.003	0.001	0.004	0.002	0.009	0.005	0.007	
	XY=2.07	XY=1.98	XY=2.01	XY=2.00	XY=1.96	XY=2.09	XY=2.04	XY=1.97	XY=2.03	XY=1.93	XY=2.02	
X_{Mg}	0.487	0.300	0.608	0.584	0.589	0.584	0.579	0.517	0.420	0.420	0.418	
X_{Fe}	0.513	0.700	0.392	0.416	0.411	0.416	0.421	0.483	0.580	0.580	0.582	

Superscripts T = tetrahedral
o = octahedral

Table 7 Chemical compositions of amphiboles from charnockitic granulites from the Adirondack Mts., N.Y. together with calculated formulae.

AMPHIBOLES

Oxides \ Sp.No.	J-35	J-44	J-50	J-80	J-99	J-103	J-105B	J-106	Av.
SiO_2	39.09	39.86	39.96	38.46	41.07	39.11	39.60	39.25	39.55
Al_2O_3	11.14	11.34	11.53	11.31	11.28	11.40	11.23	11.18	11.30
TiO_2	2.12	2.69	2.70	2.43	2.30	2.32	2.44	2.50	2.44
Fe_2O_3	2.63	3.51	5.61	4.53	3.39	4.62	4.16	3.65	4.01
FeO	18.23	22.15	14.65	15.38	18.36	20.30	20.26	20.21	18.69
MgO	7.04	4.23	8.61	8.08	6.93	5.93	6.29	6.02	6.64
MnO	0.12	0.32	0.07	0.12	0.13	0.26	0.21	0.23	0.18
CaO	13.80	9.44	11.08	13.80	10.07	9.56	9.76	10.93	11.06
Na_2O	1.50	1.81	1.15	1.44	1.52	1.82	1.77	1.79	1.60
K_2O	1.86	1.74	2.04	1.67	1.99	1.88	1.83	1.84	1.86
Total*	97.53	97.14	97.40	97.22	97.04	97.20	97.55	97.60	97.33

Numbers of ions on the basis of 23 oxygens

	J-35		J-44		J-50		J-80		J-99		J-103		J-105B		J-106	
Si	6.103	Z=8.00	6.285	Z=8.00	6.122	Z=8.00	5.979	Z=8.00	6.352	Z=8.00	6.147	Z=8.00	6.185	Z=8.00	6.148	Z=8.00
$(Al)^T$	1.897		1.715		1.878		2.021		1.648		1.853		1.815		1.852	
$(Al)^O$	0.154	XY=4.75	0.393	XY=5.09	0.204	XY=5.01	0.052	XY=4.75	0.409	XY=5.06	0.260	XY=5.17	0.253	XY=5.17	0.212	XY=5.02
Ti	0.249		0.319		0.311		0.284		0.268		0.274		0.287		0.294	
Fe^{3+}	0.309		0.417		0.647		0.530		0.395		0.546		0.489		0.430	
Fe^{2+}	2.381		2.921		1.877		2.000		2.375		2.669		2.646		2.647	
Mg	1.638		0.994		1.966		1.672		1.597		1.389		1.464		1.405	
Mn	0.016		0.043		0.009		0.016		0.017		0.035		0.028		0.031	
Ca	2.309	W=3.13	1.595	W=2.50	1.819	W=2.56	2.299	W=3.06	1.669	W=2.52	1.610	W=2.54	1.633	W=2.53	1.834	W=2.75
Na	0.454		0.553		0.342		0.434		0.456		0.555		0.536		0.544	
K	0.371		0.350		0.399		0.331		0.393		0.977		0.365		0.368	
X_{Mg}	0.408		0.254		0.512		0.484		0.402		0.342		0.356		0.347	
X_{Fe}	0.592		0.746		0.488		0.516		0.598		0.658		0.644		0.653	

* Volatiles not determined

Superscripts T = tetrahedral
O = octahedral

Table 8 Chemical compositions of garnets from charnockitic granulites from the Adirondack Mts., N.Y. together with calculated formulae.

GARNETS

Oxides \ Sp.No.	J-35	J-50	J-63A	J-66	J-80	J-81	J-99	J-105B	Av
SiO_2	38.39	38.40	36.87	38.90	36.21	36.22	38.36	37.58	37.62
Al_2O_3	20.70	20.68	20.71	19.85	20.71	21.67	20.58	22.18	20.89
TiO_2	0.05	0.06	0.02	0.00	0.04	0.08	0.06	0.09	0.05
Fe_2O_3	0.29	1.06	0.99	1.91	1.35	0.28	0.12	0.34	0.79
FeO	29.89	28.28	30.10	29.79	28.67	29.51	29.79	29.72	29.47
MgO	2.43	4.06	3.32	3.14	3.01	2.94	2.37	2.12	2.92
MnO	1.19	0.72	0.85	0.97	1.41	1.13	1.28	1.52	1.13
CaO	7.67	6.21	5.77	6.31	7.13	7.62	6.28	5.82	6.60
Na_2O	0.03	0.02	0.08	0.05	0.01	0.08	0.04	0.08	0.05
K_2O	0.04	0.02	0.03	0.04	0.01	0.07	0.05	0.04	0.04
Total	100.68	99.51	98.74	100.96	98.55	99.60	98.93	99.49	99.56

Numbers of ions on the basis of 24 oxygens

	J-35		J-50		J-63A		J-66		J-80		J-81		J-99		J-105B	
Si	6.074	Z=6.07	6.077	Z=6.08	5.954	Z=6.00	6.130	Z=6.13	5.874	Z=6.00	5.815	Z=6.00	6.151	Z=6.15	5.991	Z=6.00
$(Al)^T$	0.0		0.0		0.047		0.0		0.126		0.186		0.0		0.009	
$(Al)^O$	3.861	Y=3.90	3.858	Y=3.99	3.896	Y=4.02	3.688	Y=3.91	3.835	Y=4.01	3.916	Y=3.96	3.891	Y=3.91	4.160	Y=4.21
Ti	0.006		0.007		0.002		0.0		0.005		0.010		0.007		0.011	
Fe^{3+}	0.035		0.126		0.120		0.227		0.165		0.034		0.015		0.041	
Fe^{2+}	3.955	X=6.01	3.743	X=5.86	4.065	X=6.01	3.926	X=5.88	3.890	X=6.06	3.962	X=6.17	3.995	X=5.84	3.963	X=5.70
Mn	0.159		0.097		0.116		0.130		0.194		0.154		0.174		0.205	
Mg	0.573		0.958		0.799		0.737		0.728		0.704		0.566		0.504	
Ca	1.300		1.053		0.998		1.065		1.239		1.311		1.079		0.994	
Na	0.009		0.006		0.025		0.015		0.003		0.025		0.012		0.025	
K	0.008		0.004		0.006		0.008		0.002		0.014		0.010		0.008	
X_{Mg}	0.427		0.204		0.164		0.158		0.158		0.151		0.124		0.113	
X_{Fe}	0.873		0.796		0.836		0.842		0.842		0.849		0.876		0.887	

Superscripts

T = tetrahedral

O = octahedral

Table 9. Electron microprobe analysis of J-105B biotite from charnockitic granulite from the Adirondack Mts., N.Y. together with calculated formula

Oxide	Wt %	Ion	Number of ions on the basis of 22 oxygens	
SiO_2	36.21	Si	5.661	Z = 7.95
Al_2O_3	12.43	Al	2.291	
TiO_2	4.36	Ti	0.513	XY = 5.76
Total Fe as FeO	21.76	Fe^{2+}	2.845	
MgO	10.32	Mg	2.404	
MnO	0.00	Mn	0.000	
CaO	0.03	Ca	0.005	WW = 1.93
Na_2O	0.10	Na	0.030	
K_2O	9.50	K	1.895	
Total	94.71			

Table 10

Electron microprobe analyses of coexisting magnetite (Mt) and ilmenite (Ilm) solid solutions. With S=0.59, C=1.17 for IFe as FeO and S=0.99, C=2.02 for TiO_2.

Sp.No. / Min / Oxides	J-35		J-44		J-50	J-63A		J-66		J-80		J-81		J-99	J-103		J-105B	J-106	
	Mt	Ilm	Mt	Ilm	Ilm	Mt	Ilm	Mt	Ilm	Mt	Ilm	Mt	Ilm	Ilm	Mt	Ilm	Ilm	Mt	Ilm
IFe as FeO	96.64	50.90	91.31	49.59	51.74	92.90	50.72	91.97	48.91	81.95	44.44	91.21	50.07	47.16	91.84	48.26	47.15	92.42	47.72
TiO_2	0.05	50.35	0.96	49.00	47.00	0.56	48.22	0.58	50.53	0.19	46.98	0.73	50.58	52.42	0.23	53.01	53.76	1.00	51.55
Total	96.69	101.25	92.27	98.59	98.74	93.46	98.94	92.55	99.44	82.14	91.42	91.94	100.65	99.58	92.07	101.27	100.91	93.42	99.27

VI INTRACRYSTALLINE ION EXCHANGE

The Mössbauer Effect

The Mössbauer effect is the recoil-free emission and resonant absorption of nuclear γ-rays in the crystals. The theory and principles of the Mössbauer effect and its applications are readily available in the literature regarding the solid state, e.g. Wertheim (1964). The complex theoretical aspects will not be described in this thesis. In brief, however, there are three important hyperfine parameters in the Mössbauer effect. These are:

(1) Isomer or chemical shift (I.S.) - the electric monopole interaction between nuclear charge and electron density at the nucleus.

(2) Quadrupole splitting (Q.S.) - interaction between electric quadrupole moment and electric field gradient tensor at the nuclear site.

(3) Magnetic hyperfine splitting (M.H.S.) - interaction between magnetic dipole moment and local magnetic field at the nuclear site.

The importance of Mössbauer-effect studies in mineralogy, crystal chemistry and petrology is that from the study of the hyperfine parameters, produced by the transition metal ions in crystals (in the present study, Fe) information is obtained on several important crystal chemical

factors. These are (1) magnitude and symmetry of the crystal fields at the lattice site, (2) number of non-equivalent sites occupied by the isotope (^{57}Fe), (3) the site population, (4) oxidation state and (5) ordering of the isotopes in complex crystal structures. Studies of this kind have been carried out by Alff and Wertheim (1961), Annersten (1974), Bancroft et al. (1967, a, b, c, 1968), Burns (1970, p115), de Coster et al. (1963), Dowty and Lindsley (1973), Dowty et al. (1972), Dundon and Walter (1967), Evans et al. (1967), Finger et al. (1972), Gay et al. (1970), Ghose (1965a, b), Ghose and Hafner (1967, 1968), Ghose et al. (1972), Hafner (1968), Hafner and Virgo (1970), Hogarth et al. (1970), Kalvius and Hafner (1968), Nicholson and Burns (1964), Virgo and Hafner (1968, 1969, 1970), Saxena and Ghose (1970, 1971), and Zverev et al. (1971).

A practical aspect of the Mössbauer spectroscopy is the quantitative estimate of the Fe^{2+}/Fe^{3+} ratio in crystals, and when combined with chemical analyses, one may determine the number of ferrous and ferric ions in the different co-ordination sites in the crystal structure. Such information may not otherwise be determined by X-ray methods including the X-ray diffraction techniques (Bancroft et al., 1967b; Ghose 1965b) or by conventional chemical analysis. Furthermore even the more accurate wet chemical methods cannot avoid some oxidation of Fe^{2+} or reduction of Fe^{3+}, whereas the Mössbauer technique does not pose such problems. This is the most accurate method of determining

the Fe^{2+}/Fe^{3+} ratio in lattice sites in solid materials, provided that concentrations of the chemical species are high enough for detection (Bancroft et al., 1967c, p2223; Hogarth et al., 1970, p720). The technique may also be used to check the FeO and Fe_2O_3 determined by wet chemical analyses as to the correctness of the ratio or proportion. Or, quite rapidly and precisely, it may be employed to determine FeO and Fe_2O_3 (Fe^{2+} and Fe^{3+}) in silicate minerals, in conjunction with the electron microprobe.

The present study will make use of the Mössbauer technique to determine (1) the oxidation state of iron, in orthopyroxene, clinopyroxene, and garnet; and (2) the site populations of Fe^{2+} and Mg in the lattice sites of orthopyroxenes in the charnockitic granulites from the Adirondack Mountains.

Crystal Structure of Orthopyroxene, Clinopyroxene and Garnet

The crystal structure of an orthopyroxene with 50% Fe^{2+} (i.e. $Fe^{2+}/Fe^{2+} + Mg = 0.5$) was described by Ghose (1965a). It consists of infinite chains of SiO_4 tetrahedra, linked by bands of Mg and Fe cations, extending along the c-axis. There are two octahedral sites which are designated M_1 and M_2. M_1 site cations are surrounded by six oxygen ions each linked to one silicon atom. Cations in the M_2 sites are surrounded by four oxygen ions each linked to one silicon atom, and two bridging oxygen atoms each shared by two silicon atoms. The symmetry of M_1 sites is approximately

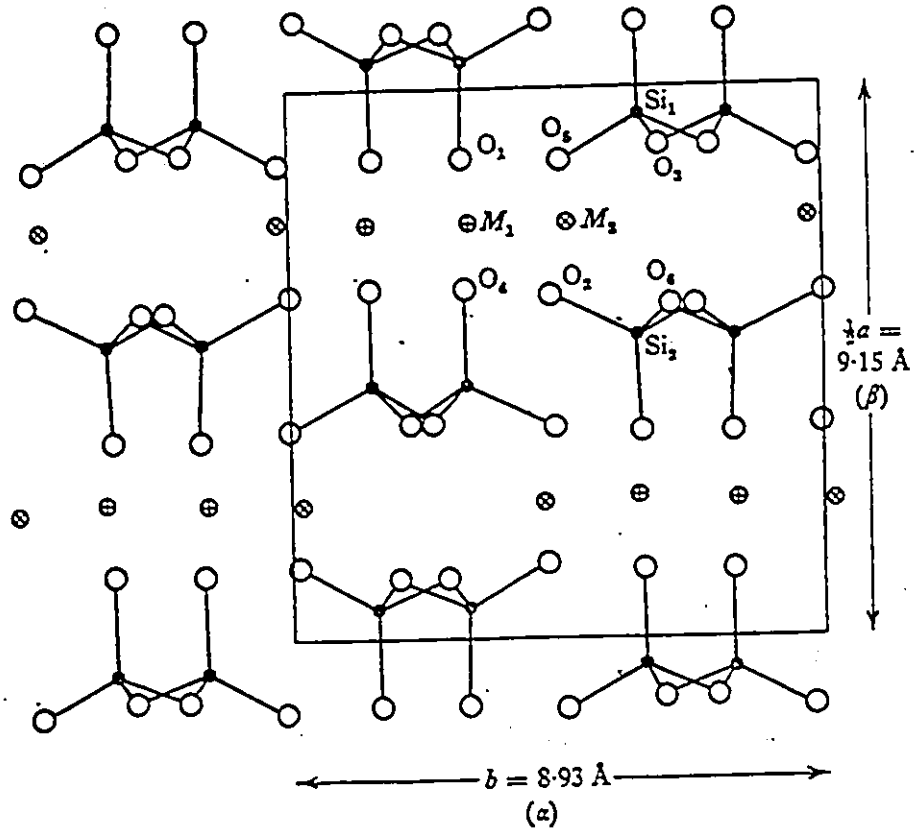
octahedral while the M_2 site is considerably distorted from octahedral (Fig. 5). The crystal structure of clinopyroxene is similar to that of the orthopyroxene, except that the cations in the M_2 sites (the distorted octahedrons), chiefly Ca^{2+} with some Fe^{2+} and Na, are eight co-ordinated with oxygen. The M_1 site is octahedral and is occupied by Fe^{2+} and Mg. The M_1 octahedron in clinopyroxene is more distorted than in orthopyroxene, and the neighbouring M_2 polyhedron is irregular (Warren and Bragg, 1929, p168; Deer et al., 1966, p102-103; Bancroft et al., 1967c, p2227; Ghose and Hafner, 1968, pGH-20).

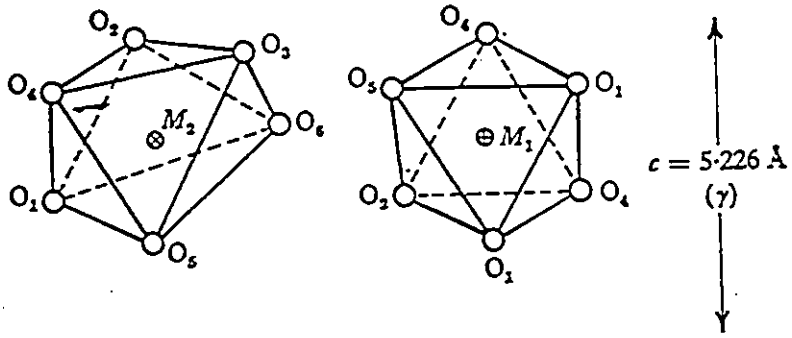
The structure of garnet consists of independent SiO_4 tetrahedra linked by a trivalent cation in octahedral co-ordination and divalent cations in eight-fold co-ordination (Abrahams and Geller, 1958; Gibbs and Smith, 1965; Deer et al., 1966; Bancroft et al., 1967c). Thus the Fe^{2+}, Mg^{2+}, Ca^{2+}, and Mn ions in garnet are eight-fold co-ordinated whereas Fe^{3+}, and Al are six-fold co-ordinated. In the ferrimagnetic garnets such as andradite and some synthetic rare-earth iron garnets, however, considerable amount of Fe^{3+} may be present in the octahedral site (Nicholson and Burns, 1964 pA1568).

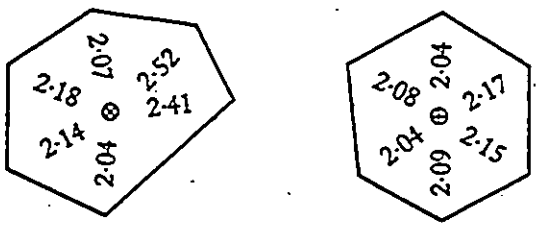
The Mössbauer Experiment

Eight mineral samples, including four orthopyroxenes (J-35, J-80, J-105B and J-106, representing two major mineral

Figure 5. The orthopyroxene crystal structure (after Burns, 1970). The figure shows the structure projected onto (001). Oxygen co-ordination polyhedra ((100) projections) and metal-oxygen distances in each site are indicated (Å); ⊕ M_1; ⊗ M_2; • silicon; ○ oxygen. Atomic co-ordinates and cell parameters from Ghose (1965).


Si1
O5
O1
O3
⊕M1
⊗M2
O4
O2
O6
Si2
½a = 9·15 Å
(β)
b = 8·93 Å
(α)


O2
O3
O4
⊗M2
O6
O1
O5
O4
O5
O1
⊖M1
O2
O4
O3
c = 5·226 Å
(γ)


2·07
2·52
2·18
⊗
2·41
2·14
2·04
2·08
2·04
2·17
2·04
⊖
2·15
2·09

assemblages of the present charnockitic granulites), three clinopyroxenes (J-80, J-105B and J-106) and one garnet (J-80) were purified (>99% purity), and polycrystalline powders (100-150μ) were prepared into the form of thin discs, each approximately 30 mm in diameter and about ½ mm in thickness. Approximately 80 to 100 mg of sample were used in each preparation. Sample powders were simply glued on to a cellophane sheet by using a commercial acrylic spray. The conventional method of adding leucite or other type of matrix was not used.

The Mössbauer resonance experiment was performed in 1972 by scientists of the Mines Branch, Department of Energy, Mines and Resources, Ottawa. A model S3 Mössbauer spectrometer of the constant acceleration type was used, in conjunction with an NS-600 512-channel multichannel analyzer. ^{57}Co embedded in a copper matrix was used as the source for the required 14.4 keV gamma rays, and stainless steel and iron foil were used as standards. Spectral measurements of samples J-35 and J-80 ortho- and clino-pyroxenes together with the J-80 garnet were measured at room temperature and pressure. J-35, J-80, J-105B and J-106 orthopyroxenes and the J-80, J-105B, J-106 clinopyroxenes were measured at 77°K and atmospheric pressure, by holding the absorbers at the liquid nitrogen temperature. All absorption spectra were analyzed and fitted into Lorenzian lines by the aid of a CDC 6400 computer.

Mössbauer absorption spectra of pyroxenes, taken at room temperature, are shown in Figs. 6 to 10. None of these spectra show resolution of Fe^{2+} at the non-equivalent M_1 and M_2 sites, whereas those measured at 77°K give complete resolution of the peaks, as shown in Figs. 11 to 17. The spectra obtained at 77°K enable precise evaluation of the hyperfine parameters and area underneath the peaks produced by iron. Thus pertinent information may be obtained on the magnitude and symmetry of the crystal fields at the lattice sites, the number of non-equivalent sites, site populations, oxidation states and ordering of Fe-Mg within the crystals. Since no further improvement on spectral resolution was obtained at temperatures lower than 77°K (down to 1.7°K) as has been demonstrated by Virgo and Hafner (1968, p269), the Mössbauer spectra are generally best obtained at temperature close to 77°K (Ghose and Hafner, 1968, p4-5; Virgo and Hafner, 1968, p256-259, 1969, p72). Detailed considerations of the Mg-Fe^{2+} distribution and oxidation state of iron in pyroxenes and garnet will therefore be based entirely on the spectral data obtained at 77°K.

Interpretation

A typical Mössbauer spectrum of garnet is a simple two-line spectrum (Nicholson and Burns, 1964, pA1508; Bancroft et al., 1967c, p2234). The Mössbauer spectrum of the analyzed almandine garnet (J-80, Fig. 10) shows such a

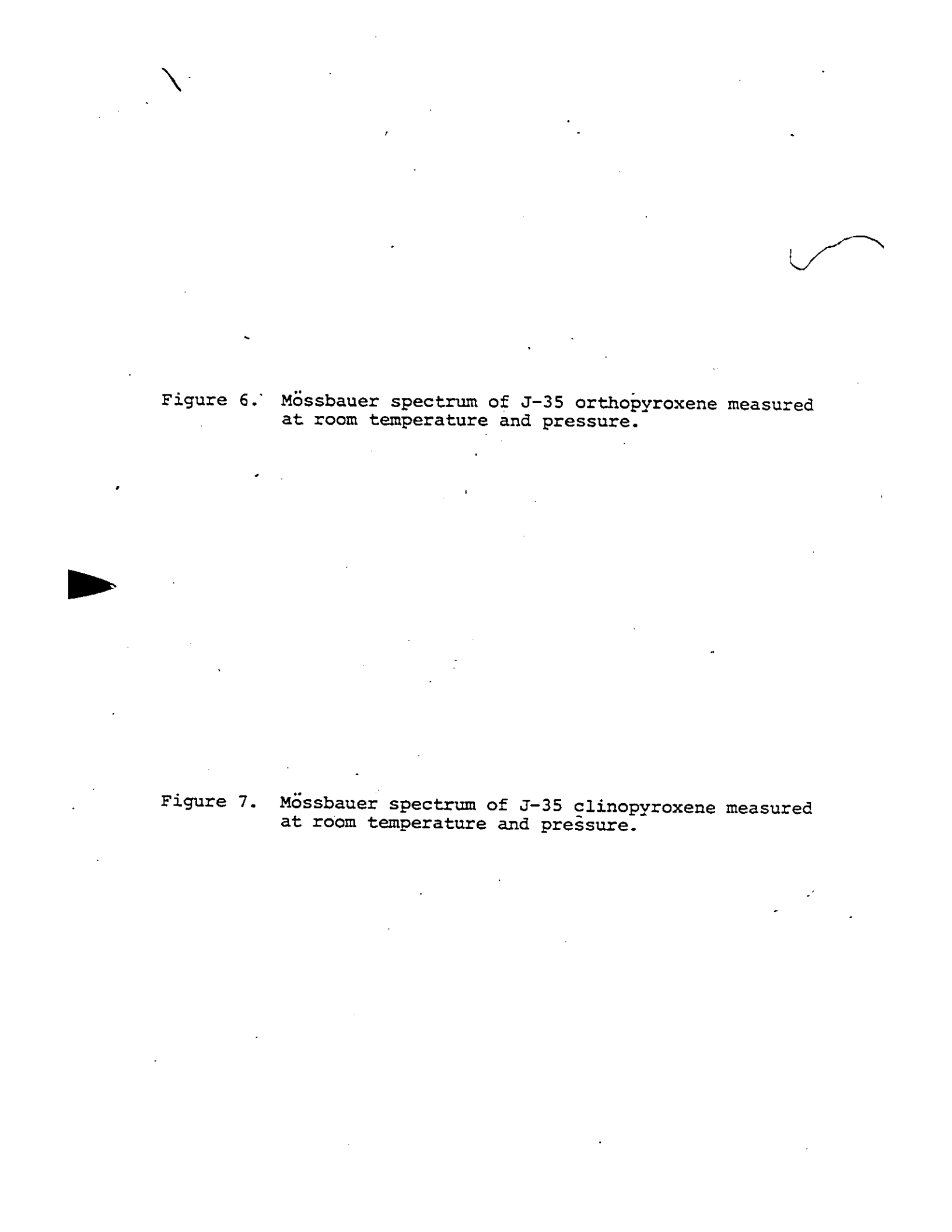
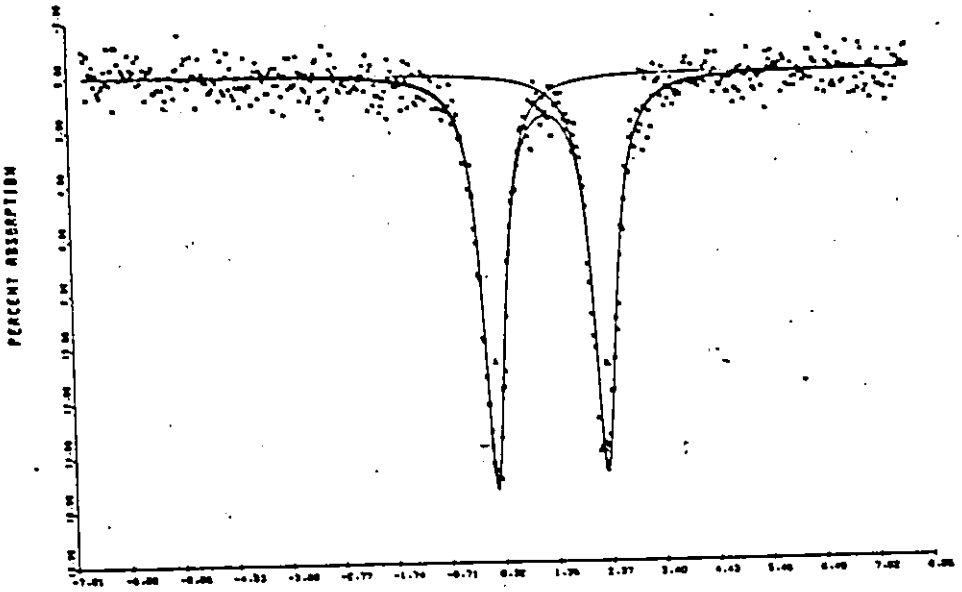


Figure 6. Mössbauer spectrum of J-35 orthopyroxene measured at room temperature and pressure.

Figure 7. Mössbauer spectrum of J-35 clinopyroxene measured at room temperature and pressure.


PERCENT ABSORPTION
MM/S RELATIVE TO STAINLESS STEEL

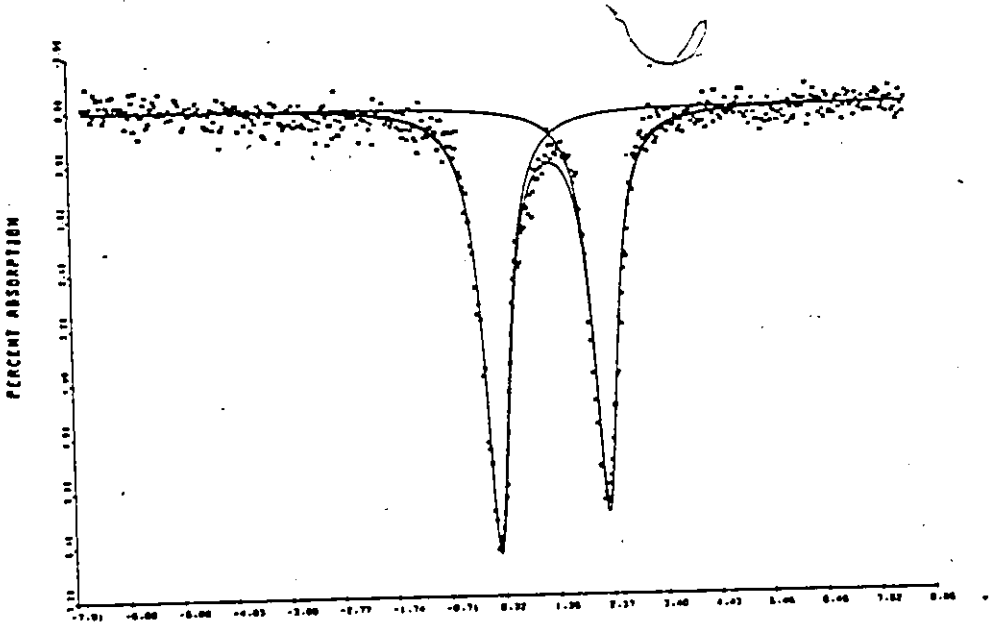
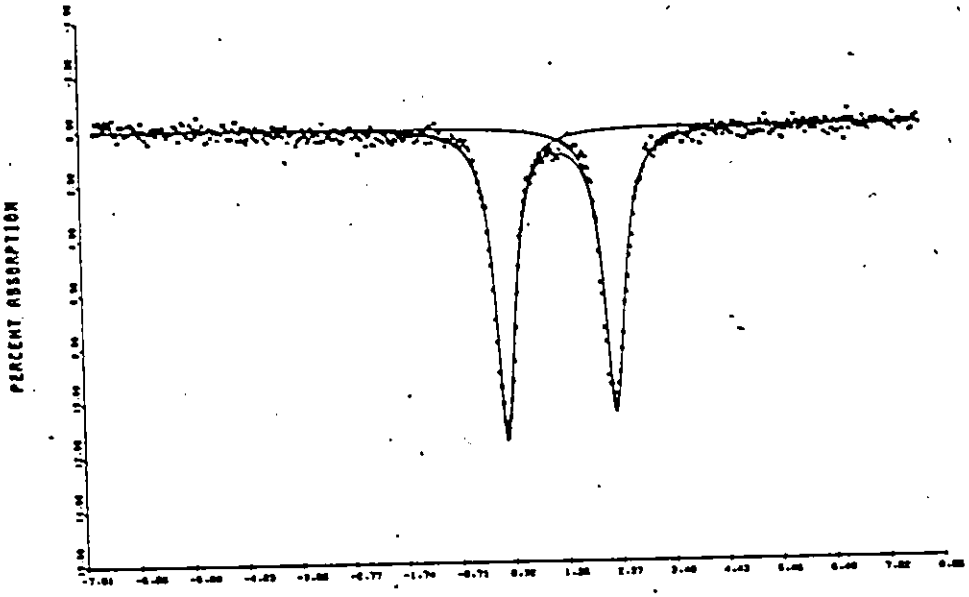

PERCENT ABSORPTION
MM/S RELATIVE TO STAINLESS STEEL

Figure 8. Mössbauer spectrum of J-80 orthopyroxene measured at room temperature and pressure.

Figure 9. Mössbauer spectrum of J-80 clinopyroxene measured at room temperature and pressure.


PERCENT ABSORPTION
MM/S RELATIVE TO STAINLESS STEEL

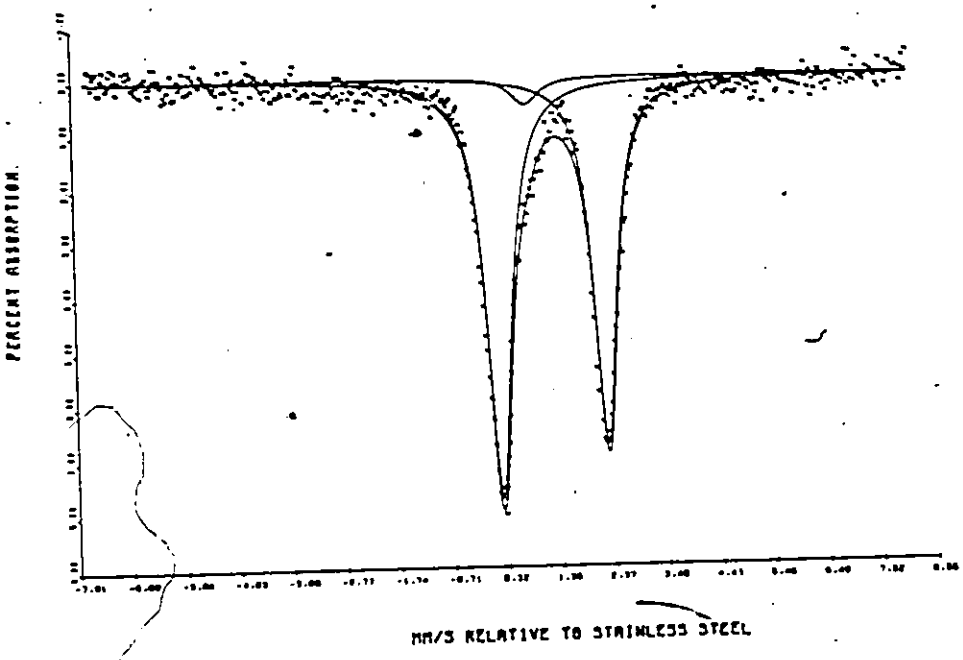
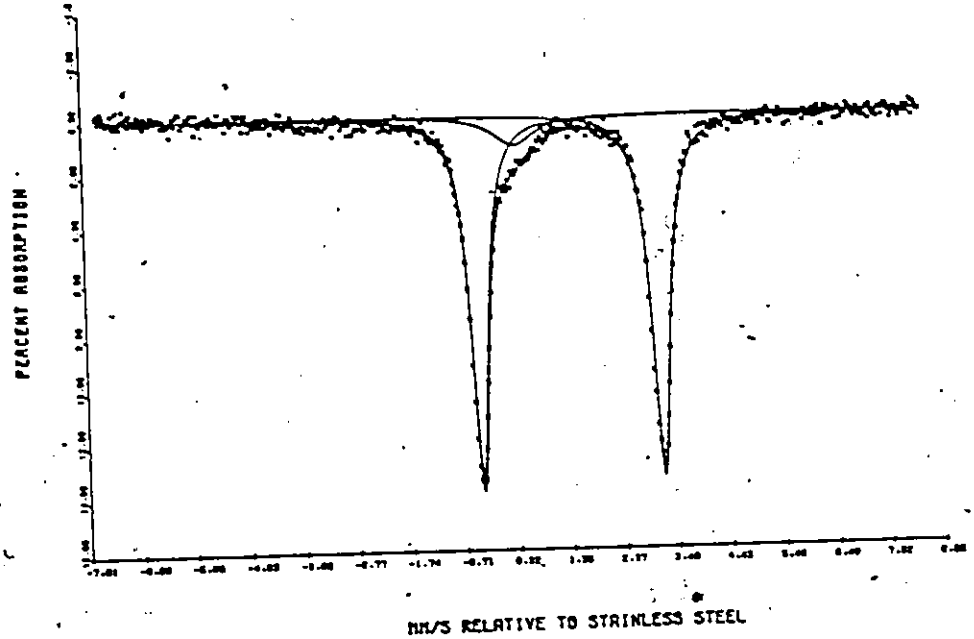

PERCENT ABSORPTION
MM/S RELATIVE TO STAINLESS STEEL

Figure 10. Mössbauer spectrum of J-80 almandine garnet measured at room temperature and pressure.

Figure 11. Mössbauer spectrum of J-35 orthopyroxene measured at T=77°K, P=1 atm.


PERCENT ABSORPTION
MM/S RELATIVE TO STRINLESS STEEL

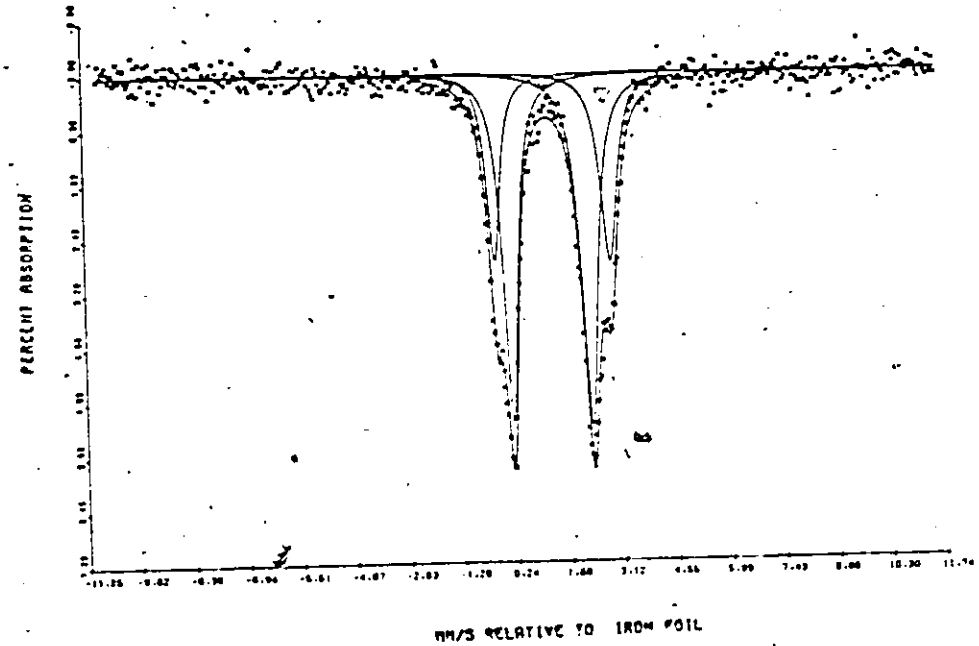
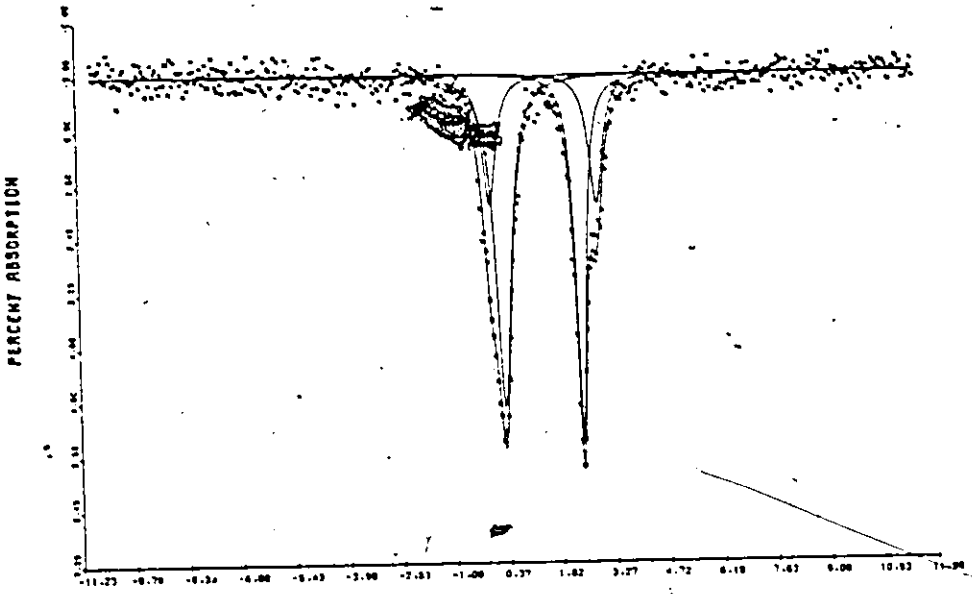

PERCENT ABSORPTION
MM/S RELATIVE TO IRON FOIL

Figure 12. Mössbauer spectrum of J-80 orthopyroxene measured at T=77°K, P=1 atm.

Figure 13. Mössbauer spectrum of J-80 clinopyroxene measured at T=77°K, P=1 atm.


PERCENT ABSORPTION
MM/S RELATIVE TO STAINLESS STEEL

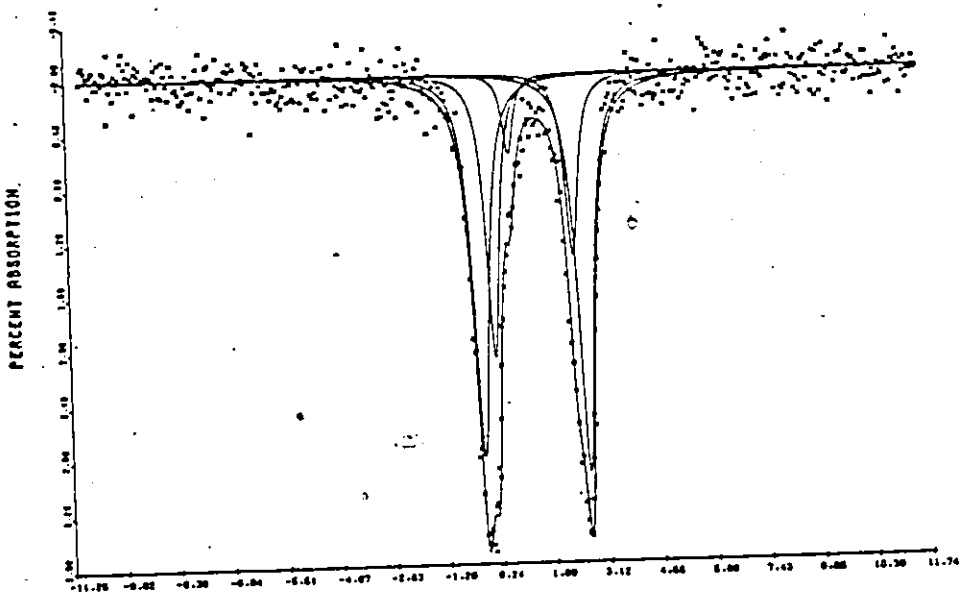
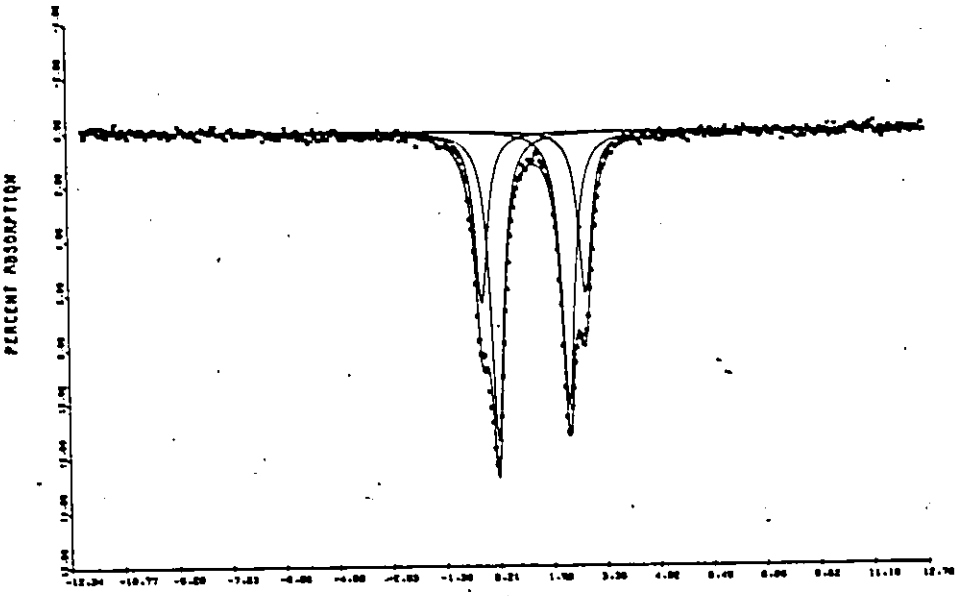

PERCENT ABSORPTION
MM/S RELATIVE TO IRON FOIL

Figure 14. Mössbauer spectrum of J-105B orthopyroxene measured at T=77°K, P=1 atm.

Figure 15. Mössbauer spectrum of J-105B clinopyroxene measured at T=77°K, P=1 atm.


PERCENT ABSORPTION
MM/S RELATIVE TO IRON FOIL

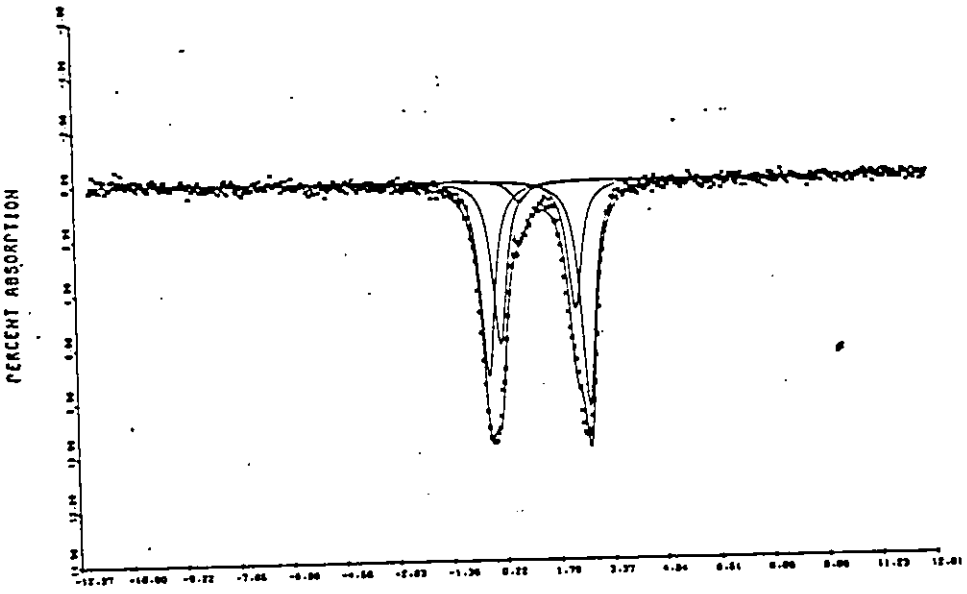
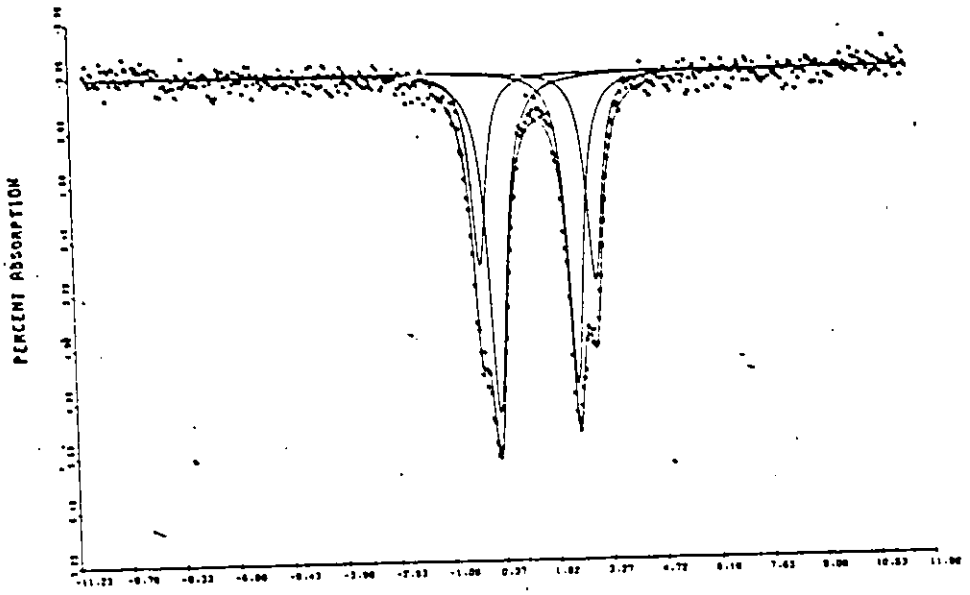
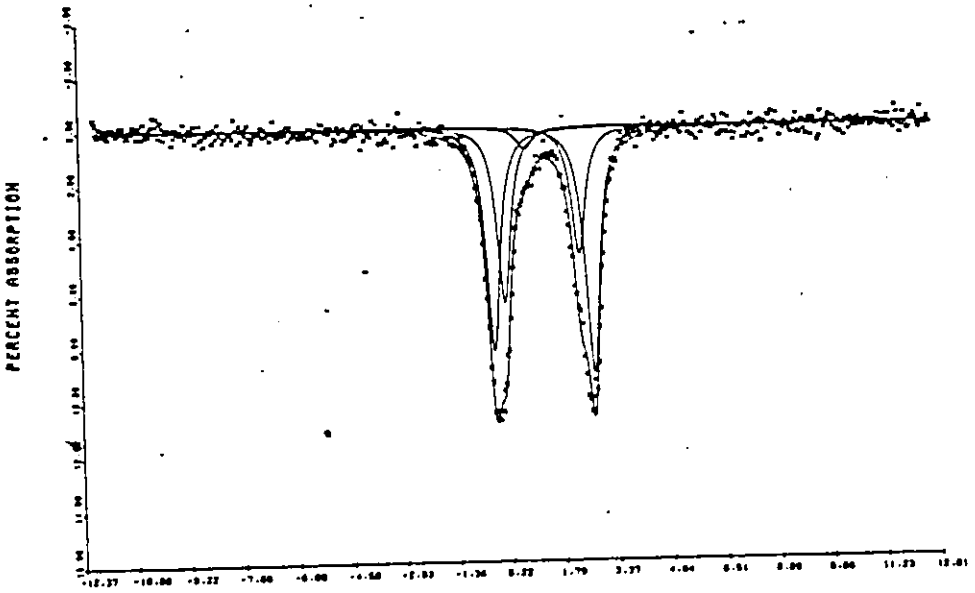

PERCENT ABSORPTION
MM/S RELATIVE TO IRON FOIL

Figure 16. Mössbauer spectrum of J-106 orthopyroxene measured at T=77°K, P=1 atm.

Figure 17. Mössbauer spectrum of J-106 clinopyroxene measured at T=77°K, P=1 atm.


PERCENT ABSORPTION
MM/S RELATIVE TO STAINLESS STEEL


PERCENT ABSORPTION
MM/S RELATIVE TO IRON FOIL

typical absorption doublet. This gives an isomer shift of 1.39 mm/sec and a very large quadrupole splitting of 3.51 mm/sec, which, from the Q.S. strongly indicates the presence of iron in the ferrous state, and, from the I.S. its presence in eight-fold co-ordination. Little Fe^{3+} is present, and is indicated by the small peak. These data, combined with chemical analyses have shown that the sample is evidently the most Fe^{2+}-rich garnet so far investigated by Mössbauer spectroscopy. All of the Fe^{2+} ions are in eight-fold co-ordination, all of the Mg will presumably also occupy that site.

With reference to the pyroxenes, there are lower velocity peaks, A_1 and A_2, and higher velocity peaks, B_2 and B_1. For example, in Fig. 12, the lower velocity peaks A_1 and A_2 have peak positions, in terms of velocites, at -0.060 and 0.299 mm/sec relative to stainless steel, whereas the higher velocity peaks B_2 and B_1 are 2.402 and 2.854 mm/sec respectively. The inner two peaks, A_2 and B_2, represent Fe^{2+} at the M_2 site; the outer two peaks A_1 and B_1 represent Fe^{2+} at the M_1 site (Bancroft et al., 1967a, b, c, 1968; Evans et al., 1967; Dundon and Walter, 1967; Ghose and Hafner, 1968; Virgo and Hafner, 1968, 1969). The inner two peaks are invariably more intense, indicating that the Fe^{2+} ions are concentrated in the M_2 site in the orthopyroxene structure.

These results, as shown in Figs. 11, 12, 14, 16, are similar to those found by Ghose (1965a, p81) and Bancroft et al. (1967a, p1223). However, the present orthopyroxenes are eulite in composition, and some complexities due to the high Fe^{2+} content will be discussed in a later chapter.

The assignment of relative intensities in clinopyroxene is the reverse of that of the orthopyroxene. The outer two peaks, representing Fe^{2+} in the M_1 site, are invariably more intense (Bancroft et al., 1967c, p2227). The present clinopyroxene spectra determined at low T (Figs. 13, 15 and 17) are consistent with these expectations. A small peak, having a velocity of 0.641 mm/sec relative to iron foil, is shown in Fig. 13, which contains the spectrum of J-80 clinopyroxene. This peak (the C peak, as distinct from the A and B peaks, indicates the presence of more than 5 per cent of the total iron in the ferric state. Small amounts of Fe^{3+} are also present in J-105B and J-106 clinopyroxenes (Figs. 15 and 17). These results are in agreement with the chemical analyses.

The site occupancy numbers (or factors) $X_{Fe}^{M_1}$ and $X_{Fe}^{M_2}$ for M_1 and M_2 sites respectively in the pyroxenes are the mole fraction $Fe^{2+}/(Fe^{2+}+Mg)$ at each site and may be calculated by use of the following equations:

$$X_{Fe}^{M_1} = (A_1+B_1)/(A_1+A_2+B_2+B_1) \times 2Fe^{2+}/(Fe^{2+}+Mg) \quad (7)$$

$$X_{Fe}^{M_2} = (A_2+B_2)/(A_1+A_2+B_2+B_1) \times 2Fe^{2+}/(Fe^{2+}+Mg) \quad (8)$$

where A_1, A_2 are areas underneath peaks A_1 and A_2 respectively,

B_1, B_2 " " " " B_1 and B_2 "

Substituting IxΓ (where I is the intensity, Γ is the half-width of a Mössbauer resonance peak) for area, equations (7) and (8) become identical with the equations given by Saxena and Ghose (1971, p539). Virgo and Hafner (1970, p206) have used the intensity alone instead of the products of intensity and halfwidth, or area underneath peak. This procedure yields somewhat different results. Since the data of the present study will be compared with the experimental data of Saxena and Ghose (1971), the area method was used, in conjunction with the intensity-halfwidth-product method, to compute the site occupancy numbers for each site. Calculations of the site populations of Fe^{2+} and Mg in each site in the pyroxenes are based on the site occupancy numbers so calculated, and are given in Table 11.

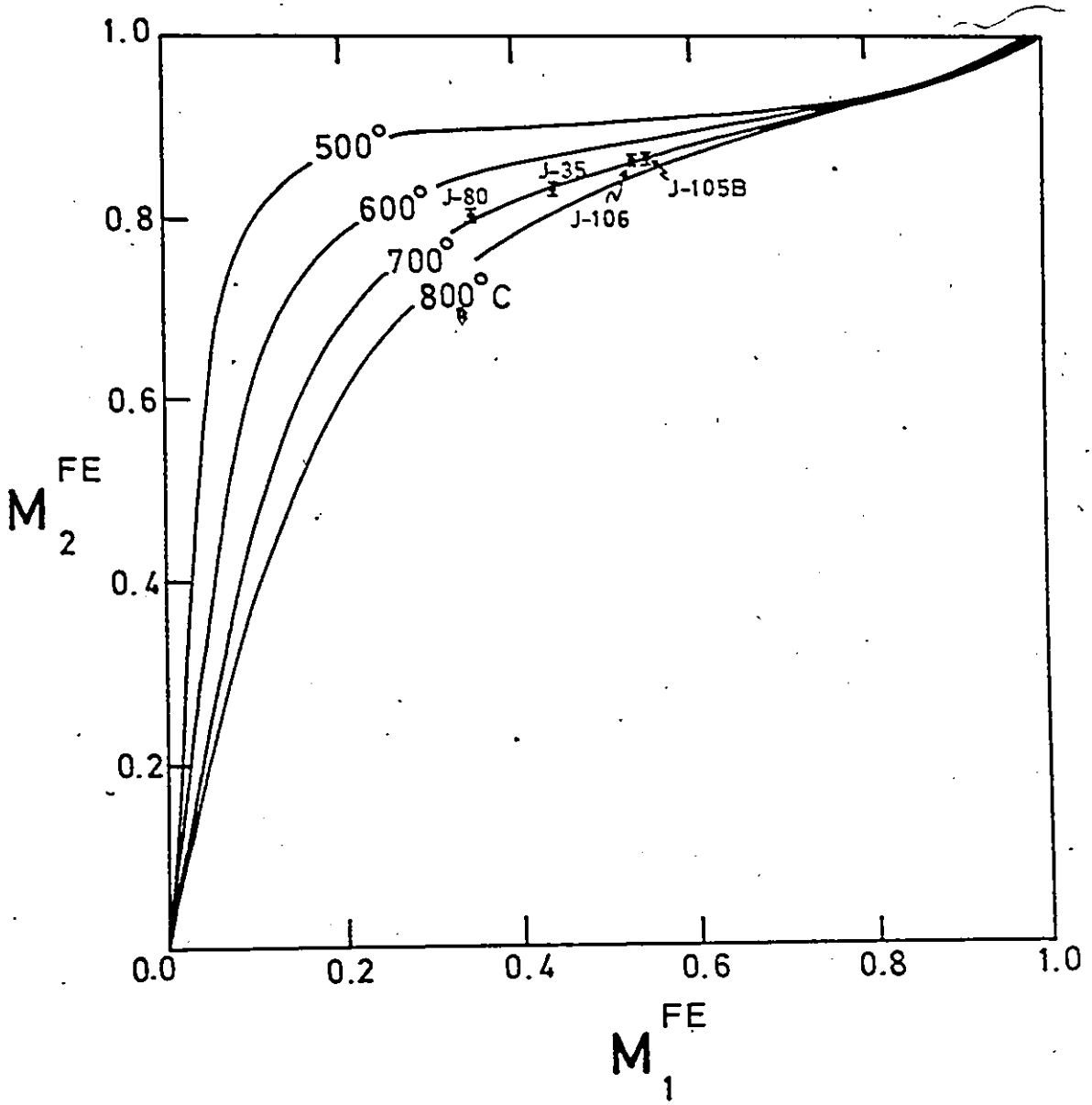
From the heating experiments of Virgo and Hafner (1969, 1970) and, Saxena and Ghose (1971), distribution isotherms for the distribution of Fe^{2+} and Mg between M_1 and M_2 sites in orthopyroxenes were obtained. These isotherms, as shown in Fig. 18 may provide information on the temperature of equilibration of naturally crystallized orthopyroxenes.

Table 11 Site occupancy (Fe^{2+}) numbers for four orthopyroxenes from charnockitic granulites from the Adirondack Mts., N.Y.

Site \ Sp.No.	J-35	J-80	J-105B	J-106
M_1	0.442±0.004	0.349±0.007	0.544±0.007	0.529±0.003
M_2	0.832±0.004	0.809±0.007	0.868±0.007	0.871±0.003

The data points for the distribution of Fe^{2+} and Mg in orthopyroxene of the present study fall very close to the 700°C isotherm of Saxena and Ghose (1971, p535), as shown in Fig. 18. Since ordering reactions could be induced in orthopyroxenes at temperature as low as 480°C by Virgo and Hafner (1969, 1970) it is surprising that the slowly-cooled orthopyroxenes of the present study did not achieve a greater degree of ordering. However since the nature and strength of the kinetic barriers to ordering are not yet perfectly understood (Mueller, 1962, 1967, 1969, 1970) it is possible that the ordering reaction was for some reason retarded in nature, and that the presently-found cation distribution represents a frozen-in ion exchange equilibrium. If so, the equilibrium temperature can be taken as 700°±25°C. It is possible, of course, that the temperature of crystallization or the peak of metamorphism was higher than this, say 800°C, and that some ordering took place in all four crystals, causing the data points in Fig. 18 to shift toward the 700°C isotherms.

Figure 18. Distribution isotherms for the distribution of Fe^{2+} and Mg between M_1 and M_2 sites in orthopyroxene, according to Saxena and Ghose (1971). Data points for 4 orthopyroxenes from the present study are shown. M_2^{Fe}= Fe/Fe + Mg atomic ratio in M_2 sites and M_1^{Fe}= Fe/Fe + Mg atomic ratio in M_1 sites.


1.0
0.8
0.6
0.4
0.2
0.0
0.2
0.4
0.6
0.8
1.0
500°
600°
700°
800°C
J-80
J-35
J-106
J-105B
M_2^{FE}
M_1^{FE}

VII INTERCRYSTALLINE ION EXCHANGE EQUILIBRIUM: ORTHOPYROXENE-CLINOPYROXENE-AMPHIBOLE-GARNET

(I) ORTHOPYROXENE-CLINOPYROXENE

Distribution of Mg and Fe^{2+} Between Coexisting Orthopyroxene and Clinopyroxene

The general Mg-Fe^{2+} exchange reaction between coexisting orthopyroxene (opx) and clinopyroxene (cpx) has been considered by numerous authors, notably Kretz (1961, 1963), Mueller (1960), Bartholome (1962), Saxena (1968), and Perchuk (1968). In this treatment, the distribution of Mg and Fe^{2+} within the crystals is disregarded. The reaction may be written as follows (with Fe^{2+} written as Fe):

$$Fe^{opx} + Mg^{cpx} = Mg^{opx} + Fe^{cpx} \qquad (9)$$

The equilibrium constant for this reaction is:

$$K(9) = \frac{a_{Mg}^{opx}\, a_{Fe}^{cpx}}{a_{Fe}^{opx}\, a_{Mg}^{cpx}} = \frac{X_{Mg}^{opx}\,(1-X_{Mg}^{cpx})}{(1-X_{Mg}^{opx})\,X_{Mg}^{cpx}} \cdot \frac{\gamma_{Mg}^{opx}\,\gamma_{Fe}^{cpx}}{\gamma_{Fe}^{opx}\,\gamma_{Mg}^{cpx}} \qquad (10)$$

Substituting K_D for the expression that contains the X terms, and K_γ for the expression that contains the γ terms, equation (10) becomes

$$K(9) = K_D \cdot K_\gamma = \exp \frac{-\Delta G^\circ(9)}{RT} \qquad (11)$$

Here a is activity, γ is activity coefficient, X is the mole fraction or atomic fraction, $X_{Mg} = Mg/Mg + Fe^{2+}$, $\Delta G^\circ(9)$ is the standard molar free energy change for reaction (9),

R is the gas constant, T is the absolute temperature, and K_D is the distribution coefficient. If the coexisting phases are ideal solid solutions of Mg and Fe^{2+} end members, $a = X$, $K_\gamma = 1$ and K_D becomes identical to K(9).

Theoretically, K and K_D depend on T and P; T appears to dominate. If both pyroxene phases behave as ideal solutions, K_D is independent of composition (Ramberg and DeVore, 1951; Kretz, 1959, 1961, 1963, 1964). Some studies have shown that K_D for natural mineral pairs may also depend on composition (Davidson, 1968; Saxena and Ghose, 1971; Fleet, 1974; Maxey and Vogel, 1974).

Model 1. Ideal Solutions

The Mg/Mg + Fe ratios for coexisting orthopyroxene and clinopyroxene in charnockitic granulites from the Adirondack Mts. (present study) and from Madras, India (Howie, 1955) are listed in Table 12. These data are plotted in Figs. 19 and 20. K_D for all of these mineral pairs does not vary greatly, as shown in Table 13; the average value is 0.57. The data from India are included for comparison and to provide a greater range in Mg/Fe ratio in the mineral pairs. Notice (Fig. 19) that, in the central part of the diagram, the data points from the two sources nearly coincide, suggesting that the metamorphic condition in the Madras area may have been similar to those in the Adirondacks, and that the Madras data may therefore provide a continuation of the distribution curve obtained from the present study.

Table 12. Mole fractions of Mg (X_{Mg}) and Fe^{2+} (X_{Fe}) for coexisting orthopyroxene and clinopyroxene from mafic charnockitic granulites from the Adirondack Mts., (present study), and from Madras, India (Howie, 1955)

		Orthopyroxene (opx)		Clinopyroxene (cpx)	
		X_{Mg}	X_{Fe}	X_{Mg}	X_{Fe}
Adirondacks	J-35	0.363	0.637	0.487	0.513
	J-44	0.218	0.782	0.300	0.700
	J-66	0.439	0.561	0.589	0.411
	J-80	0.421	0.579	0.584	0.416
	J-81	0.434	0.566	0.579	0.421
	J-103	0.297	0.703	0.420	0.580
	J-105B	0.294	0.706	0.420	0.580
	J-106	0.300	0.700	0.418	0.582
Madras	3709	0.758	0.242	0.850	0.150
	4645	0.736	0.264	0.845	0.155
	2270	0.617	0.383	0.752	0.248
	2941	0.544	0.456	0.680	0.320
	4642A	0.430	0.570	0.570	0.430

Figure 19. Distribution of Mg and Fe^{2+} between coexisting orthopyroxene and clinopyroxene from the charnockitic granulites.

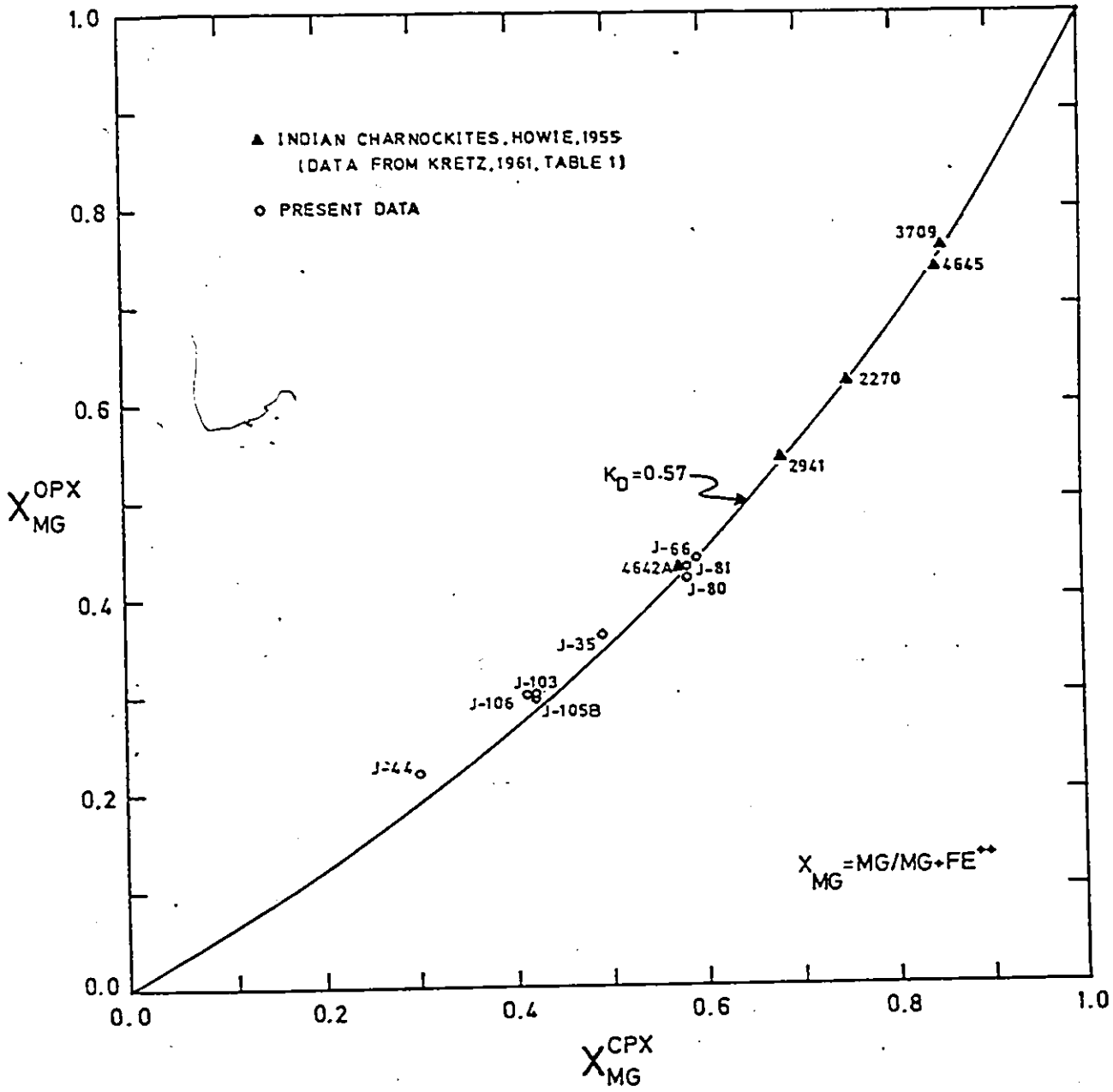

▲ INDIAN CHARNOCKITES, HOWIE, 1955
(DATA FROM KRETZ, 1961, TABLE 1)
o PRESENT DATA
3709
4645
2270
2941
K_D=0.57
J-66
4642A
J-81
J-80
J-35
J-103
J-106
J-105B
J-44
X_{MG}=MG/MG+FE**
X_{MG}^{OPX}
X_{MG}^{CPX}
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0

Figure 20. Distribution of Mg and Fe^{2+} between coexisting orthopyroxene and clinopyroxene from the charnockitic granulites, in terms of a $(\frac{X}{1-X})^{opx}_{Mg}$ vs $(\frac{X}{1-X})^{cpx}_{Mg}$ plot.

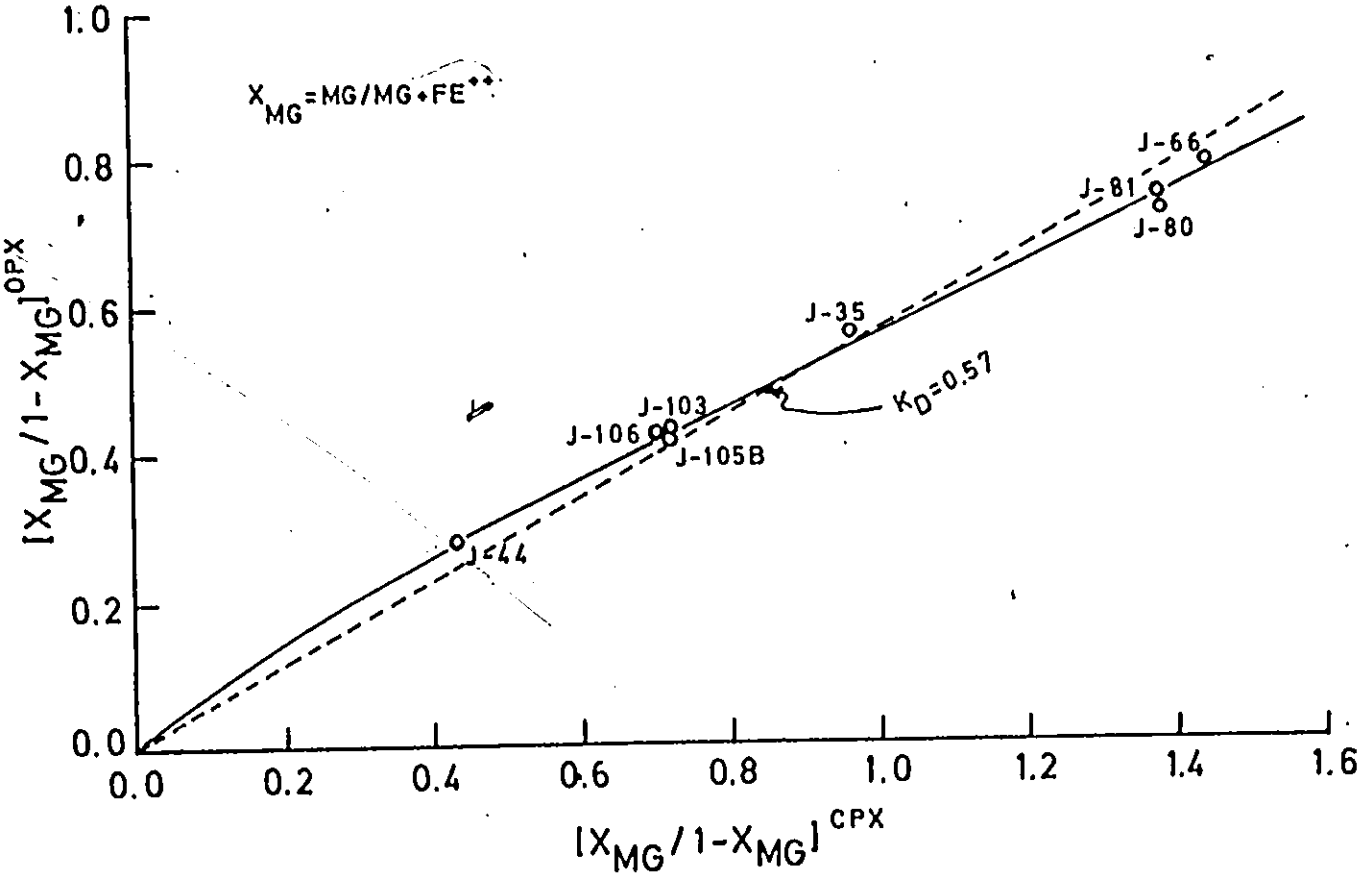

$X_{MG}=MG/MG+FE^{++}$
$[X_{MG}/1-X_{MG}]^{OPX}$
$[X_{MG}/1-X_{MG}]^{CPX}$
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
J-66
J-81
J-80
J-35
J-103
J-106
J-105B
J-44
$K_D=0.57$

Table 13. Distribution coefficients for the coexisting orthopyroxene and clinopyroxene from the Madras Area (India), and the Adirondack Mts., N.Y.

Adirondack pyroxenes	K_D
J-35	0.60
J-44	0.65
J-66	0.55
J-80	0.52
J-81	0.56
J-103	0.58
J-105B	0.58
J-106	0.60
Madras pyroxenes	
3709	0.55
4645	0.51
2270	0.53
2941	0.56
4642A	0.57
Average	0.57

The two-ideal-solution model presumes that both minerals behave as ideal solutions. This model will be considered briefly even though orthopyroxene is obviously not an ideal solution, for it is partly ordered, as discussed in the preceding chapter. It is possible that a mineral may possess near-ideal behaviour in the sense that 'macroscopic' activity of a component is equal to its mole fraction, even though internally it is partly ordered.

In the two-ideal-solution model, K_D is constant at a given T and P, and is independent of composition. Notice (Fig. 19) that this model provides a fairly good 'fit' to the data, particularly in the Mg-rich composition range.

It is interesting to note that Lindsley et al. (1974) recently carried out an experimental determination of K_D(Mg) for coexisting augite and hypersthene at 810°C and obtained a value of 0.690. A variation in K_D could not be detected by the experimental methods employed. Since the experimental K_D is considerably greater than 0.57 obtained for the Madras and Adirondack rocks, the crystallization temperature for these rocks was evidently lower than 810°C.

Model 2. Non-ideal Solutions

We shall now adapt a model which assumes both minerals to be simple mixtures rather than ideal mixtures.

Equation (10) may be written as

$$\ln K = \ln K_D + \ln\gamma_{Mg}^{opx} - \ln\gamma_{Fe}^{opx} + \ln\gamma_{Fe}^{cpx} - \ln\gamma_{Mg}^{cpx} \qquad (12)$$

where K and K_D are the equilibrium constant and distribution coefficient respectively for the non-ideal-solutions model.

The simple mixture solution model (Guggenheim, 1967) has been applied to minerals by Mueller (1964), Muan, Nafziger and Roeder (1964), Kitayama (1970), Kitayama and Katsura (1968), Williams (1971), and Froese and Gordon (1974). We shall presume that both orthopyroxene and clinopyroxene are simple solutions; consequently the activity coefficients will be as follow

$$\ln\gamma_{Mg}^{opx} = \alpha^{opx} (1-X_{Mg}^{opx})^2 \qquad (13)$$

$$\ln\gamma_{Fe}^{opx} = \alpha^{opx} (X_{Mg}^{opx})^2 \qquad (14)$$

$$\ln\gamma_{Mg}^{cpx} = \alpha^{cpx} (1-X_{Mg}^{cpx})^2 \qquad (15)$$

$$\ln\gamma_{Fe}^{cpx} = \alpha^{cpx} (X_{Mg}^{cpx})^2 \qquad (16)$$

In the above expressions, γ's are the activity coefficients and α's are the natural logarithms of the activity coefficients at infinite dilution. For the two components of a given binary solution, the α values for the two components are the same.

Substituting equations (13) to (16) into equation (12) the following equation is obtained

$$\ln K = \ln K_D - \alpha^{cpx}(1-2X_{Mg}^{cpx}) + \alpha^{opx}(1-2X_{Mg}^{opx}) \quad (17)$$

or

$$\ln X_{Mg}^{opx} - \ln(1-X_{Mg}^{opx}) + \alpha^{opx}(1-2X_{Mg}^{opx}) = \ln K + \ln X_{Mg}^{cpx} - \ln(1-X_{Mg}^{cpx}) + \alpha^{cpx}(1-2X_{Mg}^{cpx}) \quad (18)$$

Equation (17) was previously derived by Mueller (1964) and was later used by Saxena (1969, 1970, 1971, 1973) and Froese and Gordon (1974).

S.K. Saxena has kindly solved equation (17) for the data of Table 12 using a least square method. The results are: $K = 0.684$, $\alpha^{opx} = 0.670$, $\alpha^{cpx} = 0.816$. These values may be inserted into equation (18) to plot the distribution curve shown in Fig. 21. This curve provides an improved 'fit' to the data points for the natural mineral pairs. The activity coefficients of the thirteen pairs of pyroxenes may now be calculated using equations (13) and (15). The results are shown in Table 14. These values indicate a positive deviation from ideality ($\gamma > 1.0$), in agreement with the result of Saxena (1969a, b, 1971) and Saxena and Ghose (1971) and contrary to those of Olsen and Bunch (1970) and Blander (1972).

The results of the above analysis may be compared with those obtained by Froese and Gordon (1974) for the Quairading pyroxenes (Davidson, 1968) as follows:

Figure 21. Distribution of Mg and Fe^{2+} between coexisting orthopyroxene and clinopyroxene from the charnockitic granulites.

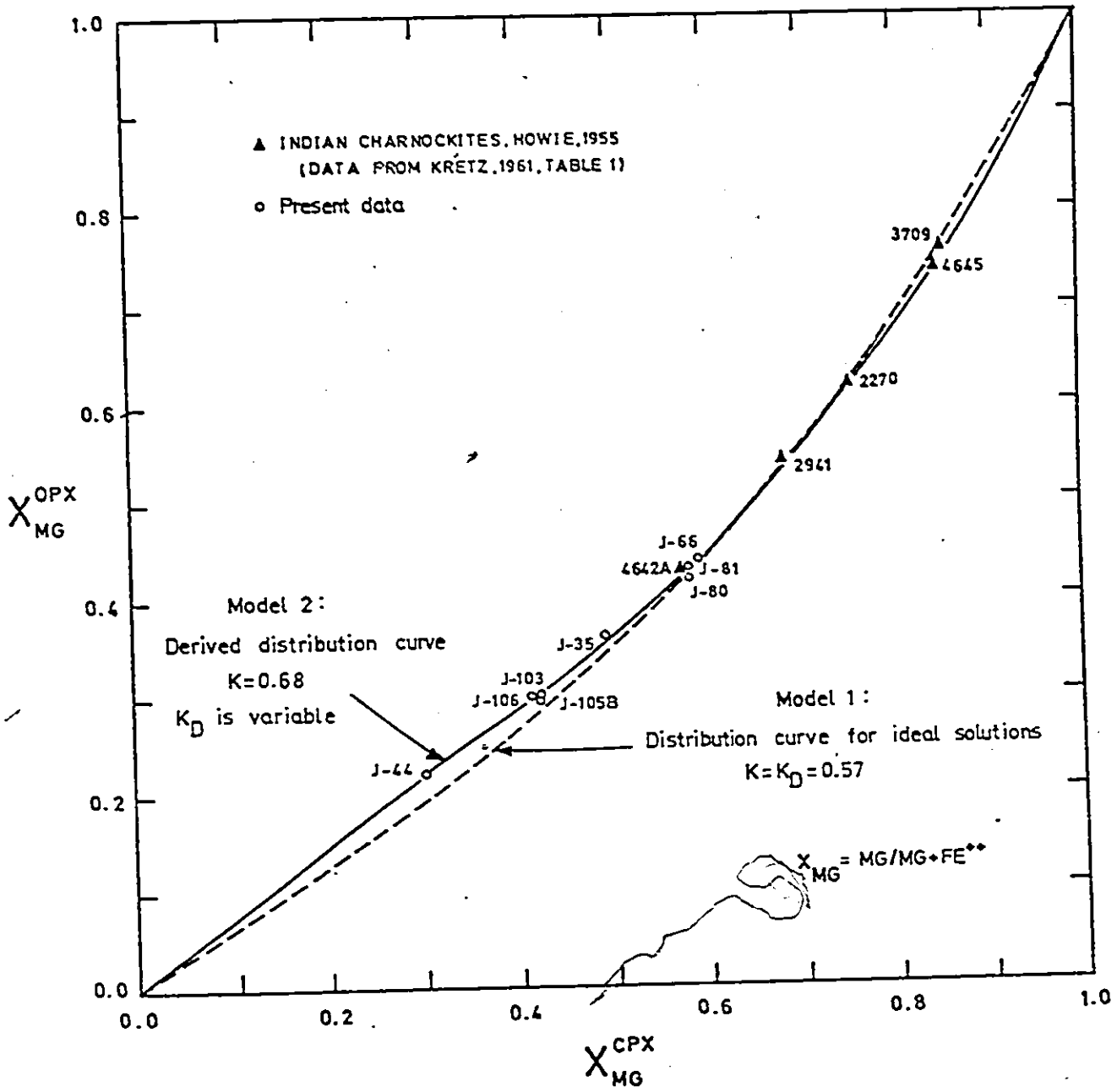

▲ INDIAN CHARNOCKITES, HOWIE, 1955
(DATA FROM KRETZ, 1961, TABLE 1)
o Present data
3709
4645
2270
2941
J-66
4642A
J-81
J-80
J-35
J-103
J-106
J-105B
J-44
Model 2:
Derived distribution curve
K=0.68
K_D is variable
Model 1:
Distribution curve for ideal solutions
$K=K_D=0.57$
X_{MG} = MG/MG+FE**
X^{OPX}_{MG}
X^{CPX}_{MG}
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0

Table 14. Activity coefficients of the Adirondack and Madras orthopyroxene (γ^{opx}) and clinopyroxene (γ^{cpx})

	Orthopyroxene		Clinopyroxene	
	γ^{opx}_{Mg}	γ^{opx}_{Fe}	γ^{cpx}_{Mg}	γ^{cpx}_{Fe}
Adirondack Pyroxenes				
J-35	1.313	1.092	1.240	1.213
J-44	1.517	1.032	1.491	1.076
J-66	1.235	1.139	1.148	1.328
J-80	1.252	1.126	1.152	1.321
J-81	1.240	1.135	1.155	1.315
J-103	1.392	1.061	1.316	1.155
J-105B	1.403	1.060	1.316	1.155
J-106	1.391	1.062	1.319	1.154
Madras Pyroxenes				
3709	1.040	1.477	1.019	1.804
4645	1.047	1.438	1.020	1.790
2270	1.103	1.291	1.052	1.586
2941	1.150	1.226	1.086	1.458
4642A	1.243	1.132	1.162	1.302

Present study		Froese and Gordon
α^{opx}	0.670	0.447
α^{cpx}	0.816	0.625
K	0.684	0.662

From the data of Tables 12 and 14, the activities for the thirteen pairs of pyroxenes may be calculated. The results are shown in Table 15. Activity-composition diagrams for orthopyroxene and clinopyroxene may also be constructed and are shown in Figs. 22 and 23.

The two-simple-solutions model for coexisting orthopyroxene and clinopyroxene is evidently superior to the two-ideal-solutions model, for it provides a better 'fit' to the data of the present study, as well as data from other sources (Fig. 24). However different combinations of various kinds of solutions would presumably produce models that would 'fit' the data equally well. Obviously, experimental studies are now needed to provide further information in activity-composition relation in the pyroxene minerals.

A comparison with data on pyroxenes from other well known charnockitic areas in the world is shown in Fig. 24.

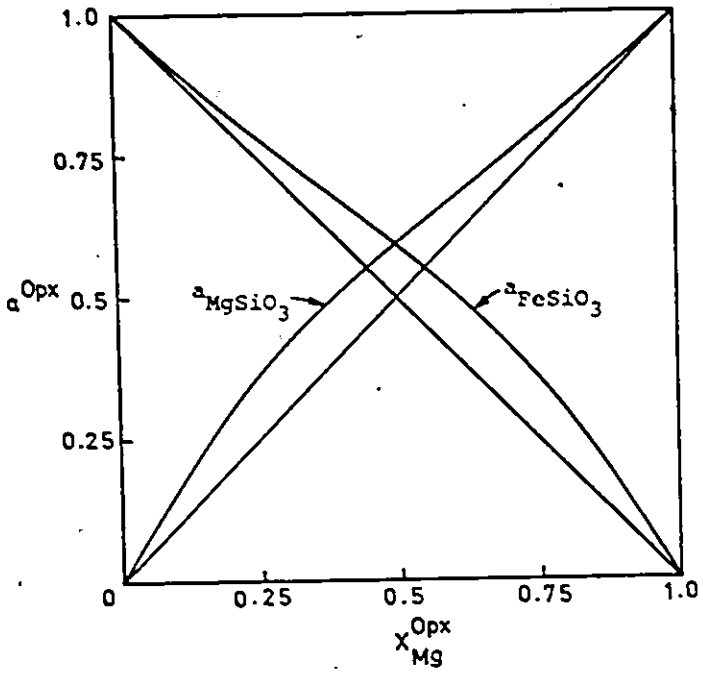
In order to illustrate the observed variation in calcium content in the pyroxenes of the present study, the Ca Mg ΣFe ratios have been calculated and plotted together with other data in Fig. 25. A vertical spread in the clino-

Table 15. Activity data of the Adirondack and Madras orthopyroxene (a^{opx}) and clinopyroxene (a^{cpx})

	Orthopyroxene		Clinopyroxene	
	a^{opx}_{Mg}	a^{opx}_{Fe}	a^{cpx}_{Mg}	a^{cpx}_{Fe}
Adirondack Pyroxenes				
J-35	0.477	0.696	0.604	0.622
J-44	0.331	0.807	0.447	0.753
J-66	0.542	0.639	0.676	0.546
J-80	0.527	0.652	0.673	0.550
J-81	0.538	0.642	0.669	0.554
J-103	0.413	0.746	0.553	0.670
J-105B	0.412	0.748	0.553	0.670
J-106	0.417	0.743	0.551	0.672
Madras Pyroxenes				
3709	0.788	0.357	0.866	0.271
4645	0.771	0.380	0.862	0.278
2270	0.681	0.494	0.791	0.393
2941	0.626	0.559	0.738	0.467
4642A	0.535	0.645	0.662	0.560

Figure 22. Activity-composition diagram for orthopyroxenes from the charnockitic granulites, using a simple solution model.

Figure 23. Activity-composition diagram for clinopyroxenes from the charnockitic granulites, using a simple solution model.


1.0
0.75
0.5
0.25
0
a^{Opx}
a_{MgSiO_3}
a_{FeSiO_3}
0.25
0.5
0.75
1.0
X_{Mg}^{Opx}

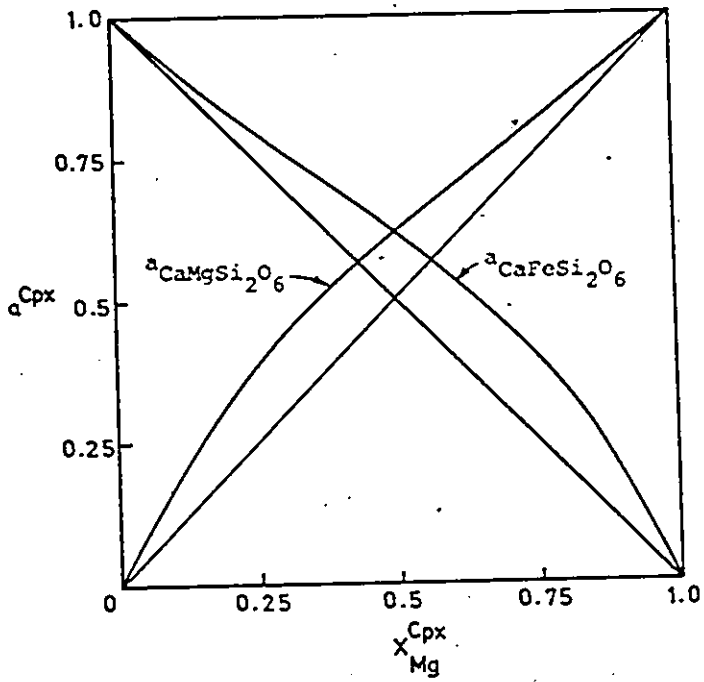

1.0
0.75
0.5
0.25
0
a^{Cpx}
$a_{CaMgSi_2O_6}$
$a_{CaFeSi_2O_6}$
0.25
0.5
0.75
1.0
X_{Mg}^{Cpx}

Figure 24. Mg-Fe^{2+} distribution diagram for the Adirondack pyroxenes (open circles), Madras pyroxenes (solid triangles, from Howie, 1955;Kretz, 1961), Quairading pyroxenes (dots, from Davidson, 1968) and high grade pyroxenes from Broken Hill (open circles with crosses, from Binns, 1962).

Equilibrium constant is the same as in Fig. 21.

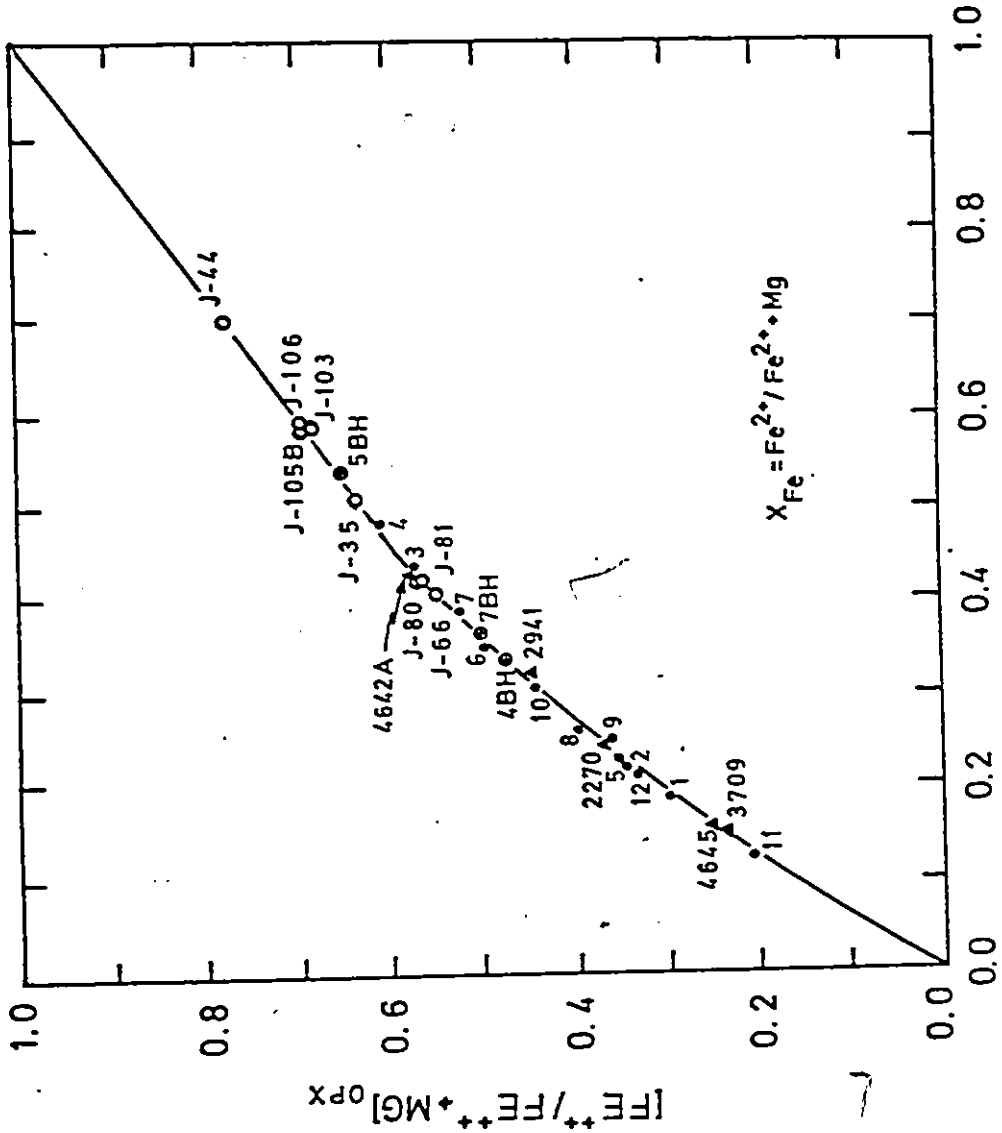
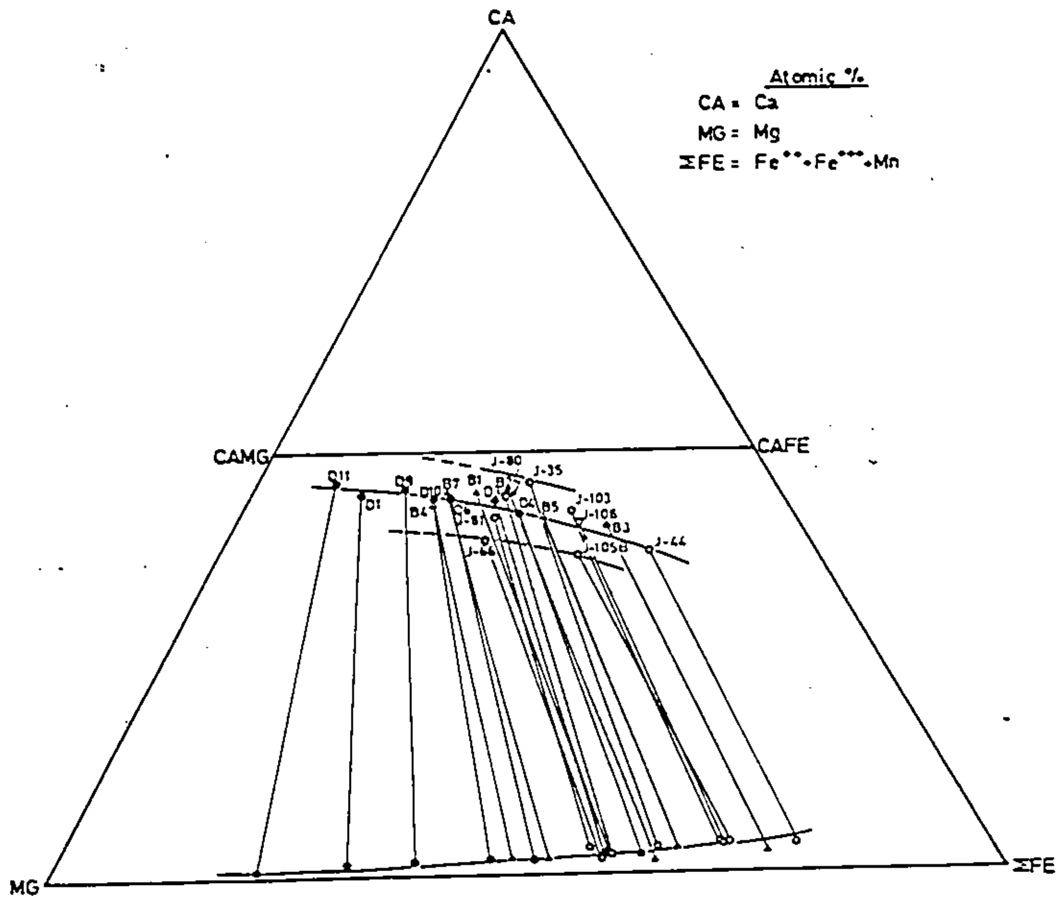

J-44
J-106
J-103
J-105B
5BH
J-35
4
3
J-81
J-80
7
J-66
6
7BH
4642A
4BH
2941
10
8
9
2270
5
12
2
1
3709
4645
11
$X_{Fe}=Fe^{2+}/Fe^{2+}+Mg$
0.0
0.2
0.4
0.6
0.8
1.0
$[FE^{++}/FE^{++}+MG]_{OPX}$
$[FE^{++}/FE^{++}+MG]_{CPX}$

Figure 25. Coexisting orthopyroxene and clinopyroxene in the Ca-Mg-Fe system. Dots - Quairading pyroxenes (Davidson, 1968); solid triangles - lower grade Broken Hill pyroxenes (Binns, 1962); open triangles - higher grade Broken Hill pyroxenes (Binns, 1962); open circles - present data. The Kondapalli and Madras charnockites (Leelanandam, 1967) occupy the field covered by D11 to J-35.


CA
Atomic %
CA = Ca
MG = Mg
ΣFE = Fe⁺⁺+Fe⁺⁺⁺+Mn
CAMG
CAFE
MG
ΣFE
D11
D1
D9
D10
B7
B1
B4
C4
B5
J-80
J-35
J-103
J-106
B3
J-105
J-44
J-81
J-66

pyroxene points has been interpreted by Davidson (1968) as resulting from differences in metamorphic grade. The charnockitic granulites of the present study were evidently equilibrated at a nearly uniform temperature and the vertical spread in these data points may be due to other factors such as analytical error, exsolution, or the effects of Al and Ti on the distribution of Ca between the minerals.

Distribution of Manganese Between Coexisting Orthopyroxene and Clinopyroxene

The general intercrystalline Mn $-(Mg + Fe^{2+})$ exchange equilibrium between coexisting orthopyroxene and clinopyroxene may be treated in terms of a Mn-Mg exchange and a Mn-Fe exchange reaction or both of these may be combined as follows:

$$(Mg,Fe)^{cpx} + Mn^{opx} = Mn^{cpx} + (Mg,Fe)^{opx} \qquad (19)$$

$$K(19) = \frac{a_{Mn}^{cpx}\, a_{Mg,Fe}^{opx}}{a_{Mg,Fe}^{cpx}\, a_{Mn}^{opx}} = \frac{X_{Mn}^{cpx}\, X_{Mg,Fe}^{opx}}{X_{Mg,Fe}^{cpx}\, X_{Mn}^{opx}} \cdot \frac{\gamma_{Mn}^{cpx}\, \gamma_{Mg,Fe}^{opx}}{\gamma_{Mg,Fe}^{cpx}\, \gamma_{Mn}^{opx}}$$

$$= \exp \frac{-\Delta G^{o}(19)}{RT} \qquad (20)$$

where $X_{Mn} = Mn^{2+}/Mn^{2+} + Fe^{2+} + Mg$, and $a_{Mg,Fe}$ is an undefined activity, depending on the Mg/Fe ratio in the mineral (Kretz, 1961). Since X_{Mn}^{opx} and X_{Mn}^{cpx} are small, the distribution coefficient may be written as:

$$K_D(Mn)^{cpx/opx} = \frac{X_{Mn}^{cpx}(1-X_{Mn}^{opx})}{(1-X_{Mn}^{cpx})X_{Mn}^{opx}} \doteq \frac{X_{Mn}^{cpx}}{X_{Mn}^{opx}} \qquad (21)$$

The distribution of Mn between pyroxene minerals of the present study is shown in Fig. 26; the mean distribution coefficient is 1.15:

$$K_D(Mn)^{opx/cpx} = \frac{X_{Mn}^{opx}}{X_{Mn}^{cpx}} = 1.15$$

This diagram demonstrates that K_γ (the expression containing the four activity coefficients in equation (20)) is independent of X_{Mn} and that equilibrium with respect to Mn-(Mg and Fe) exchange has been closely approached.

(II) DISTRIBUTION OF Mg, Fe^{2+}, AND Mn BETWEEN COEXISTING ORTHOPYROXENE AND ALMANDINE

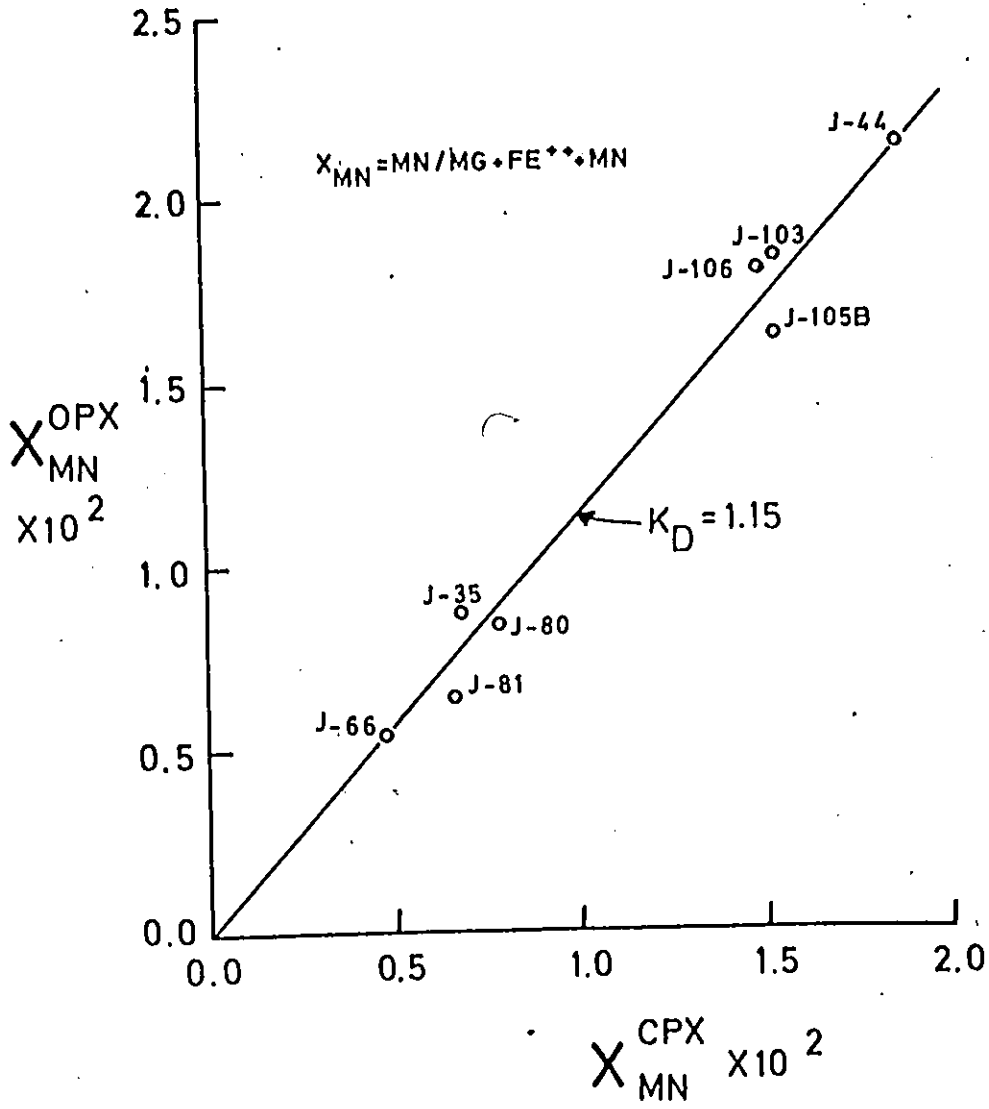
The Mg-Fe^{2+} exchange reaction for coexisting orthopyroxenes (opx) and almandine garnets (alm) (or (gar).) may be written as:

$$Fe^{opx} + Mg^{alm} = Mg^{opx} + Fe^{alm} \qquad (22)$$

Assuming almandine (alm) is an ideal solid solution of Mg and Fe^{2+}, then

$$K(22) = \frac{a_{Mg}^{opx}\, X_{Fe}^{alm}}{a_{Fe}^{opx}\, X_{Mg}^{alm}} = \exp \frac{-\Delta G^\circ(22)}{RT} \qquad (23)$$

Figure 26. Distribution of Mn between coexisting orthopyroxene and clinopyroxene from the charnockitic granulites.


2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
X_{MN}=MN/MG+FE^{++}+MN
J-44
J-103
J-106
J-105B
J-35
J-80
J-81
J-66
K_D = 1.15
X^{OPX}_{MN} X10^2
X^{CPX}_{MN} X10^2

The distribution of Mg and Fe^{2+} between coexisting orthopyroxene and almandine in the rocks of the present study (and in a few additional rocks) is shown in Figs. 27 and 28. $K_D(Mg)^{opx/alm}$ is nearly constant, with an average of 3.95. If almandine is assumed to be an ideal solution, an estimate of the equilibrium constant (K(22)) may be obtained by use of the activities for orthopyroxene that were derived previously. This yields a value of K(22) = 4.59. Departure from ideal mixing in one or both of the coexisting orthopyroxene and almandine is clearly shown in Fig. 28.

The distribution of Mn between orthopyroxene and almandine is shown in Fig. 29. Although the data points are somewhat scattered, most lie near a curve which follows the equation

$$K_D(Mn) = X_{Mn}^{opx}/X_{Mn}^{gar} = 0.21$$

(III) DISTRIBUTION OF Mg, Fe^{2+}, AND Mn BETWEEN COEXISTING CLINOPYROXENE AND ALMANDINE

The Mg-Fe^{2+} exchange equilibrium for clinopyroxene and almandine may be expressed by the following exchange reaction:

$$Mg^{alm} + Fe^{cpx} = Fe^{alm} + Mg^{cpx} \qquad (24)$$

Assuming almandine (alm) is an ideal mixture of Mg and Fe^{2+} end members, then:

$$K(24) = \frac{a_{Mg}^{cpx}\, X_{Fe}^{alm}}{a_{Fe}^{cpx}\, X_{Mg}^{alm}} = \exp \frac{-\Delta G^{\circ}(24)}{RT} \qquad (25)$$

Figure 27. Distribution of Mg and Fe^{2+} between coexisting orthopyroxene and almandine garnet from the charnockitic granulites. Data from some Indian, Swedish and Ugandan charnockites and related granulites are included.

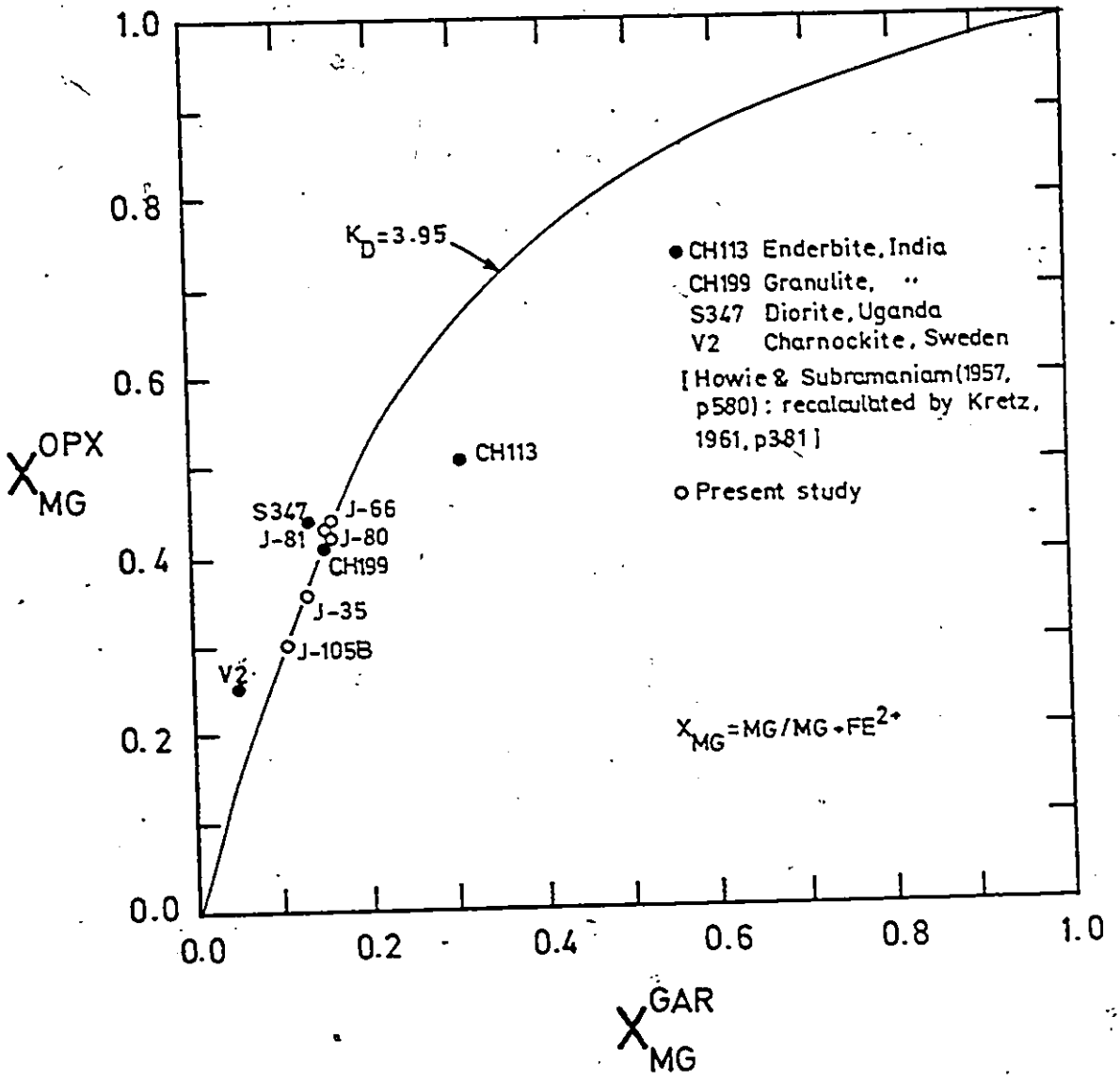

1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
X^{OPX}_{MG}
X^{GAR}_{MG}
K_D=3.95
● CH113 Enderbite, India
CH199 Granulite, "
S347 Diorite, Uganda
V2 Charnockite, Sweden
[Howie & Subramaniam (1957, p580): recalculated by Kretz, 1961, p381]
o Present study
X_{MG}=MG/MG+FE^{2+}
CH113
S347
J-66
J-81
J-80
CH199
J-35
J-105B
V2

Figure 28. Distribution of Mg and Fe^{2+} between coexisting orthopyroxene and almandine garnet from the charnockitic granulites, in terms of a $(\frac{X}{1-X})^{opx}_{Mg}$ vs $(\frac{X}{1-X})^{gar}_{Mg}$ plot. Some Indian, Swedish and Ugandan charnockites and related granulites are also plotted. Source of data as in Fig. 27.

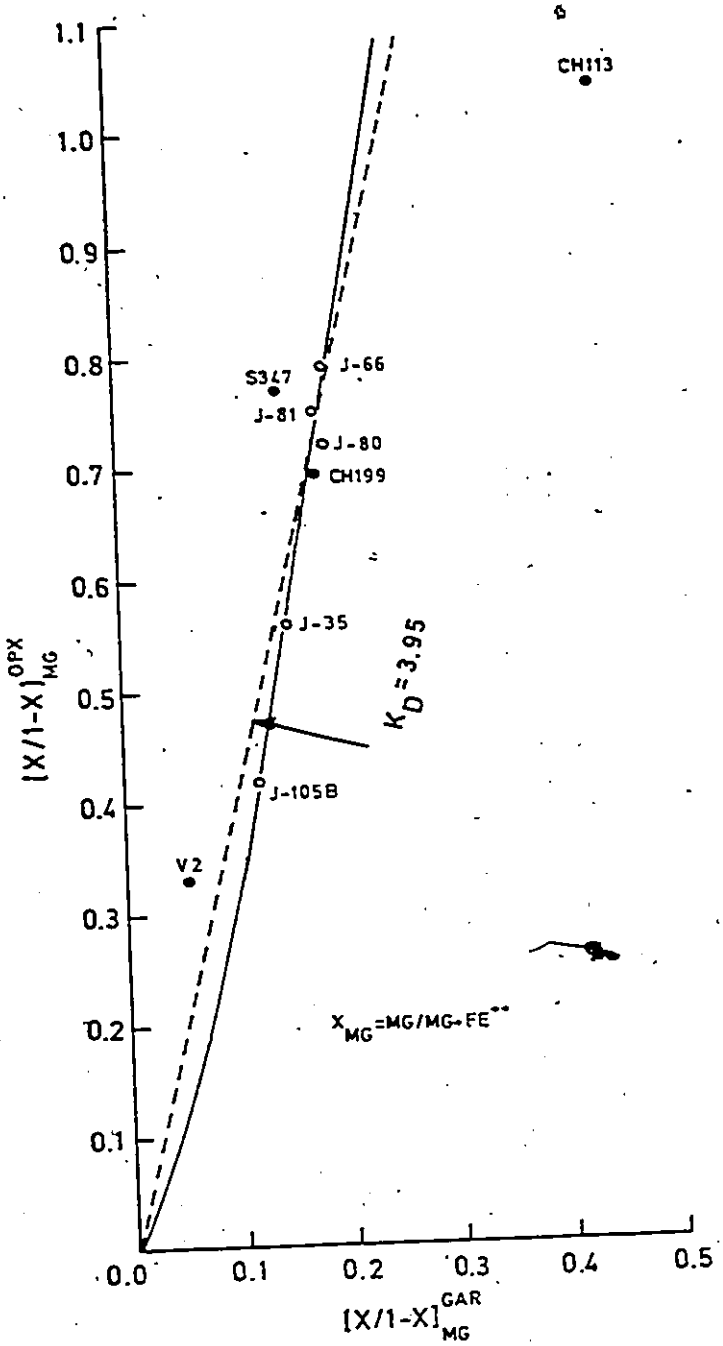
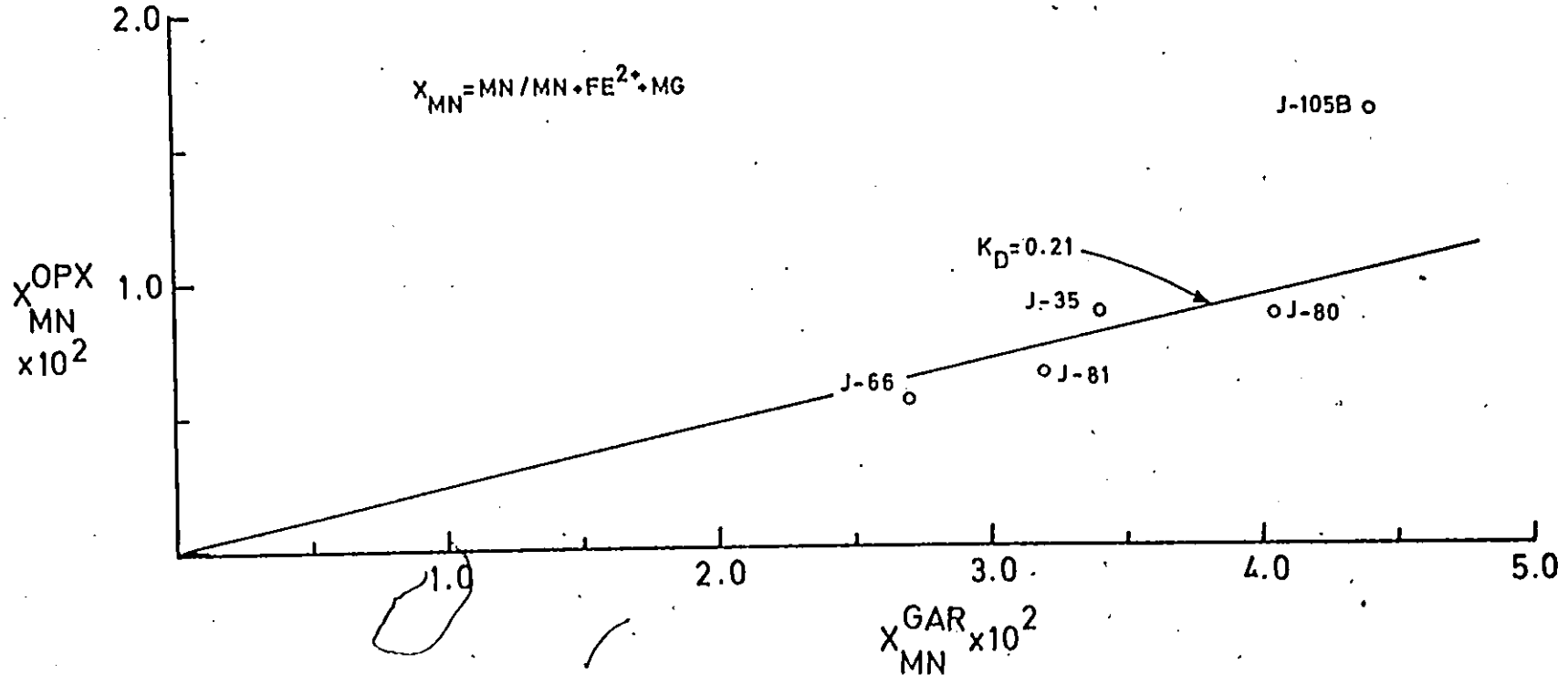

CH113
S347
J-66
J-81
J-80
CH199
J-35
J-105B
V2
K_D=3.95
X_{MG}=MG/MG+FE**
$[X/1-X]^{OPX}_{MG}$
$[X/1-X]^{GAR}_{MG}$
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.1
0.2
0.3
0.4
0.5

Figure 29. Distribution of Mn between coexisting orthopyroxene and almandine garnet from the charnockitic granulites.


2.0
1.0
$X_{MN}=MN/MN+FE^{2+}+MG$
J-105B
$K_D=0.21$
J-35
J-80
J-66
J-81
X^{OPX}_{MN} x10^2
1.0
2.0
3.0
4.0
5.0
X^{GAR}_{MN} x10^2

The distribution of Mg and Fe^{2+} between these two phases is shown in Figs. 30 and 31. For all mineral pairs except J-50, $K_D(Mg)^{cpx/alm}$ is nearly constant with an average value of 6.95. An estimate of K(24) may be obtained by use of the activities for clinopyroxene that were derived previously. This yields a value of K(24) = 6.62.

The distribution of Mn between clinopyroxene and almandine is shown in Fig. 32. All the distribution points save J-105B fall near the curve $K_D(Mn) = 0.20$.

Two aberrant distributions have appeared, namely Mg-Fe in sample J-50 and Mn-(Mg,Fe) in sample J-105B. These may be attributed to analytical error (other than lack of precision) or alternatively, to departure from exchange equilibrium.

(IV) DISTRIBUTION OF Mg, Fe^{2+}, AND Mn BETWEEN COEXISTING ORTHOPYROXENE AND AMPHIBOLE

The Mg-Fe^{2+} exchange reaction between coexisting orthopyroxene (opx) and amphibole (amph) may be expressed as follows:

$$Fe^{opx} + Mg^{amph} = Mg^{opx} + Fe^{amph} \qquad (26)$$

Assuming that the amphiboles are ideal solutions of the Mg and Fe^{2+} end members:

$$K(26) = \frac{a_{Mg}^{opx}\, X_{Fe}^{amph}}{a_{Fe}^{opx}\, X_{Mg}^{amph}} = \exp \frac{-\Delta G^{o}(26)}{RT} \qquad (27)$$

Figure 30. Distribution of Mg and Fe^{2+} between coexisting clinopyroxene and almandine garnet from the charnockitic granulites.

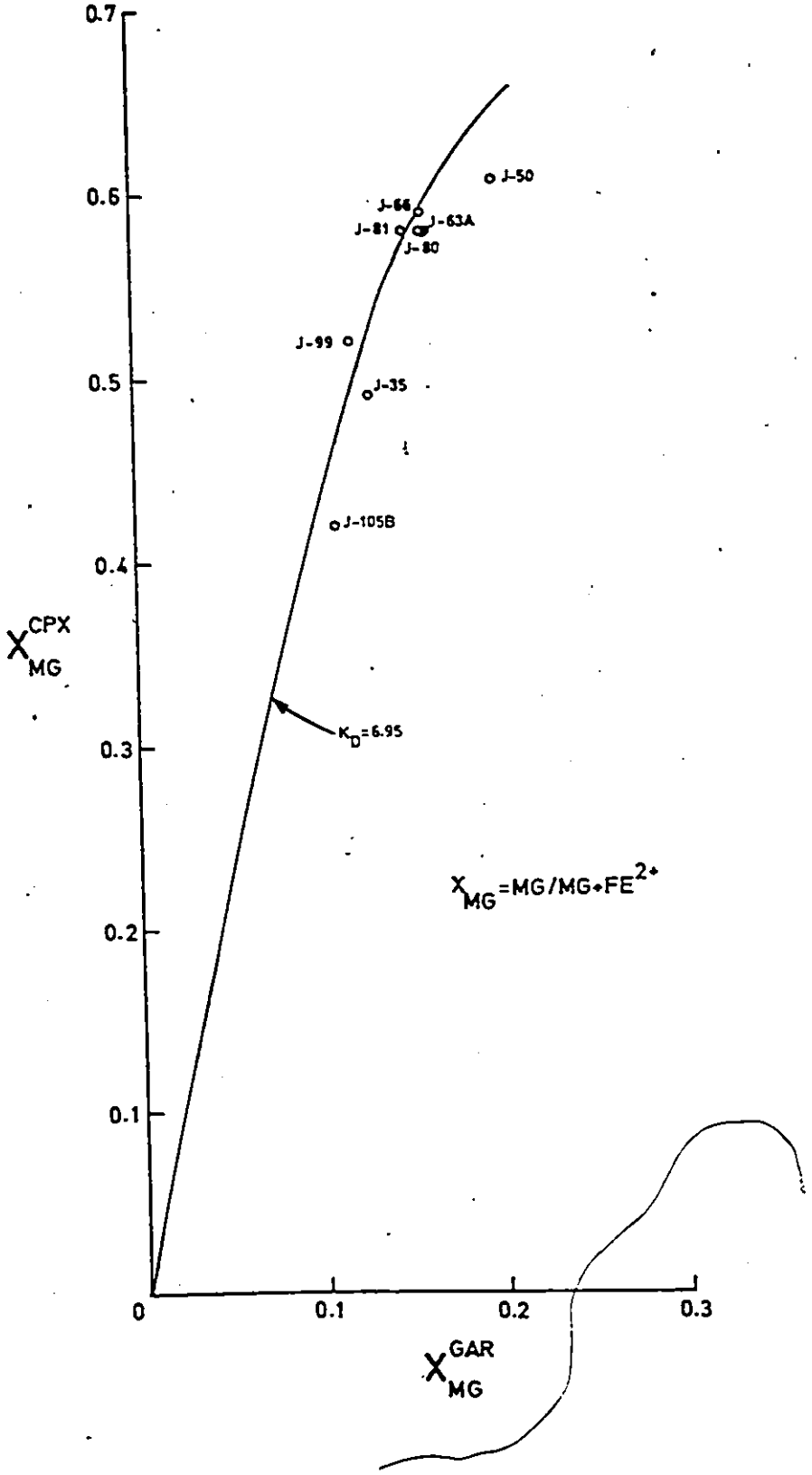

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.1
0.2
0.3
J-50
J-66
J-81
J-63A
J-80
J-99
J-35
J-105B
K_D=6.95
X^{CPX}_{MG}
X^{GAR}_{MG}
X_{MG}=MG/MG+FE^{2+}

Figure 31. Distribution of Mg and Fe^{2+} between coexisting clinopyroxene and almandine garnet from the charnockitic granulites, in terms of a $(\frac{X}{1-X})^{cpx}_{Mg}$ vs $(\frac{X}{1-X})^{gar}_{Mg}$ plot.

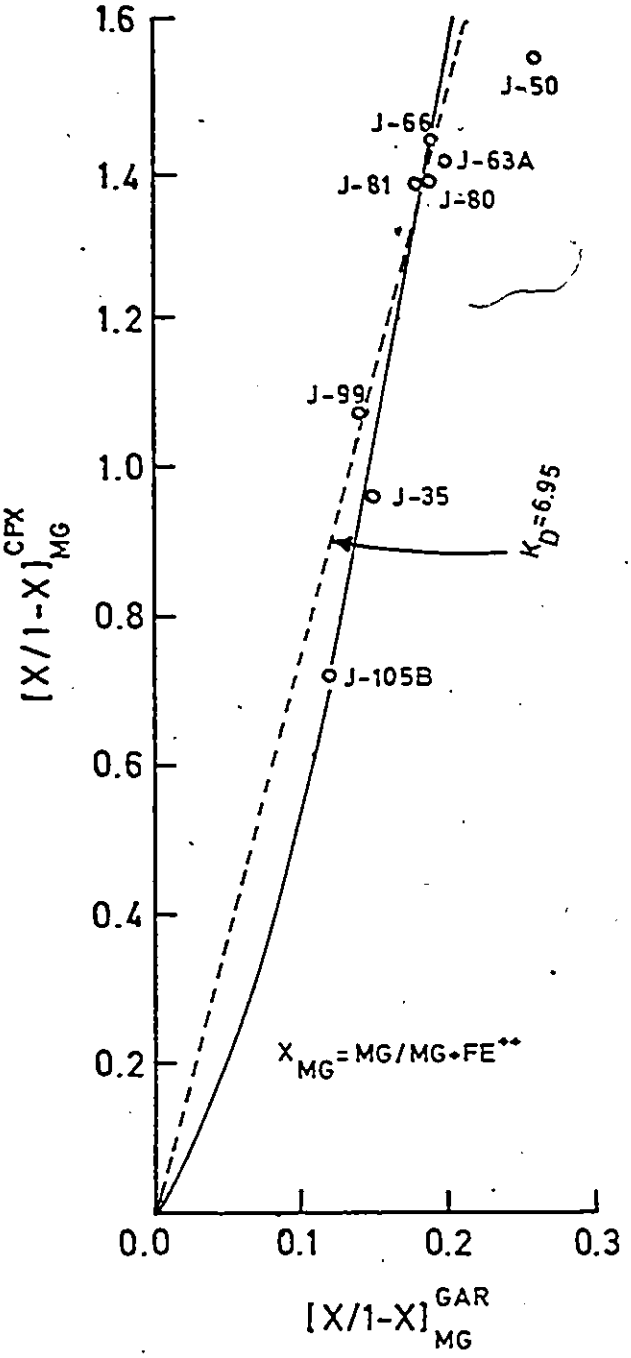
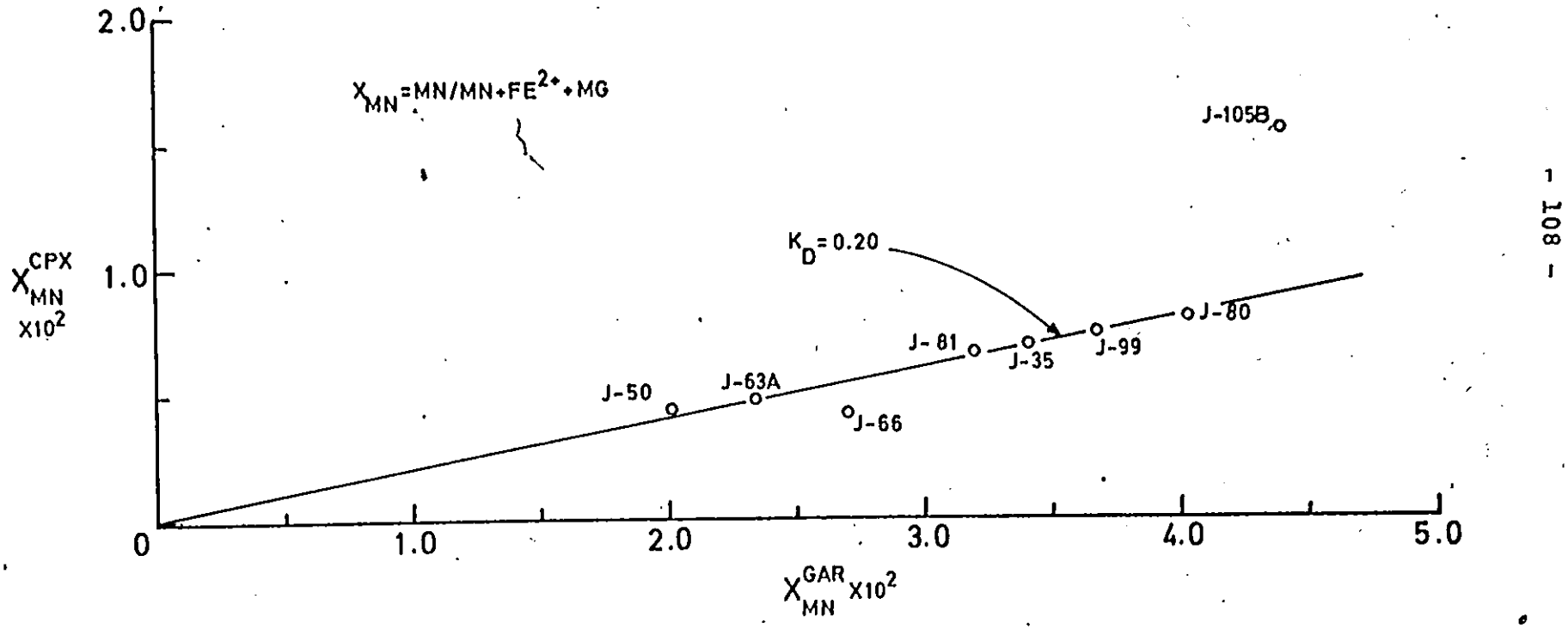

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.1
0.2
0.3
J-50
J-66
J-63A
J-81
J-80
J-99
J-35
J-105B
K_D=6.95
X_{MG}= MG/MG+FE**
$[X/1-X]^{CPX}_{MG}$
$[X/1-X]^{GAR}_{MG}$

Figure 32. Distribution of Mn between coexisting clinopyroxene and almandine garnet from the charnockitic granulites.


2.0
1.0
0
X_{MN}^{CPX} X10^2
X_{MN}=MN/MN+FE^{2+}+MG
J-105B
K_D= 0.20
J-80
J-81
J-35
J-99
J-50
J-63A
J-66
1.0
2.0
3.0
4.0
5.0
X_{MN}^{GAR} X10^2

Data from the present study and from other charnockitic areas are shown in Figs. 33 and 34. The distribution coefficient is remarkably constant, at $K_D = 0.81$. An estimate of the equilibrium constant, from equation (27) and activities for orthopyroxene derived previously is $K(26) = 1.03$. However, the very uniform value of K_D, suggests that both orthopyroxene and amphibole depart from ideal behaviour, in such a way that the expression containing the four activity coefficients remains independent of composition.

The distribution of Mn between orthopyroxene and amphibole is shown in Fig. 35. The Mn-(Mg,Fe) distribution coefficient in all specimens is very nearly 2.18.

(V) DISTRIBUTION OF Mg, Fe^{2+}, AND Mn BETWEEN COEXISTING CLINOPYROXENE AND AMPHIBOLE

The clinopyroxene-amphibole exchange equilibrium may be evaluated in terms of the reaction

$$Fe^{cpx} + Mg^{amph} = Mg^{cpx} + Fe^{amph} \qquad (28)$$

Assuming amphiboles are ideal mixtures:

$$K(28) = K_D(Mg) = \frac{a_{Mg}^{cpx}\, X_{Fe}^{amph}}{a_{Fe}^{cpx}\, X_{Mg}^{amph}} = \exp \frac{-\Delta G^{o}(28)}{RT} \qquad (29)$$

Figure 33. Distribution of Mg and Fe^{2+} between coexisting orthopyroxene and amphibole from the charnockitic granulites.

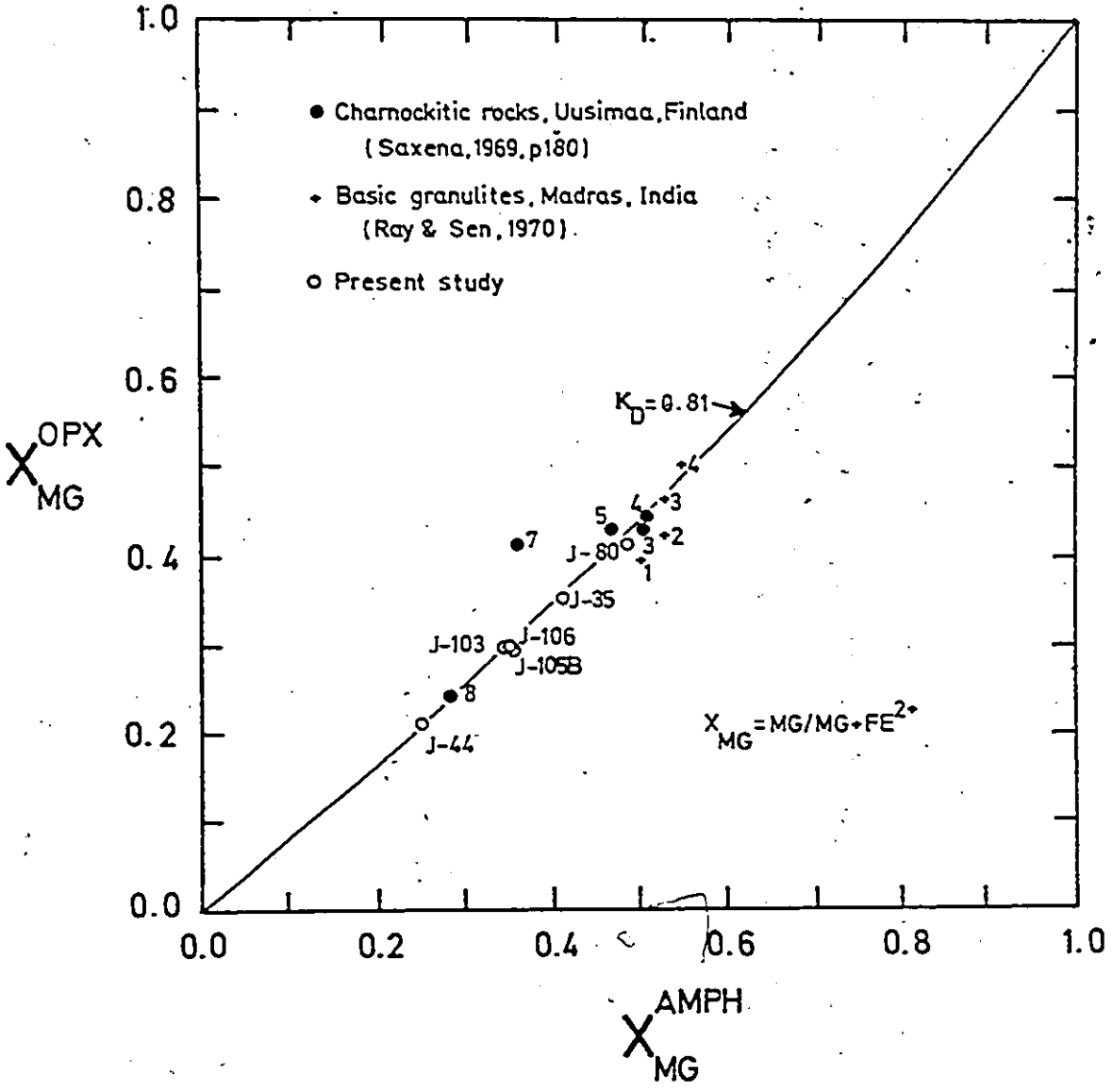

1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
● Charnockitic rocks, Uusimaa, Finland
(Saxena, 1969, p180)
+ Basic granulites, Madras, India
(Ray & Sen, 1970)
o Present study
K_D=0.81
5
4
+3
+4
+2
3
1
7
J-80
J-35
J-103
J-106
J-105B
8
J-44
X_{MG}=MG/MG+FE^{2+}
X^{OPX}_{MG}
X^{AMPH}_{MG}

Figure 34. Distribution of Mg and Fe^{2+} between coexisting orthopyroxene and amphibole from the charnockitic granulites, in terms of a $(\frac{X}{1-X})^{opx}_{Mg}$ vs $(\frac{X}{1-X})^{amph}_{Mg}$ plot.

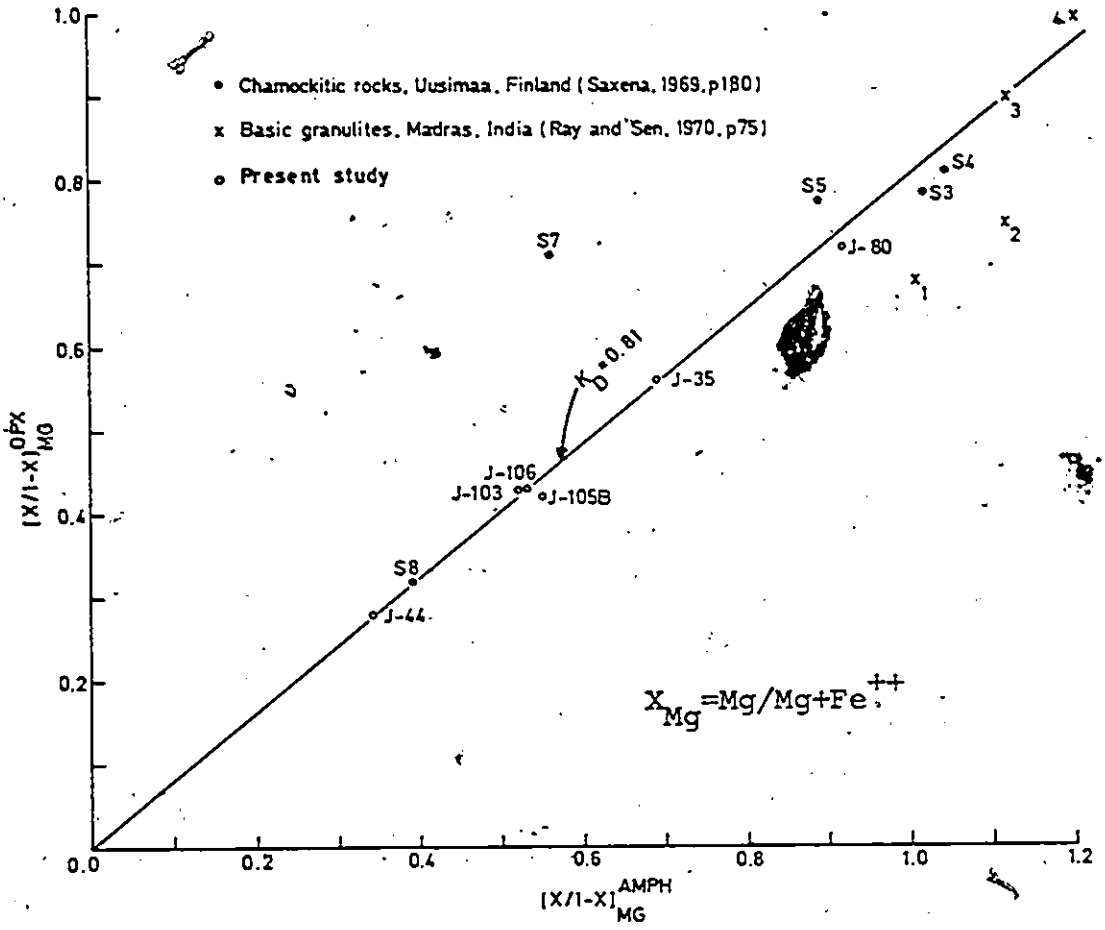
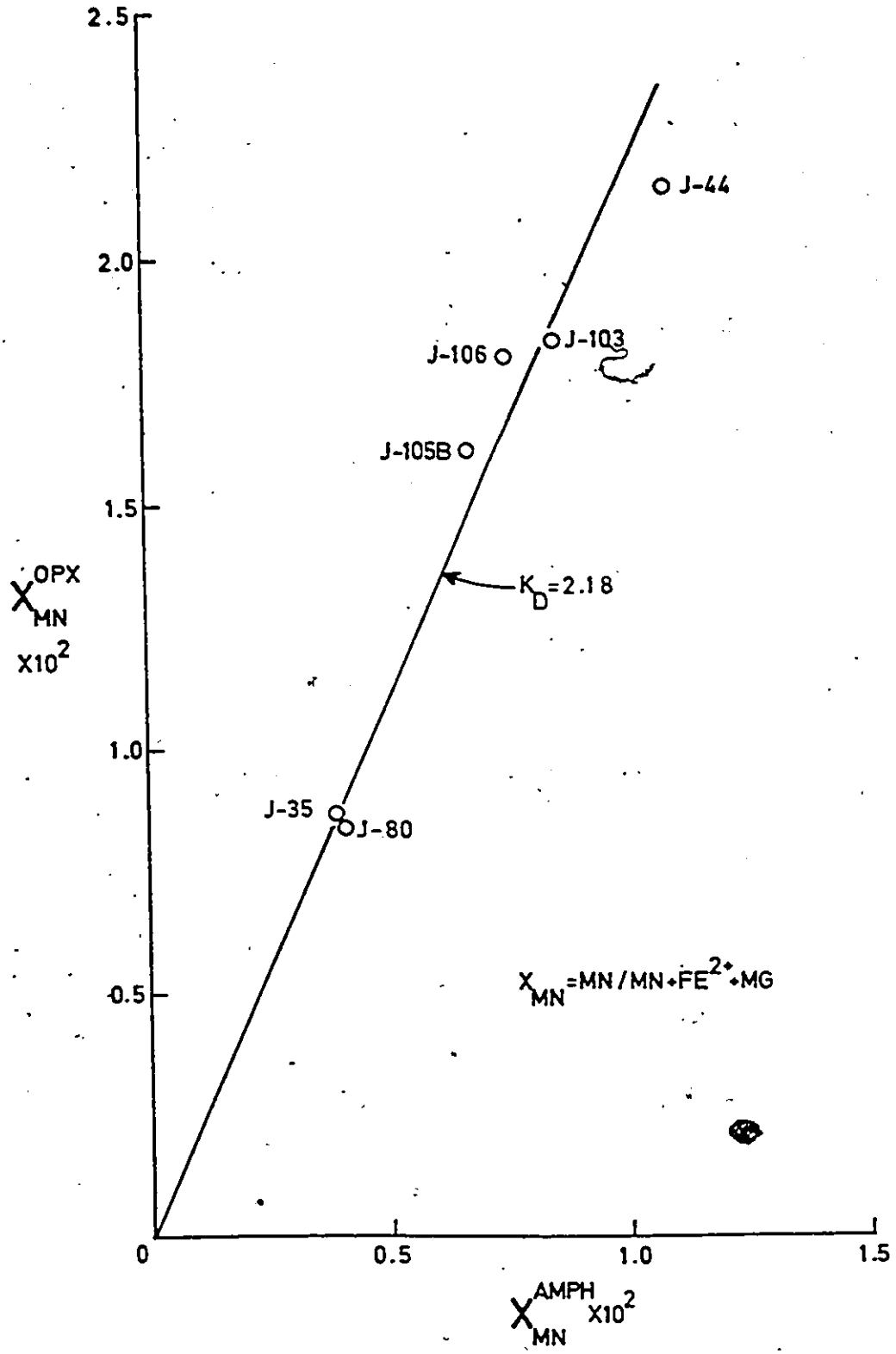

• Chamockitic rocks, Uusimaa, Finland (Saxena, 1969, p180)
x Basic granulites, Madras, India (Ray and Sen, 1970, p75)
o Present study
S7
S5
S4
S3
S8
J-80
J-35
J-106
J-103
J-105B
J-44
K_D=0.81
X_{Mg}=Mg/Mg+Fe++
$[X/1-X]^{OPX}_{MG}$
$[X/1-X]^{AMPH}_{MG}$
0.0
0.2
0.4
0.6
0.8
1.0
1.2

Figure 35. Distribution of Mn between coexisting orthopyroxene and amphibole from the charnockitic granulites.


2.5
2.0
1.5
1.0
0.5
0
0.5
1.0
1.5
J-44
J-103
J-106
J-105B
J-35
J-80
K_D=2.18
X_{MN}^{OPX} X10^2
X_{MN}^{AMPH} X10^2
X_{MN}=MN/MN+FE^{2+}+MG

The distribution of Mg and Fe^{2+} in eight pairs of coexisting clinopyroxene and amphibole is shown in Figs. 36 and 37, which contain, in addition, some data from charnockitic rocks in Finland. The distribution coefficient is nearly constant at 1.40. An estimate of K(28), employing activities for clinopyroxene reported earlier in this chapter is 1.51. The distribution of Mn is shown in Fig. 38. The distribution coefficient for Mn-(Mg,Fe^{2+}) exchange is remarkably constant, as shown in Fig. 38, with a mean value of 1.80.

(VI) DISTRIBUTION OF Mg, Fe^{2+}, AND Mn BETWEEN COEXISTING ALMANDINE AND AMPHIBOLE

The distribution of Mg and Fe^{2+} between almandine and amphibole, may be evaluated by considering the reaction:

$$Mg^{alm} + Fe^{amph} = Fe^{alm} + Mg^{amph} \qquad (30)$$

$$K(30) = \frac{a_{Fe}^{alm}\, a_{Mg}^{amph}}{a_{Mg}^{alm}\, a_{Fe}^{amph}} = \exp \frac{-\Delta G^{o}(30)}{RT} \qquad (31)$$

The distribution of Fe^{2+} and Mg in five pairs of coexisting almandine and amphibole is shown in Figs. 39 and 40. The distribution coefficient is nearly constant, at 4.54.

Figure 36. Distribution of Mg and Fe^{2+} between coexisting clinopyroxene and amphibole from the charnockitic granulites.

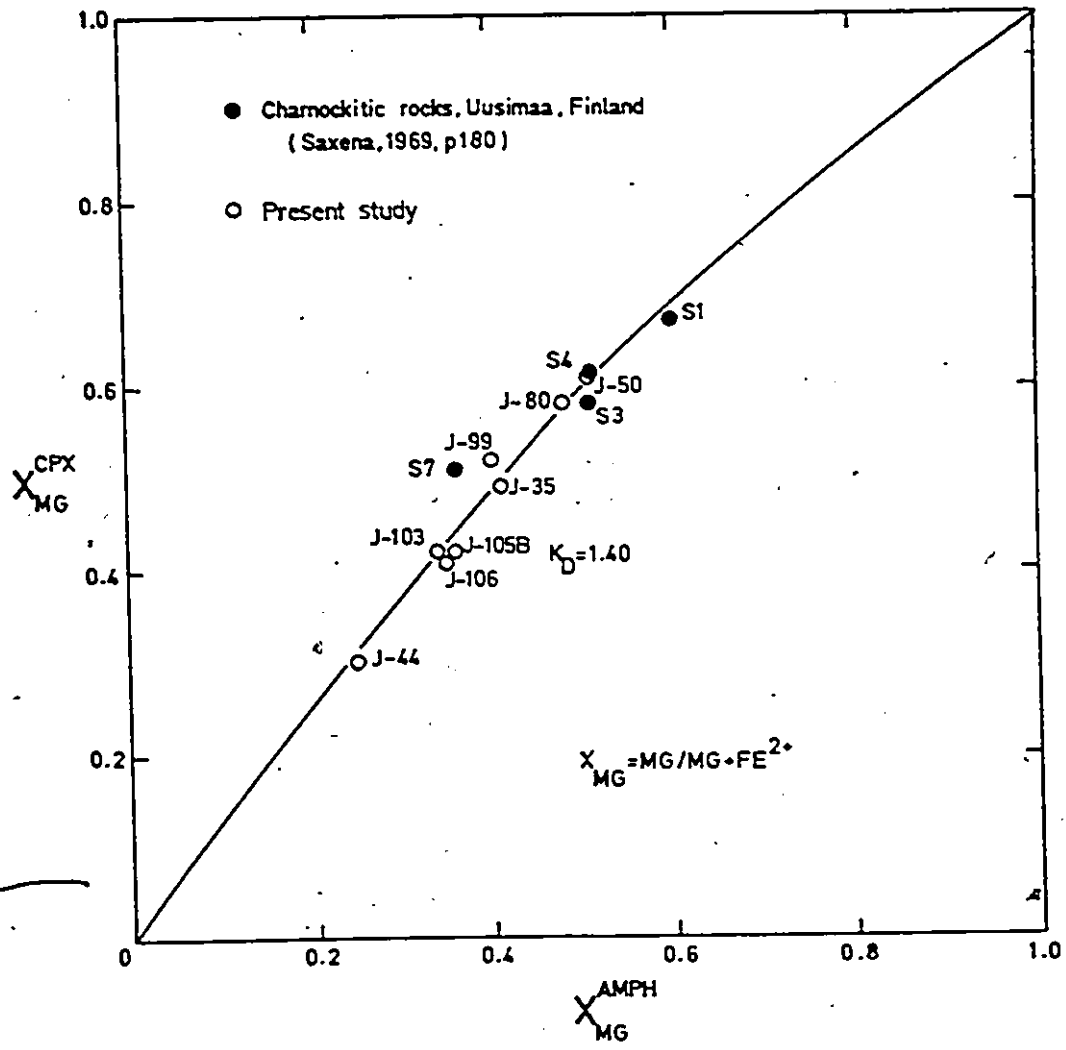
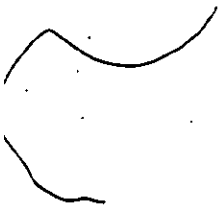

1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
● Charnockitic rocks, Uusimaa, Finland
(Saxena, 1969, p180)
○ Present study
S1
S4
J-50
J-80
S3
J-99
S7
J-35
J-103
J-105B
J-106
K_D=1.40
J-44
X_{MG}=MG/MG+FE^{2+}
X_{MG}^{CPX}
X_{MG}^{AMPH}

Figure 37. Distribution of Mg and Fe^{2+} between coexisting clinopyroxene and amphibole from the charnockitic granulites, in terms of a $(\frac{X}{1-X})^{cpx}_{Mg}$ vs $(\frac{X}{1-X})^{amph}_{Mg}$ plot.



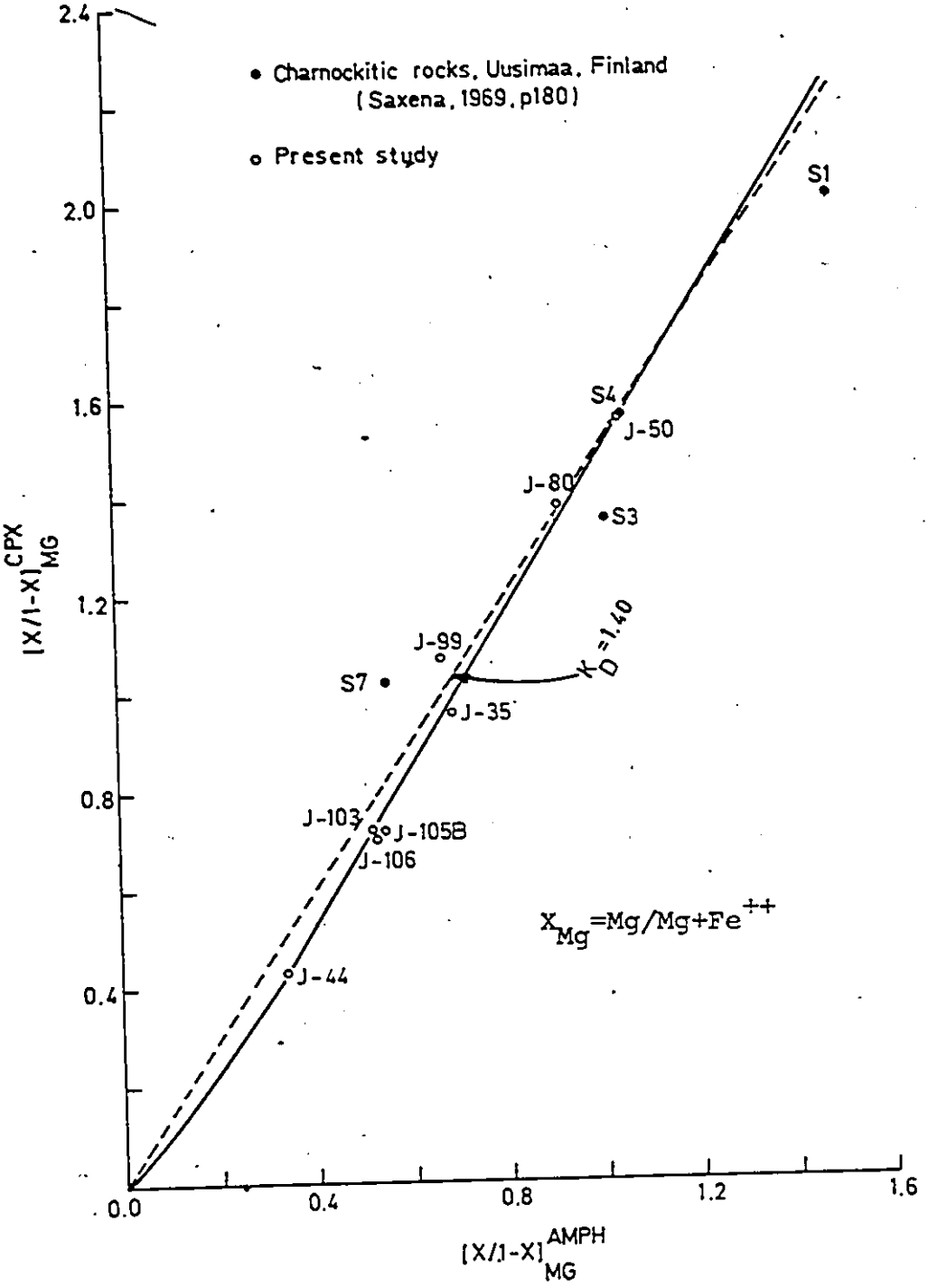

• Charnockitic rocks, Uusimaa, Finland
(Saxena, 1969, p180)
o Present study
S1
S4
J-50
J-80
S3
J-99
S7
J-35
J-103
J-105B
J-106
J-44
K_D=1.40
X_Mg=Mg/Mg+Fe++
2.4
2.0
1.6
1.2
0.8
0.4
0.0
0.4
0.8
1.2
1.6
[X/1-X]MG CPX
[X/1-X]MG AMPH

Figure 38. Distribution of Mn between coexisting clinopyroxene and amphibole from the charnockitic granulites.

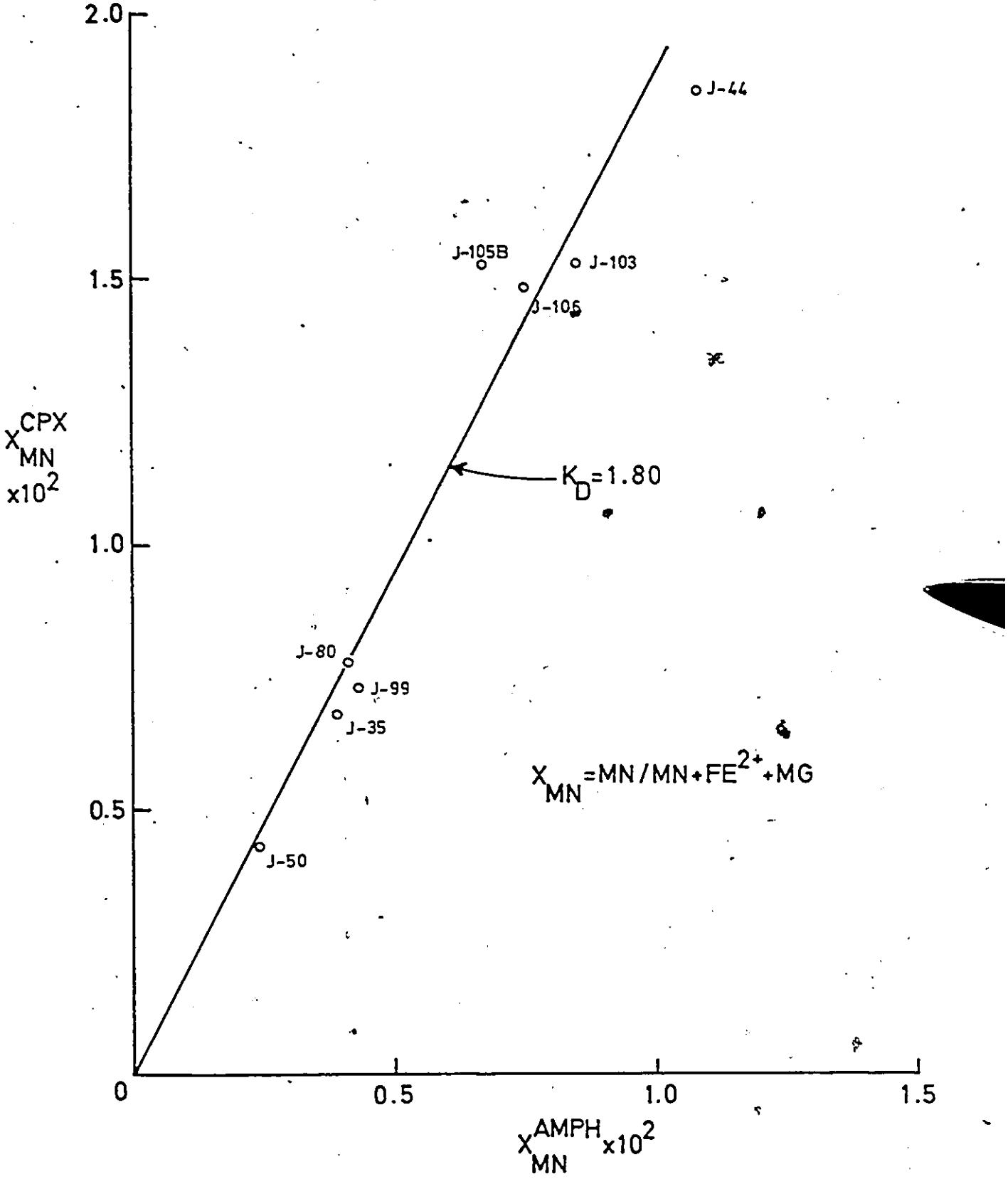

2.0
1.5
1.0
0.5
0
0.5
1.0
1.5
X_{MN}^{CPX} x10^2
X_{MN}^{AMPH} x10^2
J-44
J-105B
J-103
J-106
J-80
J-99
J-35
J-50
K_D=1.80
X_{MN}=MN/MN+FE^{2+}+MG

Figure 39. Distribution of Mg and Fe^{2+} between coexisting amphibole and almandine garnet from the charnockitic granulites.

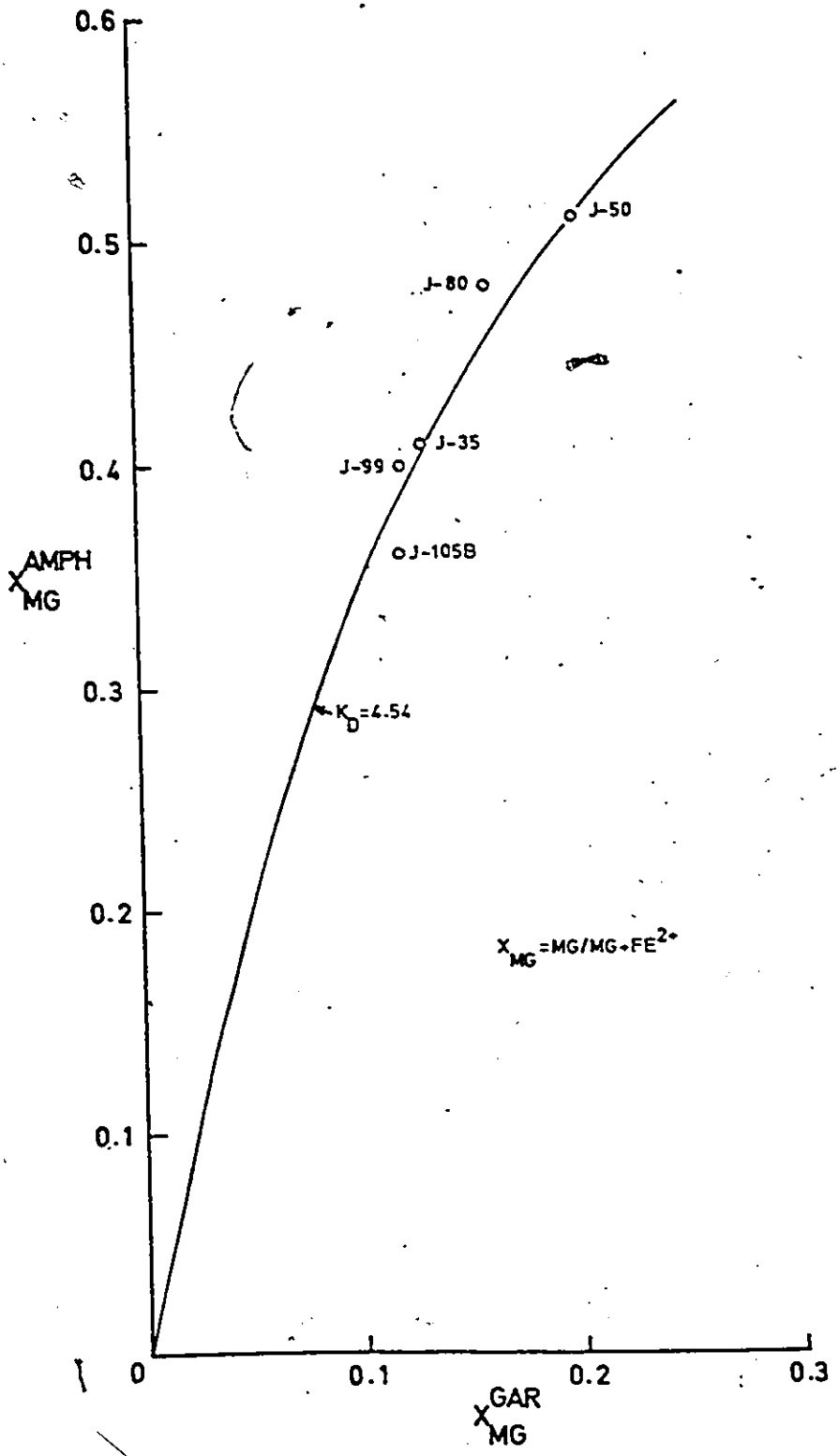
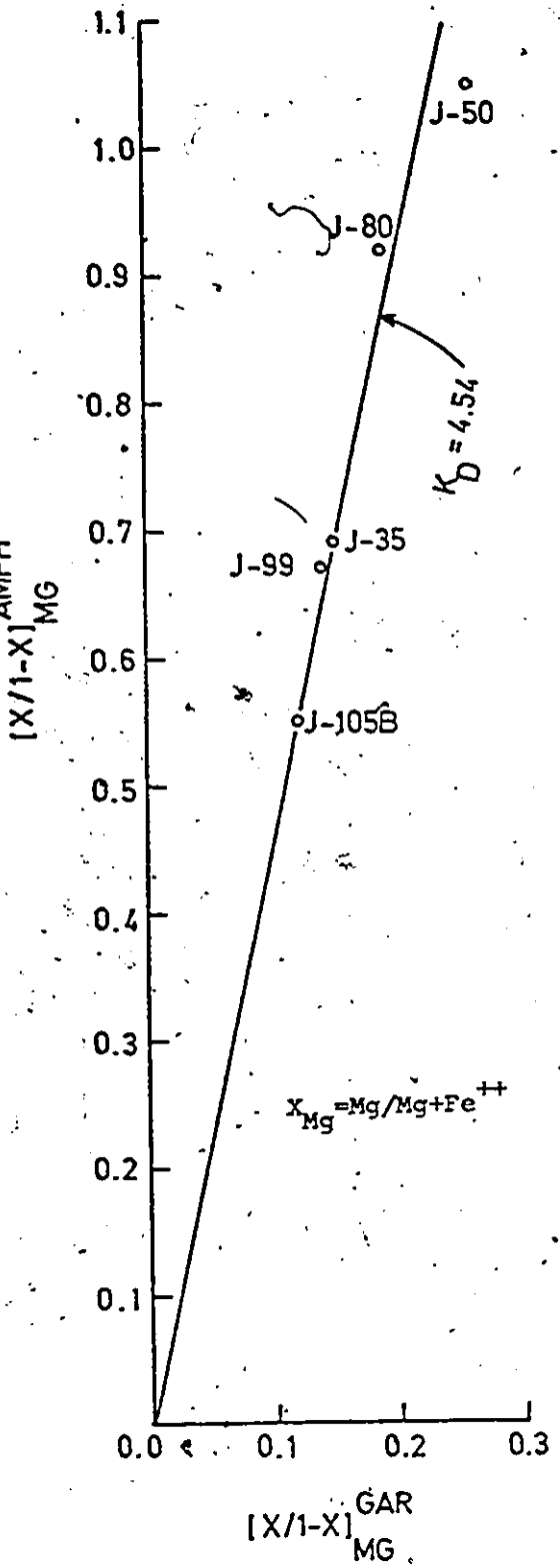

0.6
0.5
0.4
0.3
0.2
0.1
0
0.1
0.2
0.3
J-50
J-80
J-35
J-99
J-105B
K_D=4.54
X^{AMPH}_{MG}
X^{GAR}_{MG}
X_{MG}=MG/MG+FE^{2+}

Figure 40. Distribution of Mg and Fe^{2+} between coexisting amphibole and almandine garnet from the charnockitic granulites, in terms of a $(\frac{X}{1-X})^{amph}_{Mg}$ vs $(\frac{X}{1-X})^{gar}_{Mg}$ plot.


1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.1
0.2
0.3
J-50
J-80
J-35
J-99
J-105B
$K_D = 4.54$
$X_{Mg} = Mg/Mg+Fe^{++}$
$[X/1-X]^{AMPH}_{MG}$
$[X/1-X]^{GAR}_{MG}$

The distribution of Mn between the two minerals is shown in Fig. 41. The Mn-(Mg,Fe^{2+}) distribution coefficient is nearly constant, with a mean value of 8.54.

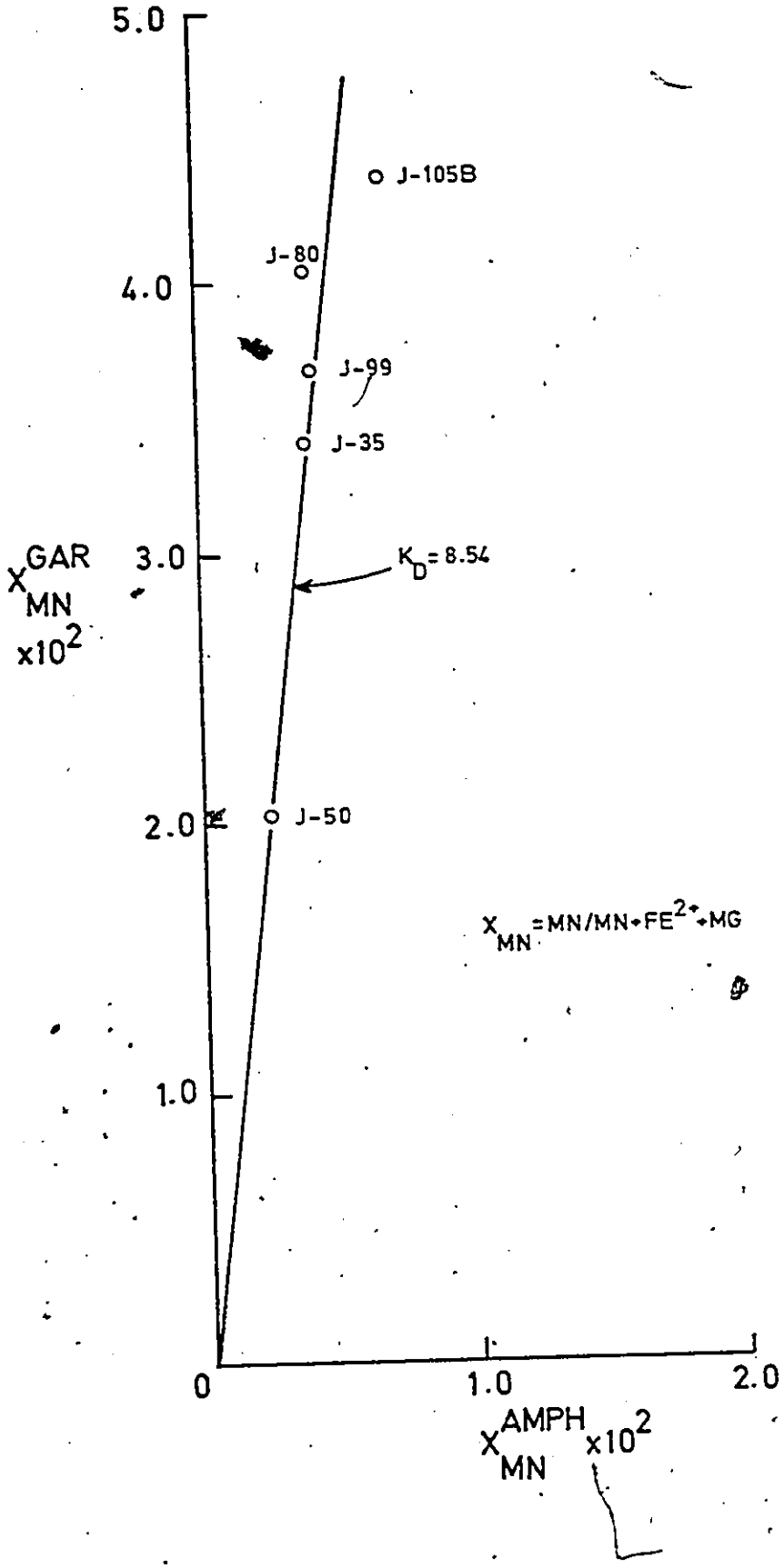
Summary

The above results show that the elements Mg, Fe^{2+}, and Mn are systematically distributed among orthopyroxene, clinopyroxene, amphibole, and garnet within the charnockitic granulites of the present study. The stepwise decrease in the affinity a mineral possesses for an element is as follows:

Mg	clinopyroxene	amphibole	orthopyroxene	almandine
Fe^{2+}	almandine	orthopyroxene	amphibole	clinopyroxene
Mn	almandine	orthopyroxene	clinopyroxene	amphibole

Moreover, with very few exceptions, the concentration of an element in one mineral bears a functional relationship with that in a coexisting mineral. The existence of these relationships and their nature are consistent with expectations based on the principle of thermodynamic equilibrium, and are taken as indication that exchange equilibrium was established and preserved in the rocks of the study area.

Figure 41. Distribution of Mn between coexisting amphibole and almandine garnet from the charnockitic granulites.


5.0
4.0
3.0
2.0
1.0
0
J-105B
J-80
J-99
J-35
J-50
$K_D = 8.54$
$X^{GAR}_{MN} \times 10^2$
$X_{MN} = MN/MN+FE^{2+}+MG$
1.0
2.0
$X^{AMPH}_{MN} \times 10^2$

The nature of the distribution patterns are capable of providing some information on the properties of the mineral solid solutions, notably the relationships between activity and concentration within them. For example, some activity-concentration relationships may be deduced for orthopyroxene and clinopyroxene, based on the distribution of Mg and Fe between them, and these indicate some departure from the ideal mixture model of solid solutions. More precise characterization of the nature of activity-concentration relationships must come from direct experimental methods.

VIII DISTRIBUTION OF IRON AND TITANIUM BETWEEN COEXISTING MAGNETITE AND ILMENITE

General Consideration

Ilmenite and magnetite are the chief iron oxides in the charnockitic granulites of the present study. Electron microprobe analyses (Table 10) shows that these minerals are solid solutions of iron and titanium oxides. Assuming that the ilmenite solid solution lies on the $FeTiO_3$ -Fe_2O_3 join and that the magnetite solid solution lies on the Fe_2TiO_4 -Fe_3O_4 join, the composition of the ilmenite solid solution (Ilm ss) may be expressed by the formula $(FeTiO_3, Fe_2O_3)$, and magnetite solid solution (Mt ss), as an inverse spinel, by $[Fe^{2+}(Fe^{2+}Ti^{4+})O_4, Fe^{3+}(Fe^{2+}Fe^{3+})O_4]$. These minerals may then be regarded as binary solid solutions, as shown in Fig. 42.

Phase Equilibrium

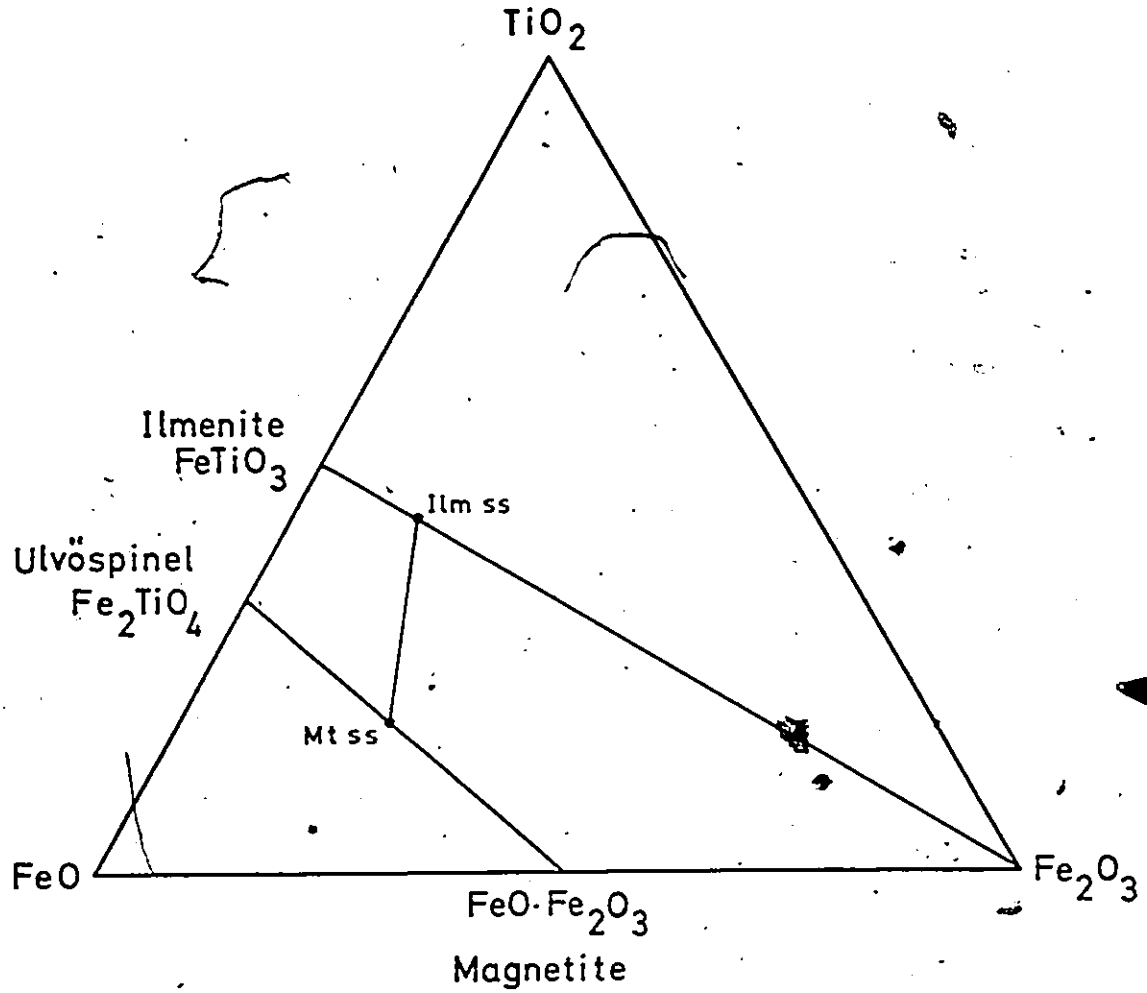
The formulas for ilmenite ss and magnetite ss, as written above, may be expressed in an alternate form, as follows:

ilmenite ss $(Fe^{2+}Ti^{4+}, Fe^{3+}Fe^{3+})O_3$

magnetite ss $Fe^{2+}(Fe^{2+}Ti^{4+}, Fe^{3+}Fe^{3+})O_4$

Consequently, equilibrium between coexisting ilmenite ss and magnetite ss, in relation to the 'slope' of the tie

Figure 42. Compositional relationships of ilmenite solid solutions (Ilm ss), magnetite solid solutions (Mt ss) and their pure end member molecules in the system TiO_2-FeO-Fe_2O_3.


TiO2
Ilmenite
FeTiO3
Ilm ss
Ulvöspinel
Fe2TiO4
Mt ss
FeO
FeO·Fe2O3
Fe2O3
Magnetite

line in Fig. 42, may be regarded as an exchange reaction, involving species Fe^{2+} Ti^{4+} and Fe^{3+} Fe^{3+}, as shown in Fig. 43. The reaction is as follows:

$$(Fe^{3+}Fe^{3+})_{Mtss} + (Fe^{2+}Ti^{4+})_{Ilmss} = (Fe^{3+}Fe^{3+})_{Ilmss} + (Fe^{2+}Ti^{4+})_{Mtss} \quad (32)$$

At equilibrium

$$\mu^{Mtss}_{Fe^{3+}Fe^{3+}} + \mu^{Ilmss}_{Fe^{2+}Ti^{4+}} = \mu^{Ilmss}_{Fe^{3+}Fe^{3+}} + \mu^{Mtss}_{Fe^{2+}Ti^{4+}} \quad (33)$$

$$K(32) = \frac{(a_{Fe^{3+}Fe^{3+}})_{Ilmss}\,(a_{Fe^{2+}Ti^{4+}})_{Mtss}}{(a_{Fe^{3+}Fe^{3+}})_{Mtss}\,(a_{Fe^{2+}Ti^{4+}})_{Ilmss}} = \exp\frac{-\Delta G^{o}(32)}{RT} \quad (34)$$

Differentiate equation (34) with respect to 1/T

$$\frac{\partial \ln K(32)}{\partial (1/T)} = \frac{-\Delta H(32)}{R} \quad (35)$$

where ΔH is the enthalpy change of reaction (32). Equation (35) gives the temperature dependence of reaction (32) and indicates that the tie line in Fig. 42 should rotate in response to temperature.

Both minerals contain Fe^{2+} and Fe^{3+}, and the composition of coexisting ilmenite ss and magnetite ss is very much dependent on oxidation-reduction equilibrium. The effect of a change in temperature and a change in the fugacity of oxygen on the location of the tie line, based on observations in nature and experiment (Buddington and Lindsley, 1964, p313), is shown in a general way in Fig. 44.

Figure 43. Exchange of iron and titanium ions between coexisting ilmenite solid solutions (Ilm ss) and magnetite solid solutions (Mt ss).

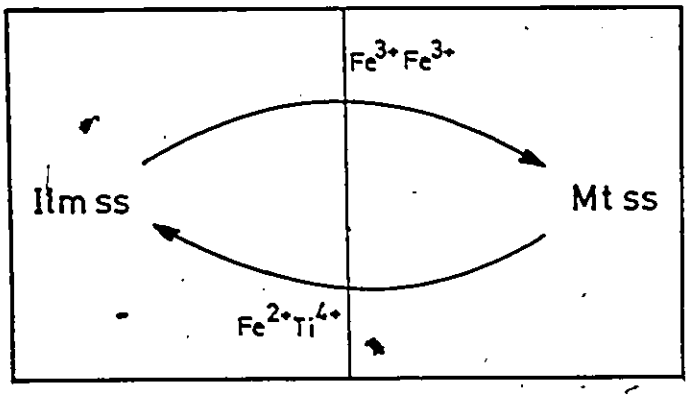

$Fe^{3+}Fe^{3+}$
Ilm ss
Mt ss
$Fe^{2+}Ti^{4+}$

Figure 44. Shift and rotation of the ilmenite-magnetite tie line, in response to a change in temperature (T) and fugacity of oxygen (fO_2), based on natural and experimental data. (Buddington and Lindsley, 1964).

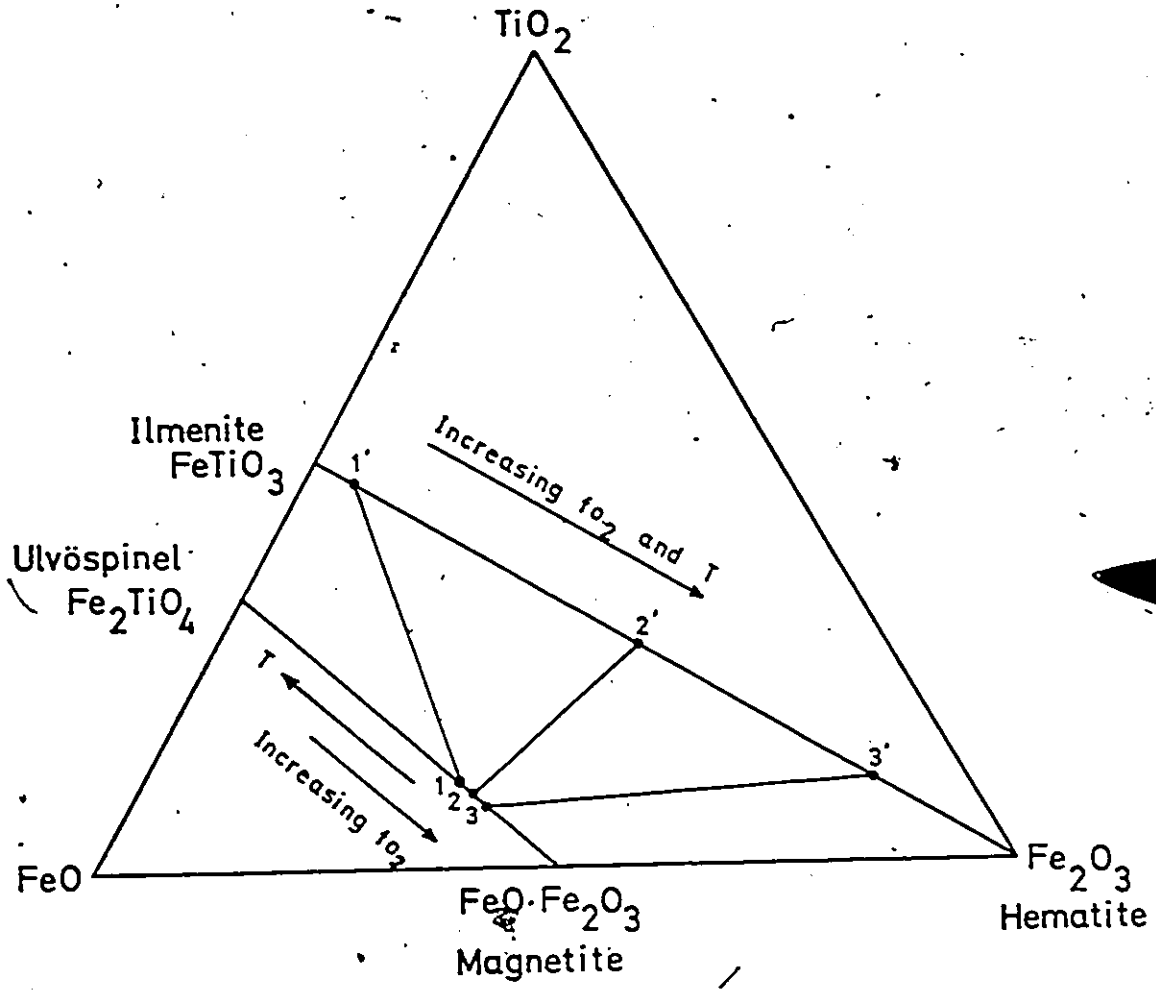
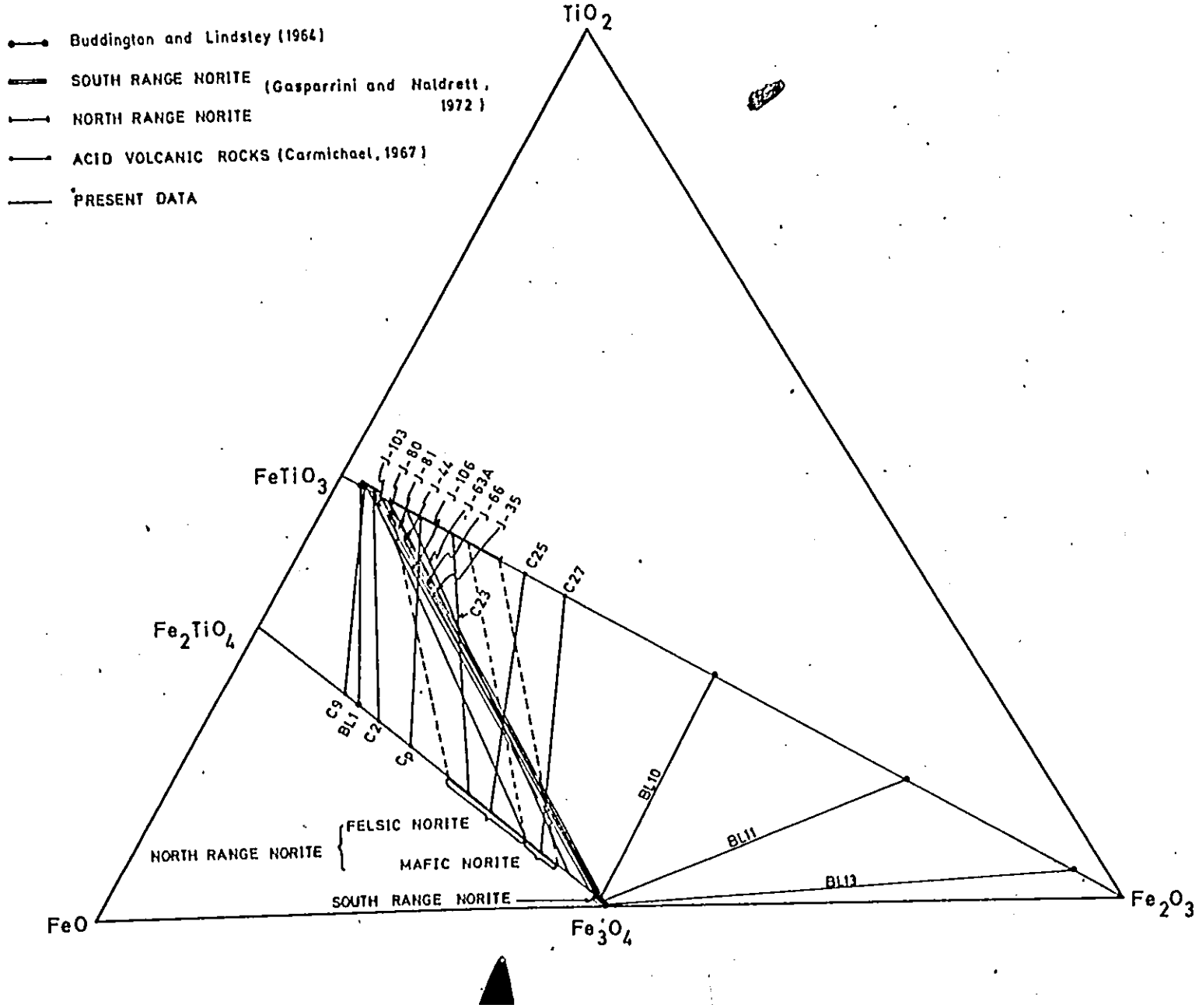

TiO_2
Ilmenite
$FeTiO_3$
Ulvöspinel
Fe_2TiO_4
Increasing fo_2 and T
T
Increasing fo_2
1'
2'
3'
1
2
3
FeO
$FeO \cdot Fe_2O_3$
Magnetite
Fe_2O_3
Hematite

Fig. 45 shows the composition of coexisting ilmenite and magnetite solid solutions from the present charnockitic granulites, together with some published results from igneous and metamorphic rocks. The composition of ilmenite ss and of magnetite ss is very close to pure ilmenite and pure magnetite respectively.

Equilibrium data on the composition of coexisting magnetite and ilmenite were obtained by Buddington and Lindsley (1964) and are presented in Fig. 46. If we assume that an equilibrium between magnetite and ilmenite in the rocks of the present study was attained and retained, then by comparison with the experimental data, the equilibrium temperature was less than 600°C, and the equilibrium oxygen fugacity was less than $10^{-18.5}$ atm. However, it is well known that exsolution reaction involving these minerals occur rather readily, and it is possible that the temperature of metamorphism was higher than that indicated above, and the oxygen fugacity was higher or lower. It is surprising that, in Fig. 45, most of the tie lines do not cross each other, and this is taken as an evidence that an equilibrium or near-equilibrium was established at a temperature below and following the peak of metamorphism.

Data of the present study may be compared with those from Sudbury. Note that tie lines for the south range

Figure 45. Phase diagram showing compositional tie lines of coexisting ilmenite solid solutions (Ilm ss) and magnetite solid solutions (Mt ss) from the charnockitic granulites together with some published results for igneous and metamorphic rocks.


Buddington and Lindsley (1964)
SOUTH RANGE NORITE (Gasparrini and Naldrett, 1972)
NORTH RANGE NORITE
ACID VOLCANIC ROCKS (Carmichael, 1967)
PRESENT DATA
TiO2
FeTiO3
Fe2TiO4
FeO
Fe3O4
Fe2O3
J-103
J-80
J-81
J-44
J-106
J-63A
J-66
J-35
C25
C27
C23
C9
BL1
C2
C9
BL10
BL11
BL13
NORTH RANGE NORITE
FELSIC NORITE
MAFIC NORITE
SOUTH RANGE NORITE

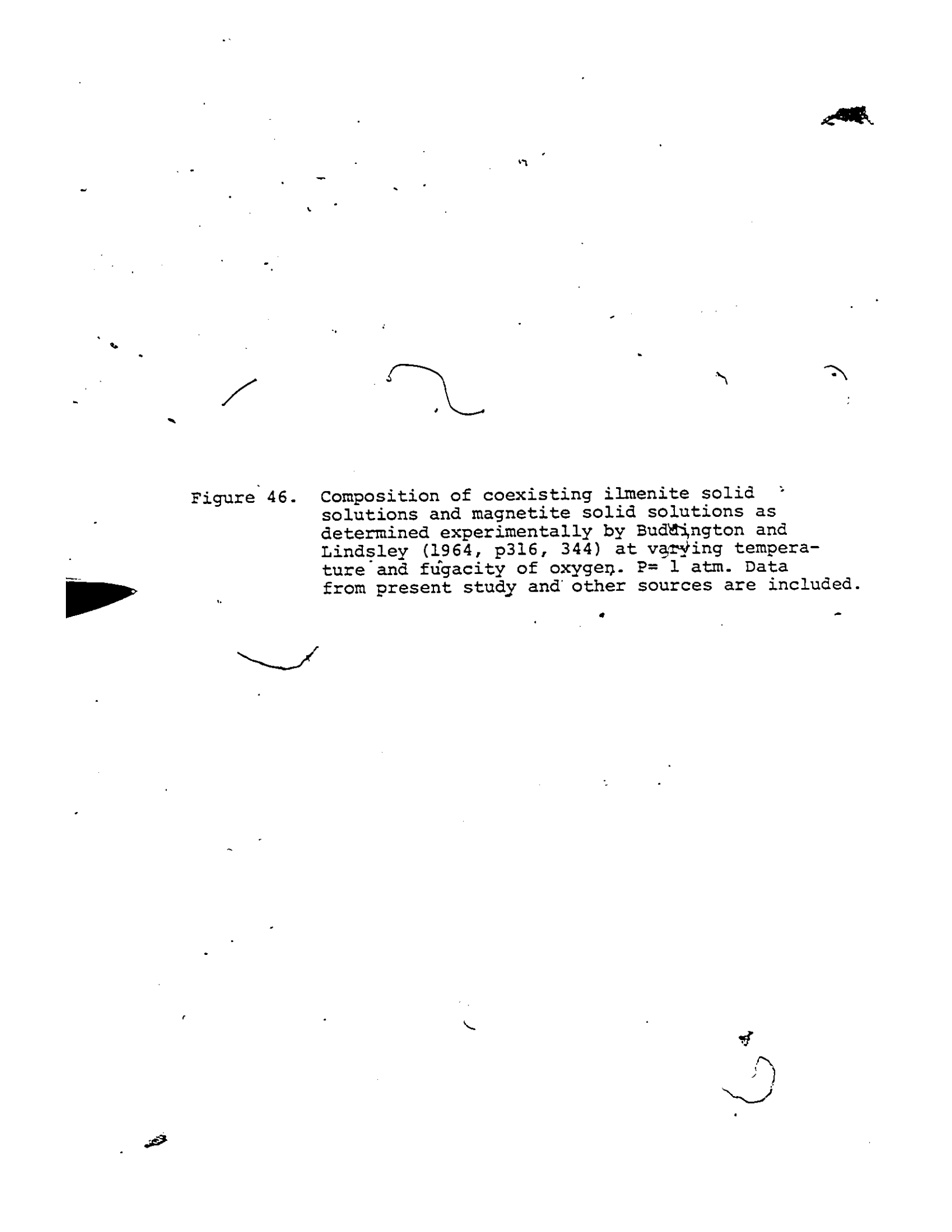
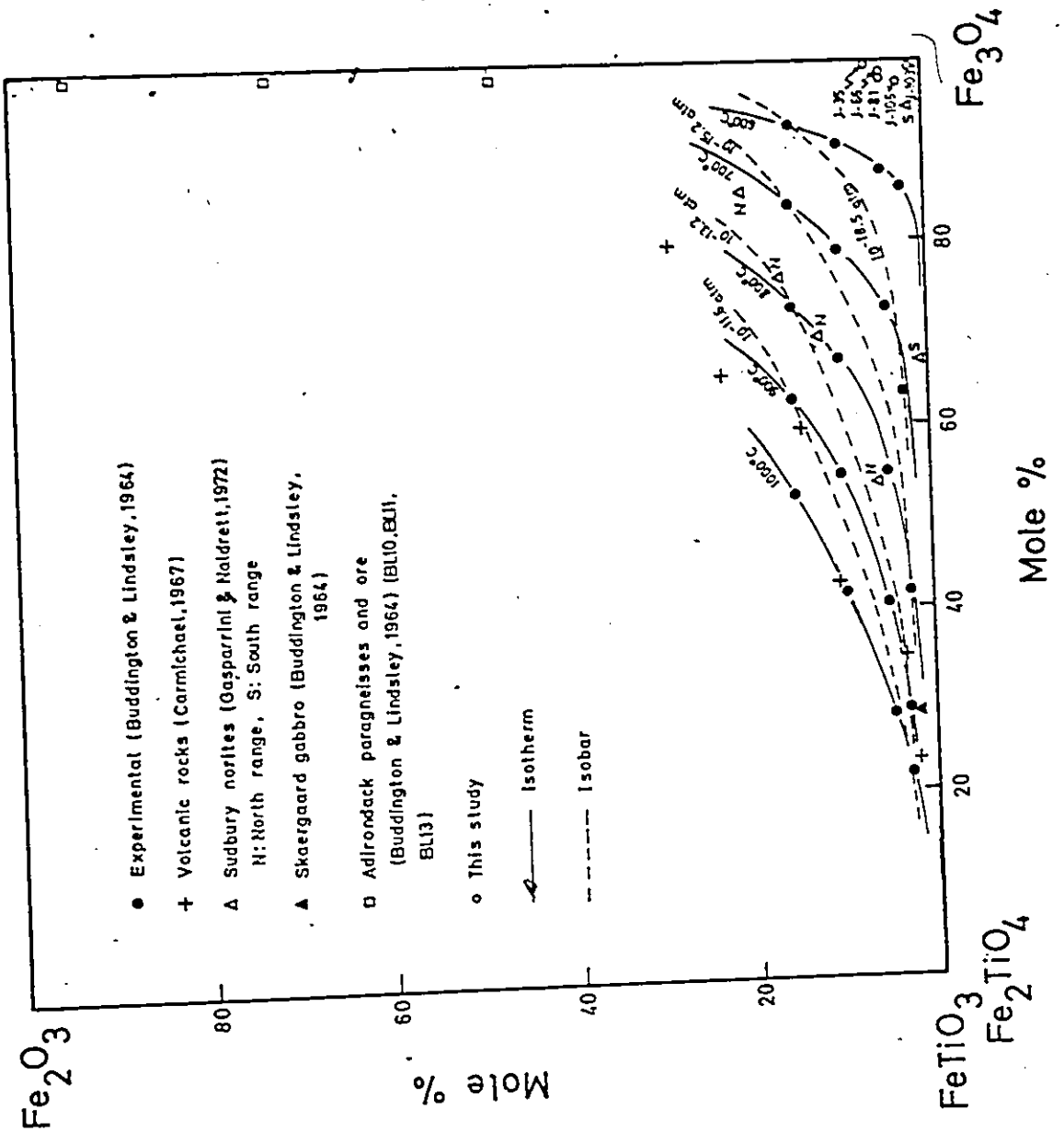


Figure 46. Composition of coexisting ilmenite solid solutions and magnetite solid solutions as determined experimentally by Buddington and Lindsley (1964, p316, 344) at varying temperature and fugacity of oxygen. P= 1 atm. Data from present study and other sources are included.


Experimental (Buddington & Lindsley, 1964)
Volcanic rocks (Carmichael, 1967)
Sudbury norites (Gasparrini & Haldrett, 1972) H: North range, S: South range
Skaergaard gabbro (Buddington & Lindsley, 1964)
Adirondack paragneisses and ore (Buddington & Lindsley, 1964) (BL10, BL11, BL13)
This study
Isotherm
Isobar
Fe2O3
Fe3O4
FeTiO3
Fe2TiO4
Mole %
Mole %
80
60
40
20
20
40
60
80

norites from the Sudbury Irruptive (Gasparrini and Naldrett, 1972) overlap those of the present study while both are crossed diagonally by tie lines of the Sudbury north range norites (Fig. 45). The north range norites were interpreted as being part of a thin periphery which was cooled relatively rapidly with the result that reaction between oxides stopped at a high temperature. The south range, being a deeper and thicker portion of the Irruptive, cooled more slowly, thus allowing the oxides to equilibrate to significantly lower temperatures (Gasparrini and Naldrett, 1972, p620). If so, the Adirondack charnockitic granulites must have been equilibrated or re-equilibrated under relatively slow cooling conditions, comparable to those of the south range norites.

Sample J-35 of the present study was collected from the same outcrop as No. 133 of Buddington and Lindsley (1964, p337; also Buddington, 1952) who obtained for their specimen a temperature of 650°±50°C, compared with <600°C for J-35. The difference may be attributed to analytical methods employed; probe analysis is more successful in avoiding small amounts of exsolved phase. According to Duchesne (1972) the temperatures determined for Adirondack rocks by Buddington and Lindsley are somewhat low and a temperature of about 700°C or slightly higher may be more realistic for the temperature of metamorphism.

PART 4

PHASE EQUILIBRIUM AND PETROGENESIS

Mineral Abbreviations Used in the Chemical Studies

Ab = albite
Alm = almandine
Amph = amphibole
An = anorthite
Anti-perth = anti-perthite
Bio = biotite
Cpx = clinopyroxene
Gar = garnet
Hb = hornblende
Ilm = ilmenite
K-feld = K-feldspar = K feld = K-f
Meso-perth = meso-perthite
Mt = magnetite
Olig = oligoclase
Opx = orthopyroxene
Or = orthoclase
Perth = perthite
Plag = plagioclase
Px = pyroxene
Qtz = quartz
2-feld = two-feldspar (plagioclase and K-feldspar)
2-px = two-pyroxene (ortho-and clino-pyroxene)

Compositions of Phases Used in Chemical Reactions

Ab = $NaAlSi_3O_8$
Alm = $(Fe, Mg)_3 Al_2Si_3O_{12}$ or $Ca (Fe, Mg)_5 Al_4Si_6O_{24}$
An = $CaAl_2Si_2O_8$
Bio = $K_2 (Fe, Mg)_{5\frac{1}{2}} Al_3Si_{5\frac{1}{2}}O_{20} (OH)_4$
Cpx = $Ca (Fe, Mg) Si_2O_6$
Hb = $NaCa_2 (Fe, Mg)_4 Al_3Si_6O_{22} (OH)_2$
Opx = $(Fe, Mg) SiO_3$
Or = $KAlSi_3O_8$
Plag = $NaAlSi_3O_8 + CaAl_2Si_2O_8$
Qtz = SiO_2

IX PHASE EQUILIBRIUM, METAMORPHIC GRADE, AND ORIGIN

Phase Equilibrium

The charnockitic granulites of the present study are characterized by the following silicate mineral assemblages:

1. Plag- Opx- Cpx- Amph- Bio- Gar- Qtz (J-35, J-66, J-80)
2. Plag- K feld- Opx- Cpx- Amph- Bio- Qtz (J-44, J-103, J-106)
3. Plag- K feld- Opx- Cpx- Amph- Bio- Gar- Qtz (J-105B)
4. Plag- K feld- Opx- Cpx- Bio- Gar- Qtz (J-81, J-63A)
5. Plag- K feld- Cpx- Amph- Gar- Bio- Qtz (J-50)
6. Plag- Cpx- Amph- Bio- Gar- Qtz (J-99).

In addition most rocks contain magnetite, ilmenite, and apatite. All are typical granulite facies rocks. In terms of major mafic silicate minerals, four distinct assemblages exist, namely:

7. Opx- Cpx- Amph- Alm- Bio (J-35, J-66, J-80, J-105B)
8. Opx- Cpx- Alm- Bio (J-81, J-63A)
9. Opx- Cpx- Amph- Bio (J-44, J-103, J-106)
10. Cpx- Amph- Alm- Bio (J-50, J-99).

It is possible to represent all assemblages except 1 and 6 (which do not contain K-feldspar) on an AFM diagram using the following definitions of components (Reinhardt, 1968):

$$A = Al_2O_3 - (CaO + Na_2O + K_2O)$$

$$F = FeO - (Fe_2O_3 + TiO_2)$$

$$M = MgO$$

This diagram could be regarded as a phase diagram for rocks that contain quartz, K-feldspar, plagioclase (of fixed composition), magnetite and ilmenite, and for constant values of P, T, and P_{H_2O}. In order to plot the composition of clinopyroxene, it is convenient to employ an orthogonal projection (Thompson, 1957) with the following axes

Vertical axis $\frac{A}{F+M}$

Horizontal axis $\frac{M}{F+M}$

The compositions of coexisting ferromagnesian silicate phases from the mineral assemblages studied are shown in Figs. 47 to 50. Assemblages in Figs. 47 to 49 represent univariant equilibrium at constant pressure and assemblages in Fig. 50 represent invariant equilibrium at constant pressure. The reason for plotting assemblages that do not apparently contain K-feldspar is because of the existence of trace to minor amounts of anti-perthitic feldspar in them. A systematic shift in phase fields indicate that rocks with the same mineral assemblages represent different equilibrium conditions. Moreover, the fact that all rocks contain 4 or 5 ferromagnesian minerals (including biotite) would, by the above analysis, indicate either non-equilibrium, or variation in metamorphic conditions.

Figure 47. Orthogonal AFM plot showing the phase relations among coexisting clinopyroxene, almandine ganet, and amphibole in the analysed charnockitic granulites along with the bulk rock compositions.

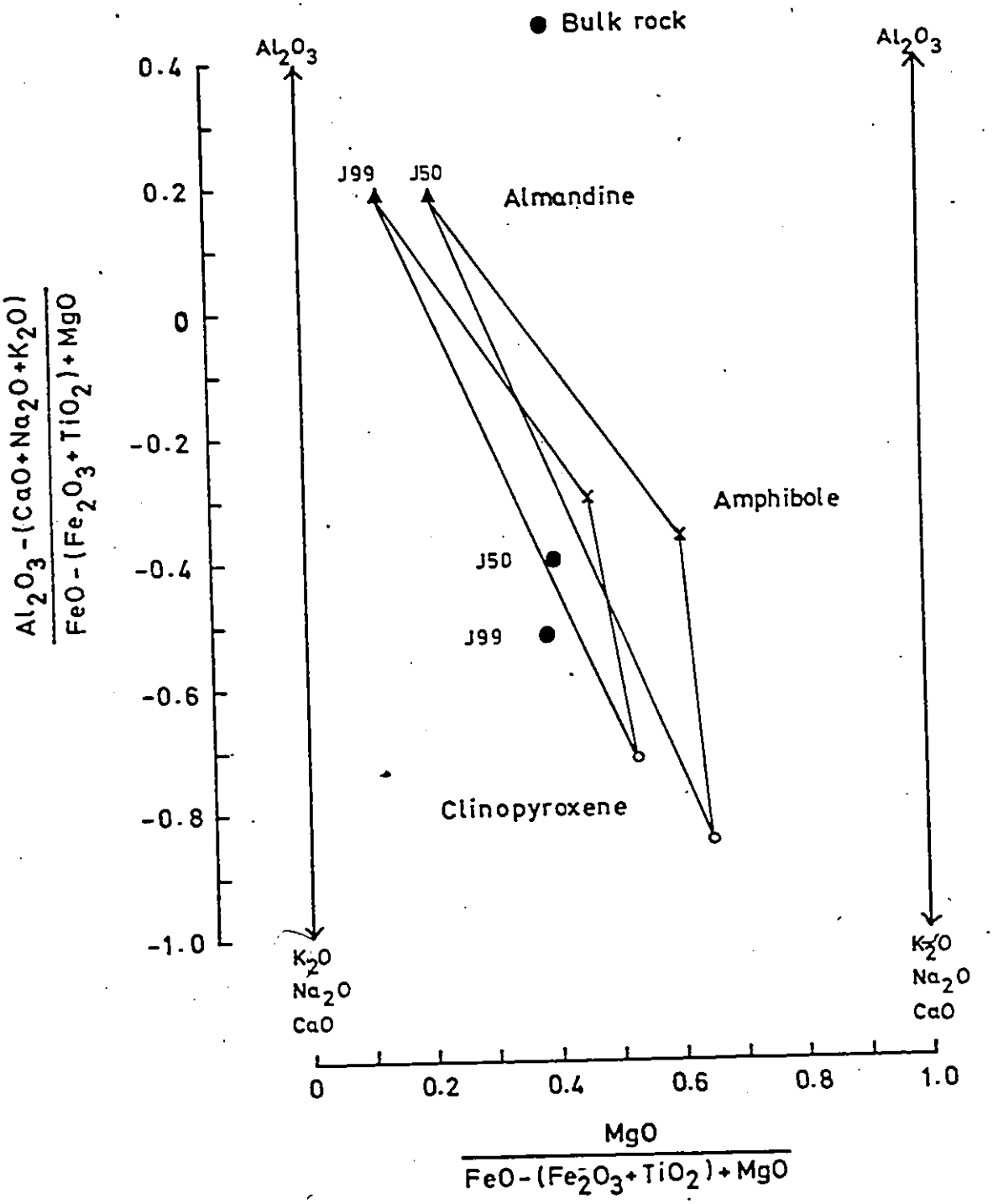

● Bulk rock
Al_2O_3
Al_2O_3
J99
J50
Almandine
Amphibole
J50
J99
Clinopyroxene
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
$\frac{Al_2O_3-(CaO+Na_2O+K_2O)}{FeO-(Fe_2O_3+TiO_2)+MgO}$
K_2O
Na_2O
CaO
K_2O
Na_2O
CaO
0
0.2
0.4
0.6
0.8
1.0
$\frac{MgO}{FeO-(Fe_2O_3+TiO_2)+MgO}$

Figure 48. Orthogonal AFM plot showing the phase relations among coexisting orthopyroxene, clinopyroxene, and amphibole in the analysed charnockitic granulites along with the bulk rock compositions.

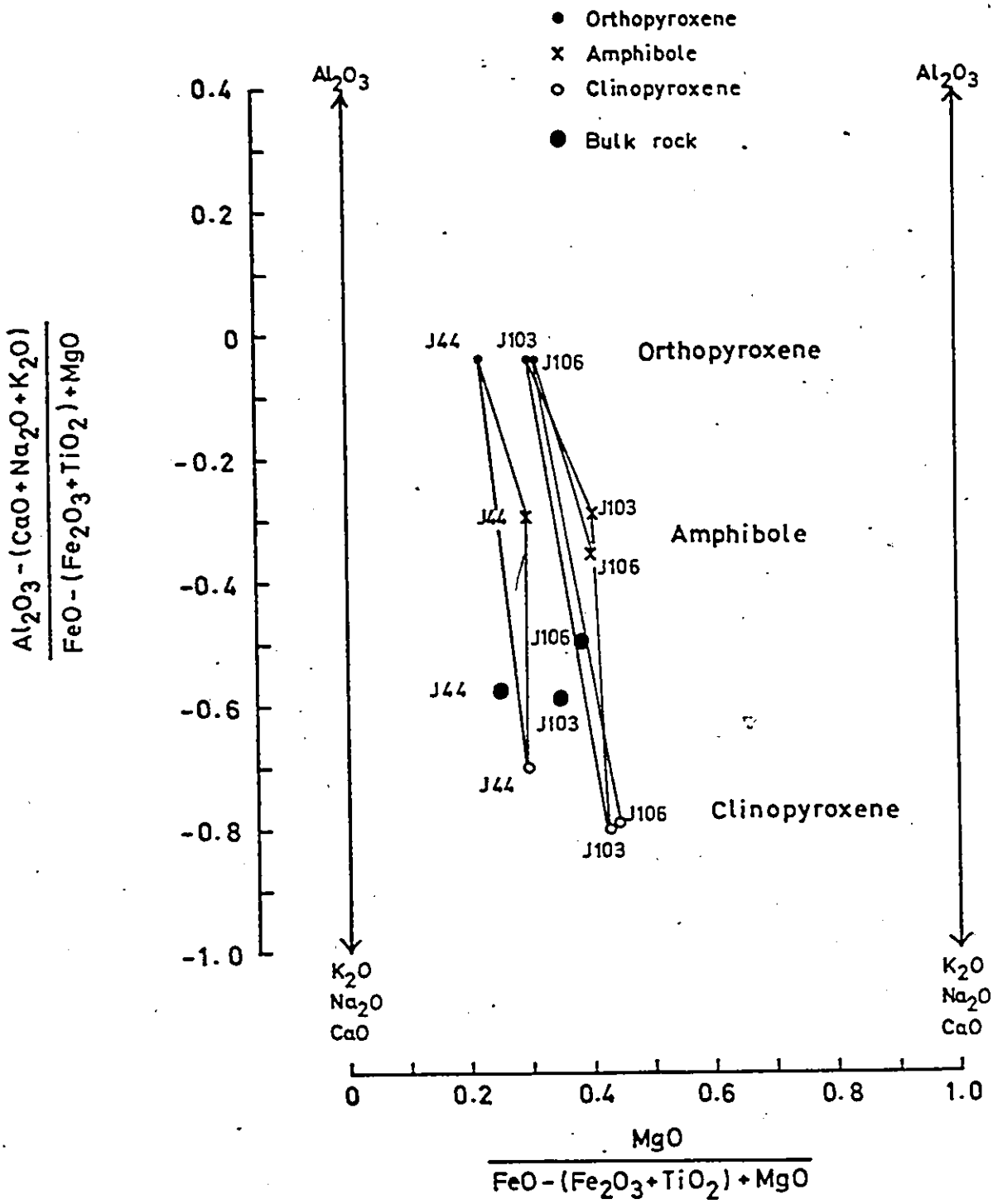

Orthopyroxene
Amphibole
Clinopyroxene
Bulk rock
Al_2O_3
K_2O
Na_2O
CaO
J44
J103
J106
Orthopyroxene
Amphibole
Clinopyroxene
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
$\frac{Al_2O_3-(CaO+Na_2O+K_2O)}{FeO-(Fe_2O_3+TiO_2)+MgO}$
0
0.2
0.4
0.6
0.8
1.0
$\frac{MgO}{FeO-(Fe_2O_3+TiO_2)+MgO}$

Figure 49. Orthogonal AFM plot showing the phase relations among coexisting orthopyroxene, clinopyroxene, and almandine garnet in the analysed charnockitic granulites along with the bulk rock compositions.

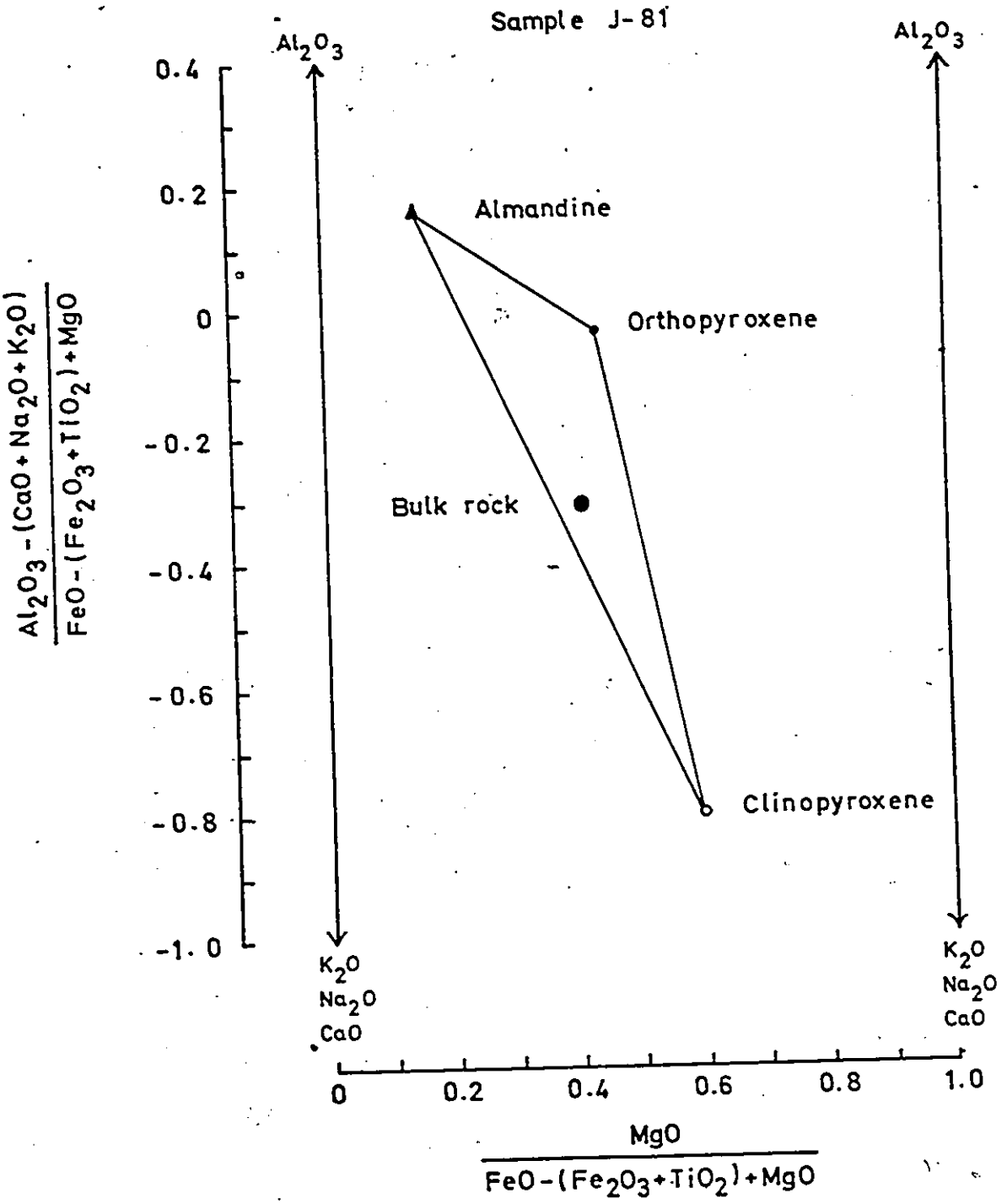
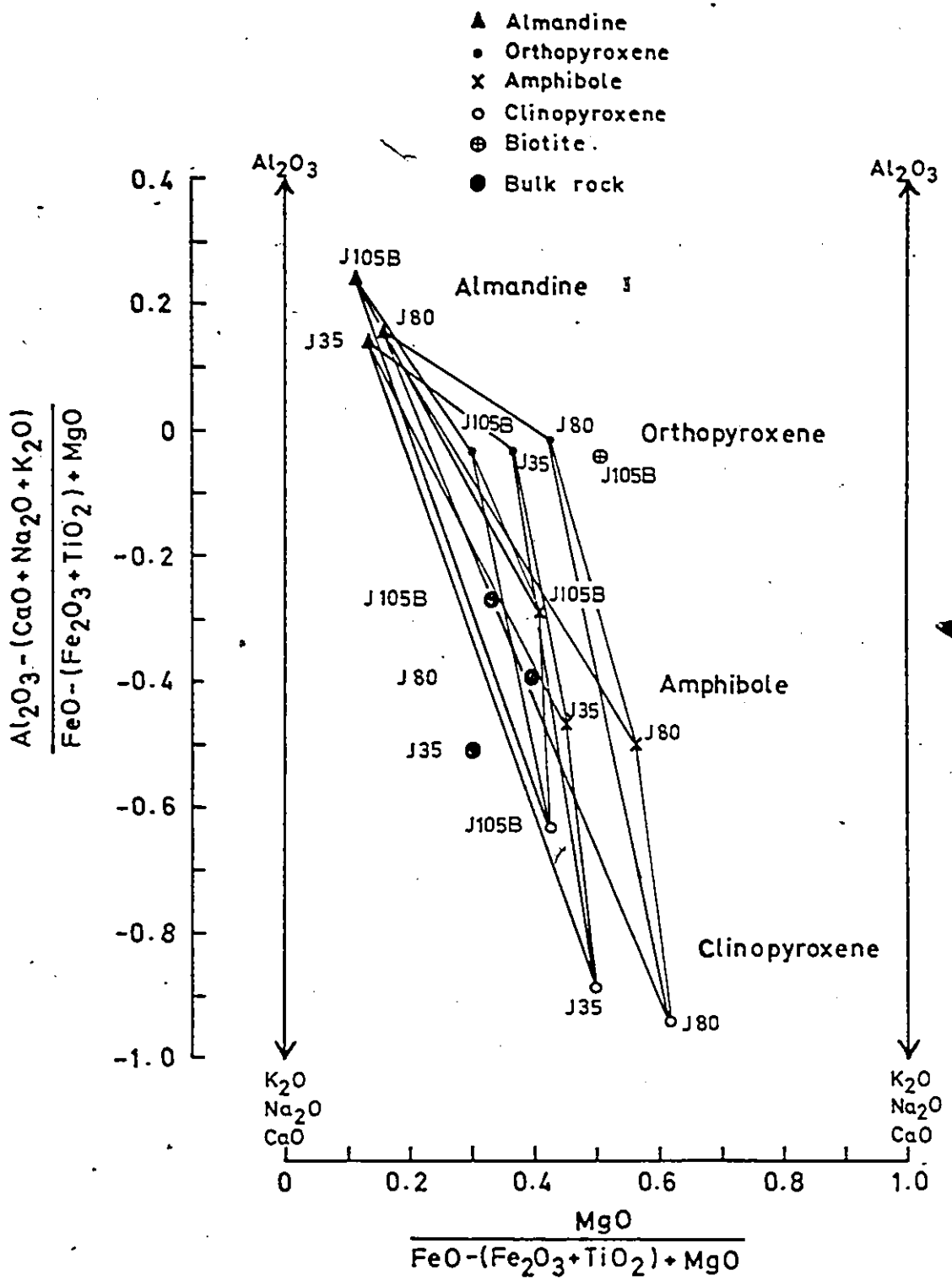

Sample J-81
Al_2O_3
Al_2O_3
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
Almandine
Orthopyroxene
Bulk rock
Clinopyroxene
K_2O
Na_2O
CaO
K_2O
Na_2O
CaO
0
0.2
0.4
0.6
0.8
1.0
$\frac{Al_2O_3-(CaO+Na_2O+K_2O)}{FeO-(Fe_2O_3+TiO_2)+MgO}$
$\frac{MgO}{FeO-(Fe_2O_3+TiO_2)+MgO}$

Figure 50. Orthogonal AFM plot showing the phase relations among coexisting orthopyroxene, clinopyroxene, almandine, and amphibole in the analysed charnockitic granulites along with the bulk rock compositions. A fifth phase, biotite, is also shown (rock J-105B). All iron in this mineral is assumed to be ferrous iron. Except for J-105B, these rocks do not contain K-feldspar.


Almandine
Orthopyroxene
Amphibole
Clinopyroxene
Biotite.
Bulk rock
Al_2O_3
Al_2O_3
K_2O
Na_2O
CaO
K_2O
Na_2O
CaO
J105B
J80
J35
Almandine
Orthopyroxene
Amphibole
Clinopyroxene
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
0
0.2
0.4
0.6
0.8
1.0
$\frac{Al_2O_3-(CaO+Na_2O+K_2O)}{FeO-(Fe_2O_3+TiO_2)+MgO}$
$\frac{MgO}{FeO-(Fe_2O_3+TiO_2)+MgO}$

From studies on the partitioning of Mg and Fe^{2+} among coexisting two-pyroxenes, amphibole and garnet, no evidence was found for gross non-equilibrium, nor for a variation in temperature among the study samples. As all of these rocks are closely associated, i.e. they all come from the same field area, large difference in load pressure may also be ruled out. Therefore, a variation in P_{H_2O} may be the principal cause for the observed shift in the phase fields; such change would be accompanied by a change in fO_2.

A variation in the composition of plagioclase, perthitic feldspar may be responsible to some extent for the fact that bulk-rock compositions plot outside the corresponding phase fields, although the exclusion of some minor components such as P_2O_5 and MnO as well as minor analytical errors may also be contributing factors.

The question of phase equilibrium may also be examined in relation to mineral reactions. The stable coexistence of five ferromagnesian minerals of known composition (J-105B), as shown in Fig. 50, in the presence of quartz, K-feldspar, plagioclase, magnetite and ilmenite, makes it possible to write five mass-balance equations (see Appendix VI), which in simplified form are as follows:

$$\text{Bio} + \text{Amph} + \text{Alm} = \text{Opx} \quad (36)$$

$$\text{Amph} + \text{Alm} = \text{Opx} + \text{Cpx} \quad (37)$$

$$\text{Amph} = \text{Bio} + \text{Opx} + \text{Cpz} \quad (38)$$

$$\text{Amph} = \text{Bio} + \text{Cpx} + \text{Alm} \quad (39)$$

$$\text{Bio} + \text{Cpx} + \text{Alm} = \text{Opx} \quad (40)$$

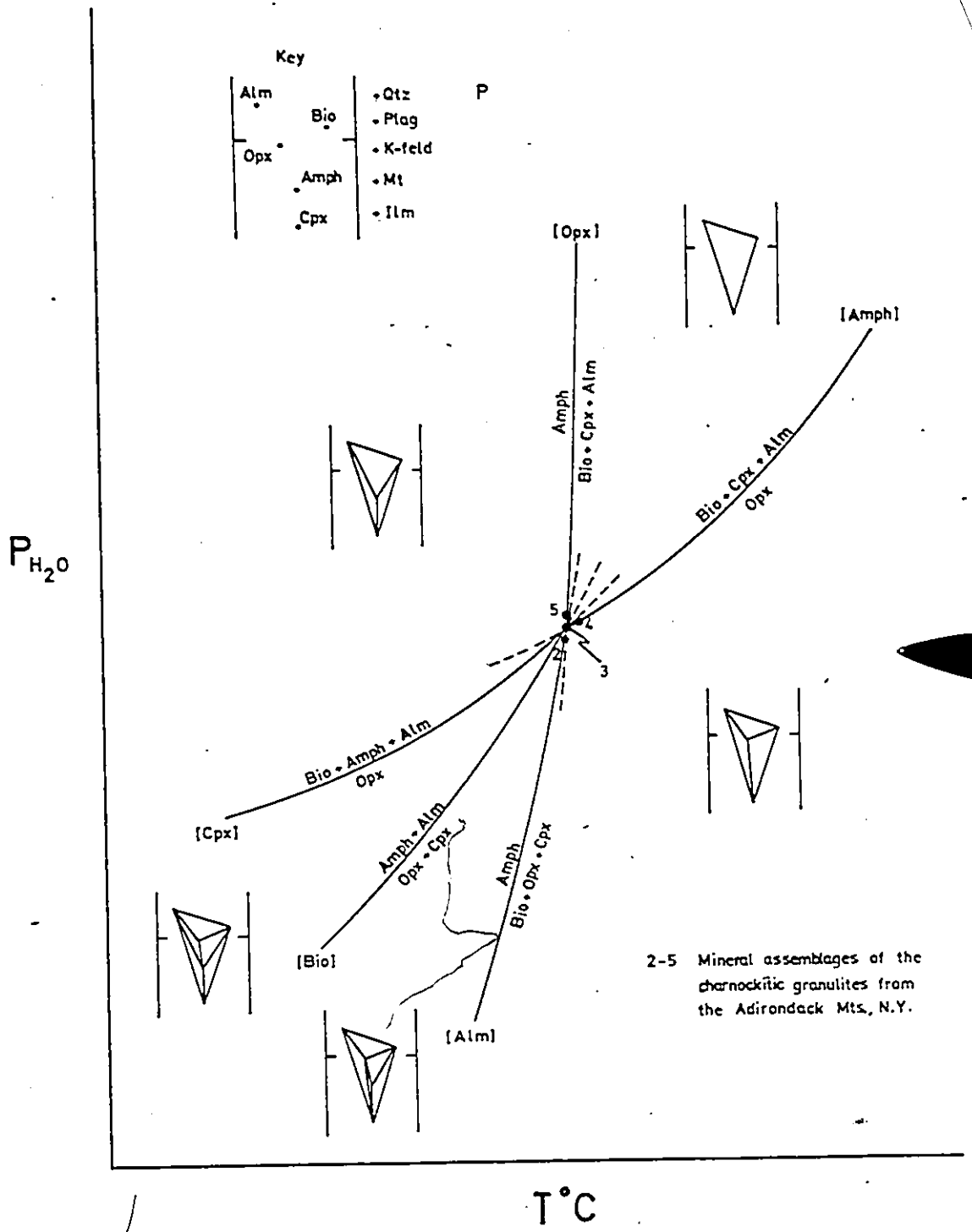
At constant pressure, the five reactions plot as univariant curves on a P_{H_2O}-T diagram and meet at an invariant point. These relations are shown schematically in Fig. 51. Assemblages 2, 4, and 5 correspond to three of these relations while assemblage 3 corresponds to the invariant point.

This analysis also suggests that some variation existed in the study area with regard to P_{H_2O} and T, probably mainly P_{H_2O}, to account for the observed differences in mineral assemblage and mineral composition.

Metamorphic Grade

The boundary between the almandine amphibolite facies and the hornblende granulite facies has been defined by the appearance of orthopyroxene and the boundary between the hornblende granulite facies and the pyroxene granulite facies by the disappearance of biotite and hornblende.

Figure 51. Schematic Schreinemakers bundle (Zen, 1966) in a P_{H_2O}-T field showing univariant reaction curves for reactions 36 to 40. The supposed relative position of mineral assemblages 2, 3, 4, and 5 are indicated.



2-5 Mineral assemblages of the charnockitic granulites from the Adirondack Mts, N.Y.

Therefore, de Waard (1965) suggested a set of bivariant equilibria (at constant P), characterized by the coexistence of orthopyroxene with biotite and/or hornblende, as representative of the hornblende granulite facies. The reactions are:

$$2Bio + 12\ Qtz = 8\ Opx + Alm + 4Or + 4H_2O \quad (41)$$

$$Hb + 4\ Qtz = 3\ Opx + Cpx + Ab + An + H_2O \quad (42)$$

$$Hb + 2Bio + 17\ Qtz = 15\ Opx + 4Or + Ab + 2An + 5H_2O \quad (43)$$

$$Hb + Alm + 5\ Qtz = 7\ Opx + Ab + 2An + H_2O \quad (44)$$

These reactions are represented by three-(ferromagnesian) phase assemblages as compared to the 4- and 5-phase assemblages of the rocks studied. For comparison, the four-phase assemblages of the studied rocks are plotted in Figs. 47, 48 and 49 as three-phase triangles. Although the studied rocks commonly contain four ferromagnesian minerals they satisfy the equilibria suggested by de Waard. Thus the rocks clearly belong to the hornblende granulite facies. The small amount of biotite and amphibole present suggests that the conditions were near the boundary between the hornblende granulite and pyroxene granulite facies. Rocks J-50 and J-99, do not contain orthopyroxene, but because they are associated with the others, they are assigned to the same facies.

From Fig. 51, one other important reaction applicable to the studied rocks is reaction (37) in which two pyroxenes may coexist with amphibole and almandine at univariant equilibrium.

The invariant point in Fig. 51 is represented by the coexisting five mafic silicates biotite, amphibole, orthopyroxine, clinopyroxene and almandine in rock J-105B. From the prograde metamorphism exhibited from the almandine amphibolite facies in the Northwestern Adirondack Lowland to the granulite facies in the Central and Eastern Adirondack Highland, the most likely reaction which lead to this invariant point in Fig. 51 is proposed to be a combination of reactions (41) and (42):

$$2\text{Bio} + \text{Hb} + 16\ \text{Qtz} = 11\ \text{Opx} + \text{Cpx} + \text{Alm} + 4\text{Or} + \text{Ab} + \text{An} + 5\text{H}_2\text{O} \qquad (45)$$

Position of the studied charnockitic granulites in the metamorphic zones of the Adirondacks

Five zones of metamorphism ranging between 500°C and 665°C (Engel and Engel, 1960; Buddington, 1963; Buddington and Lindsley, 1964) were recognized in the Adirondacks by Buddington (1966, p331); the mineral assemblages of these rocks were summarized by de Waard (1965, Table 1). The charnockitic, quartz-syenitic, and quartz-bearing syenitic gneisses (Zone E) were formed at the highest temperature level. The temperatures of 635°C to

665°C for the granulites of Zone E, as estimated by Buddington were considered by de Waard (1967, p228-23) to be too low. The present charnockitic granulites belong to this highest zone.

Based on the presence or absence of almandine garnet in charnockitic, metabasic and quartzofeldspathic rocks, Buddington (1963, 1965) delineated three garnet isograds in the Adirondacks which were inferred to represent a general increase in grade of regional metamorphism from the northwest to the southeast and east. This was corroborated by magnetite-ilmenite geothermometry (Buddington and Lindsley, 1964).

The first garnet isograd occurs in the Adirondack lowland in the almandine amphibolite facies terrane, whereas the second and third garnet isograds occur within the region of granulite facies rocks in the Adirondack highlands. The development of garnet in the Adirondacks was considered by Buddington (1965, 1966) to be the result of increasing temperature and pressure, but de Waard (1965a, 1967) thought that the compositional control was more important. de Waard's idea was recently supported by Martignole and Schrijver (1973).

Rejecting Buddington's vaguely defined second garnet isograd in the granulite terrane, de Waard (1964, p308; 1967, p221) proposed an orthopyroxene isograd, to separate the almandine amphibolite facies of the lowland from the hornblende granulite facies in the highland. He

also defined a garnet-clinopyroxene isograd to separate the hornblende granulite facies of the highland into a hornblende-orthopyroxene-plagioclase subfacies to the west, and a hornblende-clinopyroxene-almandine subfacies to the east. The garnet-clinopyroxene isograd, which runs almost north-south, divides the Adirondack highlands into approximately two halves. Although, in the Adirondacks, there is no sizeable regional development of the pyroxene granulite facies, in which hydrous minerals are virtually absent (de Waard, 1967, p210), the pyroxene granulite facies rocks do occur in small amounts throughout the central and eastern Adirondack highlands (de Waard, 1964, p354; Buddington and Lindsley, 1964, p337). The present granulites represent the highest temperature part of the hornblende granulite facies, as noted above. They all occur in the hornblende-clinopyroxene-almandine subfacies terrane of de Waard. The coexistence of the garnet-free and garnetiferous assemblages suggests that the subdivision of the hornblende granulite facies into the hornblende-orthopyroxene-plagioclase and hornblende-clinopyroxene-almandine subfacies in the Adirondacks by de Waard is a rather crude generalization. On the other hand, since all the present rocks represent the narrow 'zone' between hornblende granulite and pyroxene granulite facies, the temperature of formation of these rocks must have been fairly constant. Thus the development of garnet in these rocks must have been controlled

by bulk composition. Based on the breakdown reaction of hornblende (Yoder and Tilley, 1962; Binns, 1964), biotite (Eugster and Wones, 1962) and garnet (Ringwood and Green, 1964; Green and Lambert, 1965), de Waard (1967, p229-230) estimated that the temperature of metamorphism was at least 700°C at the hypersthene isograd and at least 760°C at the garnet-clinopyroxene isograd. He suggested that most of the Adirondack highlands had metamorphic temperatures of at least 800°C and a load pressure as high as 10 Kbs, or a depth of about 35 km. de Waard also pointed out (1967, p228) that the temperature range from 550°C (±50°C) near the hypersthene isograd to 650°C (±50°C) in the Central Adirondacks, as estimated by Buddington and Lindsley (1964) represents a late stage of metamorphism in which the oxide minerals have re-equilibrated upon cooling. Engel and Engel (1962, p37 and 74) estimated the temperature of metamorphism for rocks of the amphibolite facies to be 525°C, and, moving towards the hypersthene isograd of de Waard, their temperature estimates increased to 625°C. Extrapolating upward or eastward into the hornblende granulite and pyroxene granulite boundary of the Central Adirondack highlands, the temperature of metamorphism may well have been around 700°C.

From the distribution of amphibolites in the Northwestern Adirondack lowland, hornblende granulites in the Northwestern and Western to Central highland, to hornblende granulites and pyroxene granulites in the Central to

Eastern highland in the Adirondacks, the grade of metamorphism clearly increases from west to east and reaches its maximum at about the east central main anorthosite massif. The reappearance of hornblende granulites east of Elizabethtown and amphibolites in the eastern margin of the highland near Wilsboro (near Lake Champlain, outside east edge of Fig. 2) indicates a zonal or symmetrical distribution of metamorphic grade across the Adirondacks. Experimental data (Green and Lambert, 1965, p5259) have shown that the mafic assemblage Gar- Cpx forms at a higher pressure than the assemblage Opx- Cpx and Gar- Cpx- Opx. The appearance of the assemblage Opx- Cpx- Alm (present study) and Cpx- Alm (de Waard, 1965a, p189; 1967, p227-228; and present study) in the Eastern and Southeastern Central Adirondacks suggests that not only temperature of metamorphism but also P_{total} have reached their maximum.

Temperature, pressure and partial pressure of water during metamorphism

Although several experimental studies have been carried out to delineate fields of stability for minerals that occur in the rocks of the present study, most of the data available refer to pure end members, and as yet, only broad limits may be placed on the temperature and pressure of metamorphism, based on these experiments.

Since epidote was not found in any of the studied rocks, a lower limit to the temperature of metamorphism may be set approximately by the upper limit of the stability field for this mineral as defined by the reaction:

Epidote = grossularite + anorthite + magnetite + H_2O

which was determined by Liou (1973) and is shown in Fig. 52, curve 5. The limit is an approximate one because the products of the reaction occur in the studied rocks as components of solid solutions, not as pure minerals.

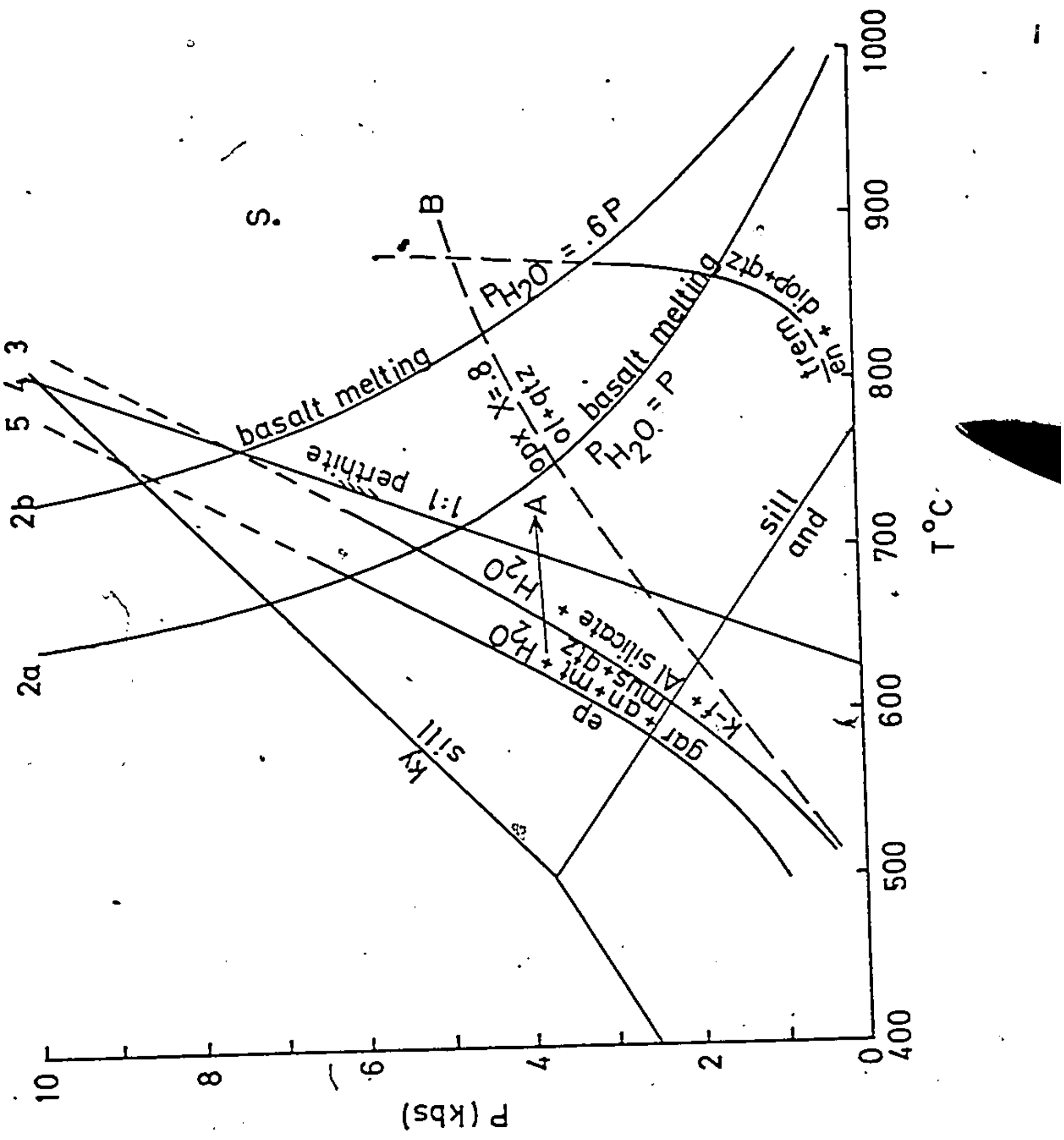
Alternatively, a lower temperature limit may be set by the upper stability field for muscovite and quartz:

Muscovite + Quartz = Sillimanite + K-feldspar + H_2O

determined by Evans (1965) and shown as curve 3 in Fig. 52. Muscovite is generally absent from the rocks of the Adirondack highland while sillimanite + K-feldspar are common (Buddington, 1963; de Waard, 1965a) and the rocks of the present study almost certainly recrystallized within the stability field of sillimanite + K-feldspar.

Since 1:1 perthites are common in the present rocks the temperature corresponding to the top of alkali feldspar solvus would provide another lower limit to temperature. One estimate of this temperature, as obtained by Luth et al. (1974), is shown in Fig. 52. Accordingly, if the pressure was 4 Kbs, the temperature of metamorphism must have exceeded about 700°C.

Figure 52. P-T field of the charnockitic granulites studied in terms of breakdown and chemical reactions of phases. Curve 1 from Boyd (1954); curves 2a and 2b from Holloway and Burnham (1972); curve 3 from Evans (1965); curve 4 from Luth et al. (1974); curve 5 from Liou (1973);arrow A, a P-T gradient of amphibolite-granulite facies rocks of northwestern Adirondacks, from Engel and Engel (1962); curve B from Olsen and Mueller (1966) and Smith (1970); point S shows the stable coexistence of an iron-rich orthopyroxene with Fe/Fe + Mg = 0.8, olivine and quartz at 900°C above 7 kbs (Smith, 1970). Shaded area is the proposed P-T field of metamorphism for the study rocks. Abbreviations: an= anorthite, and= andalusite, diop= diopside, en= enstatite, ep= epidote, gar= garnet, ky= kyanite, k-f= K-feldspar, mt= magnetite, mus= muscovite, ol= olivine, opx= orthopyroxene, qtz= quartz, sill= sillimanite, trem= tremolite.


P (kbs)
10
8
6
4
2
0
400
500
600
700
800
900
1000
T °C
2a
2b
5
4
3
ky
sill
sill
and
ep
gar+an+mt + H2O
K-f + Al silicate + H2O
mus+qtz
1:1 perthite
basalt melting
basalt melting
PH2O = .6P
PH2O = P
opx / ol+qtz X=.8
A
B
S
trem / en + diop+qtz

The temperature of intracrystalline equilibrium in orthopyroxene, determined as 700°±25°C (Chapter VI), provides another estimate of the lower limit of the temperature of metamorphism.

An upper limit to temperature may possibly be taken as the breakdown of amphibole to produce orthopyroxene. For the pure Mg end member, this temperature is high, being about 850°C for a $P_{H_2O} = P_{total}$ of 1 Kbs (Boyd, 1954). The presence of Fe in the amphibole would lower this temperature very considerably. The breakdown of phlogopite to produce orthopyroxene also occurs at a high temperature, about 1,100°C for a pressure of 3 Kbs, as determined by Yoder and Eugster (1954) and although various breakdown temperatures for Fe-Mg biotite have been determined by Eugster and Wones (1962) and Wones and Eugster (1965), these are very much dependent on the activity of oxygen. Consequently this reaction, as it occurs in nature is still imperfectly understood, and the field in which this probably takes place is large. According to Turner (1968, Fig. 4-4) the breakdown of biotite in nature, at a pressure of about 5 Kbs may take place within a temperature range of from nearly 500 to 900°C.

In an experiment on a natural rock similar to those of the present study, Binns (1964) showed that the amphibole to orthopyroxene reaction occurred at about 850°C at P_{H_2O} of 1 Kbs. He suggested a temperature of

about 800°C for the reaction in the granulite facies rock that he examined.

Finally, by comparing the K_D value of 0.57 for coexisting orthopyroxene and clinopyroxene of the present study with that of 0.69 obtained by Lindsley et al. (1974) for coexisting augite and hypersthene at 810°C, the temperature of metamorphism of the studied granulites could not have exceeded 800°C.

A lower limit to pressure may be set by the reaction

Quartz + Fe-olivine = Fe-orthopyroxene

which is displaced to the right with increasing pressure. Smith (1970) has shown experimentally that an iron-rich orthopyroxene, with Fe/Fe + Mg = 0.8, which is the most iron-rich orthopyroxene of the present study is stable relative to olivine and quartz about 7 Kbs pressure, at a temperature of 900°C (point S, Fig. 52). Using the theoretical analysis of Olsen and Mueller (1966), Curve B (Fig. 52) places an approximate lower limit to pressure of metamorphism of the terrane from which the study samples were obtained.

An upper limit to pressure might best be obtained from reasonable estimate of depth of burial, which probably would not exceed 20 km, corresponding to a pressure of 6 Kbs.

Thus the range of temperature of metamorphism is postulated to be between 700° to about 800°C, and the pressure between about 3 and 6 Kbs. The estimates of Engel and Engel (1958, 1962) for the Adirondack region west of the study area, where the highest grade attained was slightly lower, is shown as arrow A in Fig. 52, and the upper part of this arrow falls close within the limits set by the present estimates.

The question of P_{H_2O} relative to P may be examined briefly. The rocks of the present study are similar in composition to that of an alkali basalt (Cf. Yoder and Tilley, 1962) for which the minimum melting curve was determined by Holloway and Burnham (1972) and appears as Curves 2a and 2b in Fig. 52. The curve shifts to right as P_{H_2O} decreases relative to confining pressure, P. Some of the rocks of the present study contain minor feldspar-quartz and garnet-quartz intergrowths, taken as evidence of incipient melting, and hence the P-T point of metamorphism is considered to lie on or slightly to the right of this curve. Since Curve 2a cuts through the field in which the P-T point is estimated to lie, it is possible that P_{H_2O} was somewhat less than P.

A very close estimate of T-P of metamorphism of the studied rocks is difficult as appropriate experimental determinations are lacking. However, on the basis of certain assumptions, estimates may be made, as follows.

Assuming feldspar-quartz and garnet-quartz intergrowths indicate incipient melting and that the presence of mesoperthite in addition to other perthitic and/or antiperthitic feldspars suggests further homogenization of the feldspar solid solutions as a result of high T-P recrystallization, the T-P of metamorphism of the studied rocks would then be controlled by the intersection of the alkali feldspar 'solvus' curve (4) and the basalt melting curve(s) in Fig. 52. In other words, the temperature must have been above the solvus but near or slightly above the basalt melting curve(s) at different P_{H_2O} conditions. Therefore,

(1) at $P_{H_2O} = P$, the T-P of metamorphism of the studied rocks would be, allowing for experimental uncertainty, $T = 715° \pm 25°C$, $P_{H_2O} = P = 4.8$ Kbs.

(2) at $P_{H_2O} = 0.8P$, $T = 735° \pm 25°C$, $P = 6$ Kbs, $P_{H_2O} = 4.8$ Kbs.

(3) at $P_{H_2O} = 0.6P$, $T = 765° \pm 25°C$, $P = 7.4$ Kbs, $P_{H_2O} = 4.4$ Kbs.

As discussed earlier, P_{H_2O} was likely less than P; while P was unlikely to exceed 6 Kbs, corresponding to a depth of 20 km. Thus an intermediate condition between cases (1) and (3), i.e. conditions similar to case (2) would seem most likely for the present charnockitic granulites.

Origin

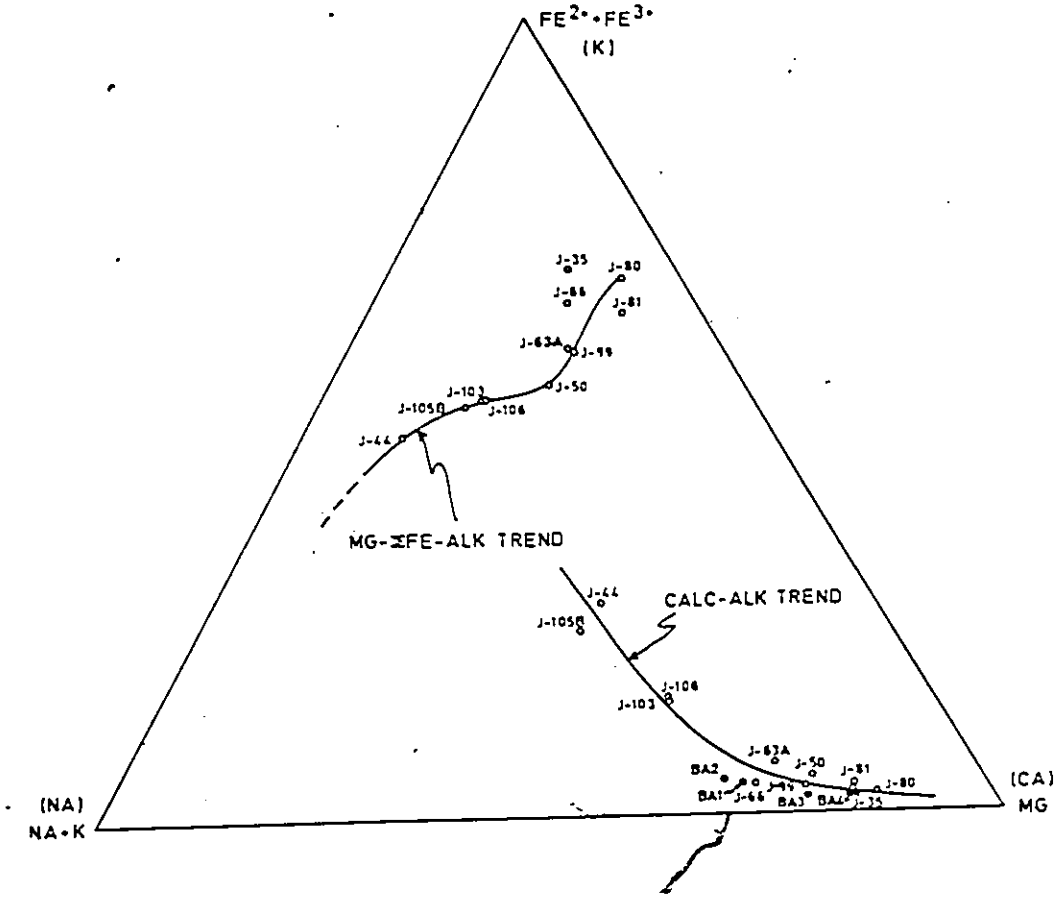
Charnockites and related granulites have been found and studied in many parts of the world, for example in Sweden (Quensel, 1951; Saxena, 1968), Finland (Eskola, 1952; Parras, 1958), Australia (Wilson, 1952, 1954, 1959, 1960a, b; Binns, 1965a, b), British Guiana (Singh, 1966), Uganda (Groves, 1935), India (Holland, 1893, 1900; Howie, 1955; Pichamuthu, 1953; Howie and Subramaniam, 1957; Subramaniam, 1959, 1962; Leelanandam, 1967), Ceylon (Corray, 1962), Canadian Shield (Roach and Duffell, 1968) and the Adirondacks of the United States (Buddington, 1939, 1950, 1952, 1963, 1966, 1969; de Waard, 1964, 1965a, b, 1967, 1969). From these studies it is evident that charnockitic rocks are generally Precambrian in age and occur in the Shield areas. Although some might have been sedimentary rocks prior to metamorphism, a meta-igneous origin is favoured in general.

The charnockitic granulites of the present study are believed to be igneous in origin, and were subsequently metamorphosed to the granulite facies. They occur as dykes and patches of irregularly shaped bodies of gabbroic and syenitic composition in the anorthosite massifs (Buddington, 1939; 1952, 1963, 1965, 1966, 1969, personal communication, 1970; de Waard, 1964, 1965).

On the variation diagram (Fig. 53), the charnockitic granulites of the present study show a continuous Mg- Fe- Alkali trend and a distinct calc- alkali trend similar to the Madras charnockite series (Howie, 1955, Figs. 1 and 2) and that of the South Savana charnockites (Singh, 1966, p188-90). These smooth curves suggest that the suite of charnockitic granulites was a series of calc-alkali magmatic differentiates rather than a group of sedimentary rocks. Some anorthosite, anorthositic gabbro and gabbroic anorthosite from the Adirondack massifs were also plotted; the analyses were reported by Buddington, (1939, p30, 36 and 235). Assuming that little or no metasomatism took place during metamorphism, some of the rocks studied (e.g. J-35, J-80 and J-81) may represent some of the earliest differentiates separated from the anorthositic or gabbroic anorthosite magma (Bowen, 1927, p89; Bailey, 1928, p173; Buddington, 1939, p235, 1969, p215, 224-230; Yoder, 1955b, p1638-1639, 1969, p13-22; Yoder, Stewart and Smith, 1957, p206-214; Turner and Verhoogen, 1960, p324-328).

From oxygen isotope studies of Adirondack igneous and metamorphic rocks, Taylor (1969, p111, 119-120) concluded that most meta-igneous rock types of the area are enriched in O^{18} relative to their unmetamorphosed counterparts in other localities, so a large fraction of the present Adirondack terrane cannot have been a closed

Figure 53. Variation diagram showing a Mg- Fe-Alk trend and a calc-alkali trend in the charnockitic granulites from the Adirondack Mts., N.Y. Atoms or ions in atomic %. BA1 to BA4 from Buddington (1939): BA1= gabbroic anorthosite, Adirondack massif (p235, d); BA2= average of 4 analyses of anorthosite from core of Adirondack massif (p30, A); BA3= anorthositic gabbro from sheet in Adirondack massif (p36, no. 25); BA4= pyroxene gabbro facies of coarse anorthositic gabbro, Adirondack massif (p36, no. 27).


FE2+FE3+
(K)
J-35
J-80
J-86
J-81
J-63A
J-99
J-101
J-50
J-105B
J-106
J-44
MG-ΣFE-ALK TREND
J-44
CALC-ALK TREND
J-105B
J-106
J-103
J-63A
J-50
J-81
BA2
J-80
BA1
J-66
J-99
BA3
BA4
J-35
(NA)
NA+K
(CA)
MG

system during metamorphism. He found only a few relatively unfoliated metagabbros and some granitic plutons have 'normal' O^{18}/O^{16} ratios (for 'normal' basalts and gabbros δ = 6.5 to 6.6). A δ value of 9.2 was obtained for a pyroxene-garnet-oligoclase granulite metagabbro collected near the present samples J-35, J-63A and J-66 and was attributed to reconstitution during metamorphism (Taylor, 1969, p119). In the Adirondacks, the most sodic plagioclase of the unmetamorphosed anorthosite series is An_{40}, and the most calcic plagioclase in the quartz-syenitic series is An_{30} (Buddington, 1969, p221). The above mentioned metagabbroic rocks have clearly undergone reconstitution during metamorphism since garnet also appears (Buddington, 1939, 1952, 1963, 1967). As a result, all rocks of the present study (except J-50) have plagioclase more sodic than An_{35}. Some of the calcium may have been used up to make garnet and calcic pyroxene. These amounts of Ca must be taken from the plagioclase. In addition, some alkalies may have been introduced to produce albite and alkalic feldspars. This is supported by the presence of slightly zoned plagioclase crystals in some rocks (e.g. J-35) with a rim less calcic than the core by an amount of about An_4 to An_5.

Apart from the possible introduction of a small amount of alkali elements, and the removal of H_2O, the rocks of the present study are considered to have recrystallized under essentially 'closed system' conditions.

From the study of coexisting iron oxides (Chapter VIII) it is evident that the present charnockitic granulites were metamorphosed and perhaps formed initially under conditions of low fO_2. This and the high iron (in particular Fe^{2+}), low Mg and low free silica nature of the rocks, together with the variation trends suggest that these rocks were early to intermediate differentiates, resulting from the fractional crystallization of a common magma, following the Fenner's trend of crystallization (Osborn, 1959, p609, 618-619). Unlike the Madras charnockites which were due to the emplacement of a charnockitic magma (Subramanian, 1962, p21-36) these rocks were more likely the gabbroic and noritic differentiates of the anorthositic or gabbroic anorthositic magma in the Adirondacks.

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APPENDIX I

A Fortran IV computer program to perform calculations from chemical analyses of pyroxenes, garnets, amphiboles and micas

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      C     A FORTRAN PROGRAM TO RECALCULATE CHEMICAL ANALYSES OF PYROXENES,          A    1
      C     AMPHIBOLES, MICAS, AND GARNETS----------L. S. JEN                        A    2
      C     THIS PROGRAM IS DESIGNED TO RUN JOB ON IBM360/65 COMPUTER                A    3
      C     (1) CALCULATION OF TOTAL WT%, MOLECULAR PROPORTION, ATOMIC               A    4
      C     PROPORTION                                                               A    5
      C     OF OXYGEN, AND ATOMIC PROPORTION OF CATIONS FROM WT% INPUT DATA          A    6
      C     (2) CALCULATION OF NUMBERS OF IONS ON THE BASIS OF 6 OXYGENS FOR         A    7
      C     PYROXENES,24(O,OH,F,CL) OR 22(O,OH,F,CL) IF H2O IS NOT ANALYSED          A    8
      C     FOR AMPHIBOLES AND MICAS, AND 24 OXYGENS FOR GARNETS                     A    9
      C     (3) CALCULATION OF VARIOUS ATOMIC RATIOS                                 A   10
      C     EXPLANATION OF ABBREVIATIONS IN OUTPUT RESULTS                           A   11
      C     APSIAL=ATOMIC PROPORTION OF SI+AL, APALT=ATOMIC PROPORTION OF            A   12
      C                                                                              A   13
      C     TETRAHEDRAL AL                                                           A   14
      C     APALO=ATOMIC PROPORTION OF OCTAHEDRAL AL, APTIT=ATOMIC PROPORTION        A   15
      C     OF                                                                       A   16
      C     TETRAHEDRAL TI, APTIO=ATOMIC PROPORTION OF OCTAHEDRAL TI,                A   17
      C     APFE3T=ATOMIC PROPORTION OF TETRAHEDRAL FERRIC IRON,APFE3O=              A   18
      C     ATOMIC PROPORTION OF OCTAHEDRAL FERRIC IRON                              A   19
      C     ALT=TETRAHEDRAL AL , ALO= OCTAHEDRAL AL , TIT=TETRAHEDRAL TI ,           A   20
      C     TIO=OCTAHEDRAL TI , FE3T=TETRAHEDRAL FERRIC IRON , FE3O=OCTAHEDRAL       A   21
      C     FERRIC IRON                                                              A   22
      C     Z=TETRAHEDRAL LATTICE SITE(OCCUPANCY)                                    A   23
      C     XY=OCTAHEDRAL LATTICE SITE(OCCUPANCY) EXCEPT IN GARNETS X=CUBIC          A   24
      C     SITE                                                                     A   25
      C     TOLERANCE OF PROGRAM ON INPUT DATA IN % OXIDES---SIO2,AL2O3,FE2O3,       A   26
      C     CR2O3,FEO,MGO,MNO,NIO,CAO,NA2O,K2O,LI2O,SRO,BAO,RB2O,H2O,F,CL            A   27
0001          DIMENSION B(4)                                                         A   28
0002          REAL W(20),MW(20),MP(20),APO(20),APC(20),X(20,2),XX(20),YY(20)         A   29
0003          DOUBLE PRECISION SI,ALT,ALO,TIT,TIO,FE3T,FE3O,CR,FE2,MG,MN,CA,NA,K     A   30
             1,LI,TI,FE3,MGMG,SRO,SR,BAO,BA,RB2O,RB,H,F,CL                           A   31
0004          READ (1,2) MO                                                          A   32
0005          DO 1 I=1,MO                                                            A   33
0006          READ (1,3) NSUB                                                        A   34
0007          IF (NSUB.EQ.1) CALL PYROX                                              A   35
0008          IF (NSUB.EQ.2) CALL AMICA                                              A   36
0009          IF (NSUB.EQ.3) CALL GARNET                                             A   37
0010        1 CONTINUE                                                               A   38
0011          STOP                                                                   A   39
      C                                                                              A   40
0012        2 FORMAT (I1)                                                            A   41
0013        3 FORMAT (I1)                                                            A   42
0014          END
```

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0001            SUBROUTINE PYROX                                                B   1
                C   A FORTRAN PROGRAM TO RECALCULATE CHEMICAL ANALYSES OF        B   2
                C   PYROXENES------                                             B   3
                C   ---L. S. JEN                                                B   4
0002            DIMENSION B(4)                                                  B   5
0003            REAL W(20),MW(20),MP(20),APO(20),APC(20),X(20,2),XX(20),YY(20)  B   6
0004            DOUBLE PRECISION SI,ALT,ALO,TIT,TIO,FE3T,FE3O,CR,FE2,MG,MN,CA,NA,K  B   7
               1,LT,TI,FE3,MGMG                                                 B   8
0005            READ (1,45) N,L                                                 B   9
0006            DO 1 I=1,N                                                      B  10
0007            READ (1,46) (X(I,J),J=1,2)                                      B  11
0008      1     CONTINUE                                                        B  12
0009            DO 2 I=1,L                                                      B  13
0010            READ (1,47) XX(I)                                               B  14
0011      2     CONTINUE                                                        B  15
0012            READ (1,48) (MW(I),I=1,N)                                       B  16
0013            READ (1,49) NO                                                  B  17
0014            DO 44 MM=1,NO                                                   B  18
0015            READ (1,50) M,(B(I),I=1,4)                                      B  19
0016            WRITE (3,51) M,(B(I),I=1,4)                                     B  20
0017            READ (1,52) (W(I),I=1,N)                                        B  21
0018            SW=0.0                                                          B  22
0019            DO 3 I=1,N                                                      B  23
0020            SW=SW+W(I)                                                      B  24
0021      3     CONTINUE                                                        B  25
0022            DO 4 I=1,N                                                      B  26
0023            IF (MW(I).EQ.0.0) GO TO 5                                       B  27
0024            MP(I)=W(I)/MW(I)                                                B  28
0025      4     CONTINUE                                                        B  29
0026      5     CONTINUE                                                        B  30
0027            APO(1)=2.0*MP(1)                                                B  31
0028            APO(2)=3.0*MP(2)                                                B  32
0029            APO(3)=2.0*MP(3)                                                B  33
0030            APO(4)=3.0*MP(4)                                                B  34
0031            APO(5)=3.0*MP(5)                                                B  35
0032            APO(6)=MP(6)                                                    B  36
0033            APO(7)=MP(7)                                                    B  37
0034            APO(8)=MP(8)                                                    B  38
0035            APO(9)=MP(9)                                                    B  39
0036            APO(10)=MP(10)                                                  B  40
0037            APO(11)=MP(11)                                                  B  41
0038            APO(12)=MP(12)                                                  B  42
0039            APO(13)=MP(13)                                                  B  43
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```
0000                  SUMAPO=0.0                                          B  44
0001                  DO 6 I=1,N                                          B  45
0002                  SUMAPO=SUMAPO+APO(I)                                B  46
0003              6   CONTINUE                                            B  47
0004                  FACT1=SUMAPO/6.0                                    B  48
0005                  APC(1)=MP(1)                                        B  49
0006                  APC(2)=2.0*MP(2)                                    B  50
0007                  APC(3)=MP(3)                                        B  51
0008                  APC(4)=2.0*MP(4)                                    B  52
0009                  APC(5)=2.0*MP(5)                                    B  53
0050                  APC(6)=MP(6)                                        B  54
0051                  APC(7)=MP(7)                                        B  55
0052                  APC(8)=MP(8)                                        B  56
0053                  APC(9)=MP(9)                                        B  57
0054                  APC(10)=MP(10)                                      B  58
0055                  APC(11)=2.0*MP(11)                                  B  59
0056                  APC(12)=2.0*MP(12)                                  B  60
0057                  APC(13)=2.0*MP(13)                                  B  61
0058                  IF (APC(1).GE.2.0*FACT1) GO TO 13                   B  62
0059                  FACT2=2.0                                           B  63
0060                  APSIAL=FACT2*FACT1                                  B  64
0061                  APALT=APSIAL-APC(1)                                 B  65
0062                  APALO=APC(2)-APALT                                  B  66
0063                  IF (APALO.GT.0.0) GO TO 12                          B  67
0064                  APALO=0.0                                           B  68
0065                  APALT=APC(2)                                        B  69
0066                  APTIT=APSIAL-APC(1)-APC(2)                          B  70
0067                  APTIO=APC(3)-APTIT                                  B  71
0068                  IF (APTIO.GT.0.0) GO TO 10                          B  72
0069                  APALT=APC(2)                                        B  73
0070                  APALO=0.0                                           B  74
0071                  APTIT=APC(3)                                        B  75
0072                  APTIO=0.0                                           B  76
0073                  APFE3T=APSIAL-APC(1)-APC(2)-APC(3)                  B  77
0074                  APFE3O=APC(4)-APFE3T                                B  78
0075                  IF (APFE3O.GT.0.0) GO TO 8                          B  79
0076                  APFE3O=0.0                                          B  80
0077                  APFE3T=APC(4)                                       B  81
0078                  SUMK=0.0                                            B  82
0079                  DO 7 I=5,N                                          B  83
0080                  SUMK=SUMK+APC(I)                                    B  84
0081              7   CONTINUE                                            B  85
0082                  SUM=SUMK+APFE3T                                     B  86
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0083                GO TO 17                                          B  87
0084          8     SUMF=0.0                                          B  88
0085                DO 9 I=5,N                                        B  89
0086                SUMF=SUMF+APC(I)                                  B  90
0087          9     CONTINUE                                          B  91
0088                SUM=SUMF+APFE30                                   B  92
0089                GO TO 17                                          B  93
0090          10    APFE3T=0.0                                        B  94
0091                APFE30=APC(4)                                     B  95
0092                SUMG=0.0                                          B  96
0093                DO 11 I=4,N                                       B  97
0094                SUMG=SUMG+APC(I)                                  B  98
0095          11    CONTINUE                                          B  99
0096                SUM=SUMG+APTIO                                    B 100
0097                GO TO 17                                          B 101
0098          12    APTIT=0.0                                         B 102
0099                APTIO=APC(3)                                      B 103
0100                APFE3T=0.0                                        B 104
0101                APFE30=APC(4)                                     B 105
0102                GO TO 15                                          B 106
0103          13    APALT=0.0                                         B 107
0104                APALO=APC(2)                                      B 108
0105                APTIT=0.0                                         B 109
0106                APTIO=APC(3)                                      B 110
0107                APFE3T=0.0                                        B 111
0108                APFE30=APC(4)                                     B 112
0109                APSIAL=APC(1)                                     B 113
0110                FACT2=APSIAL/FACT1                                B 114
0111                SUM=0.0                                           B 115
0112                DO 14 I=2,N                                       B 116
0113                SUM=SUM+APC(I)                                    B 117
0114          14    CONTINUE                                          B 118
0115          15    CONTINUE                                          B 119
0116                SUMA=0.0                                          B 120
0117                DO 16 I=3,N                                       B 121
0118                SUMA=SUMA+APC(I)                                  B 122
0119          16    CONTINUE                                          B 123
0120                SUM=APALO+SUMA                                    B 124
0121          17    CONTINUE                                          B 125
0122                FACT3=SUM/FACT1                                   B 126
0123                ST=FACT2*APC(1)/APSIAL                            B 127
0124                ALT=FACT2*APALT/APSIAL                            B 128
0125                ALO=FACT3*APALO/SUM                               B 129
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0126                TIT=FACT2*APTIT/APSIAL                                  B 130
0127                TIO=FACT3*APTIO/SUM                                     B 131
0128                TI=FACT3*APC(3)/SUM                                     B 132
0129                FE3T=FACT2*APFE3T/APSIAL                                B 133
0130                FE3O=FACT3*APFE3O/SUM                                   B 134
0131                FE3=FACT3*APC(4)/SUM                                    B 135
0132                CR=FACT3*APC(5)/SUM                                     B 136
0133                FE2=FACT3*APC(6)/SUM                                    B 137
0134                MG=FACT3*APC(7)/SUM                                     B 138
0135                MN=FACT3*APC(8)/SUM                                     B 139
0136                NI=FACT3*APC(9)/SUM                                     B 140
0137                CA=FACT3*APC(10)/SUM                                    B 141
0138                NA=FACT3*APC(11)/SUM                                    B 142
0139                K=FACT3*APC(12)/SUM                                     B 143
0140                LI=FACT3*APC(13)/SUM                                    B 144
0141                YY(1)=SI                                                B 145
0142                YY(2)=ALT                                               B 146
0143                YY(3)=ALO                                               B 147
0144                YY(4)=TIT                                               B 148
0145                YY(5)=TIO                                               B 149
0146                YY(6)=FE3T                                              B 150
0147                YY(7)=FE3O                                              B 151
0148                YY(8)=CR                                                B 152
0149                YY(9)=FE2                                               B 153
0150                YY(10)=MG                                               B 154
0151                YY(11)=MN                                               B 155
0152                YY(12)=NI                                               B 156
0153                YY(13)=CA                                               B 157
0154                YY(14)=NA                                               B 158
0155                YY(15)=K                                                B 159
0156                YY(16)=LI                                               B 160
0157                IF (ALT.GT.0.0) GO TO 19                                B 161
0158                Z=SI                                                    B 162
0159                XY=0.0                                                  B 163
0160                DO 18 I=2,L                                             B 164
0161                XY=XY+YY(I)                                             B 165
0162          18    CONTINUE                                                B 166
0163                GO TO 37                                                B 167
0164          19    Z=SI+ALT                                                B 168
0165                XY=0.0                                                  B 169
0166                DO 20 I=3,L                                             B 170
0167                XY=XY+YY(I)                                             B 171
0168          20    CONTINUE                                                B 172
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0169                IF (ALO.LE.0.0) GO TO 22                                B 173
0170                Z=SI+ALT                                                B 174
0171                XY=0.0                                                  B 175
0172                DO 21 I=3,L                                             B 176
0173                XY=XY+YY(I)                                             B 177
0174          21    CONTINUE                                                B 178
0175                GO TO 37                                                B 179
0176          22    Z=SI+ALT+ALO                                            B 180
0177                XY=0.0                                                  B 181
0178                DO 23 I=4,L                                             B 182
0179                XY=XY+YY(I)                                             B 183
0180          23    CONTINUE                                                B 184
0181                IF (TI.EQ.0.0) GO TO 31                                 B 185
0182                IF (TIT.GT.0.0) GO TO 25                                B 186
0183                Z=SI+ALT+ALO                                            B 187
0184                XY=0.0                                                  B 188
0185                DO 24 I=4,L                                             B 189
0186                XY=XY+YY(I)                                             B 190
0187          24    CONTINUE                                                B 191
0188                GO TO 37                                                B 192
0189          25    Z=SI+ALT+ALO+TIT                                        B 193
0190                XY=0.0                                                  B 194
0191                DO 26 I=5,L                                             B 195
0192                XY=XY+YY(I)                                             B 196
0193          26    CONTINUE                                                B 197
0194                IF (TIO.LE.0.0) GO TO 28                                B 198
0195                Z=SI+ALT+ALO+TIT                                        B 199
0196                XY=0.0                                                  B 200
0197                DO 27 I=5,L                                             B 201
0198                XY=XY+YY(I)                                             B 202
0199          27    CONTINUE                                                B 203
0200                GO TO 37                                                B 204
0201          28    Z=SI+ALT+ALO+TIT+TIO                                    B 205
0202                XY=0.0                                                  B 206
0203                DO 29 I=6,L                                             B 207
0204                XY=XY+YY(I)                                             B 208
0205          29    CONTINUE                                                B 209
0206                IF (FF3T.GT.0.0) GO TO 31                               B 210
0207                Z=SI+ALT+ALO+TIT+TIO                                    B 211
0208                XY=0.0                                                  B 212
0209                DO 30 I=6,L                                             B 213
0210                XY=XY+YY(I)                                             B 214
0211          30    CONTINUE                                                B 215
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```
0212                GO TO 37                                                    B 216
0213          31    Z=SI+ALT+ALO+TIT+TIO+FE3T                                   B 217
0214                XY=0.0                                                      B 218
0215                DO 32 I=7,L                                                 B 219
0216                XY=XY+YY(I)                                                 B 220
0217          32    CONTINUE                                                    B 221
0218                IF (FE30.LE.0.0) GO TO 34                                   B 222
0219                Z=SI+ALT+ALO+TIT+TIO+FE3T                                   B 223
0220                XY=0.0                                                      B 224
0221                DO 33 I=7,L                                                 B 225
0222                XY=XY+YY(I)                                                 B 226
0223          33    CONTINUE                                                    B 227
0224                GO TO 37                                                    B 228
0225          34    Z=0.0                                                       B 229
0226                DO 35 I=1,7                                                 B 230
0227                Z=Z+YY(I)                                                   B 231
0228          35    CONTINUE                                                    B 232
0229                XY=0.0                                                      B 233
0230                DO 36 I=8,L                                                 B 234
0231                XY=XY+YY(I)                                                 B 235
0232          36    CONTINUE                                                    B 236
0233          37    WRITE (3,53)                                                B 237
0234                DO 38 I=1,N                                                 B 238
0235                WRITE (3,54) (X(I,J),J=1,2),W(I),MW(I),MP(I),APO(I),APC(I)  B 239
0236          38    CONTINUE                                                    B 240
0237                WRITE (3,55) SW                                             B 241
0238                WRITE (3,56) SUMAPO                                         B 242
0239                WRITE (3,57) FACT1,FACT2,FACT3                              B 243
0240                WRITE (3,58) APSIAL,APALT,APALO                             B 244
0241                WRITE (3,59) APTIT,APTIO                                    B 245
0242                WRITE (3,60) APFE3T,APFE30,SUM                              B 246
0243                WRITE (3,61)                                                B 247
0244                DO 39 I=1,L                                                 B 248
0245                WRITE (3,62) XX(I),YY(I)                                    B 249
0246          39    CONTINUE                                                    B 250
0247                WRITE (3,63) Z,XY                                           B 251
0248                AL=ALT+ALO                                                  B 252
0249                A=AL/SI                                                     B 253
0250                IF (AL.NE.0.0) GO TO 40                                     B 254
0251                BB=0.0                                                      B 255
0252          40    BB=ALT/AL                                                   B 256
0253                C=SI/Z                                                      B 257
0254                D=ALT/Z                                                     B 258
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0255              IF (FE2.NE.0.0) GO TO 41                                  B 259
0256              E=0.0                                                     B 260
0257         41   E=MG/FE2                                                  B 261
0258              G=MG/XY                                                   B 262
0259              H=FE3/XY                                                  B 263
0260              P=MN/XY                                                   B 264
0261              Q=CA/XY                                                   B 265
0262              R=K/XY                                                    B 266
0263              S=NA/XY                                                   B 267
0264              TT=K+NA                                                   B 268
0265              IF (TT.NE.0.0) GO TO 42                                   B 269
0266              T=0.0                                                     B 270
0267              GO TO 43                                                  B 271
0268         42   T=K/(K+NA)                                                B 272
0269         43   XMG=MG/(MG+FE2)                                           B 273
0270              XFE2=FE2/(FE2+MG)                                         B 274
0271              XXMG=MG/(MG+FE2+FE3)                                      B 275
0272              XXFE2=FE2/(FE2+FE3+MG)                                    B 276
0273              XFE=(FE2+FE3)/(FE2+FE3+MG)                                B 277
0274              F=XMG/(1-XMG)                                             B 278
0275              FF=XFE2/(1-XFE2)                                          B 279
0276              U=XFE2/XMG                                                B 280
0277              V=XMG/XFE2                                                B 281
0278              CC=MN/(MG+FE2+MN)                                         B 282
0279              FEMN=FE2+FE3+MN                                           B 283
0280              DD=CA+MG+FE2+FE3                                          B 284
0281              MGMG=MG/DD*100.0                                          B 285
0282              FEFE=(FE2+FE3)/DD*100.0                                   B 286
0283              CACA=CA/DD*100.0                                          B 287
0284              WRITE (3,64) A,BB                                         B 288
0285              WRITE (3,65) C                                            B 289
0286              WRITE (3,66) D,E                                          B 290
0287              WRITE (3,67) G,H                                          B 291
0288              WRITE (3,68) P,Q                                          B 292
0289              WRITE (3,69) R,S                                          B 293
0290              WRITE (3,70) T,XMG                                        B 294
0291              WRITE (3,71) XFE2                                         B 295
0292              WRITE (3,72) XXMG                                         B 296
0293              WRITE (3,73) XXFE2                                        B 297
0294              WRITE (3,74) XFE                                          B 298
0295              WRITE (3,75) F,FF                                         B 299
0296              WRITE (3,76) U,V                                          B 300
0297              WRITE (3,77) CC                                           B 301
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0298                  WRITE (3,78) FEMN                                                  B 302
0299                  WRITE (3,79)                                                       B 303
0300                  WRITE (3,80) MGMG,FEFE,CACA                                        B 304
0301            44    CONTINUE                                                           B 305
0302                  RETURN                                                             B 306
                C                                                                        B 307
0303            45    FORMAT (2I3)                                                       B 308
0304            46    FORMAT (2A3)                                                       B 309
0305            47    FORMAT (A4)                                                        B 310
0306            48    FORMAT (13F6.2)                                                    B 311
0307            49    FORMAT (I2)                                                        B 312
0308            50    FORMAT (A4,4A4)                                                    B 313
0309            51    FORMAT ('1','0',2X,'SAMPLE J-',A4,5X,4A4)                          B 314
0310            52    FORMAT (13F6.2)                                                    B 315
0311            53    FORMAT ('0',5X,'OXIDES',12X,'WT %',10X,'MOL WT',8X,'MOL PROP',6X,' B 316
                     1ATOMIC PROP OXYGEN',2X,'ATOMIC PROP CATIONS')                      B 317
0312            54    FORMAT ('0',5X,2A3,8X,3(F10.5,5X),5X,F10.5,12X,F10.5)              B 318
0313            55    FORMAT ('0',5X,'TOTAL WT %=',1X,F10.5)                             B 319
0314            56    FORMAT ('0',5X,'TOTAL ATOMIC PROPORTION OF OXYGEN=',1X,F10.5)      B 320
0315            57    FORMAT ('0',5X,'FACT1=',1X,F10.5,10X,'FACT2=',1X,F10.5,10X,'FACT3= B 321
                     1',1X,F10.5)                                                        B 322
0316            58    FORMAT ('0',5X,'APSIAL=',1X,F10.5,5X,'APALT=',1X,F10.5,5X,'APALO=' B 323
                     1,1X,F10.5)                                                         B 324
0317            59    FORMAT ('0',5X,'APTIT=',1X,F10.5,5X,'APTIO=',1X,F10.5)             B 325
0318            60    FORMAT ('0',5X,'APFE3T=',1X,F10.5,5X,'APFE3O=',1X,F10.5,5X,'SUM=', B 326
                     11X,F10.5)                                                          B 327
0319            61    FORMAT ('0',/,5X,'NUMBERS OF IONS ON THE BASIS OF 6 OXYGENS')      B 328
0320            62    FORMAT ('0',15X,A4,5X,F10.5)                                       B 329
0321            63    FORMAT ('0',15X,'Z=',1X,F10.5,10X,'XY=',1X,F10.5)                  B 330
0322            64    FORMAT ('0',1X,'AL/SI=',1X,F10.5//(2X,'ALT/AL=',1X,F10.5))         B 331
0323            65    FORMAT ('0',1X,'SI/Z=',1X,F10.5)                                   B 332
0324            66    FORMAT ('0',1X,'ALT/Z=',1X,F10.5//(2X,'MG/FE2=',1X,F10.5))         B 333
0325            67    FORMAT ('0',1X,'MG/XY=',1X,F10.5//(2X,'FE3/XY=',1X,F10.5))         B 334
0326            68    FORMAT ('0',1X,'MN/XY=',1X,F10.5//(2X,'CA/XY=',1X,F10.5))          B 335
0327            69    FORMAT ('0',1X,'K/XY=',1X,F10.5//(2X,'NA/XY=',1X,F10.5))           B 336
0328            70    FORMAT ('0',1X,'K/(K+NA)=',1X,F10.5//(2X,'XMG=MG/(MG+FE2)=',1X,F10 B 337
                     1.5))                                                               B 338
0329            71    FORMAT ('0',1X,'XFE2=FE2/(FE2+MG)=',1X,F10.5)                      B 339
0330            72    FORMAT ('0',1X,'XXMG=MG/(MG+FE2+FE3)=',1X,F10.5)                   B 340
0331            73    FORMAT ('0',1X,'XXFE2=FE2/(FE2+FE3+MG)=',1X,F10.5)                 B 341
0332            74    FORMAT ('0',1X,'XFF=(FE2+FE3)/(FE2+FE3+MG)=',1X,F10.5)             B 342
0333            75    FORMAT ('0',1X,'XMG/(1-XMG)=',1X,F10.5//(2X,'XFE2/(1-XFE2)=',1X,F1 B 343
                     10.5))                                                              B 344
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0334        76    FORMAT ('0',1X,'XFE2/XMG=',1X,F10.5//(2X,'XMG/XFE2=',1X,F10.5))      B 345
0335        77    FORMAT ('0',1X,'MN/(MG+FE2+MN)=',1X,F10.5)                           B 346
0336        78    FORMAT ('0',1X,'FE2+FE3+MN=',1X,F10.5)                               B 347
0337        79    FORMAT ('0',/,5X,'RECALCULATION OF MG,FE AND CA TO 100 %')           B 348
0338        80    FORMAT ('0',14X,'MG=',1X,F10.5//(15X,'FE=',1X,F10.5)//(15X,'CA=',1X  B 349
                                                                                       B 350
                 1X,F10.5))                                                            B 351
0339              END
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0001            SUBROUTINE AMICA                                                    C    1
                C   A FORTRAN PROGRAM TO RECALCULATE CHEIEMICAL ANALYSES OF AMPHIBOLES C    2
                C   AND MICAS----------L. S. JEN                                    C    3
                C                                                                   C    4
0002            DIMENSION B(4)                                                      C    5
0003            REAL W(20),MW(20),MP(20),APO(20),APC(20),X(20,2),XX(20),YY(20)      C    6
0004            DOUBLE PRECISION SI,AL T,ALO,TIT,TIO,FE3T,FE3O,CR,FE2,MG,MN,CA,NA,K C    7
               1,LI,TI,FE3,MGMG                                                     C    8
0005            READ (1,23) N,L                                                     C    9
0006            DO 1 I=1,N                                                          C   10
0007            READ (1,24) (X(I,J),J=1,2)                                          C   11
0008      1     CONTINUE                                                            C   12
0009            DO 2 I=1,L                                                          C   13
0010            READ (1,25) XX(I)                                                   C   14
0011      2     CONTINUE                                                            C   15
0012            READ (1,26) (MW(I),I=1,N)                                           C   16
0013            READ (1,27) NO                                                      C   17
0014            DO 22 NM=1,NO                                                       C   18
0015            READ (1,28) M,(B(I),I=1,4)                                          C   19
0016            WRITE (3,29) M,(B(I),I=1,4)                                         C   20
0017            READ (1,30) (W(I),I=1,N)                                            C   21
0018            SW=0.0                                                              C   22
0019            DO 3 I=1,N                                                          C   23
0020            SW=SW+W(I)                                                          C   24
0021      3     CONTINUE                                                            C   25
0022            WF=W(12)*16.0/(2.0*19.0)                                            C   26
0023            WCL=W(13)*16.0/(2.0*35.457)                                         C   27
0024            TOTALW=SW-WF-WCL                                                    C   28
0025            DO 4 I=1,N                                                          C   29
0026            IF (MW(I).EQ.0.0) GO TO 5                                           C   30
0027            MP(I)=W(I)/MW(I)                                                    C   31
0028      4     CONTINUE                                                            C   32
0029      5     CONTINUE                                                            C   33
0030            APO(1)=2.0*MP(1)                                                    C   34
0031            APO(2)=3.0*MP(2)                                                    C   35
0032            APO(3)=2.0*MP(3)                                                    C   36
0033            APO(4)=3.0*MP(4)                                                    C   37
0034            APO(5)=MP(5)                                                        C   38
0035            APO(6)=MP(6)                                                        C   39
0036            APO(7)=MP(7)                                                        C   40
0037            APO(8)=MP(8)                                                        C   41
0038            APO(9)=MP(9)                                                        C   42
0039            APO(10)=MP(10)                                                      C   43
0040            APO(11)=MP(11)
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0041                APO(12)=MP(12)                                          C  44
0042                APO(13)=MP(13)                                          C  46
0043                APO(14)=MP(14)                                          C  47
0044                SUMAPO=0.0                                              C  48
0045                DO 6 I=1,N                                              C  49
0046                SUMAPO=SUMAPO+APO(I)                                    C  50
0047          6     CONTINUE                                                C  51
0048                APF=MP(13)/2.0                                          C  52
0049                APCL=MP(14)/2.0                                         C  53
0050                TOTALO=SUMAPO-APF-APCL                                  C  54
0051                DO 7 I=1,N                                              C  55
0052                IF (APO(12).NE.0.0) GO TO 8                             C  56
0053                APC(I)=22.0/TOTALO*APO(I)                               C  57
0054          7     CONTINUE                                                C  58
0055                GO TO 10                                                C  59
0056          8     DO 9 I=1,N                                              C  60
0057                APC(I)=24.0/TOTALO*APO(I)                               C  61
0058          9     CONTINUE                                                C  62
0059          10    SI=APC(1)/2.0                                           C  63
0060                AL=APC(2)*2.0/3.0                                       C  64
0061                TI=APC(3)/2.0                                           C  65
0062                FE3=APC(4)*2.0/3.0                                      C  66
0063                FE2=APC(5)                                              C  67
0064                MG=APC(6)                                               C  68
0065                LI=APC(7)*2.0                                           C  69
0066                MN=APC(8)                                               C  70
0067                CA=APC(9)                                               C  71
0068                NA=APC(10)*2.0                                          C  72
0069                K=APC(11)*2.0                                           C  73
0070                H=APC(12)*2.0                                           C  74
0071                F=APC(13)                                               C  75
0072                CL=APC(14)                                              C  76
0073                IF (SI.GE.8.0) GO TO 11                                 C  77
0074                ALT=8.0-SI                                              C  78
0075                ALO=AL-ALT                                              C  79
0076                GO TO 12                                                C  80
0077          11    ALT=0.0                                                 C  81
0078                ALO=AL                                                  C  82
0079          12    IF (ALO.GT.0.0) GO TO 13                                C  83
0080                ALT=AL                                                  C  84
0081                ALO=0.0                                                 C  85
0082          13    YY(1)=SI                                                C  86
0083                YY(2)=ALT
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0084                YY(3)=ALO                                                      C  87
0085                YY(4)=TI                                                       C  88
0086                YY(5)=FE3                                                      C  89
0087                YY(6)=FE2                                                      C  90
0088                YY(7)=MG                                                       C  91
0089                YY(8)=LI                                                       C  92
0090                YY(9)=MN                                                       C  93
0091                YY(10)=CA                                                      C  94
0092                YY(11)=NA                                                      C  95
0093                YY(12)=K                                                       C  96
0094                YY(13)=H                                                       C  97
0095                YY(14)=F                                                       C  98
0096                YY(15)=CL                                                      C  99
0097                IF (ALT.NE.0.0) GO TO 14                                       C 100
0098                Z=SI                                                           C 101
0099                XY=ALT+ALO+TI+FE3+FE2+MG+MN+LI                                 C 102
0100                GO TO 15                                                       C 103
0101          14    Z=SI+ALT                                                       C 104
0102                XY=ALO+TI+FE3+FE2+MG+MN+LI                                     C 105
0103          15    WW=CA+NA+K                                                     C 106
0104                OHFCL=H+F+CL                                                   C 107
0105                WRITE (3,31)                                                   C 108
0106                DO 16 I=1,N                                                    C 109
0107                WRITE (3,32) (X(I,J),J=1,2),W(I),MW(I),MP(I),APO(I),APC(I)     C 110
0108          16    CONTINUE                                                       C 111
0109                WRITE (3,33) SW,TOTALW                                         C 112
0110                WRITE (3,34)                                                   C 113
0111                DO 17 I=1,L                                                    C 114
0112                WRITE (3,35) XX(I),YY(I)                                       C 115
0113          17    CONTINUE                                                       C 116
0114                WRITE (3,36) Z,XY,WW,OHFCL                                     C 117
0115                AL=ALT+ALO                                                     C 118
0116                A=AL/SI                                                        C 119
0117                IF (AL.NE.0.0) GO TO 18                                        C 120
0118                BB=0.0                                                         C 121
0119          18    BB=ALT/AL                                                      C 122
0120                C=SI/Z                                                         C 123
0121                D=ALT/Z                                                        C 124
0122                IF (FE2.NE.0.0) GO TO 19                                       C 125
0123                E=0.0                                                          C 126
0124          19    E=MG/FE2                                                       C 127
0125                G=MG/XY                                                        C 128
0126                H=FE3/XY                                                       C 129
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0127                P=MN/XY                                                  C 130
0128                Q=CA/XY                                                  C 131
0129                R=K/XY                                                   C 132
0130                S=NA/XY                                                  C 133
0131                TT=K+NA                                                  C 134
0132                IF (TT.NE.0.0) GO TO 20                                  C 135
0133                T=0.0                                                    C 136
0134                GO TO 21                                                 C 137
0135          20    T=K/(K+NA)                                               C 138
0136          21    XMG=MG/(MG+FE2)                                          C 139
0137                XFF2=FF2/(FE2+MG)                                        C 140
0138                XXMG=MG/(MG+FE2+FE3)                                     C 141
0139                XXFE2=FF2/(FE2+FE3+MG)                                   C 142
0140                XFE=(FE2+FE3)/(FE2+FE3+MG)                               C 143
0141                F=XMG/(1-XMG)                                            C 144
0142                FF=XFE2/(1-XFE2)                                         C 145
0143                U=XFE2/XMG                                               C 146
0144                V=XMG/XFE2                                               C 147
0145                CC=MN/(MG+FE2+MN)                                        C 148
0146                GG=LI/XY                                                 C 149
0147                PP=100*MG/(MG+FE2+FE3+MN)                                C 150
0148                WRITE (3,37) A,BB                                        C 151
0149                WRITE (3,38) C                                           C 152
0150                WRITE (3,39) D,E                                         C 153
0151                WRITE (3,40) G,H                                         C 154
0152                WRITE (3,41) P,Q                                         C 155
0153                WRITE (3,42) R,S                                         C 156
0154                WRITE (3,43) T,XMG                                       C 157
0155                WRITE (3,44) XFE2                                        C 158
0156                WRITE (3,45) XXMG                                        C 159
0157                WRITE (3,46) XXFE2                                       C 160
0158                WRITE (3,47) XFE                                         C 161
0159                WRITE (3,48) F,FF                                        C 162
0160                WRITE (3,49) U,V                                         C 163
0161                WRITE (3,50) CC,GG                                       C 164
0162                WRITE (3,51) PP                                          C 165
0163          22    CONTINUE                                                 C 166
0164                RETURN                                                   C 167
                    C                                                        C 168
                    C                                                        C 169
0165          23    FORMAT (2I3)                                             C 170
0166          24    FORMAT (2A3)                                             C 171
0167          25    FORMAT (A4)                                              C 172
0168          26    FORMAT (13F6.2,2X)
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0169          27    FORMAT (I2)                                                                                C 173
0170          28    FORMAT (A4,4A4)                                                                            C 174
0171          29    FORMAT ('1','0',2X,'SAMPLE J=',A4,5X,4A4)                                                  C 175
0172          30    FORMAT (13F6.2)                                                                            C 176
0173          31    FORMAT ('0',5X,'OXIDES',12X,'WT %',10X,'MOL WT',8X,'MOL PROP',6X,'                         C 177
                   1ATOMIC PROP OXYGEN',4X,'ATOMIC PROP CATIONS')                                             C 178
0174          32    FORMAT ('0',5X,2A3,8X,3(F10.5,5X),5X,F10.5,12X,F10.5)                                      C 179
0175          33    FORMAT ('0',2X,('SUM OF WT %=',1X,F10.5)/(2X,'CORRECTED       TOTA                         C 180
                   1L WT %=',1X,F10.5))                                                                       C 181
0176          34    FORMAT ('0',/,5X,'NUMBERS OF IONS ON THE BASIS OF 24(O,OH,F,CL) OR                         C 182
                   1, ON THE BASIS OF 22(O,OH,F,CL) IF H2O IS NOT ANALYZED')                                  C 183
0177          35    FORMAT ('0',15X,A4,5X,F10.5)                                                               C 184
0178          36    FORMAT ('0',15X,'Z=',1X,F10.5,10X,'XY=',1X,F10.5,10X,'WW=',1X,F10.                         C 185
                   15,10X,'OH+CL=',1X,F10.5)                                                                  C 186
0179          37    FORMAT ('0',1X,'AL/SI=',1X,F10.5//(2X,'ALT/AL=',1X,F10.5))                                 C 187
0180          38    FORMAT ('0',1X,'SI/Z=',1X,F10.5)                                                           C 188
0181          39    FORMAT ('0',1X,'ALT/Z=',1X,F10.5//(2X,'MG/FE2=',1X,F10.5))                                 C 189
0182          40    FORMAT ('0',1X,'MG/XY=',1X,F10.5//(2X,'FE3/XY=',1X,F10.5))                                 C 190
0183          41    FORMAT ('0',1X,'MN/XY=',1X,F10.5//(2X,'CA/XY=',1X,F10.5))                                  C 191
0184          42    FORMAT ('0',1X,'K/XY=',1X,F10.5//(2X,'NA/XY=',1X,F10.5))                                   C 192
0185          43    FORMAT ('0',1X,'K/(K+NA)=',1X,F10.5//(2X,'XMG=(MG+FE2)=',1X,F10.5)                         C 193
                   1)                                                                                         C 194
0186          44    FORMAT ('0',1X,'XFE2=FE2/(FE2+MG)=',1X,F10.5)                                              C 195
0187          45    FORMAT ('0',1X,'XXMG=MG/(MG+FE2+FE3)=',1X,F10.5)                                           C 196
0188          46    FORMAT ('0',1X,'XXFE2=FE2/(FE2+FE3+MG)=',1X,F10.5)                                         C 197
0189          47    FORMAT ('0',1X,'XFE=(FE2+FE3)/(FE2+FE3+MG)=',1X,F10.5)                                     C 198
0190          48    FORMAT ('0',1X,'XMG/(1-XMG)=',1X,F10.5//(2X,'XFE2/(1-XFE2)=',1X,F1                         C 199
                   10.5))                                                                                     C 200
0191          49    FORMAT ('0',1X,'XFE2/XMG=',1X,F10.5//(2X,'XMG/XFE2=',1X,F10.5))                            C 201
0192          50    FORMAT ('0',1X,'MN/(MG+FE2+MN)=',1X,F10.5//(2X,'LI/XY=',1X,F10.5))                         C 202
0193          51    FORMAT ('0',1X,'100MG/(MG+FE2+FE3+MN)=',1X,F10.5)                                          C 203
0194                END                                                                                        C 204
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0001            SUBROUTINE GARNET                                                   D    1
                C   A FORTRAN PROGRAM TO RECALCULATE CHEMICAL ANALYSES OF            D    2
                C   GARNETS-+-------                                                 D    3
                C     --L. S. JEN                                                   D    4
0002            DIMENSION B(4)                                                      D    5
0003            REAL W(20),MW(20),MP(20),APO(20),APC(20),X(20,2),XX(20),YY(20)      D    6
0004            DOUBLE PRECISION SI,ALT,ALO,TIT,TIO,FE3T,FE30,CR,FE2,MG,MN,CA,NA,K  D    7
               1,LI,TI,FE3,MGMG                                                     D    8
0005            READ (1,20) N,L                                                     D    9
0006            DO 1 I=1,N                                                          D   10
0007            READ (1,21) (X(I,J),J=1,2)                                          D   11
0008          1 CONTINUE                                                            D   12
0009            DO 2 I=1,L                                                          D   13
0010            READ (1,22) XX(I)                                                   D   14
0011          2 CONTINUE                                                            D   15
0012            READ (1,23) (MW(I),I=1,N)                                           D   16
0013            READ (1,24) NO                                                      D   17
0014            DO 19 NM=1,NO                                                       D   18
0015            READ (1,25) M,(B(I),I=1,4)                                          D   19
0016            WRITE (3,26) M,(B(I),I=1,4)                                         D   20
0017            READ (1,27) (W(I),I=1,N)                                            D   21
0018            SW=0.0                                                              D   22
0019            DO 3 I=1,N                                                          D   23
0020            SW=SW+W(I)                                                          D   24
0021          3 CONTINUE                                                            D   25
0022            DO 4 I=1,N                                                          D   26
0023            IF (MW(I).EQ.0.0) GO TO 5                                           D   27
0024            MP(I)=W(I)/MW(I)                                                    D   28
0025          4 CONTINUE                                                            D   29
0026          5 CONTINUE                                                            D   30
0027            APO(1)=2.0*MP(1)                                                    D   31
0028            APO(2)=3.0*MP(2)                                                    D   32
0029            APO(3)=2.0*MP(3)                                                    D   33
0030            APO(4)=3.0*MP(4)                                                    D   34
0031            APO(5)=3.0*MP(5)                                                    D   35
0032            APO(6)=MP(6)                                                        D   36
0033            APO(7)=MP(7)                                                        D   37
0034            APO(8)=MP(8)                                                        D   38
0035            APO(9)=MP(9)                                                        D   39
0036            APO(10)=MP(10)                                                      D   40
0037            APO(11)=MP(11)                                                      D   41
0038            APO(12)=MP(12)                                                      D   42
0039            APO(13)=MP(13)                                                      D   43
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0040                  APO(14)=MP(14)                                    D  44
0041                  APO(15)=MP(15)                                    D  45
0042                  SUMAPO=0.0                                        D  46
0043                  DO 6 I=1,N                                        D  47
0044                  SUMAPO=SUMAPO+APO(I)                              D  48
0045            6     CONTINUE                                          D  49
0046                  DO 7 I=1,N                                        D  50
0047                  APC(I)=24.0/SUMAPO*APO(I)                         D  51
0048            7     CONTINUE                                          D  52
0049                  SI=APC(1)/2.0                                     D  53
0050                  AL=APC(2)*2.0/3.0                                 D  54
0051                  TI=APC(3)/2.0                                     D  55
0052                  CR=APC(4)*2.0/3.0                                 D  56
0053                  FE3=APC(5)*2.0/3.0                                D  57
0054                  FE2=APC(6)                                        D  58
0055                  MN=APC(7)                                         D  59
0056                  MG=APC(8)                                         D  60
0057                  LI=APC(9)*2.0                                     D  61
0058                  CA=APC(10)                                        D  62
0059                  NA=APC(11)*2.0                                    D  63
0060                  K=APC(12)*2.0                                     D  64
0061                  SR=APC(13)                                        D  65
0062                  BA=APC(14)                                        D  66
0063                  RB=APC(15)*2.0                                    D  67
0064                  IF (SI.GE.6.0) GO TO 8                            D  68
0065                  ALT=6.0-SI                                        D  69
0066                  ALO=AL-ALT                                        D  70
0067                  GO TO 9                                           D  71
0068            8     ALT=0.0                                           D  72
0069            9     IF (ALO.GT.0.0) GO TO 10                          D  74
0070                  ALT=AL                                            D  75
0071                  ALO=0.0                                           D  76
0072           10     YY(1)=SI                                          D  77
0073                  YY(2)=ALT                                         D  78
0074                  YY(3)=ALO                                         D  79
0075                  YY(4)=TI                                          D  80
0076                  YY(5)=CR                                          D  81
0077                  YY(6)=FE3                                         D  82
0078                  YY(7)=FE2                                         D  83
0079                  YY(8)=MN                                          D  84
0080                  YY(9)=MG                                          D  85
0081                  YY(10)=LI                                         D  86
0082                  YY(11)=CA                                         D  87
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0083                YY(12)=NA                                                    D  88
0084                YY(13)=K                                                     D  89
0085                YY(14)=SR                                                    D  90
0086                YY(15)=BA                                                    D  91
0087                YY(16)=RB                                                    D  92
0088                IF (ALO.NE.0.0) GO TO 11                                     D  93
0089                Z=SI                                                         D  94
0090                Y=ALT+ALO+TI+CR+FE3                                          D  95
0091                XSITE=MN+FE2+MG+CA+NA+K+LI                                   D  96
0092                GO TO 12                                                     D  97
0093          11    Z=SI+ALT                                                     D  98
0094                Y=ALO+TI+FE3+CR                                              D  99
0095                XSITE=MN+FE2+MG+CA+NA+K+LI                                   D 100
0096                XY=XSITE+Y                                                   D 101
0097          12    WRITE (3,28)                                                 D 102
0098                DO 13 I=1,N                                                  D 103
0099                WRITE (3,29) (X(I,J),J=1,2),W(I),MW(I),MP(I),APO(I),APC(I)   D 104
0100          13    CONTINUE                                                     D 105
0101                WRITE (3,30) SW                                              D 106
0102                WRITE (3,31)                                                 D 107
0103                DO 14 I=1,L                                                  D 108
0104                WRITE (3,32) XX(I),YY(I)                                     D 109
0105          14    CONTINUE                                                     D 110
0106                WRITE (3,33) Z,Y,XSITE                                       D 111
0107                AL=ALT+ALO                                                   D 112
0108                A=AL/SI                                                      D 113
0109                IF (AL.NE.0.0) GO TO 15                                      D 114
0110                BR=0.0                                                       D 115
0111          15    BR=ALT/AL                                                    D 116
0112                C=SI/Z                                                       D 117
0113                D=ALT/Z                                                      D 118
0114                IF (FE2.NE.0.0) GO TO 16                                     D 119
0115                E=0.0                                                        D 120
0116          16    E=MG/FE2                                                     D 121
0117                G=MG/XSITE                                                   D 122
0118                H=FE3/Y                                                      D 123
0119                P=MN/XSITE                                                   D 124
0120                Q=CA/XSITE                                                   D 125
0121                R=K/XSITE                                                    D 126
0122                S=NA/XSITE                                                   D 127
0123                TT=K+NA                                                      D 128
0124                IF (TT.NE.0.0) GO TO 17                                      D 129
0125                T=0.0                                                        D 130
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0126                  GO TO 18                                                    D 131
0127            17    T=K/(K+NA)                                                  D 132
0128            18    XMG=MG/(MG+FE2)                                             D 133
0129                  XFE2=FE2/(FE2+MG)                                           D 134
0130                  XXMG=MG/(MG+FE2+FE3)                                        D 135
0131                  XXFE2=FE2/(FE2+FE3+MG)                                      D 136
0132                  XFE=(FE2+FE3)/(FE2+FE3+MG)                                  D 137
0133                  F=XMG/(1-XMG)                                               D 138
0134                  FF=XFE2/(1-XFE2)                                            D 139
0135                  U=XFE2/XMG                                                  D 140
0136                  V=XMG/XFE2                                                  D 141
0137                  CC=MN/(MG+FE2+MN)                                           D 142
0138                  GG=LI/XY                                                    D 143
0139                  WRITE (3,34) A,BB                                           D 144
0140                  WRITE (3,35) C                                              D 145
0141                  WRITE (3,36) D,E                                            D 146
0142                  WRITE (3,37) G,H                                            D 147
0143                  WRITE (3,38) P,Q                                            D 148
0144                  WRITE (3,39) R,S                                            D 149
0145                  WRITE (3,40) T,XMG                                          D 150
0146                  WRITE (3,41) XFE2                                           D 151
0147                  WRITE (3,42) XXMG                                           D 152
0148                  WRITE (3,43) XXFE2                                          D 153
0149                  WRITE (3,44) XFE                                            D 154
0150                  WRITE (3,45) F,FF                                           D 155
0151                  WRITE (3,46) U,V                                            D 156
0152                  WRITE (3,47) CC,GG                                          D 157
0153            19    CONTINUE                                                    D 158
0154                  RETURN                                                      D 159
                C                                                                 D 160
                      FORMAT (2I3)                                                D 161
0155            20    FORMAT (2A3)                                                D 162
0156            21    FORMAT (A4)                                                 D 163
0157            22    FORMAT (13F6.2,2X)                                          D 164
0158            23    FORMAT (I2)                                                 D 165
0159            24    FORMAT (A4,4A4)                                             D 166
0160            25    FORMAT ('1','0',2X,'SAMPLE J=',A4,5X,4A4)                   D 167
0161            26    FORMAT (13F6.2)                                             D 168
0162            27    FORMAT ('0',5X,'OXIDES',12X,'WT %',10X,'MOL WT',8X,'MOL PROP',6X,'  D 169
0163            28   1ATOMIC PROP OXYGEN',4X,'ATOMIC PROP CATIONS')               D 170
                      FORMAT ('0',5X,2A3,8X,3(F10.5,5X),5X,F10.5,12X,F10.5)       D 171
0164            29    FORMAT ('0',2X,'TOTAL WT %=',1X,F10.5)                      D 172
0165            30    FORMAT ('0',/,5X,'NUMBERS OF IONS ON THE BASIS OF 24(O)')   D 173
0166            31
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0167          32    FORMAT ('0',15X,A4,5X,F10.5)                                                    D 174
0168          33    FORMAT ('0',15X,'Z=',1X,F10.5,10X,'Y =',1X,F10.5,10X,'X =',1X,F10.              D 175
                   15)                                                                             D 176
0169          34    FORMAT ('0',1X,'AL/SI=',1X,F10.5//(2X,'ALT/AL=',1X,F10.5))                      D 177
0170          35    FORMAT ('0',1X,'SI/Z=',1X,F10.5)                                                D 178
0171          36    FORMAT ('0',1X,'ALT/Z=',1X,F10.5//(2X,'MG/FE2=',1X,F10.5))                      D 179
0172          37    FORMAT ('0',1X,'MG/X =',1X,F10.5//(2X,'FE3/Y =',1X,F10.5))                      D 180
0173          38    FORMAT ('0',1X,'MN/X =',1X,F10.5//(2X,'CA/X =',1X,F10.5))                       D 181
0174          39    FORMAT ('0',1X,'K/X =',1X,F10.5//(2X,'NA/X =',1X,F10.5))                        D 182
0175          40    FORMAT ('0',1X,'K/(K+NA)=',1X,F10.5//(2X,'XMG=(MG+FE2)=',1X,F10.5)              D 183
                   1)                                                                              D 184
0176          41    FORMAT ('0',1X,'XFE2=FE2/(FE2+MG)=',1X,F10.5)                                   D 185
0177          42    FORMAT ('0',1X,'XXMG=MG/(MG+FE2+FE3)=',1X,F10.5)                                D 186
0178          43    FORMAT ('0',1X,'XXFE2=FE2/(FE2+FE3+MG)=',1X,F10.5)                              D 187
0179          44    FORMAT ('0',1X,'XFE=(FE2+FE3)/(FE2+FE3+MG)=',1X,F10.5)                          D 188
0180          45    FORMAT ('0',1X,'XMG/(1-XMG)=',1X,F10.5//(2X,'XFE2/(1-XFE2)=',1X,F1              D 189
                   10.5))                                                                          D 190
0181          46    FORMAT ('0',1X,'XFE2/XMG=',1X,F10.5//(2X,'XMG/XFE2=',1X,F10.5))                 D 191
0182          47    FORMAT ('0',1X,'MN/(MG+FE2+MN)=',1X,F10.5//(2X,'LI/X =',1X,F10.5))              D 192
0183                END                                                                             D 193-
```

APPENDIX II

A Fortran IV computer program for analyses of grain transitions (randomness test) based on chi square test

```
C  A FORTRAN PROGRAM TO CALCULATE CRYSTAL SPATIAL DISTRIBUTION DATA-----00000000
C                                                                       00000010
C     -----L. S. JEN                                                    00000020
C     --- PART (I) RANDOMNESS DATA                                      00000030
C     (1) CALCULATION OF SUMS OF INDIVIDUAL ROWS AND COLUMNS            00000040
C     AND THE TOTAL SUM OF THE TRANSITION TABLE A(I,J)                  00000050
C     (2) CALCULATION OF THE TRANSITION MATRIX T                        00000060
C     AND PRINT OUT THE VALUES IN MATRIX FORM                           00000070
C     (3) CALCULATION OF THE FIXED VECTOR PI                            00000080
C     AND PRINT OUT THE VALUES IN VECTOR FORM                           00000090
C     (4) CALCULATION OF THE EXPECTED MATRIX E                          00000100
C     AND PRINT OUT THE VALUES IN MATRIX FORM                           00000110
C     (5) CALCULATION OF THE INDIVIDUAL AND TOTAL CRYSTAL OR            00000120
C     MINERAL CHI SQUARE                                                00000130
C     (6) PRINTING OUT OF A(I,J) AND E(I,J)                             00000140
C     FOR COMPARISON OF THESE TWO MATRICES                              00000150
C     (7) LISTING OF THEORETICAL CHI SQUARE VALUES AT THE 95%           00000160
C     AND 99% SIGNIFICANCE LEVELS FOR COMPARISON WITH                   00000170
C     THE CALCULATED OBSERVED CRYSTAL CHI SQUARES                       00000180
0001        IMPLICIT REAL*8(A-H,O-Z)                                    00000190
0002        DIMENSION A(10,10), SX(10), SY(10), T(10,10), PI(10),       00000200
           1E(10,10), CHISQR(10,10), X(10), Y(10)                       00000210
0003        READ (1,130) (X(I), Y(I), I=2,10)                           00000220
0004      130 FORMAT (2(F7.3, 6X))                                      00000230
0005        WRITE (3,340)                                               00000240
0006      340 FORMAT (20X, 'THEORETICAL CHI SQUARES AT THE 95% AND 99% SIGNIFICA00000250
           1NCE LEVELS WITH DEGREES OF FREEDOM=1,4,9,16,25,36,49,64,AND 81  00000260
           2RESPECTIVELY')                                              00000270
0007        I=2                                                         00000280
0008       33 N=I-1                                                     00000290
0009        M=N*N                                                       00000300
0010        WRITE (3,230) M, X(I), M, Y(I)                              00000310
0011      230 FORMAT ('0', 19X, 'X**2, 95%(', I3, ')=', 1X, F8.3, 20X, 'X**2, 9900000310
           1%(', I3, ')=', 1X, F8.3)                                    00000320
                                                                        00000330
0012        I=I+1                                                       00000340
0013        IF(I.GT.10) GO TO 44                                        00000350
0014        GO TO 33                                                    00000360
0015       44 CONTINUE                                                  00000370
0016      111 READ (1,210,END=6000) M                                   00000380
0017      210 FORMAT (A4)                                               00000390
0018        WRITE (3,220) M                                             00000400
0019      220 FORMAT ('1', '0', 4X, 'SAMPLE J=', A4)                    00000410
0020        READ (1,10) N                                               00000420
0021       10 FORMAT (I5)
```

```
0022          DO 222 I=1,10                                                  00000430
0023          DO 222 J=1,10                                                  00000440
0024        222 A(I,J)=0.0                                                   00000450
0025          DO 11 I=1,N                                                    00000460
0026           11 READ (1,20) (A(I,J), J=1,N)                                00000470
0027           20 FORMAT (10F6.0)                                            00000480
0028          DO 25 I=1,N                                                    00000490
0029          SX(I)=0.0                                                      00000500
0030           25 SY(I)=0.0                                                  00000510
0031          DO 35 I=1,N                                                    00000520
0032          DO 35 J=1,N                                                    00000530
0033           35 SX(I)=SX(I)+A(I,J)                                         00000540
0034          WRITE (3,30)                                                   00000550
0035           30 FORMAT ('0', 6X, 'THE VALUES OF SX(I) ARE')                00000560
0036          DO 37 I=1, N                                                   00000570
0037          WRITE (3,400) I, SX(I)                                         00000580
0038        400 FORMAT ('0', 7X, 'SX(', I3, ')=', 1X, 10(F6.1, 3X))          00000590
0039           37 CONTINUE                                                   00000600
0040          DO 49 J=1,N                                                    00000610
0041          DO 49 I=1,N                                                    00000620
0042           49 SY(J)=SY(J)+A(I,J)                                         00000630
0043          WRITE (3,40)                                                   00000640
0044           40 FORMAT ('0', 6X, 'THE VALUES OF SY(J) ARE')                00000650
0045          DO 47 J=1,N                                                    00000660
0046          WRITE (3, 800) J, SY(J)                                        00000670
0047        800 FORMAT ('0', 7X, 'SY(', I3, ')=', 1X, 10(F6.1, 3X))          00000680
0048           47 CONTINUE                                                   00000690
0049          SUMSX=0.0                                                      00000700
0050          SUMSY=0.0                                                      00000710
0051          DO 55 I=1,N                                                    00000720
0052           55 SUMSX=SUMSX+SX(I)                                          00000730
0053          DO 57 J=1,N                                                    00000740
0054           57 SUMSY=SUMSY+SY(J)                                          00000750
0055          TOTAL1=SUMSX                                                   00000760
0056          TOTAL2=SUMSY                                                   00000770
0057          WRITE (3,50) SUMSX, SUMSY, TOTAL1, TOTAL2                      00000780
0058           50 FORMAT ('0', 6X,('SUMSX=', 1X, F6.1), 6X, ('SUMSY=', 1X, F6.1),  00000790
              16X, ('TOTAL1=', 1X, F6.1), 6X, ('TOTAL2=', 1X, F6.1))       00000800
0059          DO 333 I=1,10                                                  00000810
0060          DO 333 J=1,10                                                  00000820
0061        333 T(I,J)=0.0                                                   00000830
0062          DO 75 I=1,N                                                    00000840
0063          DO 75 J=1,N                                                    00000850
```

```
0064          T(I,J)=A(I,J)/SX(I)                                              00000860
0065       75 CONTINUE                                                         00000870
0066          WRITE (3,60)                                                     00000880
0067       60 FORMAT ('0', 6X, 'TRANSITION MATRIX T=')                         00000890
0068          DO 61 I=1,N                                                      00000900
0069       61 WRITE (3,900) (T(I,J), J=1,N)                                    00000910
0070      900 FORMAT ('0', 6X, 10(F7.3, 2X))                                   00000920
0071          DO 444 J=1,10                                                    00000930
0072      444 PI(J)=0.0                                                        00000940
0073          DO 85 J=1,N                                                      00000950
0074       85 PI(J)=SY(J)/SUMSY                                                00000960
0075          WRITE (3,70) (PI(J), J=1,N)                                      00000970
0076       70 FORMAT ('0', 6X, 'FIXED VECTOR PI=', 2X, 10(F7.3, 2X))           00000980
0077          DO 555 I=1,10                                                    00000990
0078          DO 555 J=1,10                                                    00001000
0079      555 E(I,J)=0.0                                                       00001010
0080          DO 95 I=1,N                                                      00001020
0081          DO 95 J=1,N                                                      00001030
0082          E(I,J)=SX(I)*PI(J)                                               00001040
0083       95 CONTINUE                                                         00001050
0084          WRITE (3,80)                                                     00001060
0085       80 FORMAT ('0', 6X, 'EXPECTED MATRIX E=')                           00001070
0086          DO 81 I=1,N                                                      00001080
0087       81 WRITE (3,700) (E(I,J), J=1,N)                                    00001090
0088      700 FORMAT ('0', 6X, 10(F7.3, 2X))                                   00001100
0089          CHISQR(I,J)=0.0                                                  00001110
0090          DO 105 I=1,N                                                     00001120
0091          DO 105 J=1,N                                                     00001130
0092          CHISQR(I,J)=(E(I,J)-A(I,J))**2/E(I,J)                            00001140
0093      105 CONTINUE                                                         00001150
0094          WRITE (3,500)                                                    00001160
0095      500 FORMAT ('0', 6X, 'INDIVIDUAL CHI SQUARE IS CHISQR=')             00001170
0096          DO 91 I=1,N                                                      00001180
0097       91 WRITE (3,90) (CHISQR(I,J), J=1,N)                                00001190
0098       90 FORMAT ('0', 6X, 10(F7.3))                                       00001200
0099          SUMCHI=0.0                                                       00001210
0100          DO 110 I=1,N                                                     00001220
0101          DO 110 J=1,N                                                     00001230
0102      110 SUMCHI=SUMCHI+ CHISQR(I,J)                                       00001240
0103          WRITE (3,300) SUMCHI                                             00001250
0104      300 FORMAT ('0', 6X, 'SUMCHI=', 2X, F8.3)                           00001260
0105          WRITE (3,1000)                                                   00001270
0106     1000 FORMAT ('0', 15X, 'A(I,J) VS E(I,J)')                           00001280
```

```
0107            WRITE (3, 4000)                                                  00001290
0108         4000 FORMAT ('0', 6X, 'THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,00001300
                 1J)=')                                                          00001310
                 DO 125 I=1,N                                                    00001320
0109             WRITE (3,2000) (A(I,J), J=1,N)                                  00001330
0110         125 FORMAT ('0', 6X, 10(F7.3, 2X))                                  00001340
0111         2000 WRITE (3, 5000)                                                00001350
0112            FORMAT ('0', 6X, 'THE EXPECTED TRANSITION MATRIX E(I,J)=')       00001360
0113         5000 DO 135 I=1,N                                                   00001370
0114            WRITE (3,3000) (E(I,J), J=1,N)                                   00001380
0115         135 FORMAT ('0', 6X, 10(F7.3, 2X))                                  00001390
0116         3000 GO TO 111                                                      00001400
0117            STOP                                                            00001410
0118         6000 END                                                           00001420
0119
```

APPENDIX III

A sample calculation of test for randomness of crystals in a rock

A sample calculation of test for randomness of crystals in a rock:

SAMPLE J- 35

THE OBSERVED TRANSITION AS TRANSITION MATRIX A (I, J)=

	F	H	C	A	D	O
F	51.000	6.000	39.000	14.000	26.000	23.000
H	4.000	1.000	4.000	1.000	0.0	2.000
C	42.000	3.000	12.000	1.000	21.000	26.000
A	12.000	0.0	1.000	4.000	6.000	5.000
D	21.000	2.000	24.000	5.000	0.0	25.000
O	25.000	0.0	27.000	5.000	24.000	38.000

THE VALUES OF SX(I) ARE

SX(1)= 159.0
SX(2)= 12.0
SX(3)= 105.0
SX(4)= 28.0
SX(5)= 77.0
SX(6)= 119.0

THE VALUES OF SY(J) ARE

SY(1)= 155.0
SY(2)= 12.0
SY(3)= 107.0
SY(4)= 30.0
SY(5)= 77.0
SY(6)= 119.0

SUMSX= 500.0 SUMSY= 500.0

TOTAL1= 500.0 TOTAL2= 500.0

PROBABILITY TRANSITION MATRIX T=

	F	H	C	A	D	O
F	0.321	0.038	0.245	0.088	0.164	0.145
H	0.333	0.083	0.333	0.083	0.0	0.167
C	0.400	0.029	0.114	0.010	0.200	0.248
A	0.429	0.0	0.036	0.143	0.214	0.179
D	0.273	0.026	0.312	0.065	0.0	0.325
O	0.210	0.0	0.227	0.042	0.202	0.319

FIXED VECTOR PI= 0.310 0.024 0.214 0.060 0.154 0.238

EXPECTED MATRIX E=

F	49.290	3.816	34.026	9.540	24.486	37.842
H	3.720	0.288	2.568	0.720	1.848	2.856
C	32.550	2.520	22.470	6.300	16.170	24.990
A	8.680	0.672	5.992	1.680	4.312	6.664
D	23.870	1.848	16.478	4.620	11.858	18.326
O	36.890	2.856	25.466	7.140	18.326	28.322

INDIVIDUAL CHI SQUARE IS CHISQR=

F	0.059	1.250	0.727	2.085	0.094	5.821
H	0.021	1.760	0.799	0.109	1.848	0.257
C	2.744	0.091	4.879	4.459	1.443	0.041
A	1.270	0.672	4.159	3.204	0.661	0.416
D	0.345	0.013	3.434	0.031	11.858	2.431
O	3.832	2.856	0.092	0.641	1.757	3.307

SUMCHI=$\Sigma\chi^2_M$=69.463

The distribution of crystals in this rock is not random since:

$$\left[\Sigma\chi^2_M = 69.463\right] > \left[\chi^2_{0.95}(\nu=25) = 37.652\right].$$

APPENDIX IV

Observed and expected transition matrices for charnockitic granulites from the Adirondack Mts., New York

The observed and expected transition matrices for rock sample J-35. F--feldspar, H--orthopyroxene, C--clinopyroxene, A--amphibole, G--garnet, D--opaque minerals, O--others.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	F	H	C	A	G	D	O
F	51.000	6.000	39.000	14.000	7.000	26.000	16.000
H	4.000	1.000	4.000	1.000	0.0	0.0	2.000
C	42.000	3.000	12.000	1.000	16.000	21.000	10.000
A	12.000	0.0	1.000	4.000	2.000	6.000	3.000
G	9.000	0.0	15.000	2.000	0.0	16.000	15.000
D	21.000	2.000	24.000	5.000	16.000	0.0	9.000
O	16.000	0.0	12.000	3.000	18.000	8.000	5.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

F	49.290	3.816	34.026	9.540	18.762	24.486	19.080
H	3.720	0.288	2.568	0.720	1.416	1.848	1.440
C	32.550	2.520	22.470	6.300	12.390	16.170	12.600
A	8.680	0.672	5.992	1.680	3.304	4.312	3.360
G	17.670	1.368	12.198	3.420	6.726	8.778	6.840
D	23.870	1.848	16.478	4.620	9.086	11.858	9.240
O	19.220	1.488	13.268	3.720	7.316	9.548	7.440

The observed and expected transition matrices for rock sample J-44.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	F	H	C	A	D	O
F	358.000	29.000	20.000	20.000	14.000	20.000
H	32.000	6.000	7.000	5.000	4.000	9.000
C	19.000	6.000	4.000	3.000	6.000	7.000
A	18.000	3.000	4.000	1.000	5.000	7.000
D	13.000	8.000	3.000	3.000	0.0	7.000
O	18.000	11.000	7.000	7.000	5.000	2.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

F	241.311	43.178	30.841	26.729	23.302	35.639
H	42.919	5.420	3.878	3.361	2.930	4.482
C	30.657	3.878	2.770	2.401	2.093	3.201
A	25.868	3.275	2.339	2.027	1.767	2.703
D	23.163	2.930	2.093	1.814	1.581	2.419
O	34.063	4.309	3.078	2.668	2.326	3.557

The observed and expected transition matrices

for rock sample J-50.

THE OBSERVED TRANSITION AS TRANSITION TABLE A[I,J]=

	P	H	C	A	C	D	O
P	247.000	6.000	40.000	12.000	26.000	13.000	9.000
H	5.000	0.0	3.0	2.000	2.000	1.000	1.000
C	40.000	1.000	12.000	6.000	8.000	4.000	8.000
A	14.000	2.000	4.000	4.000	5.000	7.000	3.000
C	21.000	1.000	13.000	2.000	0.0	6.000	6.000
D	16.000	1.000	6.000	7.000	5.000	0.0	4.000
O	7.000	1.000	4.000	6.000	5.000	8.000	1.000

THE EXPECTED TRANSITION MATRIX E[I,J]=

P	204.862	7.025	46.247	22.831	29.856	23.416	18.733
H	6.385	0.219	1.441	0.711	0.930	0.730	0.584
C	45.854	1.572	10.350	5.109	6.682	5.240	4.192
A	22.637	3.776	5.109	2.522	3.299	2.587	2.070
C	28.441	0.975	6.420	3.169	4.144	3.250	2.600
D	23.217	0.796	5.240	2.587	3.383	2.653	2.123
O	18.574	0.637	4.192	2.070	2.706	2.123	1.698

The observed and expected transition matrices

for rock sample J-63A.

THE OBSERVED TRANSITION AS TRANSITION TABLE A[I,J]=

	P	H	C	C	D	O
P	180.000	7.000	39.000	94.000	20.000	36.000
H	8.000	2.000	6.000	6.000	3.000	4.000
C	50.000	7.000	21.000	21.000	10.000	12.000
C	87.000	7.000	32.000	0.0	20.000	20.000
D	14.000	2.000	15.000	22.000	0.0	10.000
O	34.000	4.000	13.000	21.000	13.000	6.000

THE EXPECTED TRANSITION MATRIX E[I,J]=

P	165.778	12.889	56.000	72.889	29.333	39.111
H	12.786	0.994	4.319	5.622	2.262	3.017
C	53.349	4.148	18.021	23.456	9.440	12.586
C	73.189	5.690	24.723	32.180	12.953	17.267
D	27.777	2.160	9.383	12.213	4.915	6.553
O	40.122	3.119	13.553	17.641	7.099	9.466

The observed and expected transition matrices for rock sample J-66.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	F	H	C	G	D	O
F	180.000	23.000	51.000	72.000	31.000	43.000
H	25.000	7.000	12.000	2.000	13.000	13.000
C	44.000	15.000	22.000	11.000	16.000	18.000
G	71.000	2.000	11.000	0.0	34.000	14.000
D	37.000	7.000	16.000	27.000	0.0	18.000
O	47.000	17.000	11.000	20.000	14.000	23.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

F	167.115	29.269	50.879	54.632	44.674	53.361
H	30.081	5.266	9.158	9.828	8.041	9.605
C	52.641	9.251	16.027	17.200	14.072	16.809
G	55.148	9.692	16.790	18.019	14.743	17.609
D	43.868	7.709	13.356	14.333	11.727	14.007
O	55.148	9.692	16.790	18.019	14.743	17.609

The observed and expected transition matrices for rock sample J-80.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	F	H	C	A	G	D	O
F	60.000	20.000	8.000	15.000	13.000	22.000	26.000
H	26.000	67.000	44.000	18.000	2.000	35.000	26.000
C	18.000	38.000	13.000	5.000	7.000	21.000	17.000
A	12.000	21.000	9.000	9.000	3.000	11.000	7.000
G	9.000	8.000	4.000	7.000	0.0	5.000	4.000
D	24.000	42.000	11.000	8.000	10.000	0.0	26.000
O	16.000	23.000	24.000	9.000	6.000	28.000	10.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

F	32.138	42.656	22.010	13.829	7.012	23.762	22.594
H	42.720	56.701	29.257	18.382	9.321	31.587	30.033
C	22.340	29.651	15.299	9.613	4.874	16.518	15.705
A	14.109	18.727	9.663	6.071	3.078	10.432	9.919
G	7.251	9.624	4.966	3.120	1.582	5.361	5.097
D	23.711	31.471	16.239	10.203	5.173	17.532	16.670
O	22.732	30.171	15.568	9.781	4.960	16.808	15.981

The observed and expected transition matrices for rock sample J-81.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	F	H	C	G	D	O
F	148.000	34.000	33.000	31.000	21.000	20.000
H	36.000	29.000	26.000	25.000	27.000	15.000
C	30.000	49.000	35.000	12.000	23.000	23.000
G	27.000	15.000	23.000	0.0	22.000	9.000
D	21.000	28.000	17.000	19.000	0.0	18.000
O	20.000	15.000	26.000	9.000	13.000	6.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

F	89.430	53.912	50.740	30.444	33.615	28.859
H	49.233	29.680	27.934	16.760	18.506	15.887
C	53.596	32.309	30.409	18.245	20.146	17.295
G	29.914	18.033	16.972	10.183	11.244	9.653
D	32.055	19.328	18.210	10.926	12.064	10.357
O	27.733	16.718	15.735	9.441	10.424	8.949

The observed and expected transition matrices for rock sample J-92.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	F	H	C	A	D	O
F	333.000	38.000	13.000	3.000	12.000	44.000
H	35.000	3.000	3.000	1.000	7.000	11.000
C	11.000	4.000	1.000	1.000	1.000	0.0
A	4.000	1.000	1.000	0.0	1.000	0.0
D	13.000	8.000	3.0	1.000	3.0	2.000
O	45.000	8.000	0.0	1.000	2.000	13.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

F	314.594	44.229	12.841	4.994	16.407	49.936
H	42.609	5.990	1.739	0.676	2.222	6.763
C	12.783	1.797	0.522	0.203	0.667	2.029
A	4.971	0.699	0.203	0.079	0.259	0.789
D	17.043	2.396	0.696	0.271	0.889	2.705
O	49.000	6.889	2.000	0.778	2.556	7.778

The observed and expected transition matrices for rock sample J-99.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	P	C	A	G	D	O
P	117.000	66.000	47.000	39.000	29.000	23.000
C	58.000	33.000	35.000	40.000	19.000	23.000
A	59.000	32.000	14.000	4.000	21.000	11.000
G	39.000	34.000	10.000	1.000	23.000	19.000
D	33.000	23.000	15.000	22.000	0.0	15.000
O	24.000	22.000	13.000	20.000	11.000	2.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

P	105.374	67.322	43.581	40.679	33.498	30.246
C	68.280	43.623	28.239	26.553	21.706	19.599
A	44.216	28.313	19.228	17.234	14.088	12.720
G	41.362	26.426	17.106	16.085	13.149	11.877
D	34.468	22.021	14.255	13.404	10.957	9.894
O	30.201	19.295	12.493	11.745	9.601	8.669

The observed and expected transition matrices for rock sample J-103.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	P	H	C	A	D	O
P	250.000	30.000	45.000	17.000	27.000	24.000
H	36.000	11.000	11.000	2.000	6.000	9.000
C	41.000	11.000	8.000	4.000	6.000	10.000
A	17.000	4.000	2.000	3.000	1.000	0.0
D	24.000	9.000	7.000	1.000	0.0	2.000
O	24.000	10.000	9.000	0.0	4.000	3.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

P	230.623	44.124	48.243	15.885	25.886	28.240
H	44.012	8.421	9.207	3.031	4.940	5.389
C	46.546	8.902	9.820	3.234	5.269	5.749
A	15.844	3.031	3.314	1.091	1.778	1.940
D	25.234	4.828	5.278	1.738	2.832	3.090
O	29.341	5.614	6.138	2.021	3.293	3.593

The observed and expected transition matrices for rock sample J-106.

THE OBSERVED TRANSITION AS TRANSITION TABLE A(I,J)=

	F	H	C	A	D	O
F	286.000	55.000	38.000	31.000	29.000	29.000
H	47.000	5.000	8.000	1.000	10.000	9.000
C	48.000	3.000	6.000	5.000	8.000	3.000
A	24.000	3.000	6.000	1.000	7.000	7.000
D	35.000	7.000	11.000	4.000	0.0	3.000
O	28.000	7.000	5.000	5.000	5.000	1.000

THE EXPECTED TRANSITION MATRIX E(I,J)=

F	279.724	47.816	46.023	28.092	35.264	31.080
H	47.816	8.174	7.867	4.802	6.028	5.313
C	43.632	7.458	7.179	4.382	5.501	4.848
A	28.690	4.904	4.720	2.881	3.617	3.188
D	35.862	6.130	5.900	3.602	4.521	3.985
O	32.276	5.517	5.310	3.241	4.069	3.586

APPENDIX V

Transition series for

charnockitic granulites from the Adirondack Mts., New York

Abbreviations used in Appendix V

1. Mineral

F = feldspar
H = orthopyroxene
C = clinopyroxene
A = amphibole
G = garnet
D = opaque minerals
O = all other minerals, e.g. biotite + apatite + zircon

2. Spatial distribution

NR = not random
R = random
Rg = regular
ARg= anti-regular
C = clustered
AC = anti-clustered

3. Uncertainty of spatial distribution indicated by

(s) = similar values of chi squares and/or similar values of observed and expected transitions
(l) = very low values of observed and expected transitions, e.g. less than 4 or 5

Transition matrices of transition series I for rock sample J-35. Total transitions measured = 500

Transition Series I (in matrix form)	Degrees of freedom	$\Sigma\chi^2_M$	$\chi^2_{.95}$	Distribution
FHCAGDO	36	113.126	50.998	NR
FHCADO	25	69.463	37.652	"
FHCAO	16	42.224	26.296	"
FHCO	9	20.005	16.919	"
FHAO	"	17.746	"	"
FCAO	"	32.657	"	"
HCAO	"	28.588	"	"
FHO	4	4.567	9.488	R
FCO	"	11.606	"	NR
FAO	"	12.217	"	"
HCO	"	10.641	"	"
HAO	"	6.202	"	R
CAO	"	25.037	"	NR
HO	1	1.848	3.841	R
AO	"	3.610	"	" (s)
CO	"	7.857	"	NR
FO	"	0.126	"	R

Transition matrices of
transition series II for rock sample J-35

Transition series II	$\Sigma\chi^2_M$	$\Sigma\chi^2_{.95}$	Observed	Expected	Distribution
Two-phase Transition matrices					
AA			4	1.680	R (1)
CC			12	22.470	AC
HH			1	0.288	R (1)
FF			51	49.290	"
FH { FH			6	3.720	"
FH { HF			4	3.720	"
FC { FC			39	34.036	Rg
FC { CF			42	32.550	
FA { FA			14	9.540	"
FA { AF			12	8.680	
HC { HC			4	2.568	" (1)
HC { CH			3	2.520	
HA { HA			1	0.720	R (1)
HA { AH			0	0.672	"
CA { CA			1	6.300	ARg (1)
CA { AC			1	5.992	"
HO { HO	1.848	3.841	11	11.712	R (s)
HO { OH			11	11.712	
AO { AO	3.610	"	24	26.320	" (s)
AO { OA			26	28.320	
CO { CO	7.857		93	82.530	Rg
CO { OC			95	84.530	
FO { FO	0.126	"	108	109.710	R
FO { OF			104	105.710	

Transition matrices of transition series I for rock J-44. Total transition measurements = 731

Transition series I	Degrees of freedom	$\Sigma\chi^2_M$	$\chi^2_{.95}$	Distribution
FHCADO	25	134.620	37.652	NR
FHCAO	16	118.950	26.296	"
FHCO	9	99.532	16.919	"
FHAO	"	108.667	"	"
FCAO	"	99.964	"	"
HCAO	"	9.319	"	R
FHO	4	97.644	9.488	NR
FCO	"	94.486	"	"
FAO	"	97.831	"	"
HCO	"	5.549	"	R
HAO	"	1.559	"	"
CAO	"	2.716	"	"
HO	1	0.072	3.841	"
AO	"	0.580	"	"
CO	"	0.620	"	"
FO	"	93.887	"	NR

Transition matrices of transition series II for rock sample J-44

Transition series II Two-phase Transition matrices		$\Sigma\chi^2_M$	$\chi^2_{.95}$	Observed	Expected	Distribution
AA				1	2.027	R (1)
CC				4	2.770	" (1)
HH				6	5.436	"
FF				398	341.310	C
FH	FH			29	43.178	ARg
	HF			32	42.919	
FC	FC			20	30.841	"
	CF			19	30.657	
FA	FA			20	26.729	"
	AF			18	25.888	
HC	HC			7	3.878	R
	CH			6	3.878	
HA	HA			5	3.361	" (1)
	AH			3	3.275	
CA	CA			3	2.401	" (1)
	AC			4	2.339	
HO	HO	0.072	3.841	57	57.570	" (s)
	OH			57	57.570	
AO	AO	0.580	"	37	35.973	" (s)
	OA			38	36.973	
CO	CO	0.620	"	41	42.230	" (s)
	OC			41	42.230	
FO	FO	93.887	"	103	159.689	ARg
	OF			100	159.689	

Transition matrices of transition series I for rock sample J-50. Total transition measurements = 603

Transition	Series I	Degrees of freedom	Σx^2_M	$x^2_{.95}$	Distribution
FHCAGDO		36	118.266	50.998	NR
FHCAGO		25	97.766	37.652	"
FHCAO		16	68.271	26.296	"
FHCO		9	62.679	16.919	"
FHAO		"	55.843	"	"
FCAO		"	62.927	"	"
HCAO		"	8.315	"	R
FHO		4	50.467	9.488	NR
FCO		"	58.403	"	"
FAO		"	52.790	"	"
HCO		"	2.506	"	R
HAO		"	6.000	"	"
CAO		"	1.836	"	"
HO		1	0.228	3.841	"
AO		"	0.989	"	"
CO		"	0.348	"	"
FO		"	49.748	"	NR

Transition matrices of transiton series II for rock sample J-50

Transition Series II Two-phase Transition matrices		Σx_M^2	$x^2_{.95}$	Observed	Expected	Distribution
AA				4	2.522	R
CC				12	10.350	"
HH				0	0.219	" (1)
FF				247	204.892	C
FH	FH			6	7.025	ARg (s)
	HF			5	6.385	
FC	FC			40	46.247	"
	CF			40	45.854	
FA	FA			12	22.831	"
	AF			14	22.637	
HC	HC			0	1.441	R (1)
	CH			1	1.572	
HA	HA			2	0.711	" (1)
	AH			2	0.776	
CA	CA			6	5.109	" (s)
	AC			4	5.109	
HO	HO	0.228	3.841	11	10.781	"
	OH			12	11.781	
AO	AO	0.989	"	35	36.478	"
	OA			35	36.478	
CO	CO	0.348	"	67	68.650	"
	OC			67	68.650	
FO	FO	49.748	"	106	148.108	ARg
	OF			103	145.108	

Transition matrices of transition series I for rock sample J-63A. Total transition measurements = 846

Transition Series I	Degrees of freedom	Σx^2_M	$x^2_{.95}$	Distribution
FHCGDO	25	99.730	37.652	NR
FHCGO	16	77.686	26.296	"
FHCO	9	20.674	16.919	"
FHO	4	10.136	9.488	"
FCO	"	11.756	"	"
HCO	"	5.735	"	R
HO	1	1.091	3.841	"
CO	"	0.675	"	"
FO	"	3.928	"	NR (s)

Transition matrics of transition series II for rock sample J-63A

Transition Series II Two-phase Transition matrices		Σx^2_M	$x^2_{.95}$	Observed	Expected	Distribution
CC				21	18.021	R
HH				2	0.994	" (1)
FF				180	165.778	C (s)
FH	FH			7	12.889	ARg
	HF			8	12.786	
FC	FC			39	56.000	"
	CF			50	53.349	
HC	HC			6	4.319	R
	CH			7	4.148	
HO	HO	1.091	3.841	27	28.006	"
	OH			27	28.006	
CO	CO	0.675	"	100	102.979	"
	OC			105	107.979	
FO	FO	3.928	"	196	210.222	ARg(s)
	OF			193	207.222	

Transition matrices of transition series I for rock sample J-66. Total transition measurements = 967

Transition Series I	Degrees of freedom	ΣX^2_M	$X^2_{.95}$	Distribution
FHCGDO	25	129.616	37.652	NR
FHCGO	16	86.213	26.296	"
FHCO	9	14.733	16.919	R
FHO	4	5.237	9.488	"
FCO	"	6.984	"	"
HCO	"	11.172	"	NR
HO	1	0.648	3.841	R
CO	"	2.933	"	"
FO	"	2.911	"	"

Transition matrices for transition series II for rock sample J-66

Transition Series II Two-phases Transition matrices		Σx^2_M	$x^2_{.95}$	Observed	Expected	Distribution
CC				22	16.027	R
HH				7	5.286	"
FF				180	167.115	"
FH	FH			23	29.369	"
	HF			25	30.081	
FC	FC			51	50.879	" (s)
	CF			44	52.641	
HC	HC			12	9.158	Rg
	CH			15	9.251	
HO	HO	0.648	3.841	65	66.714	R
	OH			64	65.714	
CO	CO	2.933	"	104	109.973	"
	OC			101	106.973	
FO	FO	2.911	"	220	232.885	"
	OF			224	236.885	

Transition matrices of transition series I for rock sample J-80. Total transition measurements = 842

Transition Series I	Degrees of freedom	Σx^2_M	$x^2_{.95}$	Distribution
FHCAGDO	36	143.926	50.998	NR
FHCAGO	25	95.660	37.652	"
FHCAO	16	71.942	26.296	"
FHCO	9	67.405	16.919	"
FHAO	"	50.548	"	"
FCAO	"	51.773	"	"
HCAO	"	32.316	"	"
FHO	4	47.914	9.488	NR
FCO	"	45.243	"	"
FAO	"	41.094	"	"
HCO	"	25.291	"	"
HAO	"	6.701	"	R
CAO	"	4.838	"	"
HO	1	3.412	3.841	"
AO	"	1.687	"	"
CO	"	0.462	"	"
FO	"	37.310	"	NR

Transition matrices of
transition series II for rock sample J-80

Transition Series II Two-phase Transition matrices		$\Sigma\chi^2_M$	$\chi^2_{.95}$	Observed	Expected	Distribution
AA				9	6.071	R
CC				13	15.299	"
HH				67	56.701	"
FF				60	32.138	C
FH	FH			20	42.656	ARg
	HF			26	42.720	
FC	FC			8	22.009	"
	CF			18	22.340	
FA	FA			15	13.829	" (s)
	AF			12	14.109	
HC	HC			44	29.257	Rg
	CH			38	29.651	
HA	HA			18	18.382	R (s)
	AH			21	18.727	
CA	CA			5	9.613	"
	AC			9	9.663	
HO	HO	3.412	3.841	151	161.299	"
	OH			152	162.299	
AO	AO	1.687	"	63	65.929	"
	OA			62	64.929	
CO	CO	0.462	"	101	98.701	"
	OC			100	97.701	
FO	FO	37.310	"	104	131.862	ARg
	OF			105	132.862	

Transition matrices of transition series I for rock sample J-81. Total transition measurements=905

Transition Series I	Degrees of freedom	$\Sigma\chi^2_M$	$\chi^2_{.95}$	Distribution
FHCGDO	25	160.777	37.652	NR
FHCGO	16	123.631	26.296	"
FHCO	9	95.138	16.919	"
FHO	4	89.122	9.488	"
FCO	"	84.350	"	"
HCO	"	17.074	"	"
HO	1	13.108	3.841	"
CO	"	0.197	"	R
FO	"	81.600	"	NR

Transition matrices of
transition series II of rock samples J-81

Transition Series II Two-phase Transition matrices		$\Sigma\chi^2_M$	$\chi^2_{.95}$	Observed	Expected	Distribution
CC				26	27.934	R
HH				49	32.309	C
FF				148	89.430	C
FH	FH			34	53.912	ARg
	HF			30	53.596	
FC	FC			33	50.740	"
	CF			36	49.233	
HC	HC			35	30.409	Rg
	CH			29	29.680	
HO	HO	13.108	3.841	123	139.691	ARg
	OH			121	137.691	
CO	CO	0.197	"	132	130.066	R
	OC			134	132.066	
FO	FO	81.600	"	139	197.570	ARg
	OF			134	192.570	

Transition matrices of transition series I for rock sample J-92. Total transition measurements=621

Transition Series I	Degrees of freedom	$\Sigma\chi^2_M$	$\chi^2_{.95}$	Distribution
FHCADO	25	60.634	37.652	NR
FHCAO	16	38.519	26.296	"
FHCO	9	28.808	16.919	"
FHAO	"	28.638	"	"
FCAO	"	21.880	"	"
HCAO	"	13.784	"	R
FHO	4	25.137	9.488	NR
FCO	"	14.768	"	"
FAO	"	14.575	"	"
HCO	"	6.267	"	R
HAO	"	2.150	"	"
CAO	"	7.129	"	"
HO	1	1.836	3.841	"
AO	"	0.081	"	"
CO	"	0.465	"	"
FO	"	12.961	"	NR

Transition matrices of
transition series II for rock sample J-92

Transition Series II Two-phase Transition matrices	$\Sigma\chi^2_M$	$\chi^2_{.95}$	Observed	Expected	Distribution
AA			0	0.079	R
CC			1	0.522	"
HH			3	5.990	"
FF			333	314.594	C
FH {FH			38	44.229	ARg
FH {HF			35	42.609	ARg
FC {FC			13	12.841	" (s)
FC {CF			11	12.783	" (s)
FA {FA			3	4.994	" (1)
FA {AF			4	4.971	" (1)
HC {HC			3	1.739	R (1)
HC {CH			4	1.797	R (1)
HA {HA			1	0.676	" (1)
HA {AH			1	0.699	" (1)
CA {CA			1	0.203	" (1)
CA {AC			1	0.203	" (1)
HO {HO	1.836	3.841	57	54.010	"
HO {OH	1.836	3.841	59	56.010	"
AO {AO	0.081	"	7	6.921	"
AO {OA	0.081	"	7	6.921	"
CO {CO	0.465	"	17	17.478	"
CO {OC	0.465	"	17	17.478	"
PO {PO	12.961	"	110	128.406	ARg
PO {OP	12.961	"	108	126.406	ARg

Transition matrices of transition series I for rock sample J-99. Total transition measurements=987

Transition Series I	Degrees of freedom	ΣX_M^2	$X^2_{.95}$	Distribution
FCAGDO	25	97.760	37.652	NR
FCAGO	16	77.141	26.296	"
FCAO	9	20.037	16.919	"
FCO	4	12.734	9.488	"
FAO	"	9.553	"	"
CAO	"	6.295	"	R
AO	1	1.370	3.841	"
CO	"	4.148	"	NR
FO	"	2.830	"	R

Transition matrices of transition series II for rock sample J-99.

Transition Series II Two-phase Transition matrices		$\Sigma\chi^2_M$	$\chi^2_{.95}$	Observed	Expected	Distribution
AA				14	18.328	R
CC				33	43.623	AC
FF				117	105.374	R
FC	FC			66	67.322	ARg
	CF			58	68.280	
FA	FA			47	43.581	Rg
	AF			53	44.316	
CA	CA			35	28.239	R
	AC			32	28.313	
AO	AO	1.370	3.841	121	116.672	ARg
	OA			120	115.672	
CO	CO	4.148	"	175	164.377	Rg
	OC			174	163.377	
FO	FO	2.830	"	204	215.626	R
	OF			207	218.626	

Transition matrices of transition series I for rock sample J-103. Total transition measurements=668

Transition Series I	Degrees of freedom	$\Sigma\chi^2_M$	$\chi^2_{.95}$	Distribution
FHCADO	25	39.993	37.652	NR
FHCAO	16	34.711	26.296	"
FHCO	9	24.302	16.919	"
FHAO	"	25.622	"	"
FCAO	"	22.747	"	"
HCAO	"	7.811	"	R
FHO	4	16.976	9.488	NR
FCO	"	11.697	"	"
FAO	"	18.741	"	"
HCO	"	2.684	"	R
HAO	"	5.461	"	"
CAO	"	4.870	"	"
HO	1	0.994	3.841	"
AO	"	3.625	"	" (s)
CO	"	0.437	"	"
FO	"	9.572	"	NR

Transition matrices of
transition series II for rock sample J-103

Transition Series II Two-phase Transition matrices		$\Sigma\chi^2_M$	$\chi^2_{.95}$	Observed	Expected	Distribution
AA				3	1.091	R (1)
CC				8	9.820	"
HH				11	8.421	"
FF				250	230.623	C
FH	FH			30	44.124	ARg
	HF			36	44.012	
FC	FC			45	48.242	"
	CF			41	46.946	
FA	FA			17	15.885	Rg
	AF			17	15.844	
HC	HC			11	9.207	R
	CH			11	8.982	
HA	HA			2	3.031	" (1)
	AH			4	3.031	
CA	CA			4	3.234	" (1)
	AC			2	3.314	
HO	HO	0.994	3.841	64	66.569	"
	OH			64	66.569	
AO	AO	3.625	"	24	25.909	"
	OA			24	25.909	
CO	CO	0.437	"	72	70.180	"
	OC			74	72.180	
FO	FO	9.579	"	143	162.377	ARg
	OF			142	161.377	

Transition matrices of transition series I for rock sample J-106. Total transition measurements=783

Transition Series I	Degrees of freedom	$\Sigma\chi^2_M$	$\chi^2_{.95}$	Distribution
FHCADO	25	44.354	37.652	NR
FHCAO	16	37.642	26.296	"
FHCO	9	14.682	16.919	R
FHAO	"	21.213	"	NR
FCAO	"	11.947	"	R
HCAO	"	13.685	"	"
FHO	4	6.573	9.488	"
FCO	"	7.019	"	"
FAO	"	5.748	"	"
HCO	"	5.854	"	"
HAO	"	8.710	"	"
CAO	"	1.913	"	"
HO	1	1.529	3.841	"
AO	"	1.392	"	"
CO	"	0.237	"	"
FO	"	0.870	"	"

Transition matrices of
transition series of rock sample J-106

Transition Series II Two-phase Transition matrices		$\Sigma\chi^2_M$	$\chi^2_{.95}$	Observed	Expected	Distribution
AA				1	2.881	R (1)
CC				6	7.179	" (s)
HH				5	8.174	"
FF				286	279.724	"
FH	FH			55	47.816	"
	HF			47	47.816	
FC	FC			38	46.023	"
	CF			48	43.632	
FA	FA			31	28.092	"
	AF			24	28.690	
HC	HC			8	7.867	"
	CH			3	7.458	
HA	HA			1	4.802	" (1)
	AH			3	4.904	
CA	CA			5	4.382	"
	AC			6	4.720	
HO	HO	1.529	3.841	75	71.826	"
	OH			75	71.826	
AO	AO	1.392	"	47	45.119	"
	OA			46	44.119	
CO	CO	0.237	"	67	65.821	"
	OC			71	69.821	
FO	FO	0.870	"	182	188.276	"
	OF			182	188.276	

APPENDIX VI

Mass-balance of chemical reactions

36-40

Mass-balance of chemical reactions

Short form

Bio + Amph + Gar = Opx
Amph = Cpx + Gar + Bio
Amph = Opx + Cpx + Bio
Bio + Gar + Cpx = Opx
Amph + Gar = Opx + Cpx

Mass-balanced form

1.0 Qtz + 0.04671 Bio + 0.24333 Amph + 0.16942 Gar = 0.98212 Opx + 0.17574 Kf + 0.49233 An + 0.13157 Ab + 0.02761 Mt + 0.09272 Ilm + 0.33675 H_2O

0.53957 Amph + 0.61956 Qtz + 0.05387 Kf = 1.0 Cpx + 0.0696 Gar + 0.12945 Bio + 0.14688 An + 0.23387 Ab + 0.11013 Mt + 0.08176 Ilm + 0.28067 H_2O

0.63 Amph + 0.99121 Qtz = 0.365 Opx + 1.0 Cpx + 0.11209 Bio + 0.32985 An + 0.28276 Ab + 0.01145 Kf + 0.12039 Mt + 0.11621 Ilm + 0.40582 H_2O

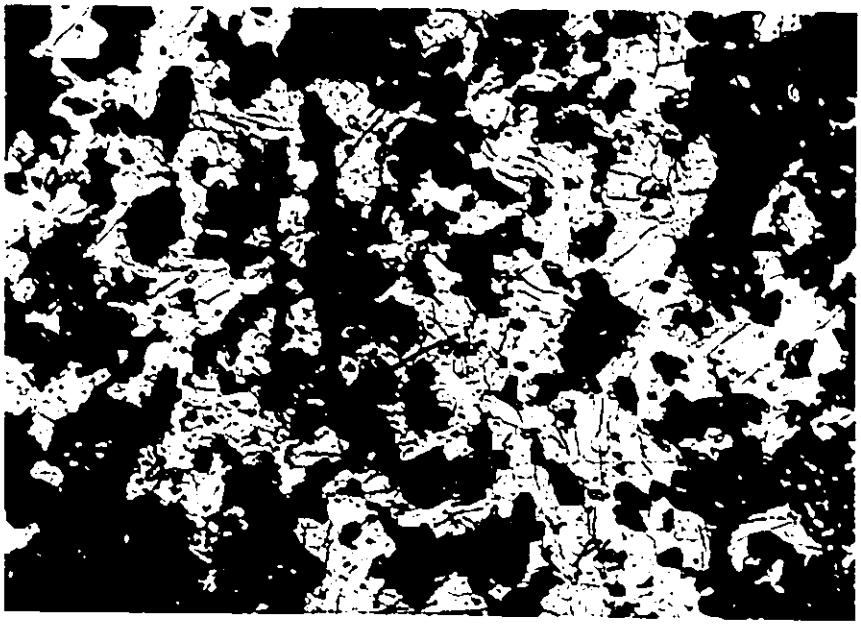
0.107 Bio + 0.20142 Gar + 0.45918 Cpx + 0.73372 Qtz + 0.02246 Mt = 1.0 Opx + 0.43385 An + 0.02658 Ab + 0.20368 Kf + 0.05686 Ilm + 0.214 H_2O

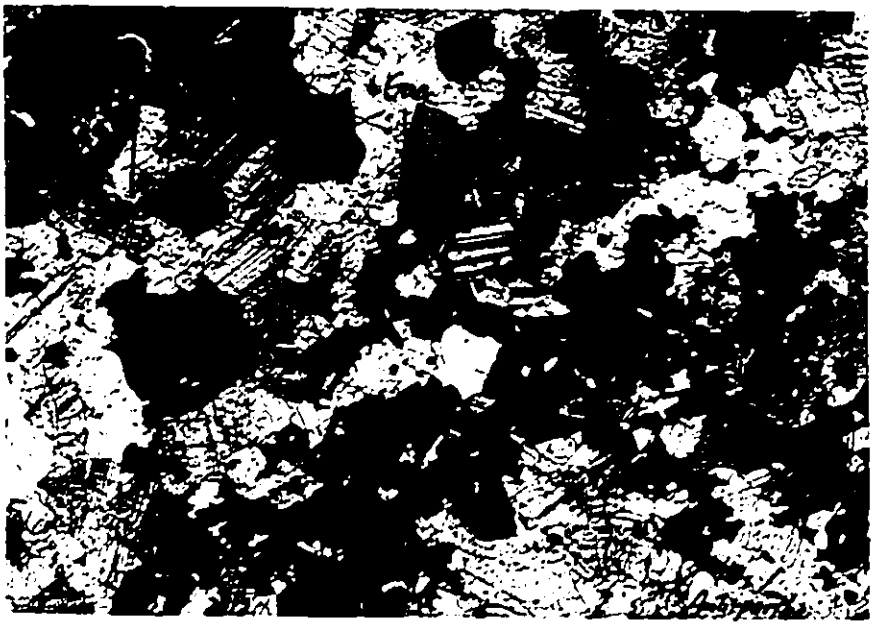
0.358 Amph + 0.11989 Gar + 1.0 Qtz = 0.80267 Opx + 0.29492 Cpx + 0.44569 An + 0.1765 Ab + 0.12774 Kf + 0.05505 Mt + 0.09989 Ilm + 0.358 H_2O

PLATES

J-35 Representative of the plagioclase-two pyroxene-garnet-amphibole-biotite-quartz-iron oxide mafic granulites (noritic to gabbroic) showing fine grained, granoblastic texture. Certain mafic minerals appear to associate preferentially. (Plane polarized light)

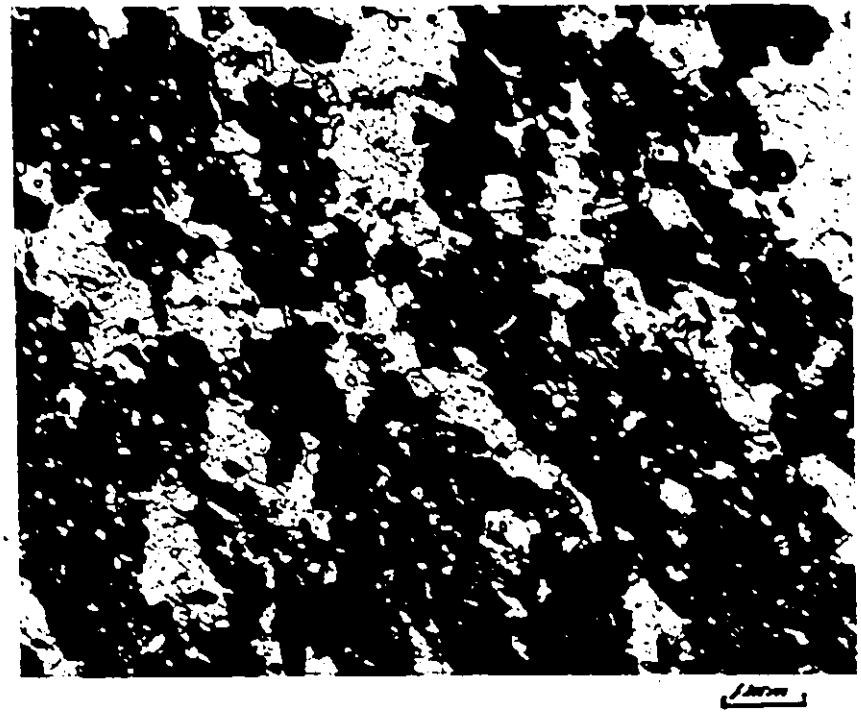
J-50 Fine to medium grained two feldspar-clinopyroxene-amphibole-garnet-biotite-quartz-iron oxide mafic granulite showing slight porphyroblastic texture. Also note the euhedral or idioblastic garnet, antiperthite, and ilmenite rimmed by quartz. Feldspars appear to be clustered. (Partial polarized light)

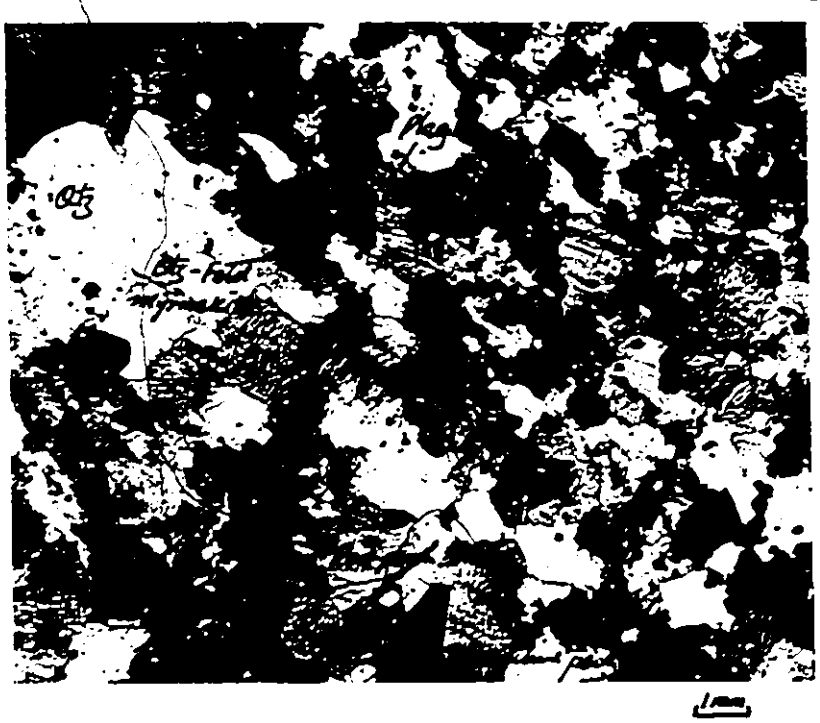

1mm


1mm

J-81 Fine grained two feldspar-two pyroxene-garnet-biotite-quartz-iron oxide mafic granulite (noritic to gabbroic) showing granoblastic-foliated texture. Mafic minerals appear to be clustered. (Plane polarized light)

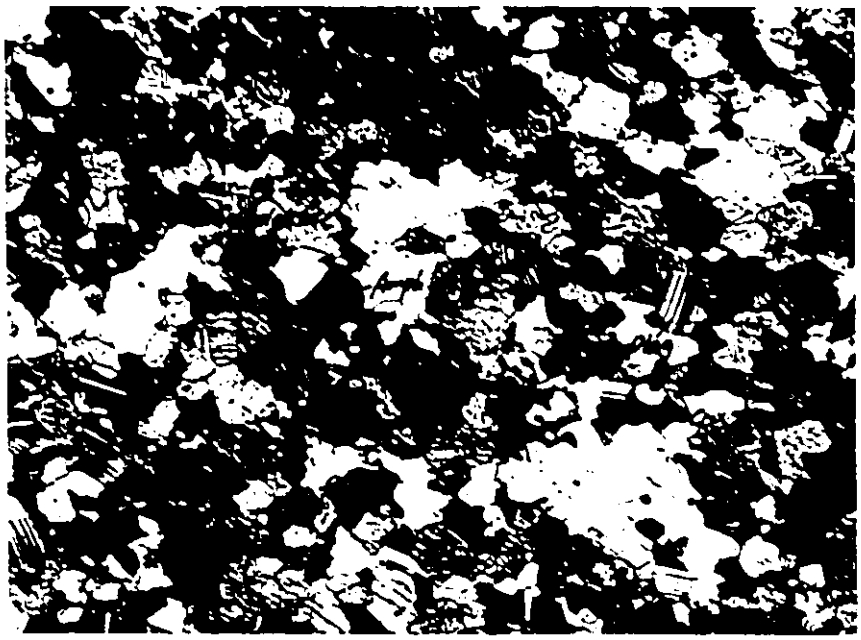
J-92 Fine to medium grained, intermediate, K-feldspar-rich two feldspar-two pyroxene-garnet-biotite-quartz-iron oxide farsundite showing serial porphyroblastic texture. Also note the feldspar-quartz myrmekite and the coexistence of rod perthite, mesoperthite, and microcline perthite. Preferred mineral association is not obvious here. (Partial polarized light)



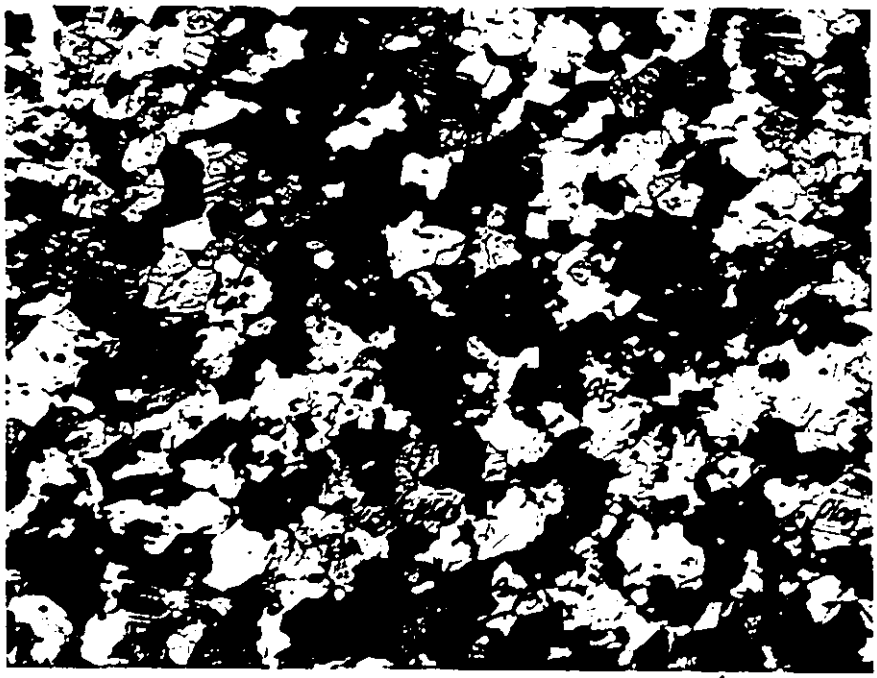


J-99 Fine grained equigranoblastic plagioclase-clinopyroxene-amphibole-garnet-biotite-quartz-iron oxide mafic granulite (anorthositic to gabbroic). Garnet symplektite with quartz, iron oxide and plagioclase are shown. Most minerals appear to be randomly distributed. (Polarized light)

J-106 Fine grained equigranoblastic two feldspar-two pyroxene-amphibole-biotite-quartz-iron oxide mafic granulite (gabbroic to noritic). Minerals appear to be randomly distributed. (Partial polarized light)



1 mm



1 mm