

MINERAL CHEMISTRY OF SOME MAFIC GRANULITES FROM THE ADIRONDACK REGION

L.S. JEN* AND R. KRETZ

Department of Geology, University of Ottawa, Ottawa, Ontario K1N 9B4

ABSTRACT

Results of chemical analyses are presented for 8 intermediate to iron-rich orthopyroxenes, 11 clinopyroxenes, 8 hornblendes and 8 garnets from mafic granulites of the northeastern Adirondacks in New York. A reaction bundle containing an invariant point for granulite-facies metamorphism is proposed, based on the apparent compatibility of five co-existing ferromagnesian minerals (those listed above plus biotite), together with plagioclase, quartz and alkali feldspar. Equilibrium with regard to the reaction hornblende + quartz = orthopyroxene + clinopyroxene + plagioclase + H₂O is suggested by a relation between the Mg:Fe²⁺ ratio of hornblende and the composition of plagioclase. A close approach to exchange equilibrium is indicated by a regular distribution of Mg, Fe²⁺ and Mn among the four principal ferromagnesian minerals. The distribution of Mg and Fe²⁺ between orthopyroxene and clinopyroxene in the Adirondacks is identical with that found in Indian and Australian granulites; a new compilation of data suggests that the previously observed slight decrease in the distribution coefficient with increasing Fe extends over the entire substitution range. In one Adirondack granulite, the Mg:Fe²⁺ ratios in all distorted octahedral sites (M1 orthopyroxene, M1 clinopyroxene, M2 hornblende) at the time of metamorphism are estimated to be equal, whereas this ratio differs greatly in the associated distorted cubic sites (M2 orthopyroxene, {X} garnet, M2 clinopyroxene). Thus the distribution of Mg and Fe²⁺ among the ferromagnesian minerals is largely dependent on the composition of the distorted cubic sites, in which the Mg:Fe²⁺ ratio is a positive function of the Ca content of the sites.

Keywords: Adirondack granulites, New York, orthopyroxene, clinopyroxene, Ca amphibole, garnet, reaction bundle, phase relations, distribution coefficients, interphase-, intracrystalline distribution, site occupancy.

SOMMAIRE

On présente les résultats d'analyses chimiques

*Present address: Mineral Policy Sector, Department of Energy, Mines & Resources, Ottawa, Ontario K1A 0E4.

de huit orthopyroxènes (intermédiaires à ferrifères), onze clinopyroxènes, huit hornblendes et huit grenats provenant de granulites mafiques du secteur nord-est du bloc Adirondack (New-York). Une famille de réactions et un point invariant, appropriés pour les conditions de métamorphisme dans le facies granulite, découlent de la compatibilité apparente de cinq minéraux ferromagnésiens coexistants (les quatre nommés ci-dessus ainsi que la biotite) avec plagioclase, quartz et feldspath alcalin. L'état d'équilibre pour la réaction hornblende + quartz = orthopyroxène + clinopyroxène + plagioclase + H₂O serait à l'origine d'une relation observée entre le rapport Mg/Fe²⁺ dans la hornblende et la composition du plagioclase. Un équilibre d'échange semble indiqué par la distribution régulière des atomes Mg, Fe²⁺ et Mn parmi les quatre minéraux ferromagnésiens principaux. La répartition de Mg et Fe²⁺ entre orthopyroxène et clinopyroxène dans ces roches est identique à celle qui caractérise les granulites d'Australie et de l'Inde. Une nouvelle compilation de données indique que la légère diminution du coefficient de distribution, notée antérieurement lorsqu'augmente la teneur en fer, serait valide dans tout le domaine de substitution. On estime que dans l'un des échantillons, le rapport Mg/Fe²⁺ était le même dans tous les sites octaédriques difformes (M1 orthopyroxène, M1 clinopyroxène, M2 hornblende) au cours du métamorphisme, tandis qu'il varie fortement dans les sites cubiques difformes (M2 orthopyroxène, {X} grenat, M2 clinopyroxène). La distribution de Mg et de Fe²⁺ parmi les minéraux ferromagnésiens dépend donc largement du chimisme des sites cubiques difformes, dans lesquels le rapport Mg/Fe²⁺ varie directement avec la teneur en Ca.

(Traduit par la Rédaction)

Mots-clés: granulites, Adirondacks (New-York), orthopyroxène, clinopyroxène, amphibole calcique, grenat, famille de réactions, relations de phases, coefficients de distribution, distribution intercrystalline, distribution intracrystalline, occupation de sites.

INTRODUCTION

The Adirondack region, which forms the southern extension of the Precambrian Grenville province, is one of the best-known anorthosite-granulite terranes in the world. Although

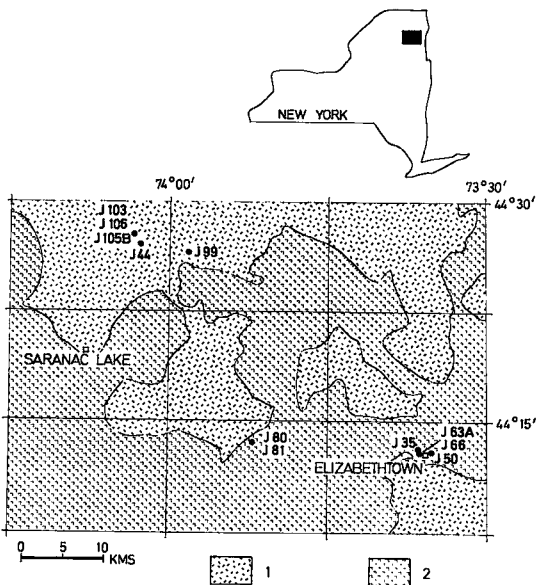


FIG. 1. Simplified geological map showing sample locations. Map units are (1) mangerite, charnockite, syenite, granite, metagabbro, minor metasediment, and (2) meta-anorthosite and anorthositic gneiss. Data from Isachsen & Fischer (1970).

Buddington (1952), Engel & Engel (1960) and Engel *et al.* (1964) obtained numerous analyses of ferromagnesian minerals from this terrane, detailed mineral studies of the charnockitic rocks, comparable to Howie's (1955) classical study of Indian charnockites, were not undertaken until recently. Some years ago one of us (Jen 1975) completed a study of ferromagnesian minerals from the northeastern Adirondacks, and the results are presented here as a complement to the numerous microprobe analyses that were subsequently obtained by Bohlen & Essene (1978, 1979) and by Jaffe *et al.* (1978).

Some of the Adirondack granulites contain as many as five ferromagnesian minerals, thus providing an opportunity to re-examine possible phase relations under granulite-facies conditions, a subject previously considered by de Waard (1965), Carmichael (1974) and others. The hornblende and pyroxene analyses presented here will enable us to examine one aspect of the phase relations (the hornblende-breakdown reaction) in some detail, thereby contributing to the detailed discussion of this reaction previously presented by Sen (1970).

A slight compositional dependence of the distribution of Mg and Fe²⁺ between inter-

TABLE 1. MODAL AND CHEMICAL COMPOSITION OF ROCKS

	1	2	3	4	5	6	7	8	9	10	11
	J-44	J-105B	J-106	J-103	J-63A	J-50	J-99	J-81	J-66	J-35	J-80
Plagioclase	45.1	33.6	51.8	51.7	50.8	59.1	43.1	30.0	48.6	45.4	22.8
Alkali Feldspar	29.2	26.8	9.7	16.6	Trace	7.6	-	3.1	-	Trace	1.0
Orthopyroxene	7.8	9.2	10.8	10.3	2.2	-	-	15.8	5.3	3.7	23.6
Clinopyroxene	6.2	3.4	8.7	9.0	15.7	15.3	28.2	20.0	15.6	17.9	13.5
Amphibole	7.9	2.5	9.6	4.5	0.1	4.8	11.1	-	2.7	7.1	8.3
Biotite	Trace	1.4	Trace	Trace	Trace	-	0.4	Trace	Trace	0.3	0.1
Garnet	-	8.3	-	-	20.9	9.1	7.8	16.0	15.8	13.2	8.5
Quartz	0.5	6.5	1.6	1.0	0.4	0.5	0.1	0.5	0.7	0.6	-
Opaque Minerals*	2.0	3.3	5.0	4.8	6.8	3.2	6.8	8.5	8.1	10.5	14.2
Apatite	0.9	2.4	2.8	1.8	2.8	0.2	2.4	5.9	2.6	1.2	8.0
Zircon	0.4	0.3	-	Trace	-	-	-	-	Trace	Trace	-
Calcite	Trace	2.3	Trace	0.2	0.4	0.1	0.1	0.2	0.4	Trace	-
Plagioclase % An	23	28	28	26	32	42	35	32	32	32	29
SiO ₂	60.55	57.50	53.30	53.00	47.70	49.50	46.40	42.10	45.50	40.80	41.05
Al ₂ O ₃	12.85	13.40	13.30	13.60	14.50	19.20	14.20	11.80	14.40	13.20	8.70
TiO ₂	1.35	2.30	2.80	2.85	3.65	2.60	3.75	4.65	4.25	5.35	4.75
Fe ₂ O ₃	1.46	1.84	2.10	1.38	2.05	1.77	1.66	2.81	2.05	1.80	5.24
FeO	8.81	10.03	11.09	11.62	14.38	9.31	14.09	19.53	17.18	19.16	21.49
MgO	1.26	2.03	2.33	2.35	3.59	2.58	3.63	5.27	3.43	3.21	5.20
MnO	0.21	0.18	0.23	0.26	0.24	0.13	0.25	0.35	0.27	0.32	0.36
CaO	4.76	4.16	6.74	7.08	8.90	10.47	11.02	10.20	7.62	12.31	10.47
Na ₂ O	3.69	3.72	3.86	4.06	2.98	2.76	3.01	1.99	2.97	2.49	1.72
K ₂ O	4.93	3.77	2.98	2.97	1.28	1.05	0.96	0.71	0.69	0.68	0.46
Total	99.87	98.93	98.73	99.17	99.27	99.37	98.97	99.41	98.36	99.32	99.44

*Magnetite, ilmenite, pyrite, pyrrhotite. J-99 is free of magnetite; J-50 is free of pyrrhotite.

mediate to Mg-rich orthopyroxene and associated clinopyroxene in granulite-facies rocks from Australia was previously demonstrated by Binns (1962) and Davidson (1968). The present results on intermediate to Fe-rich pyroxenes, together with those of Jaffe *et al.* (1978), also from the Adirondacks, provide an opportunity to determine if the compositional dependence of the distribution coefficient holds for the entire range of composition.

Between-crystal distribution relations are governed by the more fundamental between-site distribution relations, such as that between the *M1* and *M2* sites of orthopyroxene, for which some experimental information is available. Data on the Mg:Fe²⁺ ratio in orthopyroxene, clinopyroxene, amphibole and garnet, as here reported, may be combined with these experimental data to deduce the relative Mg:Fe²⁺ ratio of various pairs of similar coexisting sites, such as {*X*} garnet and *M2* clinopyroxene, or *M1* orthopyroxene and *M2* hornblende, as they existed during metamorphism. This important aspect of mineral chemistry is examined with regard to one of the Adirondack granulites.

OCCURRENCE

The plutonic rocks of the Adirondack region, as described by Buddington (1939, 1952), consist mainly of deformed and metamorphosed anorthosite, gabbro and pyroxene-hornblende granite and syenite. The study specimens were obtained from small plutons and dykes in and adjacent to the main anorthosite body, in the Elizabeth, Mt. Marcy, Lake Placid and Saranac quadrangles, within what is here referred to as the Lake Placid area (Fig. 1). Further information on the geology of this area is provided by de Waard (1968) and by Jaffe *et al.* (1978).

METHODS

Of 100 specimens that were collected and examined microscopically, the 11 specimens listed in Table 1 were chosen for detailed study. A magnetic separator and heavy liquids were used to separate ferromagnesian minerals to a purity greater than 99% (Jen 1975). All rock and mineral samples were analyzed in duplicate for Fe(total), Mg, Ca, Mn, Na and K by atomic absorption spectroscopy, using instrumentation and procedures previously described by Kretz (1970). FeO was determined by titration using a method that was developed by Jen (1973). All of these analyses were carried out by the first author. Si, Al and Ti were determined at

TABLE 2. ACCURACY AND PRECISION

Analytical Method	Standard	Oxide	Recommended*	Found**		
				\bar{x}	s	v
Micro-probe	NASA	SiO ₂	51.61	50.6	0.96	2
	Pyroxene (LUD)	Al ₂ O ₃	5.92	5.9	0.16	3
		TiO ₂	0.27	0.21	0.05	22
Atomic Absorption (FeO by Titration)	USGS	FeO	9.08	9.10	0.16	2
	BCR-1	Fe ₂ O ₃	3.20	3.17	0.18	6
		MgO	3.46	3.58	0.14	4
		MnO	0.18	0.19	0.01	5
		CaO	6.92	6.81	0.40	6
		Na ₂ O	3.27	3.47	0.19	6
		K ₂ O	1.70	1.70	0.06	4

* N.D. Macrae (unpublished); Flanagan (1973). ** \bar{x} : mean of 10-15 determinations; s: estimate of standard deviation; v: coefficient of variation (in percent).

the Geological Survey of Canada using instrumental methods (rock analyses), and at Carleton University by electron microprobe (mineral analyses); all were obtained by analytical staff at the respective institutions. An estimate of the accuracy and precision of the analytical data is given in Table 2.

Formulae and atomic ratios for the minerals were calculated by computer (Jen 1975) and are available on request. The 95% confidence intervals ($x \pm c = x \pm 1.386 s$, where x is the mean of duplicate determinations and s is standard deviation, precision error) were used in propagation-of-error calculations to estimate errors in atomic ratios, which appear as error bars in the diagrams to follow. The composition of plagioclase, as indicated in Table 1, was estimated by the maximum-extinction-angle method.

THE ROCKS

Mineral assemblages, modal analyses and chemical analyses of the 11 study specimens are listed in Table 1. The specimens are fine- to

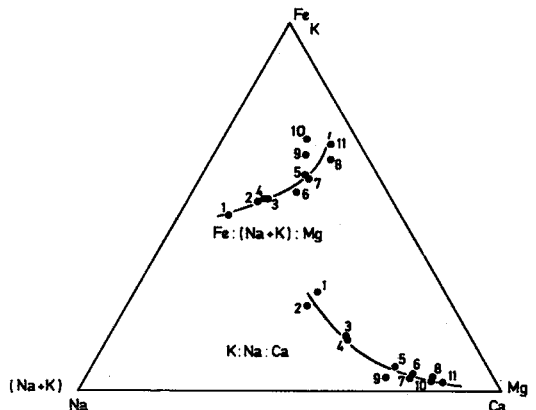


FIG. 2. Fe:(Na+K):Mg and K:Na:Ca atomic proportions of the specimens studied (Table 1).

medium-grained, homogeneous or faintly layered, and possess a granoblastic-polygonal texture as found in many granulite-facies rocks (Jen 1975).

The rocks may be divided into two groups, based on their chemical composition. Specimens 1 to 4 (Table 1) contain 3.0 to 4.9 wt. % K_2O and are relatively rich in alkali feldspar; specimen 2 is the only member of this group that contains garnet. These rocks resemble granodiorite or monzonite in composition, except that they are richer in Fe^{2+} and Ti. Specimens 5 to 11 (Table 1) contain 0.5 to 1.2 wt. % K_2O and are relatively poor in alkali feldspar; all contain garnet. These rocks resemble gabbro in composition, except that they too are relatively rich in Fe^{2+} and Ti. Specimens 5 and 9 are nearly identical in composition to a granulite described by Buddington (1952, specimen 13), obtained from the same or adjacent locality near Elizabethtown.

The $Fe:(Na+K):Mg$ and $K:Na:Ca$ ratios of the 11 study specimens are shown in Figure 2. The data define "trends", which suggest that variation in rock composition among the study specimens may be the result of some process of magmatic differentiation.

THE MINERALS

The texture of the 11 study specimens, as observed microscopically, indicates that the following mineral changes took place after the peak of metamorphism: (1) modification of

alkali feldspar to form an intergrowth of Na-rich and K-rich phases, here interpreted as the product of an exsolution reaction; (2) exsolution of calcic pyroxene lamellae from orthopyroxene (especially in 1 and 4), similar to those noted by Jaffe *et al.* (1975); (3) exsolution of lamellae of Ca-poor pyroxene from calcic clinopyroxene (especially in 2, 3 and 4), similar to those described by Jaffe *et al.* (1975), who found the lamellae to consist of orthopyroxene and pigeonite; (4) exsolution-oxidation reactions involving magnetite and ilmenite; (5) local alteration of orthopyroxene to biotite; and (6) local crystallization of secondary calcite.

We are here concerned only with the composition of the ferromagnesian minerals at the time of granulite-facies metamorphism. Grains of orthopyroxene and clinopyroxene, as found at present, are variable in composition and consist of a host and lamellae of different composition, as described by Jaffe *et al.* (1975) for clinopyroxene in other specimens from the study area. In order to arrive at an estimate of the granulite-facies composition of all the minerals, we separated for analysis grains consisting of host plus lamellae. The resulting compositions should provide good approximations of the original compositions, provided that (1) no appreciable amount of exsolved phase migrated beyond grain boundaries; (2) no appreciable exchange of ions occurred between adjacent grains during cooling, and (3) no appreciable oxidation of iron occurred within the silicates during cooling.

TABLE 3. ORTHOPYROXENE

	1	2	3	4	8	9	10	11
SiO_2	46.50	46.56	47.13	47.82	47.75	48.14	48.92	46.80
Al_2O_3	0.44	0.51	0.67	0.57	0.89	0.64	0.67	0.91
TiO	0.11	0.08	0.09	0.10	0.12	0.00	0.09	0.06
Fe_2O_3	0.92	2.30	2.10	0.80	0.24	3.25	0.43	1.35
FeO	42.05	39.37	38.36	39.70	33.87	33.44	36.00	33.89
MgO	6.57	9.21	9.23	9.41	14.59	14.71	11.53	13.81
MnO	1.16	0.90	0.99	1.04	0.38	0.32	0.49	0.49
CaO	1.58	1.70	1.70	1.69	1.54	1.03	1.53	1.15
Na_2O	0.05	0.07	0.07	0.07	0.06	0.07	0.06	0.03
K_2O	0.03	0.06	0.09	0.08	0.03	0.05	0.04	0.01
Total	99.41	100.76	100.43	101.28	99.47	101.65	99.76	98.50
$Fe^{2+}/Mg+Fe^{2+}$	0.782	0.706	0.700	0.703	0.566	0.561	0.637	0.579

TABLE 4. CLINOPYROXENE

	1	2	3	4	5	6	7	8	9	10	11
SiO_2	48.71	51.45	49.02	49.04	49.76	48.38	51.27	47.58	51.7	48.35	46.88
Al_2O_3	1.23	1.80	1.63	1.60	2.09	2.55	1.31	2.11	2.20	1.64	2.03
TiO ₂	0.19	0.19	0.17	0.17	0.13	0.27	0.17	0.23	0.14	0.10	0.19
Fe_2O_3	2.53	1.39	2.47	1.56	2.60	3.59	1.04	2.38	2.15	1.02	3.86
FeO	22.40	18.88	18.76	18.54	13.88	12.07	15.95	13.56	13.25	16.62	13.33
MgO	5.38	7.66	7.57	7.53	10.94	10.49	9.57	10.47	10.67	8.85	10.49
MnO	0.60	0.50	0.48	0.49	0.16	0.13	0.24	0.21	0.15	0.22	0.25
CaO	16.76	16.00	19.39	19.79	17.85	20.01	18.57	22.35	17.55	22.54	22.54
Na_2O	0.57	0.61	0.54	0.67	0.74	0.52	0.40	0.62	0.72	0.55	0.63
K_2O	0.03	0.09	0.13	0.17	0.05	0.06	0.04	0.08	0.07	0.06	0.02
Total	98.40	98.57	100.16	99.56	98.20	98.07	98.56	99.59	98.47	99.95	100.22
$Fe^{2+}/Mg+Fe^{2+}$	0.700	0.580	0.582	0.580	0.416	0.392	0.483	0.421	0.411	0.513	0.416

TABLE 5. AMPHIBOLE

	1	2	3	4	6	7	10	11
SiO ₂	39.86	39.60	39.25	39.11	39.96	41.07	39.09	38.46
Al ₂ O ₃	11.34	11.23	11.18	11.40	11.53	11.28	11.14	11.31
TiO ₂	2.69	2.44	2.50	2.32	2.70	2.30	2.12	2.43
Fe ₂ O ₃	3.51	4.16	3.65	4.62	5.61	3.39	2.63	4.53
FeO	22.15	20.26	20.21	20.30	14.65	18.36	18.23	15.38
MgO	4.23	6.29	6.02	5.93	8.61	6.93	7.04	8.08
MnO	0.32	0.21	0.23	0.26	0.07	0.13	0.12	0.12
CaO	9.44	9.76	10.93	9.56	11.08	10.07	13.80	13.80
Na ₂ O	1.81	1.77	1.79	1.82	1.15	1.52	1.50	1.44
K ₂ O	1.74	1.83	1.84	1.88	2.04	1.99	1.86	1.67
Total*	97.14	97.55	97.60	97.20	97.40	97.04	97.53	97.22
Fe ²⁺ /Mg+Fe ²⁺	0.746	0.644	0.653	0.658	0.488	0.598	0.592	0.516

*Volatiles not determined

TABLE 6. GARNET

	2	5	6	7	8	9	10	11
SiO ₂	37.58	36.87	38.40	38.36	36.22	38.90	38.39	36.21
Al ₂ O ₃	22.18	20.71	20.68	20.58	21.67	19.85	20.70	20.71
TiO ₂	0.09	0.02	0.06	0.06	0.08	0.00	0.05	0.04
Fe ₂ O ₃	0.34	0.99	1.06	0.12	0.28	1.91	0.29	1.35
FeO	29.72	30.10	28.28	29.79	29.51	29.79	29.89	28.67
MgO	2.12	3.32	4.06	2.37	2.94	3.14	2.43	3.01
MnO	1.52	0.85	0.72	1.28	1.13	0.97	1.19	1.41
CaO	5.82	5.77	6.21	6.28	7.62	6.31	7.67	7.13
Na ₂ O	0.08	0.08	0.02	0.04	0.08	0.05	0.03	0.01
K ₂ O	0.04	0.03	0.02	0.05	0.07	0.04	0.04	0.01
Total	99.49	98.74	99.51	98.93	99.60	100.96	100.68	98.55
Fe ²⁺ /Mg + Fe ²⁺	0.887	0.836	0.796	0.876	0.849	0.842	0.873	0.842

Orthopyroxene and clinopyroxene analyses are listed in Tables 3 and 4. The ratio Fe²⁺/(Mg+Fe²⁺) extends from 0.56 to 0.78 in orthopyroxene and from 0.39 to 0.70 in clinopyroxene. Some of the clinopyroxene analyses appear to be too low in Ca (1, 2, 5, 7, 9); these are the minerals with low totals. Fe-rich orthopyroxenes from the Lake Placid area (Mt. Marcy quadrangle), with Fe/(Mg+Fe) up to 0.95, were recently reported by Jaffe *et al.* (1975, 1978). Amphibole analyses are listed in Table 5. The Fe₂O₃/FeO weight ratio ranges from 0.14 to 0.38 (mean 0.22), which may be compared with 0.19 to 0.41 (mean 0.31) of 10 more magnesian amphiboles from Adirondack gneisses, reported by Buddington (1952). Garnet analyses are listed in Table 6, which shows this mineral to consist mainly of the almandine component; small amounts of Fe³⁺ are evidently present in the Al position.

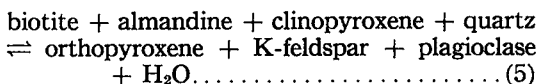
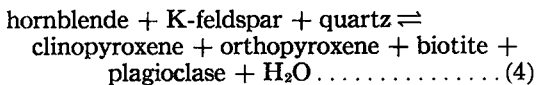
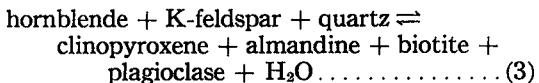
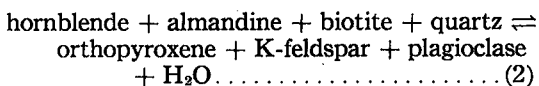
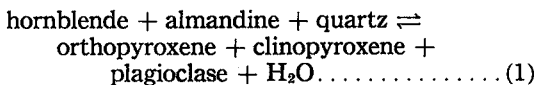
With regard to minor elements, the mineral analyses of the present study are similar to the microprobe analytical results reported for Adirondack granulites by Jaffe *et al.* (1975, 1978) and Bohlen & Essene (1979). The only notable differences are that the Al content of amphibole and the K content of clinopyroxene in our analyses are relatively high. The latter is possibly the result of biotite contamination.

PHASE RELATIONS

Various combinations of minerals occur in

the 11 study specimens, as shown in Table 1. All specimens contain plagioclase and clinopyroxene, together with some combination of alkali feldspar, orthopyroxene, amphibole (hornblende), garnet and quartz. Biotite appears to be primary in specimens 2, 7, 10 and 11. Our analysis of phase relations in these rocks follows that of Jen (1975), Froese & Jen (1979) and Froese (pers. comm.).

The mineral assemblage of specimen 2 (J-105B) permits one to write the following reaction equations:



The five reactions intersect at an invariant point on a diagram of H₂O activity versus tem-

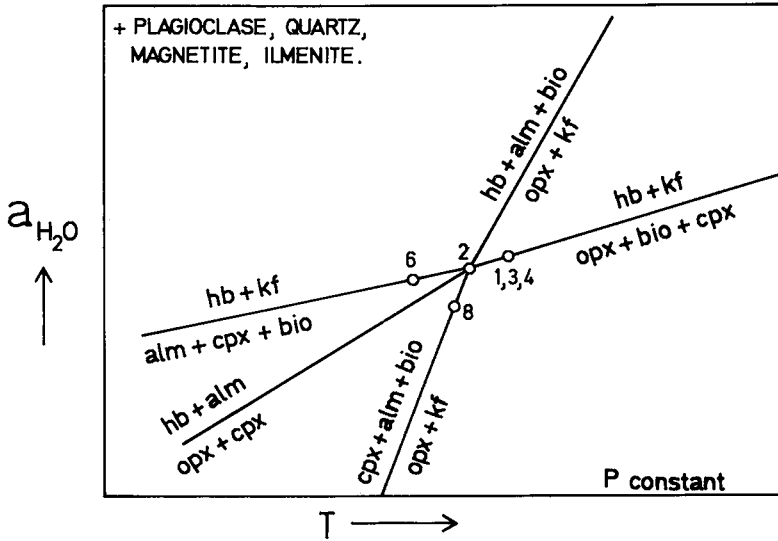
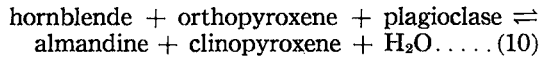
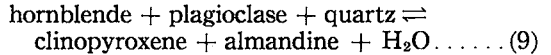
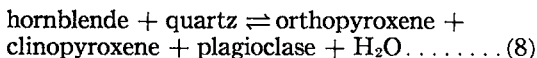
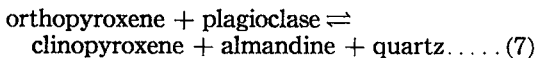
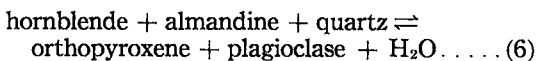


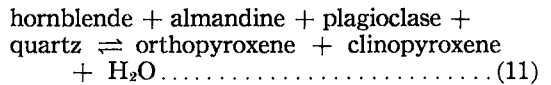
FIG. 3. Proposed mineral reactions in mafic granulites in the presence of quartz and plagioclase of fixed composition and at constant pressure. Symbols are: a activity, T temperature, hb hornblende, alm almandine, bio biotite, opx orthopyroxene, cpx clinopyroxene. Dots represent specimens studied.

perature at constant pressure. These five reactions are shown schematically as five univariant curves in Figure 3. Specimens 1, 3, 4, 6 and 8 correspond to three of these curves, whereas specimen 2 corresponds to the invariant point. Mineral assemblages from other rocks can be plotted on this diagram, suggesting slight differences in H₂O activity or temperature (or both) from rock to rock. The invariant point shown in Figure 3 was previously deduced by Mueller & Saxena (1977), based on reactions not all occurring in one rock; however, the proposed reactions differ somewhat. The topology presented here was used in a reaction grid for biotite-bearing mafic granulites by Froese & Jen (1979).

The reactions shown in Figure 3 are consistent with several reactions suggested as marking the boundary between the amphibolite and granulite facies. Thus, the following bivariant reactions, which were proposed by de Waard

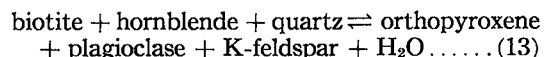
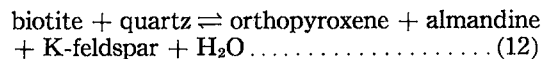


(1965, reactions 6, 7, 8), Carmichael (1974, reaction 9) and Buddington (1966, reaction 10), all intersect in the univariant reaction

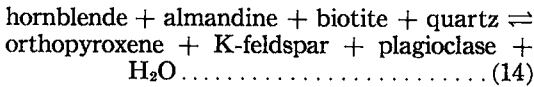


For this reason, we agree with Carmichael (1974) that all five reactions are mutually consistent. Note that reactions (7) and (10), which mark the boundary between hornblende- and pyroxene-granulite facies, obviously extend downward and intersect reaction (11) from a higher temperature and pressure.

Similarly, the following bivariant reactions,



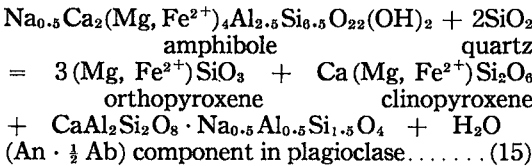
which were proposed by de Waard (1965), intersect in the univariant reaction



and, in fact, three more bivalent reactions could be written.

THE HORNBLLENDE - ORTHOPYROXENE REACTION

The most common mineral-forming reaction that takes place in mafic rocks at the amphibolite-facies/granulite-facies boundary may be reaction (8) above, which causes orthopyroxene to crystallize at the expense of hornblende. Various detailed reactions may be proposed, depending on the initial composition of hornblende. Of these, the following reaction, discussed by Sen (1970), is favored:



Five rocks (1, 2, 3, 4, 10) satisfy the conditions that all minerals of equation (15) are present and that the amphibole has been analyzed. Within the group of five amphiboles, the Na:Ca:(Mg,Fe²⁺):Al:Si ratio is generally close to that indicated by the above simplified formula. The greatest difference is found in tetrahedral Al, which is considerably less than is indicated. Equation (15) may aid in determining if a reaction relationship existed among the five minerals (together with an H₂O-bearing grain-boundary phase) at the time of metamorphism.

Sen & Ray (1971) have pointed out that because the Mg:Fe²⁺ ratio of amphibole on the left of the proposed reaction lies between that of orthopyroxene and clinopyroxene on the right, the Mg:Fe²⁺ ratios on the left and right are nearly equal. This is confirmed by specimens 10, 2 and 1 of the present study, in which the Fe²⁺/(Mg+Fe²⁺) ratios compare as follows: 0.59 and 0.61, 0.64 and 0.67, 0.75 and 0.76, respectively. Thus, unlike many other proposed reactions involving ferromagnesian minerals, the Mg:Fe²⁺ ratio does not provide an additional source of variance (Sen & Ray 1971, p. 314).

This ratio in the minerals is nevertheless important. Energy-balance considerations lead to the conclusion that in a metamorphic terrane of uniform temperature, pressure and chemical potential of H₂O [G(H₂O)], equilibrium with

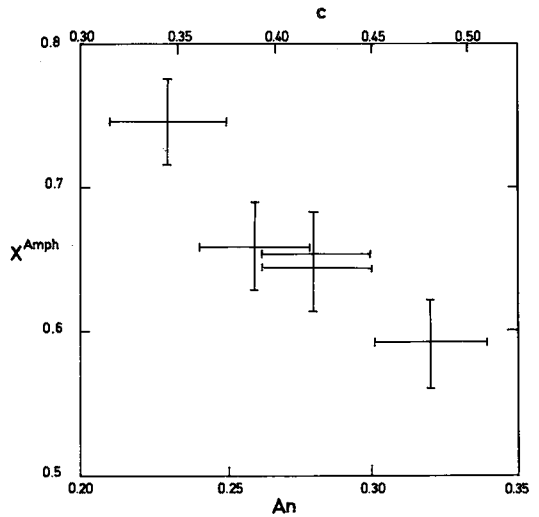


FIG. 4. Relation between the Mg:Fe²⁺ ratio of amphibole (hornblende) and the composition of associated plagioclase. X^{Amph} = Fe²⁺/(Mg+Fe²⁺) in amphibole; An = mole fraction of anorthite component in plagioclase; c (top horizontal axis) = mole fraction of (An·½Ab) component in plagioclase.

regard to equation (15) may be obtained at different places, provided that the energy term

$$\Delta G = G_{\text{amphibole}} + 2G_{\text{quartz}} - 3G_{\text{orthopyroxene}} - G_{\text{clinopyroxene}} - G(\text{H}_2\text{O}) \dots \dots \dots (16)$$

is balanced by the partial free energy of the An·½Ab component in plagioclase (G_{An·½Ab}). Now ΔG will in general be a function of the Mg:Fe²⁺ ratio of the ferromagnesian minerals (this ratio in the three minerals is interrelated, as will be shown below), whereas G_{An·½Ab} is a function of the composition of plagioclase. Hence, equilibrium in different rocks containing hornblende of different Mg:Fe²⁺ ratios may be achieved provided a complementary difference exists in the composition of the associated plagioclase. That a correlation between Fe²⁺/(Mg+Fe²⁺) in amphibole and the composition of plagioclase evidently exists in the study area is shown in Figure 4, which is taken as an indication of equilibrium with regard to reaction (15).

DISTRIBUTION OF MG, FE²⁺ AND MN AMONG COEXISTING MINERALS

The relative Mg:Fe²⁺ ratio of two associated ferromagnesian minerals in a metamorphic rock

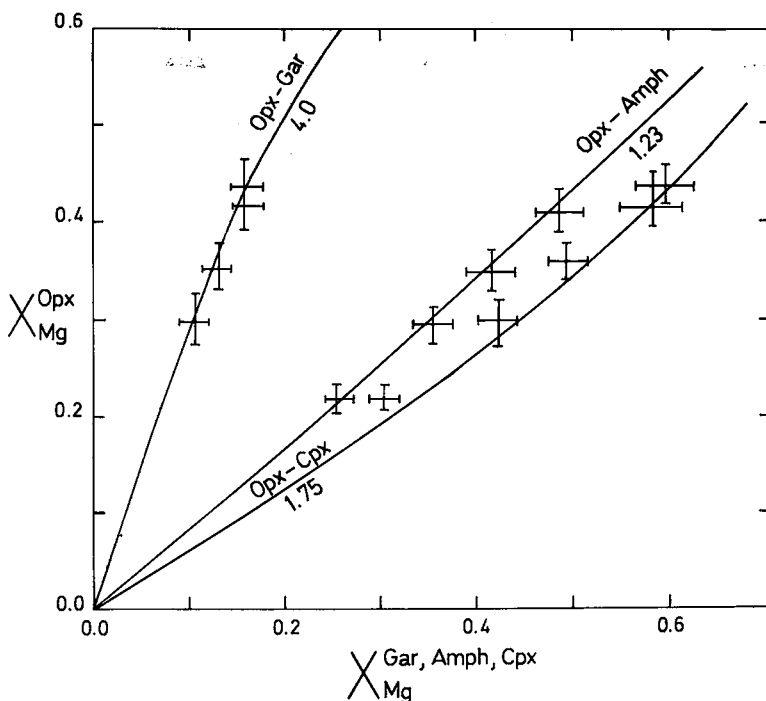
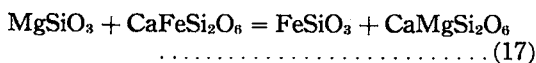


FIG. 5. Distribution of Mg and Fe²⁺ between orthopyroxene and garnet, orthopyroxene and amphibole, and orthopyroxene and clinopyroxene. $X_{Mg} = Mg / (Mg + Fe^{2+})$.

may be governed by an exchange reaction, such as the following, which refers to orthopyroxene and clinopyroxene.



The quotient

$$K_D = \frac{X_{Mg}^{Cpx}}{1 - X_{Mg}^{Cpx}} \cdot \frac{1 - X_{Mg}^{Opx}}{X_{Mg}^{Opx}} \quad (18)$$

forms a convenient empirical expression of the relative Mg:Fe²⁺ ratio of orthopyroxene (Opx) and clinopyroxene (Cpx), with $X_{Mg} = Mg / (Mg + Fe^{2+})$. For many pairs of minerals in rocks of uniform metamorphic grade, this quotient, which is referred to as the distribution coefficient (K_D), is nearly constant, as is shown for example in rocks of the upper amphibolite facies examined by Kretz (1978).

Results on the distribution of Mg and Fe²⁺ among the four minerals of the present study are compiled in Figure 5, which shows that $K_D =$ constant provides, in general, a satisfactory description of the relation between X_{Mg} of one

mineral and that of a coexisting mineral. The results may be summarized as follows: clinopyroxene ^{1.42} amphibole ^{1.23} orthopyroxene ^{4.0} garnet, where symbol > refers to X_{Mg} and the number above this symbol is the distribution coefficient for the two minerals on either side. The remaining three distribution coefficients may be obtained by calculation; for example, clinopyroxene ^{1.42 × 1.23 = 1.75} orthopyroxene.

These results confirm that the Mg:Fe²⁺ ratio of amphibole lies between that of associated orthopyroxene and clinopyroxene, as was presumed above. With regard to the amphibole-orthopyroxene distribution curve (Fig. 5), the first three data points found along this curve in moving up from the origin are (1) specimen 1, (2) specimens 2, 3 and 4 (all coincident) and (3) specimen 10, i.e., the same minerals that appear in Figure 4. The fourth data point is specimen 11, in which quartz is absent, and hence the hornblende=orthopyroxene equilibrium (15) does not apply.

The relative Mn content of two associated minerals may be governed by an exchange reaction similar to (17):

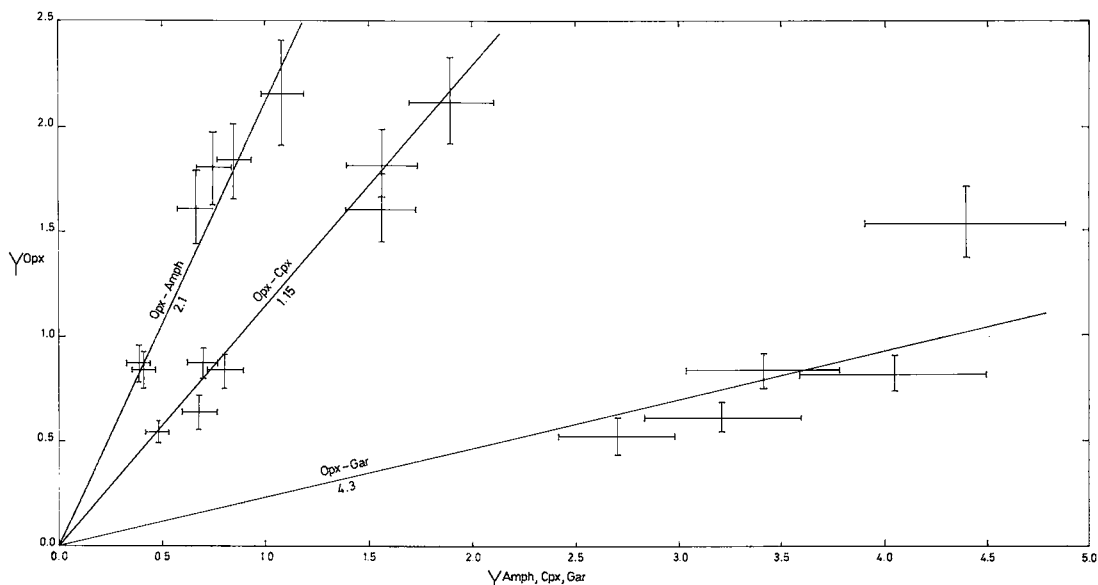
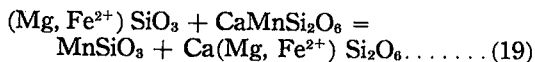


FIG. 6. Distribution of Mn between orthopyroxene and amphibole, orthopyroxene and clinopyroxene, and orthopyroxene and garnet. $Y = \text{Mn}/(\text{Mg} + \text{Fe}^{2+} + \text{Mn})$.



which leads to the following quotient:

$$K_D = Y_{\text{Mn}}^{\text{Opx}} / Y_{\text{Mn}}^{\text{Cpx}} \dots (20)$$

where $Y_{\text{Mn}} = \text{Mn}/(\text{Mg} + \text{Fe}^{2+} + \text{Mn})$. A different proposal for the reaction, such as one involving Mn-Ca exchange, will lead to a different definition of Y_{Mn} and a different value for the distribution coefficient.

The distribution of Mn among the ferromagnesian minerals of the present study is shown in Figure 6. Equation (20), with $K_D = \text{constant}$, provides a generally satisfactory expression for the relation between the Mn content of one mineral and that of an associated mineral. The results may be summarized as follows: garnet ^{4.3} orthopyroxene ^{1.15} clinopyroxene ^{1.80} amphibole. As above, the remaining distribution coefficients may be obtained by calculation.

With the exception of the anomalous distribution of Mn between orthopyroxene and garnet in one specimen (2), all the data of Figures 5 and 6 are consistent with a close approach to equilibrium during granulite-facies metamorphism in the part of the Adirondack terrane sampled, thus complementing the evidence from the phase-equilibrium relationships presented above.

REVIEW OF THE DISTRIBUTION OF Mg AND Fe^{2+} BETWEEN METAMORPHIC ORTHOPYROXENE AND CLINOPYROXENE

The new data presented here on the distribution of Mg and Fe^{2+} between orthopyroxene and clinopyroxene are now compared with similar data from two other well-studied terranes, namely, the Madras area in India (Howie 1955) and the Quairading area in Western Australia (Davidson 1968). The combined data, together with four Fe-rich mineral pairs, also from the Adirondacks (Jaffe *et al.* 1978), provide an opportunity (1) to examine the distribution relationship over virtually the entire Mg: Fe^{2+} range and (2) to reinvestigate the compositional dependence of the distribution coefficient that was found in part of the range by Binns (1962) and Davidson (1968).

The ratio $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ in the four Fe-rich mineral pairs described by Jaffe *et al.* (1978) was estimated by assuming that the ferrous iron/total iron ratios in these minerals are the same as in the most Fe-rich mineral pair of the present study (specimen 1), namely, 0.98 for orthopyroxene and 0.91 for clinopyroxene. These values are close to the average values for all the relatively Fe-rich mineral pairs of the present study and to the values arrived at by Jaffe *et al.* (1978) based on stoichiometric considerations. The resulting estimates of $\text{Fe}^{2+}/$

(Mg+Fe²⁺) for the orthopyroxenes and clinopyroxenes are as follows:

Po-13A	0.846	0.776
Po-13B	0.882	0.816
Sc-9	0.917	0.872
Po-17	0.952	0.927

The compilation is shown in Figure 7, where some of the data points represent two or three nearly identical mineral pairs from different rock specimens of the same region. Error bars based on 95% confidence limits, corresponding to an assumed 3.6% coefficient of variation on weight-percent determinations of FeO and MgO,

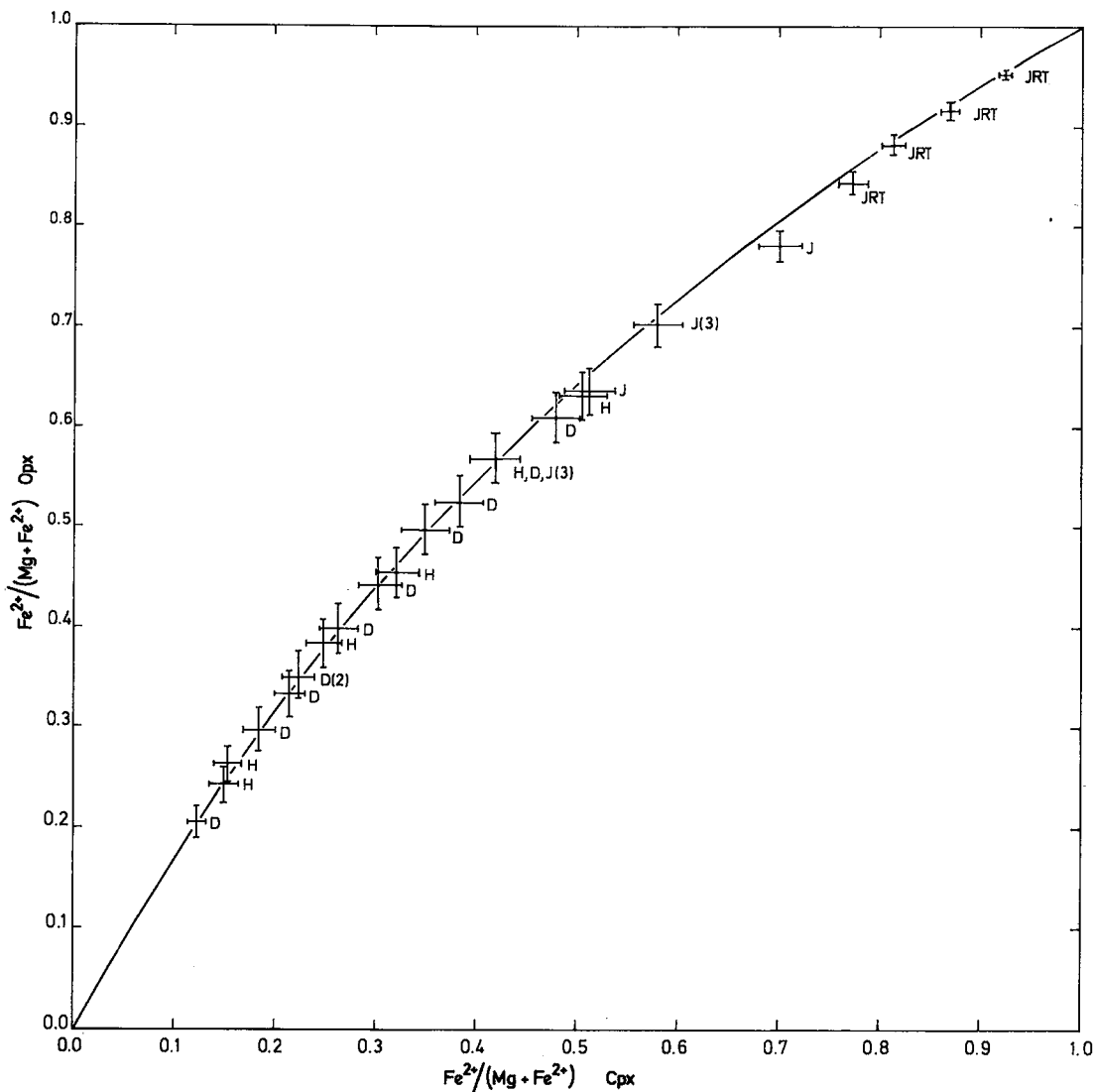


FIG. 7. Compilation of data on the distribution of Mg and Fe²⁺ between orthopyroxene and clinopyroxene in granulite-facies rocks from India (H: Howie 1955), Australia (D: Davidson 1968) and the Adirondacks, North America (J: present study, JRT: Jaffe *et al.* 1978). In brackets is the number of nearly identical mineral pairs from the same region, plotting as a single data-point. Error bars were obtained by propagation-of-error calculations assuming a 3.6% coefficient of variation (precision error) in weight percent MgO and FeO. The plotted curve follows equation (21), with $K_D = 1.80$.

were constructed on all data points. Also shown is a curve that follows equation (18), expressed in the alternate form:

$$K_D = \frac{X_{Fe}^{Opx}}{1 - X_{Fe}^{Opx}} \cdot \frac{1 - X_{Fe}^{Cpx}}{X_{Fe}^{Cpx}} \dots \dots (21)$$

with $K_D = 1.80$.

The Mg-rich part of the distribution diagram (Fig. 7) shows that granulite-facies terranes in India (H), Australia (D) and the Adirondacks (J) are all remarkably similar with regard to the distribution of Mg and Fe^{2+} between the indigenous pyroxene minerals. Moreover, all mineral pairs appear to obey the simple distribution law (equation 21), with $K_D = 1.80$. This conformity extends at least to $X_{Fe}^{Cpx} = 0.42$, where five nearly identical mineral pairs (one from India, one from Australia and three from the Adirondacks) have $X_{Fe}^{Cpx} = 0.41$ to 0.43 (mean 0.42), $X_{Fe}^{Opx} = 0.56$ to 0.58 (mean 0.57) and $K_D = 1.77$ to 1.93 (mean 1.82). With increasing Fe content, a notable departure of data points from the curve is first apparent at $X_{Fe}^{Cpx} = 0.5$, where three data points, one from each of the three localities, all lie slightly to the right of the curve. However, at $X_{Fe}^{Cpx} = 0.58$, three nearly coincident data points, all from the Adirondacks, again fall very close to the curve. The remaining five (Fe-rich) data points, one from the present study and four from Jaffe *et al.* (1978), all appear to fall to the right of the curve.

Thus, although only one of the 11 most Fe-rich mineral pairs falls entirely off the curve (taking error limits into account), the fact that all of the 11 points fall to the right of the curve, none to the left, is taken as evidence for a slight decrease of K_D in the Fe half of the distribution diagram. This indicates that the slight decrease, observed by Binns (1962) and Davidson (1968), evidently extends over the entire Fe^{2+} -Mg compositional spectrum.

DISTRIBUTION OF Mg AND Fe^{2+} BETWEEN STRUCTURALLY SIMILAR SITES IN THE ASSOCIATION ORTHOPYROXENE-CLINOPYROXENE-AMPHIBOLE-GARNET

In a rock containing orthopyroxene, clinopyroxene, hornblende and garnet, two sets of structurally similar Mg- Fe^{2+} -bearing sites may be recognized. One set consists of distorted octahedra (*M1* orthopyroxene, *M1* clinopyroxene, *M2* amphibole), and the other of more highly distorted octahedra (*M2* orthopyroxene, *M2* clinopyroxene, {*X*} garnet), which are here re-

TABLE 7. ESTIMATED $Fe^{2+}/(Mg+Fe^{2+})$ SITE-OCCUPANCY IN SPECIMEN 4 AT 800°C

	Site		
	Distorted cube	Distorted octahedron	Near-regular octahedron
Garnet	0.91	-	-
Ca pyroxene	0.96	0.54	-
Orthopyroxene	0.86	0.55	-
Hornblende	-	0.54	0.70

ferred to as distorted cubic sites. There is, in addition, a nearly regular octahedron (*M1* amphibole, *M3* amphibole) found only in one mineral. All of these sites normally contain both Mg^{2+} and Fe^{2+} ions, and the question of the distribution of the two ions between similar sites, such as {*X*} garnet and *M2* clinopyroxene, or *M1* orthopyroxene and *M2* amphibole, is now considered.

The specimen chosen for this purpose is 4(J-103), for which Kretz (1981) has estimated the Mg: Fe^{2+} ratio on the four sites (*M1* and *M2* of orthopyroxene and *M1* and *M2* of clinopyroxene) based on experimental data at 800°C, obtained by Saxena & Ghose (1971) and by McCallister *et al.* (1976). These results are listed in Table 7, together with the Mg: Fe^{2+} ratio of a garnet that would be in equilibrium with orthopyroxene in specimen 4 (garnet is not present in this specimen), as determined from Figure 4 ($K_D = 4.0$). The Mg: Fe^{2+} ratio on *M2*, *M1* and *M3* of amphibole in specimen 4 was estimated from experimental results on an amphibole from a granite obtained by Bancroft & Brown (1975), who showed that Fe^{2+} on *M1* and *M3* is similar and greater than on *M2*, with a between-site distribution coefficient (*M1*+*M3*):*M2* of approximately 2.53 (Kretz 1978). Some ordering may have occurred in these crystals during cooling, causing the distribution coefficient to increase. At granulite-facies conditions, this coefficient is therefore expected to be less than 2.53, and a value of 2.0 was arbitrarily chosen. Following the assignment of all Al^{VI} , Fe^{3+} and Ti in the amphibole from specimen 4 to the *M2* sites, the procedure used by Kretz (1981) gave estimates of $Fe^{2+}/(Mg+Fe^{2+})$ on *M2* and (*M1* + *M3*), as listed in Table 7.

Table 7 shows that the Mg: Fe^{2+} proportions in the three distorted octahedral sites in specimen 4 are all estimated to be very similar. A somewhat greater difference is estimated for the three distorted cubic sites, possibly resulting from different concentrations of Ca on these sites. Thus, the sequence of increasing $Fe^{2+}/(Mg+Fe^{2+})$, *M2* orthopyroxene, {*X*} garnet,

M2 clinopyroxene, corresponds to the sequence of increasing fraction of Ca ions on these sites, approximately 0.1, 0.2 and 0.9.

The latter conclusion is similar to that determined by Hafner *et al.* (1971) and Saxena *et al.* (1974) in their studies of the distribution of Fe²⁺ between M1 and M2 sites in clinopyroxene, where increasing Ca in the M2 sites apparently causes the Fe²⁺:Mg ratio in these sites to increase relative to that in the neighboring M1 sites.

Based on the above study, the interphase distribution of Mg and Fe²⁺ between coexisting orthopyroxene, clinopyroxene, Ca amphibole and garnet is relatively independent of the intracrystalline distribution of these ions between the slightly distorted octahedral sites. However, it is dependent on the ratio between the highly distorted cubic sites, in which the Fe²⁺:Mg ratio is a positive function of the Ca ions.

CONCLUSION

Based on the coexistence of five ferromagnesian silicate minerals, together with plagioclase, quartz, alkali feldspar and iron oxides, a reaction bundle containing an invariant point for granulite-facies metamorphism in the Adirondacks is proposed. The reaction bundle consists of five intersecting univariant reactions that are consistent with a number of bivalent reactions proposed by various authors for granulite-facies metamorphism in the Adirondacks.

New data on the distribution of Mg, Fe²⁺ and Mn among intermediate to iron-rich ferromagnesian minerals in a segment of the Adirondack region provide further evidence for a close attainment of phase equilibrium and Mg-Fe²⁺-Mn exchange equilibrium during hornblende-granulite-facies metamorphism.

A compilation of data on the distribution of Mg and Fe²⁺ between metamorphic orthopyroxene and clinopyroxene in rocks from India, Australia and the Adirondacks in North America indicates that the Binns-Davidson proposal for a slight decrease in the distribution coefficient with increasing Fe evidently extends over the entire Fe²⁺:Mg range of composition.

Preliminary estimates suggest that, during metamorphism, structurally similar sites in different associated ferromagnesian minerals contain nearly identical proportions of Mg and Fe²⁺ and that the order of increasing preference for Fe²⁺ over Mg is: distorted octahedron, nearly regular octahedron, distorted cube. Increasing Ca on distorted cubic sites evidently makes the remaining cubic sites progressively

more favorable for Fe²⁺ ions. It can be concluded that the interphase distribution of Mg and Fe²⁺ is a function of the intracrystalline distribution of these ions between the distorted cubic sites, in which the Fe²⁺:Mg ratio is a positive function of the Ca content of these sites.

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