

GARNET ZONING — PRODUCT OF A CONTINUOUS REACTION

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ABSTRACT

In the Whetstone Lake area of southeastern Ontario, the MnO-FeO zoning in garnet in metapelites is produced by the reaction: muscovite+chlorite+plagioclase+ilmenite+quartz \rightarrow garnet+biotite+rutile+H₂O where the garnet-chlorite equilibria outline a divariant envelope in the pseudo-binary system MnO-FeO. At the staurolite-biotite isograd a discontinuous reaction occurs which gives rise to an isobaric invariant point between chlorite, garnet, and staurolite in *T-X* space. From these mineral equilibria, garnet zoning in the Whetstone Lake area is shown to be a function of both temperature and initial Mn/Fe ratio of the host rock.

SOMMAIRE

Dans la région de Whetstone Lake, dans le Sud-Est de l'Ontario, le zonage MnO-FeO du grenat des roches métapélitiques a été produit par la réaction: muscovite+chlorite+plagioclase+ilmenite+quartz \rightarrow grenat+biotite+rutile+H₂O où le contenu d'équilibre grenat-chlorite à enveloppe bivalente, est situé dans système pseudo-binaire MnO-FeO. La réaction discontinue qui arrive à l'isograde staurolite-biotite produit un point invariant isobare entre la chlorite, le grenat et la staurolite dans l'espace *T-X*. A partir de ces équilibres minéralogiques, on montre que le zonage du grenat dans la région de Whetstone Lake est fonction de la température et du rapport Mn/Fe initial dans la roche mère.

INTRODUCTION

In recent years chemically zoned garnets have received considerable attention and numerous mechanisms have been proposed (Hollister 1966; Atherton 1968; Muller & Schneider 1971; Miyashiro & Shido 1973) to account for the observed zoning. The observed zoning patterns are important, for they bear directly upon the petrogenesis of the host rock and upon the constituent minerals. It is the purpose of this paper to discuss some garnet equilibria in the Whetstone Lake area, southeastern Ontario (Carmichael 1967, 1970) and then to propose a simple mechanism to explain the garnet zoning found in the area.

PETROGRAPHY

The Whetstone Lake area is underlain by heterogeneously interstratified metasedimentary and metavolcanic Precambrian rocks. The metamorphic grade varies from biotite-zone in the southeast to sillimanite-zone in the northwest (Fig. 1). A detailed geological description of the area is given by Carmichael (1967, 1970).

Samples selected for the study come from a single metapelitic unit that is oriented at a high angle to the metamorphic gradient (Fig. 1). The rocks are fine-grained and are homogeneous on a hand-specimen scale. The lowest grade assemblage is muscovite-chlorite-biotite-plagioclase-quartz-ilmenite-rutile \pm graphite. With increasing metamorphic grade garnet becomes a stable phase in the assemblage and is followed at still higher grade by the addition of staurolite. Also with increasing metamorphic grade, modal chlorite decreases and modal biotite increases. Garnets, where they occur, commonly have cores that contain inclusions of quartz, ilmenite, and fine flakes assumed to be graphite. The outer one-third of the garnets is inclusion-free. Quartz plus untwinned plagioclase constitute up to 60% of the rock. The TiO₂-bearing oxides are ubiquitous, but most commonly form less than five modal percent of the rock. The three phyllosilicates, muscovite, chlorite and biotite, commonly define a weak to moderate foliation. Staurolite is found in small (40-200 μ m) euhedral grains full of quartz inclusions.

MINERAL CHEMISTRY

More than 100 thin-sections of the pelitic formation were examined. From these, 7 were selected for electron microprobe analyses of constituent minerals. The location of these samples and several pelitic isograds are shown in Figure 1. The microprobe analyses of coexisting minerals (Table 1) indicate that, to the staurolite-biotite isograd, the major chemical changes with prograde metamorphism are increases in the ratios (Mg/(Mg+Fe) and Fe/(Fe+Mn) of the ferromagnesian silicates. However, with the entry of staurolite in the garnet-bearing assem-

blage at the staurolite-biotite isograd, these element ratios become constant for the nine-phase assemblage muscovite-chlorite-biotite-garnet-staurolite-plagioclase-quartz-rutile-ilmenite. Below the staurolite-biotite isograd, plagioclase shows no detectable zoning, but above the isograd normal zoning occurs.

Element profiles for Mn, Fe, and Mg across garnet grains show that there is little to no zoning in garnets from some samples, whereas in others there is significant zoning (Fig. 2). Because of this zoning, and because it is thought that only the outermost layer of the garnet is in chemical equilibrium with the surrounding minerals, garnet rim compositions are the only compositions used in discussing equilibria between garnet and coexisting phases.

Three rocks, one containing a highly zoned

garnet (sample #2, Table 1), one with garnet showing little to no zoning (sample #3, Table 1) and one with no garnet (sample #6, Table 1), were selected to investigate a possible relationship between the bulk-rock chemistry and garnet zoning. These rocks were pulverized and pelleted and then scanned semi-quantitatively for Mn and Fe with an XRF unit. The XRF scans (Fig. 3) show that there is a direct relationship between the Mn/Fe ratio of the rock and the amount of zoning in the garnets. In fact, where the Mn/Fe ratio is low, garnet does not appear in the rock.

CHEMOGRAPHIC RELATIONS

The major chemical changes noted across the metamorphic gradient are the increases in the

TABLE 1. MICROPROBE ANALYSES OF MINERALS

	Muscovite			Chlorite						Biotite						Plagioclase						
	#3	#4	#5	#1	#1A	#2	#3	#4	#5	#6	#1	#1A	#2	#3	#4	#5	#6	#3	#4	#5	#6	
SiO ₂	46.48	45.40	45.94	25.20	23.95	25.21	24.73	24.61	24.46	24.58	37.31	35.07	38.08	36.45	38.25	35.67	37.30	53.98	59.68	56.46		
TiO ₂	0.30	0.32	0.33	0.13	0.05	0.07	0.05	0.04	0.05	0.12	1.61	1.81	1.51	1.22	1.08	1.19	0.94	0.00	0.00	0.00		
Al ₂ O ₃	36.83	36.83	36.68	23.41	21.92	25.69	24.66	24.72	23.89	25.77	18.96	18.17	20.08	20.14	19.63	20.01	20.20	26.21	25.66	27.41		
FeO	1.02	1.04	0.91	27.17	29.49	27.08	25.17	22.19	23.86	22.56	21.83	23.03	20.63	18.96	16.89	18.04	19.02	0.09	0.00	0.00		
MnO	0.00	0.01	0.02	0.35	0.22	0.18	0.05	0.04	0.03	0.01	0.19	0.12	0.13	0.05	0.00	0.03	0.01	0.00	0.00	0.00		
MgO	0.72	0.51	0.57	12.94	12.45	13.70	13.83	15.91	16.89	14.93	8.92	8.55	9.26	9.95	11.32	11.18	10.09	10.14	8.24	9.30		
CaO	0.13	0.00	0.02	0.00	0.04	0.03	0.13	0.03	0.03	0.03	0.00	0.01	0.00	0.08	0.00	0.00	0.00	10.14	8.24	9.30		
Na ₂ O	0.63	1.22	1.02	0.00	0.01	0.00	0.00	0.14	0.14	0.00	0.00	0.06	0.00	0.00	0.00	0.17	0.00	6.43	7.07	5.99		
K ₂ O	9.44	9.29	8.89	0.00	0.01	0.00	0.00	0.00	0.00	0.00	7.89	9.39	7.40	8.22	8.21	8.44	8.35	0.13	0.00	0.06		
Total	95.55	94.62	94.38	89.20	88.14	91.96	87.64	89.71	89.71	88.00	96.71	96.21	97.09	95.07	95.38	94.72	95.91	96.98	100.65	99.22		
Cation proportions																						
Si	6.114	6.048	6.105	5.254	5.150	5.071	5.131	5.088	5.002	5.058	5.572	5.389	5.592	5.477	5.645	5.381	5.544	2.517	2.646	2.549		
Ti	0.030	0.032	0.003	0.020	0.008	0.011	0.008	0.006	0.008	0.019	0.181	0.209	0.167	0.138	0.120	0.135	0.105	0.000	0.000	0.000		
Al	5.712	5.784	5.747	5.754	5.557	6.092	6.032	6.025	5.760	6.252	3.338	3.292	3.476	3.568	3.415	3.559	3.540	1.441	1.341	1.459		
Fe	0.112	0.116	0.101	4.738	5.304	4.555	4.368	3.837	4.081	3.882	2.726	2.960	2.533	2.383	2.085	2.276	2.364	0.004	0.000	0.000		
Mn	0.000	0.001	0.002	0.062	0.040	0.031	0.009	0.007	0.005	0.002	0.024	0.016	0.016	0.006	0.000	0.003	0.001	0.000	0.000	0.000		
Mg	0.141	0.101	0.113	4.021	3.990	4.107	4.277	4.902	5.148	4.579	1.985	1.958	2.026	2.228	2.490	2.514	2.235	0.000	0.000	0.000		
Ca	0.018	0.000	0.003	0.000	0.009	0.006	0.018	0.029	0.007	0.007	0.000	0.002	0.000	0.013	0.000	0.000	0.000	0.507	0.391	0.450		
Na	0.161	0.315	0.263	0.000	0.004	0.000	0.000	0.000	0.056	0.000	0.000	0.018	0.000	0.000	0.000	0.050	0.000	0.581	0.668	0.524		
K	1.584	1.579	1.507	0.000	0.003	0.000	0.000	0.000	0.000	0.000	1.503	1.841	1.386	1.576	1.546	1.624	1.583	0.008	0.000	0.000		
O	22	22	22	28	28	28	28	28	28	28	22	22	22	22	22	22	22	8	8	8		

	Ilmenite		Rutile		Staurolite			Garnet						
	#4	#5	#4	#5	#4	#5	#6	#1A(r)*	#2(r)	#2(c)	#3(r)	#3(c)	#4(r)	#5(r)
SiO ₂	0.00	0.00	0.00	0.00	28.69	28.03	28.12	36.44	37.86	38.41	38.49	38.27	37.03	38.06
TiO ₂	53.11	53.32	99.06	98.75	0.54	0.46	0.39	0.04	0.07	0.06	0.00	0.00	0.04	0.00
Al ₂ O ₃	0.06	0.11	0.09	0.45	54.54	56.39	54.65	20.83	21.84	21.87	21.36	20.46	21.05	21.16
FeO	45.90	45.49	0.45	0.24	12.44	12.14	13.70	30.34	29.57	26.03	34.46	34.28	33.99	34.42
MnO	0.52	0.50	0.01	0.04	0.10	0.07	0.07	6.28	5.54	7.89	1.71	1.67	2.14	1.71
MgO	0.06	0.00	0.02	0.00	1.91	1.93	1.28	1.20	1.23	1.23	2.25	2.22	2.51	2.87
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.33	3.75	4.08	2.68	3.09	2.79	2.82
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.65	99.42	100.01	99.48	99.13	99.40	98.21	99.46	99.86	99.57	100.95	99.99	99.55	101.04
Cation proportions														
Si	0.000	0.000	0.000	0.000	7.826	7.592	7.751	2.977	3.034	3.068	3.054	3.073	2.996	3.023
Ti	1.008	1.012	0.994	0.993	0.111	0.094	0.081	0.002	0.004	0.004	0.000	0.000	0.002	0.000
Al	0.001	0.003	0.001	0.007	17.540	18.007	17.758	2.006	1.982	2.059	1.998	1.937	2.008	1.982
Fe	0.968	0.960	0.005	0.003	2.834	2.746	3.158	2.078	1.982	1.739	2.287	2.302	2.300	2.287
Mn	0.011	0.011	0.000	0.000	0.023	0.016	0.016	0.435	0.376	0.534	0.115	0.114	0.147	0.115
Mg	0.003	0.000	0.000	0.000	0.776	0.779	0.526	0.146	0.147	0.146	0.266	0.266	0.303	0.340
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.379	0.322	0.349	0.228	0.256	0.242	0.240
Na	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O	3	3	2	2	46	46	46	12	12	12	12	12	12	12

N.D. = not determined
 * (c) = garnet core composition; (r) = garnet rim composition

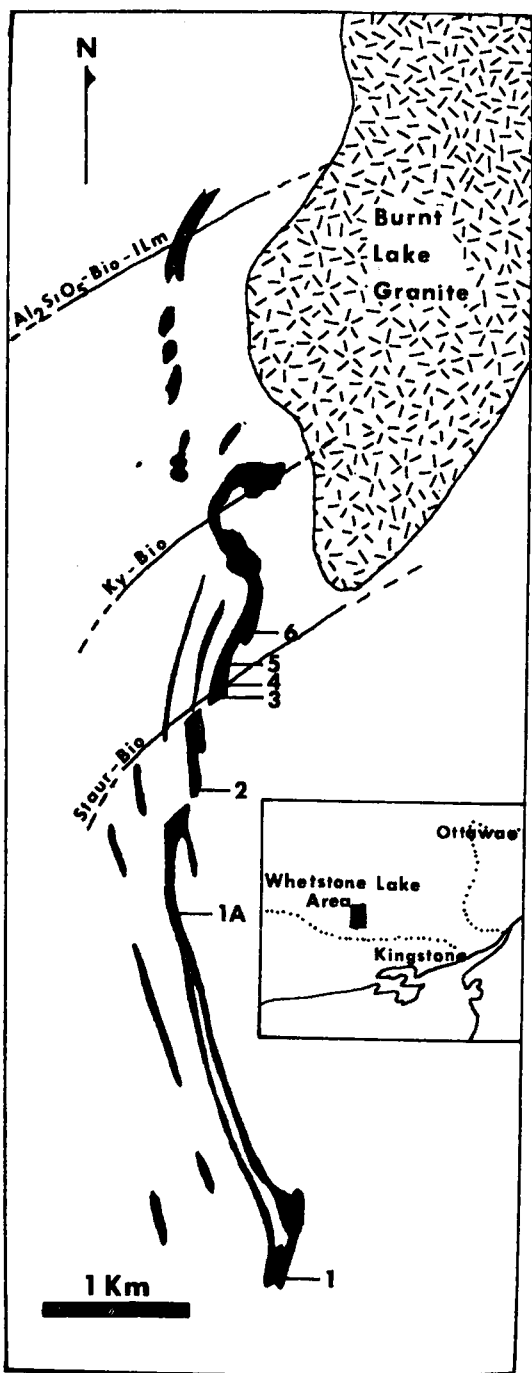


FIG. 1. Simplified map of part of the Whetstone Lake area, southeastern Ontario (after Carmichael 1967) showing only the pelitic formations. The isograds are based upon discontinuous reactions (Trzcieski 1971, 1977). The kyanite-biotite isograd is defined by garnet-free, magnesium-rich rocks.

ratios $Mg/(Mg+Fe)$ and $Fe/(Fe+Mn)$ for the ferromagnesian silicates. Phase compatibilities also change in that garnet appears near the low-grade end of the metamorphic gradient (sample #1A), followed by staurolite half-way across the gradient. Taking the microprobe analyses of all the coexisting minerals in sample #3, and using matrix algebra (Trzcieski 1971, 1977), the garnet-producing reaction is:



Reaction (1) is considered possible as long as the assemblage contains all the phases on the left-hand side of the reaction, that is, the reactants. If one of these phases is totally consumed, the reaction ceases. If the phases given in reaction (1) are present, however, the reaction progresses with continuously changing mineral compositions.

One of the continuous changes is the exchange FeO for MnO. Since chlorite is the major MnO-bearing silicate on the reactant side of the reaction, and since garnet is the major MnO-bearing silicate on the product side of the reaction, a pseudo-binary MnO-FeO diagram can be constructed for the reaction using the $Fe/(Fe+Mn)$ cation ratios of chlorite and garnet, respectively, to show the reaction behavior in $T-X$ space. To a first approximation, the temperature axis may be represented by the horizontal distance be-

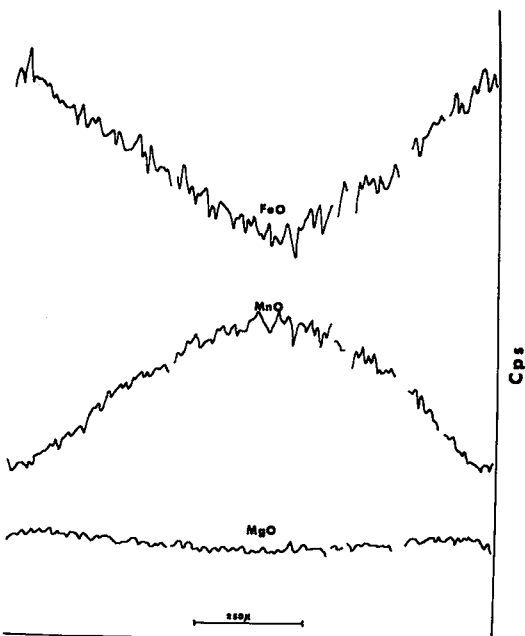


FIG. 2. Typical bell-shaped profile of Mn-Fe zoned garnet from specimen #2.

tween samples in the prograde metamorphic terrain. A plot of composition versus distance (Fig. 4) illustrates the continual change, along a divariant loop, in both the reactants (chlorite) and in the products (garnet) leading to a general decrease of MnO in the entire assemblage. This continuous change is interrupted only at the staurolite-biotite isograd (#4, Fig. 1) where staurolite enters the assemblage. As a result of the presence of staurolite, the variance of the assemblage decreases by one, and the reaction becomes a discontinuous one. The nine-phase assemblage

muscovite-chlorite-biotite-garnet-plagioclase-staurolite-quartz-ilmenite-rutile then persists for more than one km above the isograd (Trzcinski 1977).

DISCUSSION

To a first approximation, the assumption that chlorite and garnet represent the reactants and the products of the garnet-producing reaction is valid. The equilibria expressed between the two phases define a divariant loop similar to that found in numerous igneous systems, and the rules governing the recrystallization of metamorphic minerals are those of igneous petrology. Schematically (Fig. 5) garnet represents the products, and chlorite represents the reactants of the reaction. Assuming an initial $Fe/(Fe+Mn)$ ratio at N , and a temperature $< T_1$, there will be only reactants. At T_1 , reaction begins with the formation of products with an $Fe/(Fe+Mn)$ ratio C and reactants with a ratio N . With increasing temperature, the equilibria move along the two solubility curves defined by the products and the reactants. The zoning found in many garnets indicates that the bulk composition of the recrystallization matrix material lies near the solubility curve of the reactants. With tem-

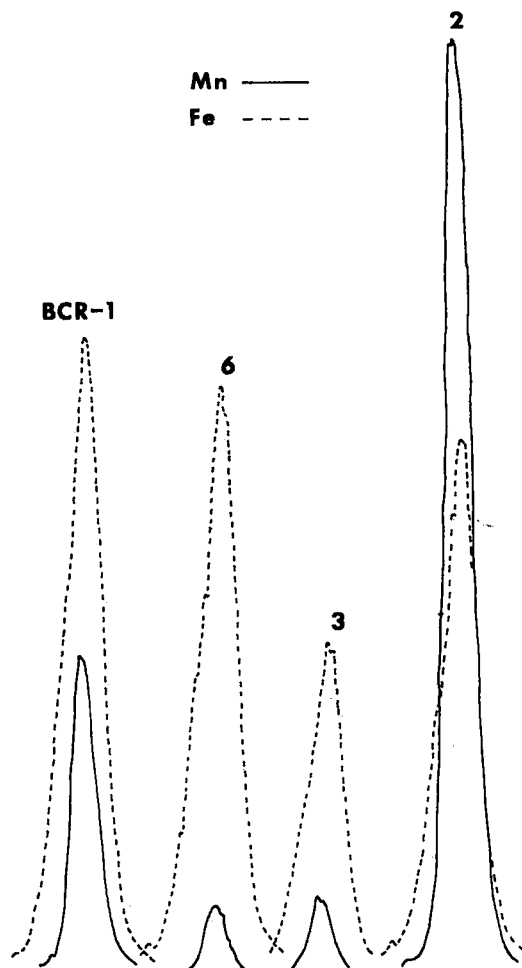


FIG. 3. XRF scans for Fe and Mn in three representative specimens. BCR-1 is a rock standard containing 11.89% FeO and 0.17% MnO. Specimen #2 contains garnet with a core content of 7.90% MnO and a rim content of 5.50% MnO. Specimen #3 contains garnet that is unzoned with 1.70% MnO; specimen #6 contains no garnet, only staurolite. The Fe and Mn peaks are not to the same scales.

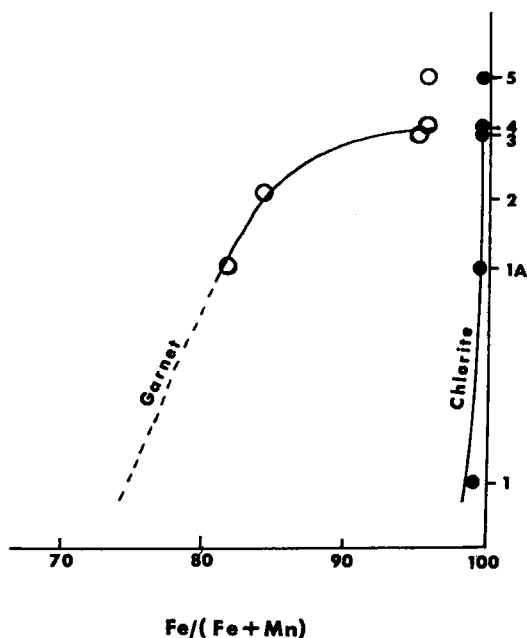


FIG. 4. Relationship between chlorite and garnet in T - X space representing the behavior of the reactants and products of reaction (1). To a first approximation, T is represented by the spatial distribution of samples in the prograde metamorphic terrain.

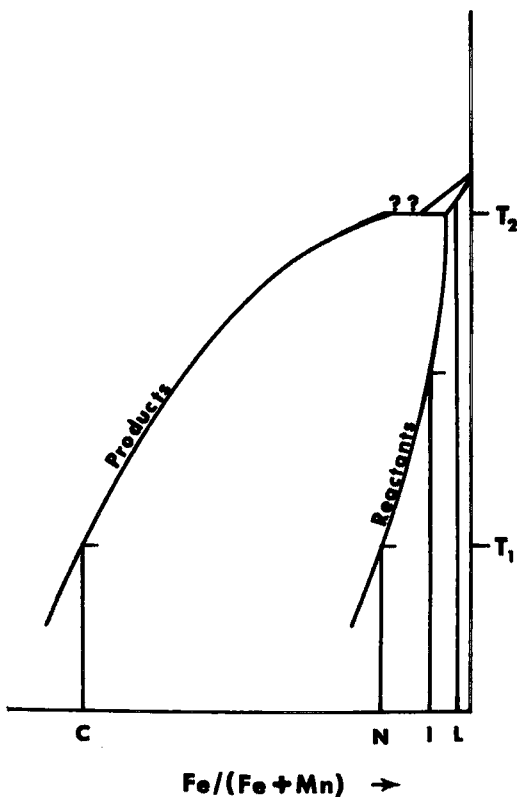


FIG. 5. Schematic representation of product (garnet) - reactant (chlorite) equilibria in T - X space. See text for discussion.

perature increasing to T_2 there is a gradual change in the composition of all participating minerals. Because garnet remains refractory (Hollister 1969), that is, it does not re-equilibrate, it records and preserves its equilibrium composition for each step of the prograde continuous reaction, thus its zoned MnO-FeO profile. The other minerals, being less refractory, re-equilibrate at each successive temperature through which they pass and retain only their composition of last re-equilibration.

TABLE 2. MINERAL ASSEMBLAGES OF THE SPECIMENS

Specimen	#1	#1A	#2	#3	#4	#5	#6
Muscovite	x	x	x	x	x	x	x
Chlorite	x	x	x	x	x	x	x
Biotite	x	x	x	x	x	x	x
Garnet		x	x	x	x	x	x
Plagioclase	x	x	x	x	x	x	x
Quartz	x	x	x	x	x	x	x
Ilmenite	x	x	x	x	x	x	x
Rutile	x	x	x	x	x	x	x
Staurolite					x	x	x

If at any point between T_1 and T_2 a reactant phase becomes totally consumed, the minerals remaining will ideally retain the $Fe/(Fe+Mn)$ ratio of the temperature at which the reactant disappears even though the remaining assemblage may continue to a higher temperature. In fact, in the Whetstone Lake area, numerous examples of the garnet-producing assemblages, minus chlorite or muscovite or ilmenite, are found well above the staurolite-biotite isograd. Another possibility is that, although all the necessary phases are present, the assemblage is raised only to some temperature intermediate between T_1 and T_2 as its maximum temperature of metamorphism. In this case the maximum possible zoning or growth of garnet would not be realized. Rather, some intermediate garnet rim composition would occur in place of a minimum MnO content. Sample #2 is an example of the rim composition, 5.54% MnO, being significantly more than the higher grade, more fully developed garnet (samples #3, #4, #5) in which the rim MnO-content is 1.70%.

At T_2 staurolite enters the assemblage. In the pseudo-binary system this point of entrance becomes an isobaric invariant point. From this temperature upward there is little to no compositional change in the garnet-rim compositions - compare assemblages #4 and #5.

In spite of the apparent refractory nature of garnet, its equilibria at and above the staurolite-biotite isograd, in the pseudo-binary system FeO-MnO, have to be reconciled with that of chlorite and that of staurolite. Between staurolite and chlorite there is no problem as there is a small divariant loop (Fig. 6) between these two phases before chlorite is totally consumed with increasing temperature (Trzcinski 1971). The equilibria between garnet and chlorite end at the invariant point. However, between garnet and staurolite there are two possibilities. One is that there is a divariant loop between garnet and staurolite (Fig. 6A). The argument favoring this interpretation is that garnet always has a lower $Fe/(Fe+Mn)$ ratio than coexisting staurolite (Trzcinski 1971; Hollister pers. comm.). The other possibility is that the FeO-MnO pseudo-binary system is a slice through n -compositional space and that the garnet-staurolite equilibria cut at a high angle another divariant envelope which, in Figure 6B, appears as a "solvus". The argument for this interpretation is that, at higher grades, garnet and staurolite act together as reactants in aluminosilicate-producing reactions (Trzcinski 1971). This requires the appearance of garnet and staurolite on the same side of the reaction field with increasing temperature.

From the schematic diagram (Fig. 5), it is

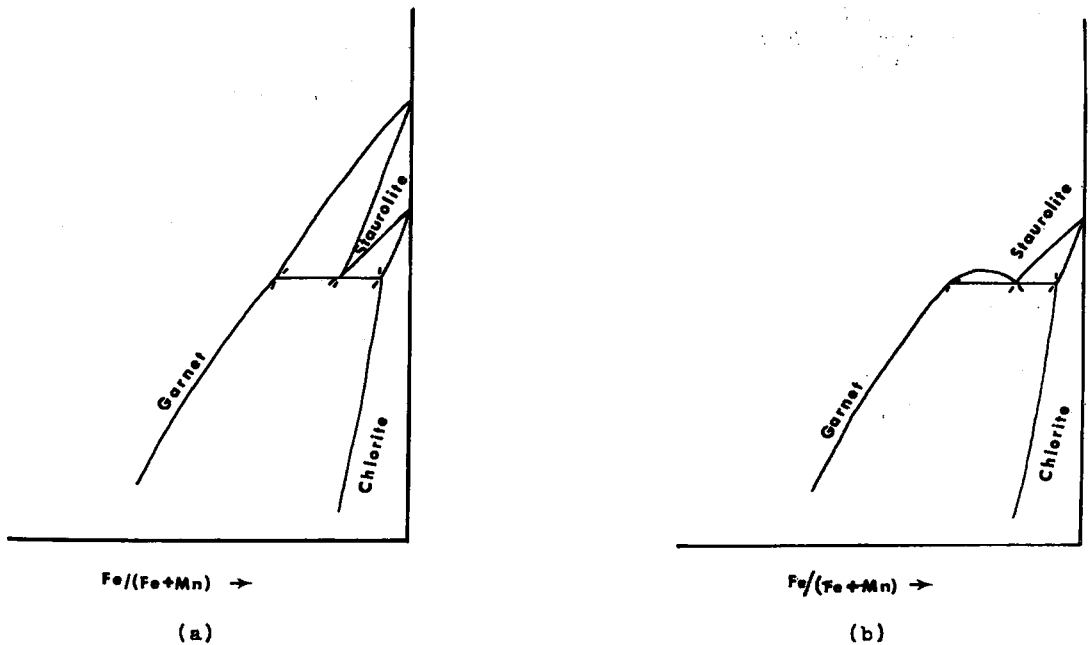


FIG. 6. Possible garnet-staurolite equilibria in $T-X$ space. (a) In this example garnet and staurolite are separated by a divariant loop based upon different $Fe/(Fe+Mn)$ ratios in garnet and staurolite. (b) In this example the garnet-staurolite equilibrium cut perpendicularly another binary loop in n -compositional space, which here appears as a solvus.

evident that the initial $Fe/(Fe+Mn)$ ratio of the rock can greatly influence the zoning profile and presence of garnet. Assuming that two different rocks, X and Y with initial $Fe/(Fe+Mn)$ ratios at N and I , respectively, pass through the same temperature interval T_1-T_2 , one would expect the garnets from rock X to be more highly zoned than those from rock Y . A rock with an initial ratio L would not contain garnet but could contain staurolite. This is the case as already shown by the XRF scans (Fig. 3) of bulk compositions. The high Mn/Fe ratio of sample #2 results in significant $Mn-Fe$ zoning of garnet (Fig. 2). Lower Mn/Fe ratios produce less zoning (sample #3), or as in the case of sample #6 where the Mn/Fe ratio is low, the garnet-producing reaction is bypassed entirely by the assemblage muscovite-chlorite-biotite-plagioclase-quartz-ilmenite-rutile. Only when the temperature attains the staurolite-biotite isograd does a new phase appear — staurolite.

SUMMARY

Unlike the models of Hollister (1966) and Atherton (1968), the zoning found in garnet does not require a constant temperature nor a changing fractionation factor. In fact, garnet zoning occurs by a continuous process over a given

temperature interval. Also, the model presented here does not require that Mn be treated as a minor component. Second, the model indicates that the presence of garnet and the amount of zoning are controlled, in part, by the initial $Fe/(Fe+Mn)$ ratio of the host rock.

ACKNOWLEDGMENTS

This paper is taken from a thesis submitted to the Graduate Faculty of McGill University in partial fulfillment of requirements for the Ph.D. Special thanks are extended to Dr. Dugald M. Carmichael, thesis advisor, for his guidance and encouragement throughout the course of research. Financial support was provided by the National Research Council of Canada. Significant improvements of the original manuscript were provided by E. Froese, E. Ghent, and T. Birkett. The remaining *trzienskelese* is not their fault, however.

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Manuscript received September 1976, emended January 1977.